



# Differentiation of pre-existing trapped methane from thermogenic methane in an igneous-intruded coal by hydrous pyrolysis



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## ABSTRACT

So as to better understand how the gas generation potential of coal changes with increasing rank, same-seam samples of bituminous coal from the Illinois Basin that were naturally matured to varying degrees by the intrusion of an igneous dike were subjected to hydrous pyrolysis (HP) conditions of 360 °C for 72 h. The accumulated methane in the reactor headspace was analyzed for  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$ , and mol percent composition. Maximum methane production (9.7 mg/g TOC) occurred in the most immature samples (0.5 % $R_o$ ), waning to minimal methane values at 2.44 % $R_o$  (0.67 mg/g TOC), and rebounding to 3.6 mg/g TOC methane in the most mature sample (6.76 % $R_o$ ). Methane from coal with the highest initial thermal maturity (6.76 % $R_o$ ) shows no isotopic dependence on the reactor water and has a microbial  $\delta^{13}\text{C}$  value of  $-61\text{‰}$ . However, methane from coal of minimal initial thermal maturity (0.5 % $R_o$ ) shows hydrogen isotopic dependence on the reaction water and has a  $\delta^{13}\text{C}$  value of  $-37\text{‰}$ . The gas released from coals under hydrous pyrolysis conditions represents a quantifiable mixture of ancient (270 Ma) methane (likely microbial) that was generated in situ and trapped within the rock during the rapid heating by the dike, and modern (laboratory) thermogenic methane that was generated from the indigenous organic matter due to thermal maturation induced by hydrous pyrolysis conditions. These findings provide an analytical framework for better assessment of natural gas sources and for differentiating generated gas from pre-existing trapped gas in coals of various ranks.

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## 1. Introduction

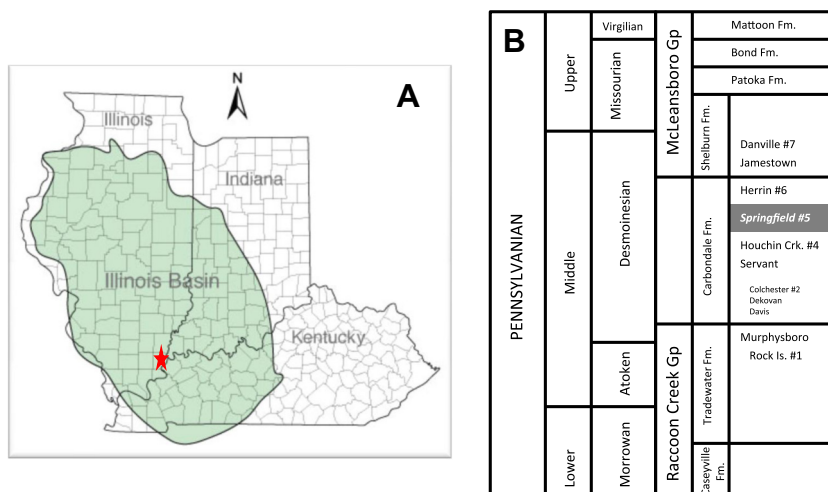
Interest in increasing the commercial viability of unconventional natural gas has spurred continued research into the sources, chemistry and kinetics of shale gas, deep gas, coalbed methane and sorption/desorption of methane from organic geochemical matrices. Of particular interest to Kotarba and Lewan (2004) was the source and nature of methane generation from high rank coals. The methane generation potential of coal samples subjected to hydrous pyrolysis conditions was observed to cease at a vitrinite reflectance of 2.0 % $R_o$ , typical of petroleum generation conditions found in sedimentary systems. However, more recent experiments showed that some overmature coals with initial vitrinite reflectance values of 4–6 % $R_o$ , indicative of metamorphic regimes, can produce up to 5 mg of methane per gram of total organic carbon (TOC) after exposure to hydrous pyrolysis conditions (Lewan and Kotarba, 2010). The precise chemical mechanism of generation remains unclear, but has been hypothesized to include: the simple release of methane sorbed to the coal matrix, continued pyrolytic degradation of ultra-refractory, high molecular weight carbon

structures, or possibly the abiotic generation of methane from graphite moieties in meta-anthracites reacting with water to form methane and carbon dioxide.

The Springfield #5 coal (Willow Lake Mine) in southeastern Illinois offers a unique opportunity to study the gas generation properties of a same-seam coal whose initial thermal maturity ranges from immature (0.5 % $R_o$ ) to overmature (% $R_o$  > 6). Located throughout the Illinois Basin, the Springfield #5 coal has been extensively studied (e.g., Hatch and Affolter, 2002 and references therein, Strapoc et al., 2007; Schimmelmann et al., 2009). The bituminous coal is middle Pennsylvanian (~325–290 Ma) in age and occupies a significant segment of the upper Carbondale Formation, typically 1–1.5 m in thickness and laterally extensive throughout Illinois, western Kentucky and Indiana. Geographic location and stratigraphy is shown in Fig. 1. The Springfield #5 coal is generally a thermally immature coal (% $R_o$  = 0.5) that is sporadically cut by peridotite igneous intrusions which alter the thermal maturity on a meter scale (% $R_o$  > 6, Stewart et al., 2005). Our specific sampling location was the Willow Lake Mine, an underground operation in Saline County (southeastern Illinois), which is actively operated by Peabody Energy (St. Louis, MO). Igneous intrusions are ubiquitous throughout the area and have been documented by Clegg (1955) and Stewart et al. (2005). Intrusions in the sampling area were argon dated ( $^{39}\text{Ar}/^{40}\text{Ar}$ ) at ~270 Ma (Fifarek

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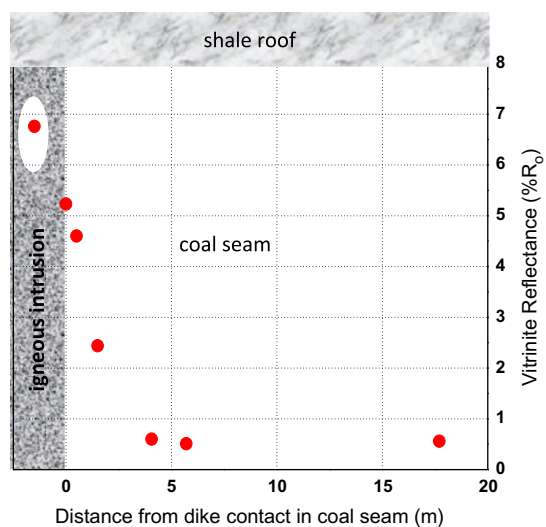
**Fig. 1.** (A) Location and extent (grayed area) of Illinois Basin within the central United States. The star represents the approximate location of the Willow Lake Mine. (B) General stratigraphy of the Pennsylvanian system within the Illinois basin (after Hatch and Affolter (2002)).

et al., 2001), with an estimated contact temperature of  $\sim 600$  °C (Stewart et al., 2005). Our samples were collected in a section of the mine where the occurrence of two intrusive dikes had forced the stoppage of mining operations. A more complete description of the sample location was made by Schimmelmann et al. (2009).

## 2. Methods

### 2.1. Sampling

Same-seam samples of bituminous coal from the Willow Lake Mine, Springfield #5 (IL) were collected for hydrous pyrolysis. Fresh, unweathered kilogram size samples were taken at increasing distance from a large igneous intrusion and one sample was taken from an enclave of coal that was entrapped within the dike. A diagram of the sampling area overlain with the respective initial thermal maturities ( $\%R_o$ ) is shown in Fig. 2. The initial relevant geochemical characteristics of the coal samples are summarized in Table 1.



**Fig. 2.** Plot of initial vitrinite reflectance ( $\%R_o$ ) of same-seam bituminous coal samples vs. their distance from the igneous intrusion. Superimposed on the plot is the approximate location of the dike and the shale roof on the upper extent of the coal seam. The thickness of the large intrusion at the sampling location is unknown (Schimmelmann et al., 2009).

**Table 1**

Relevant geochemical parameters for the same-seam coal samples from Springfield #5 used in hydrous pyrolysis reactions.  $x$  (m) = distance from igneous intrusion;  $\%R_o$  = initial vitrinite reflectance;  $\%TOC$  = wt% total organic carbon; HI = hydrogen index, mg  $S_2$ /g TOC; OI = oxygen index, mg  $S_3$ /g TOC;  $T_{max}$  = temperature at maximum  $S_2$  yield.

ID#	$x$ (m)	$\%R_o$	$\%TOC$	$T_{max}$	HI	OI
100203-7	-0.5	6.76	76.4	510	13	1
100203-5	0	5.23	53.5	500	27	6
100203-4	0.5	4.60	51.3	497	24	4
100203-3	1.5	2.44	60.4	463	42	6
100203-2	4.06	0.60	68.8	416	345	8
100203-1	5.7	0.51	72.6	418	275	10
100203-6	17.7	0.56	76.1	419	291	6

### 2.2. Hydrous pyrolysis

Hydrous pyrolysis experiments were performed as described by Kotarba and Lewan (2004). Briefly, 290–350 g of crushed, gravel sized (0.5–2.0 cm) coal was sealed in a 1000 ml 316 stainless steel Parr pressure vessel (Moline, IL). The sealed reactor was evacuated, filled with 330–350 ml of distilled, deionized water and pressurized with 241.3 kPa helium. Each reactor was heated to 360 °C for 72 h. After cooling to room temperature, the headspace gas was sampled into duplicate stainless steel vessels and the remaining reactor contents (oil, gas, water, spent coal) were separated and weighed. Table 2 details the gravimetrics of each hydrous pyrolysis experiment performed in this work.

**Table 2**

Gravimetric accounting of hydrous pyrolysis parameters. HP denotes hydrous pyrolysis experiment number. g rock = grams of coal used in HP experiment; g water = grams of reaction water used; g oil = grams of expelled oil; g gas = grams of gas;  $\%R_{oHP}$  = vitrinite reflectance of coal recovered after hydrous pyrolysis (numbers in parentheses are the standard deviation).

ID#	HP#	g Rock	g Water	g Oil	g Gas	$\%R_{oHP}$
100203-7	3461	350.1	340.8	1.72	4.01	6.88 (0.8)
100203-5	3462	350.1	340.7	0.99	3.72	5.33 (0.18)
100203-4	3463	350.0	340.6	1.44	2.56	4.63 (0.09)
100203-3	3464	300.0	350.4	2.20	2.92	2.47 (0.11)
100203-2	3470	290.4	330.6	13.45	7.98	1.50 (0.11)
100203-1	3471	290.7	330.7	13.55	8.13	1.46 (0.08)
100203-6	3469	290.5	330.7	12.14	7.96	1.41 (0.08)

### 2.3. Microscopy

Identification and reflectance determination of the vitrinite maceral (%R<sub>0</sub>) were performed with a reflected light microscope using white light and oil immersion. For this purpose, samples were prepared using the method described by Pawlewicz and Finn (2012). Briefly, coal samples were cast in epoxy then ground and polished to obtain a scratch free surface. Standard petrographic characteristics of the coal, including relative color, shape and abundance are used to distinguish the vitrinite maceral from other coal entities (Stach et al., 1982), at any level of thermal maturation. Vitrinite reflectance measurements were made using a calibrated microscope at 500× magnification under plane polarized incident white light with a 546 nm monochromatic filter in immersion oil. Typically a minimum of 25 measurements are made on a sample from which the mean reflectance is calculated (Table 2).

### 2.4. Gas compositional analysis

Gas compositional analysis was performed on each of the headspace gas samples. Briefly, chemical quantitation data were acquired using a customized Agilent 6890 series gas chromatograph (GC) that was configured by Wasson ECE Instrumentation (Ft. Collins, CO) for analysis of light natural gases. The GC contains eight columns and three detectors (1 FID and 2 TCDs) such that hydrocarbon and non-hydrocarbon components of interest are analyzed on a single injection. Standard gases of known chemical compositions were used to calibrate the system. Gas composition data are presented in Table 3 as normalized mol percent.

### 2.5. Carbon isotopic analysis

The <sup>13</sup>C/<sup>12</sup>C ratios of natural gas components were determined using methods modeled after Baylis et al. (1994). An aliquot of pyrolysis gas was introduced into a HP 6890 gas chromatograph via an autosampler through a sample-loop injector. Natural gas components were chromatographically separated on a Varian Porabond-Q column (50 m × 0.32 mm × 5 μm). Typical GC conditions were as follows: He carrier gas @ 1.5 ml/min; 40 °C initial temp; hold for 6 min; ramp to 150 °C at 15 °C/min; ramp to 250 °C at 30 °C/min; hold for 5 min. The individual components were then combusted in the He stream (with a trickle of O<sub>2</sub>) at 1050 °C in an in-line Alsint-99.7 ceramic reactor (0.5 mm I.D. × 6 mm O.D. × 500 mm length). The resulting combustion products (primarily CO<sub>2</sub> and H<sub>2</sub>O) are passed through an in-line Nafion drier and the final analyte CO<sub>2</sub> was passively drawn via open split into the source of a GV-Elementar Isoprime isotope ratio mass spectrometer for subsequent carbon isotope analysis.

Carbon isotope values from the instrument (IonVantage software) undergo off-line isotope corrections for drift, isotopic linearity and are normalized on the VPDB (Vienna Pee Dee belemnite)

scale using well calibrated, working laboratory methane standards. The final carbon isotope values represent the average of multiple replicate analyses (typically *n* = 3) with a standard deviation of generally better than 0.2‰. All final carbon isotope values are reported in del notation (δ<sup>13</sup>C, ‰) relative to the international VPDB carbonate standard.

### 2.6. Hydrogen isotope analysis

The D/H ratio of methane was determined using methods modeled after Burgoyne and Hayes (1998). An aliquot of pyrolysis gas was introduced into a HP 6890 gas chromatograph via an autosampler through a sample-loop injector. Methane was chromatographically separated on a Varian Poraplot-Q column (30 m × 0.32 mm × 1 μm). Typical GC conditions were as follows: He carrier gas at 1 ml/min; 65 °C initial temp; hold for 12 min; ramp to 225 °C at 25 °C/min; hold for 5 min. The eluent methane was then pyrolyzed in the He stream at 1450 °C in an in-line Alsint-99.7 ceramic reactor (0.5 mm I.D. × 6 mm O.D. × 500 mm length). The resulting H<sub>2</sub> analyte was passively drawn via open split into the source of a GV-Elementar Isoprime isotope ratio mass spectrometer for subsequent hydrogen isotope analysis.

Raw delta values from the instrument (IonVantage software) undergo off-line isotope corrections for drift, isotopic linearity and are normalized to the internationally accepted SMOW-SLAP hydrogen isotope scale using two well calibrated, working laboratory methane standards. The final hydrogen isotope values represent the average of multiple replicate analyses (typically, *n* = 5) with a standard deviation of better than 1‰. All final hydrogen isotope values are reported in del notation (δ<sup>2</sup>H, ‰) relative to the international standard, Vienna Standard Mean Ocean Water (VSMOW).

## 3. Results

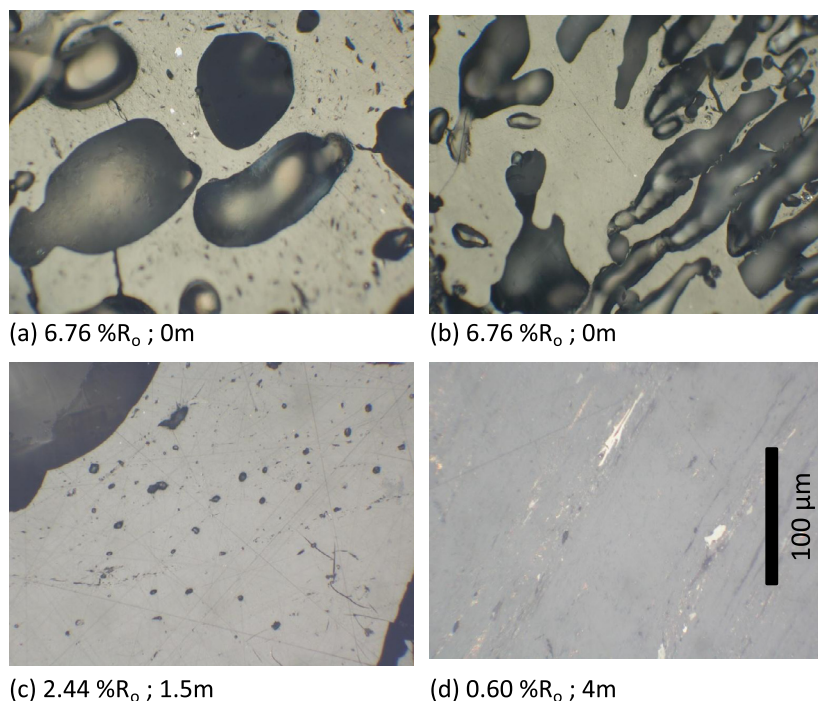
### 3.1. Microscopy

The initial %R<sub>0</sub> values for the coal samples are shown in Table 1. The %R<sub>0</sub> values range from thermally immature (0.5, farthest away from the dike) to 6.76 from the coal enclave sampled within the dike (Fig. 2). After hydrous pyrolysis, all %R<sub>0</sub> values increase (albeit marginally at very high rank), however initially immature samples (0.5 %R<sub>0</sub>) never increase beyond 1.5 %R<sub>0</sub>, consistent with thermal maturities near the end of the oil window brought on by hydrous pyrolysis conditions (Table 2). Additionally, reflected light photomicrographs were taken of each of the original coal samples. Selected pictures are shown in Fig. 3. Within the sampled coal enclave and at the contact interface, large vacuoles are observed. These vacuoles attenuate in size and frequency as the distance from the dike increases until no vacuoles are observed at a distance > 4 m from the contact interface. These vacuoles are interpreted to be the result of thermal alteration of the coal at the

**Table 3**

Gas generation details. Methane, ethane and propane are expressed in total mmol generated in each hydrous pyrolysis experiment. The parameter %C<sub>2</sub>+ is defined as the sum of all gaseous hydrocarbons (in mol%) from C<sub>2</sub> through C<sub>7</sub> divided by the number of total moles of gas per experiment. "Thermo" and "microbial" are the normalized results of our simple 2 end member mixing model based on the thermogenic (−37.4‰) and microbial (−61.0‰) isotopic signatures of methane.

ID#	HP#	Methane (mmol)	Ethane (mmol)	Propane (mmol)	%C <sub>2</sub> +	Methane (mg/gTOC)	Thermo (mg/gTOC)	Microbial (mg/gTOC)
100203-7	3461	60.58	2.01	0.71	6.7	3.62	0.00	3.62
100203-5	3462	29.07	4.77	4.06	32.1	2.48	0.20	2.29
100203-4	3463	7.98	2.50	2.86	55.9	0.71	0.11	0.60
100203-3	3464	7.56	3.53	3.41	59.0	0.67	0.13	0.53
100203-2	3470	121.65	41.82	17.30	35.0	9.74	9.74	0.00
100203-1	3471	114.97	38.77	16.28	34.8	8.72	8.72	0.00
100203-6	3469	115.11	39.40	17.47	35.6	8.33	8.33	0.00



**Fig. 3.** Reflected light photomicrographs of three of the coal samples examined in this study at different distances from the dike contact surface. The large irregular dark portions in slides a and b are vacuoles. The vacuoles are smaller and less numerous in slide c, and are not present in slide d. The photomicrographs were taken in reflected light at 500 $\times$  magnification. The solid bar in slide d represents 100  $\mu\text{m}$  and all photos are at the same scale.

time the dike intruded and are consistent with vacuoles observed by [Drobniak et al. \(2007\)](#).

### 3.2. Methane generation

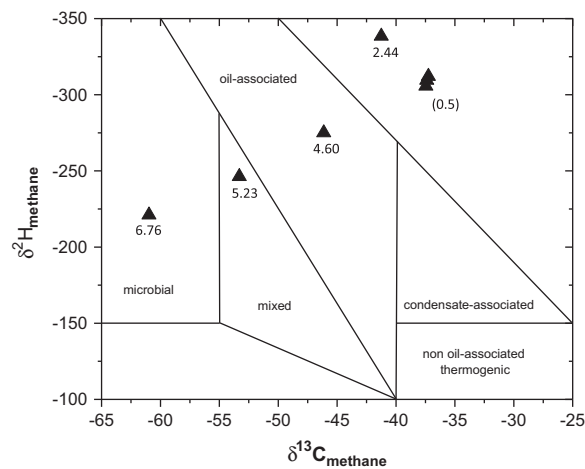
The amounts of all petroleum fluids expelled during hydrous pyrolysis are shown in [Table 2](#). However, this study focuses on the generation of methane gas and the other petroleum fluids will not be discussed further. The generation of methane ranges from 3.62 mg/g TOC at an initial 6.76 % $R_0$ , down to 0.67 mg/g TOC at 2.44 % $R_0$ , and back up to an average of 8.93 mg/g TOC for the most immature coal samples (0.5 % $R_0$ ). This is consistent with the findings of [Kotarba and Lewan \(2004\)](#) and is consistent with more recent methane generation results from the hydrous pyrolysis of higher rank coals (4–6 % $R_0$ , [Lewan and Kotarba, 2010](#)).

### 3.3. Carbon isotope analyses

$\delta^{13}\text{C}$  values for methane, ethane and propane generated from hydrous pyrolysis of the coal samples are summarized in [Table 4](#). The  $\delta^{13}\text{C}$  is most depleted (–61‰) from the coal enclave trapped within the dike, and becomes more enriched with increasing

distance (decreasing % $R_0$ ) from the contact to –37‰ at > 4 m (0.5 % $R_0$ ). A  $\delta^{13}\text{C}$  value of –37‰ is typical for methane generated by hydrous pyrolysis from a bituminous coal, the more depleted  $\delta^{13}\text{C}$  value of –61‰ is not. This value is more consistent with methane of microbial origin (e.g., [Schoell, 1983](#); [Whiticar, 1996](#); [Fig. 4](#)).

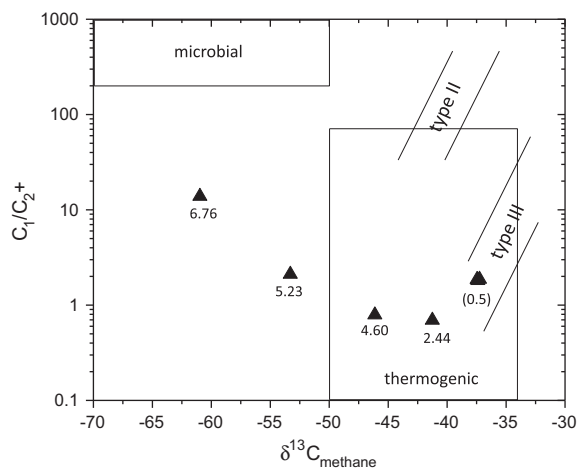
When the carbon isotopic composition of methane is considered in context with the mol% composition of the generated gases ([Fig. 5](#); after [Bernard et al., 1978](#); [Whiticar, 1996](#)), there appears to be a mixing trend between two different gases with distinct carbon isotopic sources: (1) a wet gas consistent with thermal generation from low rank, Type III coal, and (2) a second gas from extremely



**Fig. 4.** Plot of  $\delta^{13}\text{C}$  vs.  $\delta^2\text{H}$  for methane generated by hydrous pyrolysis of same-seam coals of variable initial thermal maturity due to the igneous intrusion, showing the difference in genetic characterization of the methane as described by [Schoell \(1983\)](#). The initial vitrinite reflectance values (% $R_0$ ) are given below the symbols and the value in parentheses is an average of 3 values.

**Table 4**  
Isotopic composition of recovered water and gases from hydrous pyrolysis of same-seam coal samples from Springfield #5.

ID#	HP#	$\delta^2\text{H}$		$\delta^{13}\text{C}$		
		Water	Methane	Methane	Ethane	Propane
100203-7	3461	–121	–221	–61.0	–37.8	–35.4
100203-5	3462	–117	–246	–53.2	–33.5	–32.1
100203-4	3463	–115	–275	–46.1	–35.6	–33.3
100203-3	3464	–115	–338	–41.2	–35.0	–32.6
100203-2	3470	–87	–306	–37.5	–28.1	–27.0
100203-1	3471	–91	–312	–37.2	ns	ns
100203-6	3469	–90	–310	–37.4	–27.8	–26.9



**Fig. 5.** Plot of the carbon isotope composition of methane vs. the mol% composition of the gas generated from same-seam Springfield #5 coal samples under hydrous pyrolysis conditions. The graph (after Bernard et al. (1978) and Whiticar (1996)) shows mixing of isotopically distinct methane from different genetic origins; one thermogenic and one mixed microbial. The initial vitrinite reflectance values (%R<sub>o</sub>) are given below the symbols and the value in parentheses is an average of 3 values. The parameter C<sub>1</sub>/C<sub>2</sub>+ is defined as the mol% C<sub>1</sub> divided by the sum of all gaseous hydrocarbons (in mol%) from C<sub>2</sub> through C<sub>7</sub> as per our total gas compositional analysis.

high rank coals of potential microbial or mixed microbial–thermogenic origin. Methane consistent with a thermogenic origin is to be expected from hydrous pyrolysis of low rank coals, however the observation of isotopically depleted methane with a potential microbial source is surprising.

#### 3.4. Hydrogen isotope analyses

The δ<sup>2</sup>H values for methane generated from hydrous pyrolysis of the coal samples and post-reaction water are shown in Table 4. The δ<sup>2</sup>H values of the residual water range from –121‰ to –87‰ and are consistent with depleted meteoric water from greater Denver area (~–100‰, Coplen and Kendall, 2000). The hydrogen isotope values of the residual water generally trend from depleted to more enriched as the initial thermal maturity (%R<sub>o</sub>) decreases. The δ<sup>2</sup>H values of the generated methane range from –221‰ to –338‰ and trend towards more depleted values as the initial thermal maturity of the coal samples decreases. It should be noted however, that δ<sup>2</sup>H values of –300‰ and less are a common observation for methane (and higher gaseous hydrocarbons) generated at our facility under hydrous pyrolysis conditions from any source rock due to the relatively depleted nature of the water used in our experiments.

## 4. Discussion

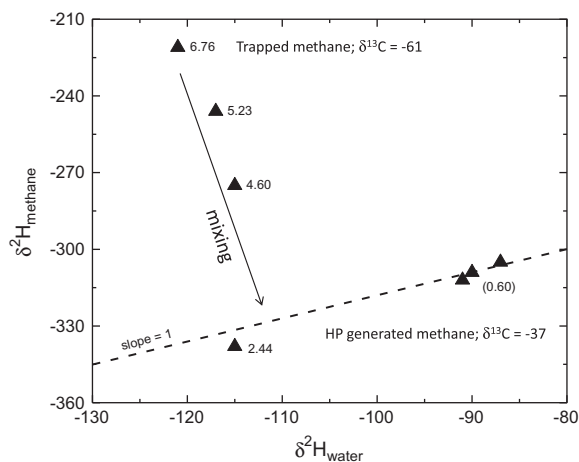
The working hypothesis to explain the isotopic variability of methane generated from these same-seam coal samples under hydrous pyrolysis conditions is the following: hydrous pyrolysis of these coal samples releases methane of two distinct origins. The first is methane thermochemically generated from the indigenous organic matter that makes up the majority of carbon in the immature coal and the second is pre-existing methane that was trapped by the metamorphism of the igneous intrusion in vacuoles and subsequently released by hydrous pyrolysis of the most thermally mature coal samples. Fig. 4 shows a standard plot of δ<sup>2</sup>H vs. δ<sup>13</sup>C of methane from the hydrous pyrolysis experiments. As is consistent with most published interpretations (e.g., Schoell, 1980, 1983; Whiticar, 1996; Sherwood-Lollar et al., 2008; McCollom et al., 2010), the methane released from the most thermally mature

sample (6.76 %R<sub>o</sub>) plots in an isotopic field typically ascribed to methane of microbial origin. Though it is possible that the origin of this methane could be due to early gas generation due to the extreme high temperature contact of the intrusion with the coal organic matter, our measured carbon and hydrogen isotopic compositions are not consistent with any instances of known early gas generation. Similarly, an abiotic source for this gas is purely speculative. However, the measured carbon and hydrogen isotopic values for this gas (–61.5‰ and –223‰, respectively) are consistent with average microbially sourced coalbed gas from the Springfield Formation (–60.5‰ and –202‰, Strapoc et al., 2007). Strapoc et al. (2007) asserted that the microbial gas currently found in the Springfield Formation is recent (i.e., Holocene). While older microbial production is possible (i.e., Middle Pennsylvanian), they argue that this scenario is unlikely as the groundwater turnover rate is on the order of several thousand years. Our results argue for a much older microbial production of methane, dating back to the late Pennsylvanian, just prior to the emplacement of the igneous intrusion. Additionally, regardless of origin, it is at this time difficult to propose a mechanism by which any gas of distinct isotopic composition was trapped in vacuoles due to the igneous intrusion to the exclusion of gas from any other source.

Fig. 4 also shows a mixing trend to a group of gases generated from the most thermally immature coals (0.5 %R<sub>o</sub>). Were it not for the anomalously depleted δ<sup>2</sup>H values (–306‰ to –312‰), these gases would generally be considered of thermogenic origin. In fact, an internal review of gas isotope analysis for samples generated by hydrous pyrolysis in Denver (regardless of organic matter source or rock type) shows δ<sup>2</sup>H values for methane consistently fall between –300‰ and –350‰ (M. Lewan, pers. comm.). This is undoubtedly due to the relatively depleted nature of the water in the local Rocky Mountains (δ<sup>2</sup>H = approx. –100‰). We therefore believe we have isotopically identified two distinct pools of methane contributing to the total natural gas derived from these hydrous pyrolysis experiments: (1) a trapped gas consistent with microbial origin (carbon and hydrogen isotopic signatures –61.5‰ and –232‰, respectively) and a thermogenic gas with an artificially depleted δ<sup>2</sup>H signal (–37‰ and –310‰, respectively).

Hydrous pyrolysis experiments in this work and that of Strapoc et al. (2007) confirm the distinction between pre-existing trapped gas and gas thermochemically generated from complex organic source material during hydrous pyrolysis. This difference is observed in the δ<sup>2</sup>H value of the methane in question. During thermochemical generation (pyrolysis) of methane (and other light hydrocarbons), the methane acquires a hydrogen atom from interstitial water in order to cap the methyl radical, forming methane gas. During this process, the methane acquires a measureable isotopic legacy from the reaction water. This is consistent with methane generated under hydrous pyrolysis conditions from the Springfield Coal by Strapoc et al. (2007) with a methane hydrogen isotopic composition of –327‰ using reaction water with an initial δ<sup>2</sup>H of –137‰. Additionally, reactions using more enriched water (+1196‰) resulted in methane generated with a more enriched hydrogen isotopic value (+363‰). It should be noted that the carbon isotope composition of the methane generated by Strapoc et al. (2007) was –34.3‰, which is consistent with the δ<sup>13</sup>C of methane generated in this work from the most thermally immature coal samples.

Methane not actively generated by hydrous pyrolysis has a δ<sup>2</sup>H value that is independent of reaction water. This is shown graphically in Fig. 6 by plotting the hydrogen isotope composition of methane vs. the associated water. A line with a slope of one is drawn indicating that methane values falling close to the line are in equilibrium with the reaction water. Methane generated from coal samples with an initial thermal maturity of 4.6 %R<sub>o</sub> and greater shows essentially no isotopic dependence on the reactor water.



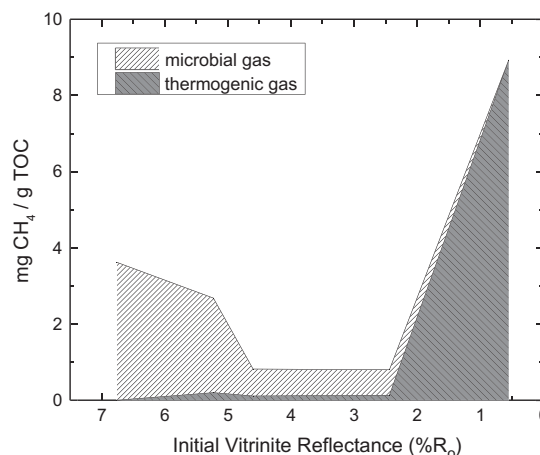
**Fig. 6.** Plot of the hydrogen isotopic composition of the methane generated from same-seam Springfield #5 coal samples under hydrous pyrolysis conditions vs. the hydrogen isotopic composition of the water used in the reactions. The methane samples that fall on the dashed line with a slope of one are likely in equilibrium with the reaction water at the time of generation. Samples that lie off the line likely have hydrogen isotopic compositions that are independent of the reaction water and were not thermochemically generated under hydrous pyrolysis conditions. The initial vitrinite reflectance values (% $R_0$ ) are given near the symbols and the value in parentheses is an average of 3 values.

The formation of vacuoles, changes in porosity, permeability and gas storage capacity of metamorphic coals is well documented (e.g., Grocke et al., 2009), including several studies involving the Springfield #5 coal (Stewart et al., 2005; Strapoc et al., 2007). We propose that very old microbial gas (mid-late Pennsylvanian) was trapped in vacuoles formed during rapid, intense heating by the intruding igneous dyke. Upon cooling, the gas became trapped and what was not trapped was lost to volatile migration out of the coal.

Hydrous pyrolysis of these same-seam coal samples liberated pre-existing gas that was trapped as a function of metamorphic heating and generated new methane from the residual organic matter still remaining. An isotopic mass balance of “liberated trapped” (microbial) methane and “newly generated” (thermogenic) methane is calculated in Table 3 and plotted in Fig. 7. For simplicity, the end members were chosen at 0.5 % $R_0$  = “thermogenic” gas and 6.76 % $R_0$  = “microbial” gas. Also, the calculation was performed using only the  $\delta^{13}C$  of the total methane released by hydrous pyrolysis for any one sample. An analogous mass balance calculation using the  $\delta^2H$  of the methane would be complicated due to the incorporation of the hydrous pyrolysis reaction water and therefore was not done. Results of the mixing model show very little thermogenic gas generated by hydrous pyrolysis down to an initial maturity of 2.4 % $R_0$ . This is consistent with findings of Kotarba and Lewan (2004) who argued that the cut-off for methane generation by high rank coals is at a vitrinite reflectance of 2.0 % $R_0$ . Any gas generation observed under hydrous pyrolysis conditions for samples with initial maturity beyond 2.0 % $R_0$  must be the result of trapped gas being liberated as a result of desorption, decrepitation of gas-filled vacuoles or some other mode of gas release unrelated to the thermochemical (pyrolytic) generation of new methane.

## 5. Conclusions

Carbon and hydrogen isotope values of methane generated from hydrous pyrolysis of organic material can be used to discern the genetic origins of natural gas. Based on isotopic analyses this work clearly demonstrates that natural gases of two distinct



**Fig. 7.** Based on isotopic mass balance, a histogram showing the relative contributions of microbial gas “liberated” and thermogenic gas “generated” from same-seam Springfield #5 coal samples under hydrous pyrolysis conditions as a function of initial vitrinite reflectance (% $R_0$ ). For low rank samples, the gas produced by hydrous conditions is primarily thermogenic in origin, however, at extreme high rank, the gas produced is being liberated from vacuoles and is of mixed or microbial origin.

sources are present upon hydrous pyrolysis conditions. The  $\delta^{13}C$  value of produced methane is useful for designating an ultimate source as thermogenic or microbial, and the  $\delta^2H$  value defines whether the gas was previously trapped and subsequently released, or was pyrolytically generated as result of the hydrous pyrolysis. In a same-seam suite of coal samples from the Springfield #5 mine, hydrous pyrolysis reactions revealed that for samples with an initial vitrinite reflectance of <2.44 % $R_0$ , the main source of resultant methane was the experimental pyrolysis (and subsequent reaction with water) of the original coal. For higher rank samples, the main source of gas was previously trapped gas that was simply released under hydrous pyrolysis conditions. This methane is hypothesized to be of microbial origin that was likely trapped in vacuoles about 270 Ma, at the time of the igneous intrusion. Whereas multiple origins for this trapped methane are possible, our isotopic and compositional data are most consistent with a trapped gas of mixed thermogenic/microbial origin. These findings provide an experimental and analytical framework for better assessment of natural gas sources by differentiating generated gas from pre-existing trapped gas in coals of various ranks.

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