



A new method for the quantification of hydrogen contribution from water to methane during hydrous kerogen pyrolysis

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ABSTRACT

Hydrogen from stratigraphic water may compensate for H-depleted kerogen, and it may produce more shale gas resources. The contribution of water-derived hydrogen to methane was calculated via deuterium atom transfer from labelled water (enriched ²H) to the methane generated from the pyrolysis experiments of high-maturity kerogen. The results showed that methane had enriched ²H up to 8040–9509 ‰ with labelled water addition. According to deuterium atom transfer calculations, we found that water contributes 12.91–15.15 % hydrogen to methane, with the contribution proportion increasing with increasing thermal maturity. These results suggest that in high-over matured shale rocks, water might contribute to shale gas reserves for late methane generation from the residual hydrogen-exhausted kerogen.

1. Introduction

Shale gas is an important unconventional natural gas resource that is primarily formed by the thermal cracking of residual organic matter in shale. The H/C atomic ratio of kerogen decreases with increasing thermal maturity, resulting in the amount of hydrogen possibly being one of the constraints for hydrocarbon generation at high-over matured shale (Seewald, 2003; Gao et al., 2020). External hydrogen plays an important role in the generation and distribution of hydrocarbons (Lewan and Roy, 2011) and oil and gas resources (Seewald, 2003). Water widely distributed in the organic and inorganic pores in shale rock (Gu et al., 2016; Cheng et al., 2018) might be one of the most important inorganic donors for supplying external hydrogen to high-over matured source rocks for hydrocarbon gas generation. Recently, Wang et al. (2022) suggested that hydrogenation of kerogen by water may be responsible for hydrocarbon yields in excess of those predicted by conventional models of source rock maturation in which hydrocarbon generation is limited by the amount of organically bonded hydrogen.

Prior hydrous pyrolysis experiments on organic matter have shown that water participates in the kerogen thermal degradation reaction (Behar et al., 2003; Su et al., 2006) and supplies its hydrogen atom to generate hydrocarbons (Lewan, 1997; Leif and Simoneit 2000; Reeves

et al., 2012). Water would not alter (Wang et al., 2011) and restrain (Lewan, 1997) the yields of gaseous hydrocarbon (such as C₁–C₅) at a relatively low thermal maturity stage of kerogen, but could enhance their yields at a high thermal maturity stage (Wang et al., 2011; Gao et al., 2020). The hydrogen isotopes of gaseous hydrocarbon products from kerogen pyrolysis are altered by the water chemical action (Wang et al., 2015; Wei et al., 2019). The interaction between water and organic matter is considered to be an important reason for the carbon isotope rollover in high-maturity shale gas (Gao et al., 2014). Additionally, the transformation of hydrogen from water to hydrocarbons also alters the hydrogen isotopic composition of hydrocarbon gases (Schimmelmann et al., 2006; Burruss and Laughrey, 2010).

A quantitative assessment of the water-derived hydrogen contribution to methane is possible via hydrogen tracing transformation. A recent study reported that hydrogen transfer from water to methane during low- and high- temperature hydrous pyrolysis of source rocks would be approximately 1–13 % and 53 %, respectively, based on the experiential ratios between δD differences of methane and water (Wei et al., 2019). Here, we devised a new method to quantify the contribution of water to methane by accurately determining the transformation amount of hydrogen atoms from water to methane from hydrous pyrolysis experiments of kerogen, which would be important for the

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assessment of water contribution to over matured shale gas.

2. Material and methods

2.1. Materials and experimental process

High-maturity shale ($R_o = 1.36\%$) from the Salgan Formation of the Middle-Upper Ordovician in the western Tarim Basin, China, was selected to simulate shale gas generation at the high-over maturity stage. It was treated with HCl/HF to isolate kerogen; the details of the treatment process can be found in [Vandenbroucke and Largeau \(2007\)](#).

Labelled water mixed with 1 % (mol/mol) heavy water (99.9 % deuterium atoms, purchased from Aldrich Corporation in the United States) and 99 % ultrapure water was prepared as a tracer reagent to prevent potential difficulties in the isotopic analysis of highly deuterated species. Both ultrapure water and the labelled water were used in subsequent experiments.

Gold tubes (length \times external diameter \times thickness: 60 mm \times 5 mm \times 0.50 mm) were used for the pyrolysis experiments, and the details of the treatment process can be found in the study by [Cheng et al. \(2020\)](#). Kerogen (approximately 100 mg) was added into each gold tube of the three groups, in which one (Group I) was selected as the anhydrous pyrolysis system. Approximately 20 mg of ultrapure water (Group II) and 20 mg of labelled water (Group III) were added to the other two groups of tubes. The amount of water added was in excess for the hydrous pyrolysis reaction of kerogen. A temperature of 365 °C, which is not beyond the critical temperature of water, was selected as the pyrolysis temperature to promote product yields as much as possible. Each group was pyrolyzed at a constant temperature of 365 °C with increasing times of 144 h, 216 h, 360 h, and 720 h to obtain the gas components at the different thermal evolution stages. The equivalent thermal maturity parameters of R_o (Easy R_o) for the pyrolysis products with rising temperatures varied from 1.38, 1.47, 1.57, and 1.73 %, respectively. These values were determined using the chemical kinetics method as described by [Sweeney and Burnham \(1990\)](#).

2.2. Instrumental analysis

Analyses performed on the calcareous mudstone included rock pyrolysis using a Rock-Eval 6.0, standard pyrolysis analyzer. Elemental analysis of kerogen was performed using a Vario EL III elemental analyzer.

The gas component analysis was performed using an Agilent 6890 GC equipped with an FID detector. Stable carbon ($\delta^{13}C$, V-PDB) and hydrogen (δD , VSMOW) isotopes were obtained using an Agilent Technologies 6890N-ISOPRIME 100 and Thermo Trace GC 1310-Delta V Advantage, respectively. Replicate analyses showed that the reproducibility of the hydrogen isotope was generally within $\pm 5\%$. The results were reported as the average of two or three runs.

3. Calculation

Under excess water conditions, the number of hydrogen atoms of methane (HA_m) generated from hydrous kerogen pyrolysis can be calculated as follows:

$$HA_m = (4 \times Y_m \times M_k \times N_A) / V_m \quad (1)$$

Among the above formula, the Y_m (ml/g), M_k (g), V_m , and N_A stand for the yield of methane, the weight of kerogen, the molar volume of the gas ($V_m = 24.5\text{L/mol}$, under the condition of 25 °C and 1 atm), and Avogadro constant ($N_A = 6.02214076 \times 10^{23}$), respectively.

Hydrogen has three types of isotopes, protium (1H), deuterium (2H or D), and tritium (3H). 3H is negligible relative to 1H and 2H in laboratory waters and kerogen and we assumed that hydrogen is composed only of 1H and 2H . The total number of hydrogen atoms in methane (HA_m) is equal to the sum of protium (1HA_m) and deuterium atoms (2HA_m), using

the following formula:

$$HA_m = ^2HA_m + ^1HA_m \quad (2)$$

Deuterium was used to trace the hydrogen transformation from water to methane in the hydrous kerogen pyrolysis experiment. The hydrogen isotopic composition of methane is usually expressed as δD values per mil (‰).

$$\delta D_m = 1000 \times (R_m - R) / R \quad (3)$$

where R_m and R are the D/H ratios of methane and international standards, respectively. The standard adopted for stable hydrogen isotopes here is the VSMOW, with an R value of 0.00015575. According to the definition of $R_m = ^2HA_m / ^1HA_m$ and (2) and (3), the deuterium atoms in methane can be expressed as

$$^2HA_m = [(10^{-3}R \times \delta D_m + R) / (10^{-3}R \times \delta D_m + R + 1)] \times HA_m \quad (4)$$

Let 2HA_m be normalized to the atom amount per mol methane, meaning that $HA_m = 4 \times N_A$ because methane has four hydrogen atoms. According to Eq. (4), 2HA_m can be expressed as follows:

$$^2HA_m(1\text{mol}) = 4 \times N_A \times (10^{-3}R \times \delta D_m + R) / (10^{-3}R \times \delta D_m + R + 1) \quad (5)$$

The chemical reaction between water and organic matter to generate methane was carried out through the oxygen atom from water attacking the carbon atom from the methyl group in the kerogen structure. The reaction rate is considered to be the same for ultrapure water and labelled water, and it is not influenced by hydrogen isotope components. In the case of excess water, the difference in the δD_m values from Groups III to II resulted from 1 % D_2O . The ratio of the water-derived deuterium to the total hydrogen in methane is denoted as r , with its calculation formula taking Group III as an example:

$$r = (^2HA_{m-III} - ^2HA_{m-II}) / HA_m \quad (6)$$

The difference in the δD_m values between the two groups resulted from the effect of 1 % deuterium oxide. According to Eqs. (5) and (6), the contribution of water-derived hydrogen to methane (C_{water}) in Group III is as follows:

$$C_{\text{water}}(\%) = \left(\frac{10^{-3}R \times \delta D_{m-III} + R}{10^{-3}R \times \delta D_{m-III} + R + 1} - \frac{10^{-3}R \times \delta D_{m-II} + R}{10^{-3}R \times \delta D_{m-II} + R + 1} \right) \times 100 \times 100\% \quad (7)$$

4. Results and discussion

The Salgan shale features an R_o of 1.36 %, TOC of 2.46 %, and a kerogen ash content of 16.23 % (Table 1). The total gaseous hydrocarbon yields from kerogen pyrolysis showed an upward tendency with increasing thermal maturity, with CO_2 slightly increasing first and then decreasing (Table 2). The methane yield and its rate of increase were evidently higher than those of the other gases. Fig. 1a shows that the addition of water did not affect the yields of methane and other gases in the current experiments. This is consistent with prior studies ([Lewan, 1997](#); [Wang et al., 2011](#)) that water does not promote the methane yield at a relatively low thermal maturity stage of kerogen.

δD_m increased with increasing Easy R_o in all the groups. Slight increases in δD_m were observed in both Group I (from -243% to -256%) and II (from -228% to -259%). However, δD_m from Group III displays an increase from 8040 ‰ to 9509 ‰, which is significantly higher than that of the other two groups (Fig. 1b). This indicates a marked influence of the water-derived hydrogen on methane generation from kerogen thermal degradation, and ultrapure water produced the effect because of the lack of deuterium as a marker.

Water-derived hydrogen is incorporated into hydrocarbons primarily through hydrogen exchange and chemical reactions between organics

Table 1

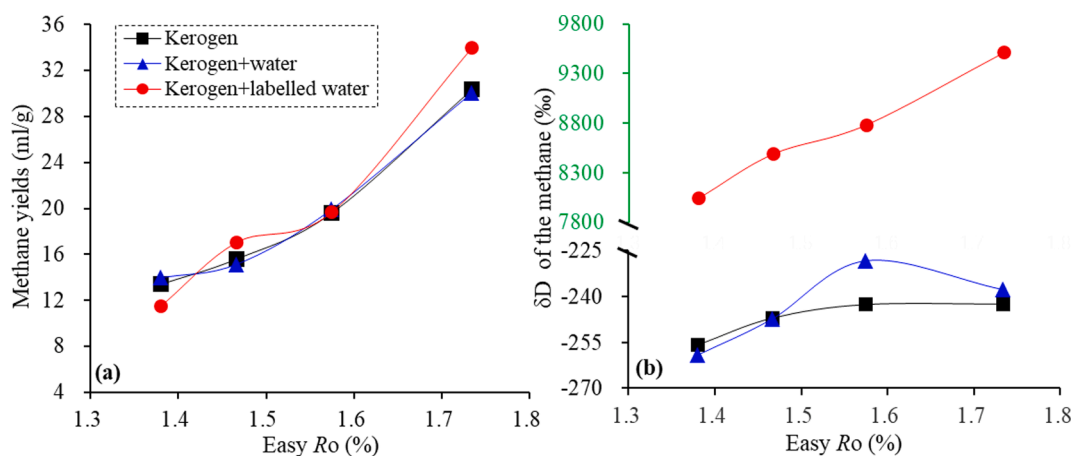
Basic geochemical data of the kerogen from Salgan shale.

Sample	Type	Element (wt %)				Atomic ratio		Ro (%)	Ash (wt %)
		C	H	O	N	H/C	O/C		
Kerogen	II	58.61	4.22	3.74	1.26	0.86	0.05	1.36	16.23

Table 2The data of C₁–C₅ gaseous hydrocarbons from the kerogen pyrolysis.

Groups	Kerogen (mg)	Temperature (°C)	Time (h)	Easy R _o (%)	Gas yield (mL/g)					C ₁ /C ₁₋₅ (%)	δD _m (‰)	C _{water} (%)
					CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄₋₅	CO ₂			
I (Kerogen)	100.19	365	144	1.38	13.40	4.49	2.05	1.06	7.76	63.80	-256	/
	100.90		216	1.47	15.60	4.33	2.58	1.49	11.01	65.03	-247	/
	100.85		360	1.57	19.60	6.34	2.82	1.57	11.34	64.62	-243	/
	99.30		720	1.73	30.32	8.54	3.78	1.61	9.94	68.52	-243	/
II (Kerogen + water)	101.89	365	144	1.38	13.97	5.07	2.52	1.31	9.21	61.09	-259	/
	101.05		216	1.47	15.15	5.95	2.63	1.41	8.03	60.24	-247	/
	101.59		360	1.57	19.94	5.16	2.82	1.42	12.06	67.98	-228	/
	100.25		720	1.73	30.05	8.13	3.53	1.47	8.77	69.59	-238	/
III (Kerogen + labelled water)	98.01	365	144	1.38	11.50	4.65	2.32	1.16	9.95	58.55	8040	12.91
	100.9		216	1.47	17.05	5.19	2.43	1.22	12.14	65.85	8487	13.58
	99.72		360	1.57	19.67	5.58	2.82	1.31	11.61	66.94	8781	14.01
	101.9		720	1.73	33.95	7.29	3.26	1.45	9.71	73.88	9509	15.15

Note: “/” represents the data were not determined or calculated.

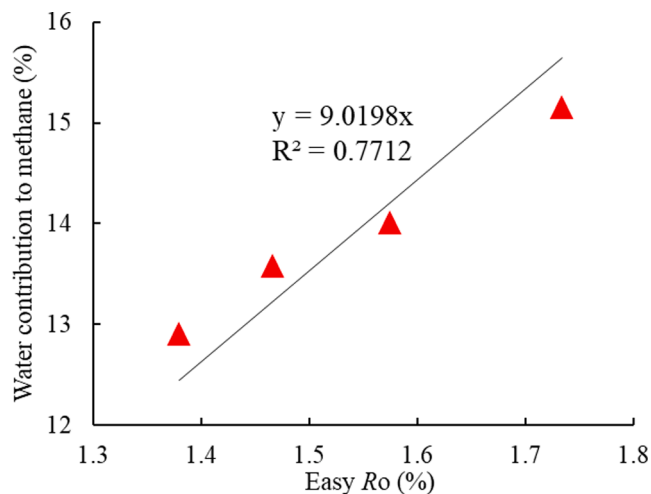
**Fig. 1.** The yields of methane (a) and its δD (b) from the pyrolysis experiments.

and water. However, the *n*-alkene from kerogen cracking would exchange its hydrogen with water and subsequently react with other alkenes to generate deuterated *n*-alkane (Leif and Simoneit 2000), which might not be the path for the generation of deuterated methane because of the restraints of the methane carbon number. The generation of deuterated methane is not a simple homogeneous exchange reaction (Lewan, 1997; Reeves et al., 2012), but from the deuteration of hydrocarbon radicals cleaved from the pyrolyzed kerogen (Lewan, 1997).

The chemical reaction between water and the carbonyl groups in kerogen is usually accompanied by an increase in CO₂ yield (Lewan, 1997). However, in our experiments, this increase was not observed. The reaction between water and organic compounds is promoted by mineral catalysis (Leif and Simoneit 2000; Reeves et al., 2012) or by increasing the reactive temperature (Lewan, 1997), but these conditions are not present in our experiments that lack catalytic minerals and were conducted at constant temperature. Depletion of carbonyl groups in the high-maturity type-II kerogen (Robin and Rouxhet, 1978) may be also responsibility for the CO₂ yield relatively constant after water addition.

The contribution of hydrogen atoms in methane from water can be determined using Eq. (7). The ratio of the contribution of water-derived hydrogen to the pool of methane hydrogen ranged from 12.91 % to

15.15 % with increasing Easy Ro (from 1.38 % to 1.73 %) in Group I

**Fig. 2.** The quantification of hydrogen transfer from water to methane.

(Table 2). Fig. 2 shows a linear increase in the water contribution to methane with higher thermal maturity, with $R^2 = 0.7712$. The contribution might be enhanced within shale rock owing to mineral catalysis, according to prior study results (Leif and Simoneit, 2000; Reeves et al., 2012).

5. Conclusion

Hydrous pyrolysis experiments were conducted on high-maturity Salgan shale kerogen to quantify the contribution of hydrogen to the production of methane using isotope tracing. The results showed that methane is markedly enriched ^2H with the addition of the hydrogen-isotope-tracing water, indicating hydrogen transfer from the water to methane. Based on the calculation of the amount of deuterium atoms transferred, we found that 12.91–15.15 % of the hydrogen atoms of methane originated from water in the hydrous kerogen pyrolysis experiment. This contribution increases with higher maturity, indicating that water has the potential to contribute to shale gas reserves at the high-over-mature stage when kerogen is generally depleted in hydrogen.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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