Methane and carbon at equilibrium in source rocks

Frank D Mango

Abstract

Methane in source rocks may not exist exclusively as free gas. It could exist in equilibrium with carbon and higher hydrocarbons: \( CH_4 + C \rightleftharpoons \text{Hydrocarbon} \). Three lines of evidence support this possibility. 1) Shales ingest gas in amounts and selectivities consistent with gas-carbon equilibrium. There is a 50% increase in solid hydrocarbon mass when Fayetteville Shale is exposed to methane (450 psi) under moderate conditions (100°C): Rock-Eval S2 (mg g\(^{-1}\)) 8.5 \rightleftharpoons 12.5. All light hydrocarbons are ingested, but with high selectivity, consistent with competitive addition to receptor sites in a growing polymer. Mowry Shale ingests butane vigorously from argon, for example, but not from methane under the same conditions. 2) Production data for a well producing from Fayetteville Shale declines along the theoretical curve for withdrawing gas from higher hydrocarbons in equilibrium with carbon. 3) A new general gas-solid equilibrium model accounts for natural gas at thermodynamic equilibrium, and C6-C7 hydrocarbons constrained to invariant compositions. The results make a strong case for methane in equilibrium with carbon and higher hydrocarbons. If correct, the higher hydrocarbons in source rocks are gas reservoirs, raising the possibility of substantially more gas in shales than analytically apparent, and far more gas in shale deposits than currently recognized.

Introduction

Few questions in geoscience are as interesting and controversial as the origin of methane in natural gas. And fewer go as far back in time. Evans proposed thermal cracking in 1971 to explain oil trending to methane with depth in a Canadian basin [1]. It was assumed that hydrocarbons cracked more or less randomly to smaller hydrocarbon and ultimately to methane. This premise had broad appeal, but no empirical or theoretical foundation. McNab had attempted to replicate methane generation from oil cracking in long-term cracking experiments in 1952, but failed [2]. Thermal cracking theory was nevertheless elevated to text-book status [3,4], but it was never to gain the empirical support McNab sought, and its predictive powers today are limited. It cannot, for example, explain the properties of natural gas, the thermal stability of its light hydrocarbons [5], their compositions in gas deposits [6], or their constraints to thermodynamic equilibrium [7].

Catalysis by transition metals explains these properties [5-7], and there is considerable experimental evidence supporting it. Source rocks release gas catalytically in laboratory experiments at ambient temperatures [8-10], and molecular probe experiments confirm natural catalytic activity as the source of gas in these experiments [11]. However, there is also experimental evidence against transition metal catalysis in natural gas generation [12].

Catalysis accounts for the composition of natural gas, but other questions remain troubling. Shales ingest and expel gas in the laboratory in ways contradicting classical physics. Non-classical behavior is apparent in chaotic generation curves [8], and in the generation of hydrocarbons in reverse-mass order [9]. It is also apparent in the molecular probe experiments [11]. Methane ingestion in Fayetteville and Mowry Shales reported here is another outstanding example.

The premise that methane should be independent of the solid hydrocarbons generating it could be flawed. If generation is catalytic and reversible, methane and its source would be more like carbon dioxide and calcite at equilibrium. Carbon dioxide is never independent of calcite. Ingested and expelled reversibly from CaCO\(_3\)/CaO, its pressure increases and falls with temperature as a thermodynamic function of the equilibrium constant. Methane could similarly exist in two states, gaseous methane and solid-state methane, at equilibrium. It accounts for the results presented here and the non-classical behavior in earlier experiments.

An equilibrium hypothesis is presented in three parts. The general concept is laid out first (Theory). The second
part is the supporting experimental evidence (Ingestion), and the third contains a kinetic model of the theoretical equilibrium (Gas-Solid Equilibrium Kinetic Simulations). A new general equilibrium model for light hydrocarbon generation summarizes the results.

**Results and discussion**

**Theory** - Solid hydrocarbons storing and generating gas is hypothetical. It considers two very different reservoirs of gas in shales. The first is open porosity storing and expelling gas as a passive container in accordance with classical theory. The second does not. It is comprised of solids like pyrobitumens, and similar high-molecular weight hydrocarbons found in organic-rich shales. It is not a passive container storing hydrocarbons in solution, however. Methane could only have a very limited solubility in solid hydrocarbons, perhaps no more than a few percent by my estimates. In the current hypothesis solid hydrocarbon reservoirs are co-polymers of methane and carbon, at equilibrium. The equilibrium in reaction (1) illustrates the concept in its simplest form.

\[ n\text{CH}_4 + n(-\text{C}_x) \leftrightarrow (-\text{CH}_2)_2n. \]  

The equilibrium hypothesis and supporting evidence are discussed below. Here, we consider the origin of solid hydrocarbons, also referred to as ‘carbon pools’. ‘Methane’ is used throughout to illustrate relationships for simplicity. All references to ‘methane’ or ‘CH4’ should apply to the higher light hydrocarbons as well, although methane is the primary focus here.

The existence of solid hydrocarbons in source rocks is not new. They have been recognized by organic geochemists for decades. Generating gas from higher hydrocarbons necessarily generates a carbon deposit to balance hydrogen. It is the text-book explanation for the origin of pyrobitumens, for example, a ubiquitous organic mineral in sources rocks with H/C ratios ranging from about .5 to 1.6 [4]. Pyrobitumens are typically rich in transition metals [13,14] and have recently been cited for catalytic activity in methane generation [15]. Solid hydrocarbons have been proposed as catalysts resembling activated carbon in the decomposition of higher hydrocarbons to gas [16]. Solid hydrocarbon pools in this model can be pyrobitumens, or any other organic solid containing a catalyst that generate gas. They are both catalysts for generating methane and reservoirs for storing it.

Solid hydrocarbons are not uncommon in transition metal catalysis. The hydrogenation of carbon monoxide to methane over nickel, ‘methanation’, is an outstanding example [17]. The intermediates to methane are distributed in pools of solid hydrocarbons associated with nickel. The nature of the carbon polymer in methanation is unclear except that it is a co-catalyst, it is unsaturated in hydrogen and it is not graphite. It is like the carbon pool proposed here, some carbon polymer between saturate hydrocarbon CH3 and graphite CH0. The activated carbon suggested by Alexander et al. [16] in the catalytic generation of natural gas is another relevant example.

How the proposed equilibrium reaction might proceed mechanistically is discussed in Gas-Solid Equilibrium Kinetic Simulations, below. We are only concerned here with overall conversion. Methane generation feeds carbon into a pool of hydrogen-unsaturated carbon, into pyrobitumens, for example.

Since source rocks possess natural catalytic activity and generate catalytic gas in the laboratory [11], we shall assume that natural methane is catalytically generated and that the catalyst resides in pools of solid hydrocarbons. Because most catalytic reactions are reversible and approach equilibrium over time, we also assume that methane generation is reversible and should bring methane and solid hydrocarbons into equilibrium over time.

Reaction (2) illustrates a general equilibrium between methane and solid hydrocarbons.

\[ x\text{CH}_4 + \text{CH}_x \leftrightarrow C_{x+1+4x} + H_2 \]  

There is a 46% mass difference in methane equivalents between a solid hydrocarbons with compositions CH0.5 and CH1.6, for example, a typical range for pyrobitumens [4]. Thus, CH0.5 can consume 46% of its mass in methane generating CH1.6 if methane exists in equilibrium with solid hydrocarbon.

However, there is nothing to suggest that methane actually reacts with solid hydrocarbons generating new compounds. It is not enough that methane merely dissolves in CHx. In that case, x in reaction (2) would be insignificant and the equilibrium in (2) meaningless.

The proposed equilibrium is purely hypothetical, but testable. Do solid hydrocarbons in source rocks consume extraordinary amounts of light hydrocarbons in ways distinguishable from simple adsorption and solution?

**Light Hydrocarbon Ingestion** - The experimental challenge is to distinguish gas addition to the solid hydrocarbons in source rocks from classical gas addition to ordinary solid hydrocarbons. There are several classical ways light hydrocarbons can add to heterogeneous materials like source rocks. They can be adsorbed on surfaces, go into liquid solutions, or into polymer solutions, for example. There is no chemical change in adsorption and solution, however. They are first-order reactions in which rates of addition are proportional to concentrations: Rate = k[X], where (X) is the concentration of free hydrocarbon X and k is the first-order rate constant. Because hydrocarbons do not compete for surface sites or positions in solution, transfer rates and solubilities are typically independent of
other hydrocarbons. Butane has about the same water solubility in helium as it has in methane, for example [18].

Assume that hydrocarbons add to the solid hydrocarbons in source rocks differently. Hydrocarbon X adds to some receptor \([\ldots]\) generating the adduct \([X]\), a process referred to here as ‘ingestion’. X disappears by second-order kinetics at rates proportional to X and \([\ldots]\): \[\text{Rate} = k^X(X)^{[\ldots]}\]. However, in contrast to adsorption and solution, hydrocarbons are mere solvents, hydrocarbon X will go into solid-solution at rates proportional to concentrations independent of other hydrocarbons. X reacts with \([\ldots]\) generating the adduct \([X]\), a process referred to here as ‘ingestion’. X disappears by second-order kinetics at rates proportional to X and \([\ldots]\)

Do hydrocarbons compete in their addition to solid hydrocarbons?

To put this question to experimental test, two vials were charged with identical amounts of Mowry Shale and an equal molar mixture of ethane, propane, iso-butane and n-butane \((C_2-C_4)\). Both vials were heated at 75°C for 200 hours. One (Vial A) was diluted with argon by 50% five times over the 200 hours and the other (Vial B) was diluted with equal amounts of methane five times. The only difference in the two reactions was dilutions with argon in one (Vial A) and dilutions with methane in the other (Vial B). Thus, \(C_2-C_4\) gas concentrations in each vial diminished equally with each argon and methane dilution. Concentrations over time should be about the same in A and B if Mowry Shale is passive and only removes \(C_2-C_4\) hydrocarbons by adsorption or solution. If it removes them by ingestion, and \(C_1-C_4\) hydrocarbons compete for \([\ldots]\), \(C_2-C_4\) concentrations in Vial A should fall progressively below those in Vial B.

Another vial (C) was charged with beach sand with a thin coating of n-octadecane (~ 1%) to assess adsorption and solution or ingestion. The only difference in the two reactions was dilutions with argon (Vial A) or methane (Vial B & C) or argon (Vial A). 2 ml. gas was removed and analyzed 5 times over 200 hours and replaced with argon (Vial A), or methane (Vials B & C). Concentrations are gas concentrations in the vials prior to each dilution calculated from the concentrations in the 2 ml. samples removed with each dilution.

**Table 1 Hydrocarbon ingestion, Mowry Shale, 75°C, 200 hours**

| VIAL A | Weight Concentrations in 200 hours | 1 | 2 | 3 | 4 | 5 | 6 |
|--------|-----------------------------------|---|---|---|---|---|---|
| \(\mu g\ C_2/g\) | 83.993 | 13.629 | 4.720 | 1.239 | 0.114 | 0.028 |
| \(\mu g\ C_3/g\) | 101.548 | 11.542 | 3.113 | 0.693 | 0.036 | 0.010 |
| \(\mu g\ IC_4/g\) | 124.533 | 13.942 | 4.059 | 1.032 | 0.065 | 0.020 |
| \(\mu g\ nC_4/g\) | 86.679 | 4.290 | 1.051 | 0.184 | 0.007 | 0.007 |

| VIAL B | Weight Concentrations in 200 hours | 1 | 2 | 3 | 4 | 5 | 6 |
|--------|-----------------------------------|---|---|---|---|---|---|
| \(\mu g\ C_2/g\) | 69.046 | 32.556 | 8.803 | 5.489 | 2.623 | 1.595 |
| \(\mu g\ C_3/g\) | 93.766 | 44.174 | 12.430 | 7.606 | 3.249 | 1.558 |
| \(\mu g\ IC_4/g\) | 119.893 | 59.328 | 19.538 | 12.789 | 5.971 | 3.032 |
| \(\mu g\ nC_4/g\) | 114.537 | 57.104 | 17.266 | 11.075 | 5.403 | 2.734 |

| VIAL C | Percent wt Compositions in \(C_2-C_4\) over time | 1 | 2 | 3 | 4 | 5 |
|--------|-----------------------------------------------|---|---|---|---|
| \(\%\ C_2/g\) | 21.17 | 31.40 | 36.47 | 39.36 | 51.16 |
| \(\%\ C_3/g\) | 25.59 | 26.59 | 24.05 | 22.00 | 16.12 |
| \(\%\ IC_4/g\) | 31.39 | 32.12 | 31.36 | 32.80 | 29.38 |
| \(\%\ nC_4/g\) | 21.85 | 9.88 | 8.12 | 5.83 | 3.34 |

| VIAL B | Percent wt Compositions in \(C_2-C_4\) over time | 1 | 2 | 3 | 4 | 5 |
|--------|-----------------------------------------------|---|---|---|---|
| \(\%\ C_2/g\) | 17.38 | 16.85 | 15.17 | 14.85 | 15.21 |
| \(\%\ C_3/g\) | 23.60 | 22.87 | 21.42 | 20.58 | 18.84 |
| \(\%\ IC_4/g\) | 30.18 | 30.71 | 33.66 | 34.60 | 34.62 |
| \(\%\ nC_4/g\) | 28.83 | 29.56 | 29.75 | 29.96 | 31.33 |

| VIAL C | Percent wt Compositions in \(C_2-C_4\) over time | 1 | 2 | 3 | 4 | 5 |
|--------|-----------------------------------------------|---|---|---|---|
| \(\%\ C_2/g\) | 17.03 | 18.05 | 33.59 | 34.52 | 34.79 |
| \(\%\ C_3/g\) | 23.88 | 24.15 | 28.26 | 27.76 | 26.54 |
| \(\%\ IC_4/g\) | 30.67 | 30.41 | 29.62 | 29.43 | 29.48 |
| \(\%\ nC_4/g\) | 28.42 | 27.39 | 8.52 | 8.29 | 9.19 |

Sample preparation and experimental procedures are described elsewhere [10]. Each 5 ml. vial was charged with 1 g shale and gas composed of a 2 ml. mixture of ethane, propane, isobutane, and n-butane, equal volumes, and about 2 ml. of either methane (Vials B & C) or argon (Vial A). 2 ml. gas was removed and analyzed 5 times over 200 hours and replaced with argon (Vial A), or methane (Vials B & C). Concentrations are gas concentrations in the vials prior to each dilution calculated from the concentrations in the 2 ml. samples removed with each dilution.

Consistent with sequential 50% dilutions, but composition of \(C_2-C_4\) remains essentially constant over time (Table 1B). The blue line passing through the B data is not the regression line for that data. It is the dilution line indicating where the data should plot if only dilution were lowering n-butane gas concentrations. Hydrocarbon concentrations in A fall sharply below the blue dilution line progressing to zero over time signaling almost total ingestion. Moreover,
n-butane was selectively withdrawn from Vial A. Percent n-butane (C₂-C₄) fell sharply in A and remained essentially constant in B (Figure 2). Concentrations at termination were 16 μg g⁻¹ in B and 0.064 μg g⁻¹ in A, a 250-fold difference.

C₂-C₄ concentrations in Vial C fell over time proportional to their molecular weights consistent with solution in n-octadecane. The ratio of iso-butane/n-butane approached equilibrium (~3 at 75°C) consistent with acid-catalyzed isomerization promoted by the mild acidity of beach sand [19]. The equivalent reaction in Vial B showed no change in iso-butane/n-butane, or in the composition of C₂-C₄. Thus, Mowry Shale in B showed no evidence of isomerization activity or adsorption under the reaction conditions.

We conclude from this that the solubility of hydrocarbons in Mowry Shale by solution in liquid and solid hydrocarbons is relatively insignificant under these conditions.

Mowry Shale in argon thus consumed C₂-C₄ hydrocarbons vigorously and selectively at 75°C over 200 hours. The same shale in methane totally rejected the same C₂-C₄ hydrocarbons under the same conditions.

**Methane ingestion:** Fayetteville Shale was exposed to nine sequential cycles of methane pressurization and exhaustion at 100°C. Vessels filled with shale were pressurized (450 psi), sealed, and slowly vented. The shale released only trace amounts of C₂ and higher hydrocarbons during exhaustion. There was no evidence of free methane in the shale after these experiments. Heating vented samples in Argon at 100°C produced only trace amounts of methane and higher hydrocarbons, substantially less than the original sample.

Methane was indeed consumed by Fayetteville Shale, but not as free methane. It appeared in the solid hydrocarbons, in the Rock-Eval S2 peak, not in the free hydrocarbon S1 peak (Figure 3 and Table 2). Remarkably, the shale returned to its original Rock-Eval composition when exposed to the same exhaustion experiments in 2% methane. Thus, the solid S2 hydrocarbons in Fayetteville Shale had increased in
Table 2 Rock-Eval analysis of Fayetteville Shale before and after exposure to methane 450 psi, 100°C

| Samples | S1 | S2 | S3 | TOC | Tmax |
|---------|----|----|----|-----|------|
| Starting | 4.2 | 8.3 | 0.27 | 3.35 | 446 |
| 100% CH₄ | 3.67 | 12.45 | 0.28 | 3.69 | 443 |
| 2% CH₄ | 3.56 | 7.97 | 0.25 | 3.35 | 443 |

Shale was prepared for analysis by grinding in argon to 60 mesh. Three aliquots were treated as follows: Aliquot 1: analyzed directly by Rock-Eval. Aliquot 2: Rock-Eval analysis after 9 exposures to methane (450 psi, 100°C, 10 min.). Aliquot 3: Rock-Eval analysis after 9 exposures to methane (450 psi, 100°C, 10 min.) followed by 5 exposures to 2% methane in helium (450 psi, 100°C, 10 min.). Samples in sealed brass containers were pressurized to 450 psi at 100°C for 10 minutes in each exposure, and slowly vented (1 minute) to atmospheric pressure. Samples showed no evidence of adsorbed methane after sequential exposures to methane; standard gc analysis: 1 g shale in 5 ml Ar, 100°C, 1 hr. S1 = mg g⁻¹ volatile hydrocarbons, < 300°C; S2 = mg g⁻¹ solid hydrocarbon cracking, 350 – 550°C; S3 = mg CO₂ g⁻¹; TOC = % organic carbon. Values of starting shale are averages of triplicate analyses with sd: S1 ± 0.3; S2 ± 0.3; TOC ± 1.4; TMAX ± 3. Values for products are single analyses, although one (100% CH₄) was verified in a second analysis.

A hydrogen balance is ignored throughout this scheme. All hydrocarbons in brackets are unsaturated, CₙH₂ₙ₊₂, and those in parentheses are saturated, CₙH₂n+2. Thus, reaction (3) is hydrogen neutral. Reaction (4), however, is not, and should be ([Cₙ] + H₂ = (Cₙ) + [⋯]) [10]. We assume for simplicity that hydrogen is in excess and that it moves easily from the pool to [Cₙ] generating (Cₙ) and from (Cₙ) to the pool generating [Cₙ]

Reactions (3) and (4) are within a closed system, a sealed source rock, for example. Gas escapes confinement through reaction (5).

\[(Cₙ) \rightarrow (Cₓ)\] (5)

Reaction (6) summarizes the kinetic steps interconverting free gas and solid-state gas as symbolized by [Cₙ] and [Cₓ].

\[[Cₙ] + [⋯] \leftrightarrow [Cₓ] \leftrightarrow (Cₓ) + [⋯]\] (6)

The rate of [Cₙ] generation is proportional to [⋯]* [Cₙ]. Because [Cₙ] is constant and [⋯] becomes constant over time (steady-state), the rate of gas generation from solid hydrocarbon is constant over time. It will continue generating [Cₙ] and free gas (Cₓ) until their concentrations become sufficiently high to promote reverse reactions at rates equal to forward reactions. At that point, reaction (6) is at steady-state (equilibrium). (Cₓ) and [Cₓ] are then at their maximum concentrations, and [⋯] is at its minimum concentration. This is the state of a sealed (closed) source rock in the subsurface. We are interested in the dynamics of that system when the rock is opened, and reaction (5) is significant. How will (Cₓ) decline over time when the system is at equilibrium and the rate of reaction (5) exceeds the rate of generation (reaction 3)?

Three possibilities are considered in the following kinetic simulations. The first is classical first-order expulsion without generation or equilibrium of any kind. The kinetic model thus contains only free, in-place gas (Cₓ). [Cₙ] and [Cₓ] are at equilibrium, and after gas generation does not attend gas release, in other words. In the third, reaction (6) is fully operative, two reservoirs of gas, [Cₙ] and (Cₓ), at equilibrium, are depleted while [Cₓ] is generated at a constant rate from [Cₙ].

Each possibility is treated assuming equal rate constants and equivalent intermediate concentrations. Figure 4 displays a schematic of the reactions used in the kinetic simulations. A small fraction of gas in reservoir A was removed by first-order kinetics in each iteration, \(Δ(Cₙ) = (0.2*(Cₙ))\), and all other concentrations altered accordingly as described in Figure 3. Thus, \(Δ(Cₙ)\) over iterations simulates expulsion rates over time. \(Δ(Cₙ)\) is henceforth referred to as ‘rate’ denoted R and iteration as ‘time’ (t). Figure 5 shows the decline curves, R vs. t, for three hypothetical rocks. In the first (no catalytic activity) R
declines exponentially (ED) as expected, thus describing the straight line on log scale. In the equilibrium models, R declines by double exponential decay (DED) without generation and by double exponential decay with a constant (DED1) with generation, (equation 7), where \( R_t \) is the expulsion rate at time \( t \), \( R_i \) is the initial expulsion rate for free gas \([C_x]\), \([R]\)i is the initial expulsion rate for solid hydrocarbon gas \([C_x]\), and \( C \) is the constant for rate of generation from \([C_n]\).

\[
R_t = (R)_i e^{-at} + [R]_i e^{-bt} + C
\]  

(7)

Figure 6 shows DED1 curves with different values of \( C \) reflecting different levels of generation attending production. Therefore, rates of production from source rocks releasing gas in equilibrium (reaction 6) should decline by DED1 reflecting free gas declining exponentially, solid-state gas declining exponentially, and generated gas at a constant rate \( C \).
equation line to the data. Showing the theoretical curve superimposed on field data in this way illustrates the remarkable fit between theory and field data. Regressing Miller Heirs data to DED1 gives an exact fit ($R^2 = 0.99$), while regressing the data to single exponential decay gives a substantially poorer fit, $R^2 = 0.84$. The constant $C$ in the DED1 regression equation was significant throughout production, accounting for 37% of produced gas at 25 months.

Regressing the same data to double exponential decay without a constant ($C = 0$) (DED) between 0 and 50 months gives an equally strong correlation ($R^2 = 0.99$), however. It is therefore impossible to evaluate the constant $C$ from the data fit to DED1 in Figure 7. If the data has genuine linearity – two sources of gas declining exponentially and one constant - then any DED equation that fits the data between time 0 and $n$ will necessarily underestimate the data beyond $n$. The DED line will fall exponentially while the data approaches the constant $C$. Therefore, the test for linearity ($C$) lies beyond $n$, where the respective regression curves predict the future.

The Miller Heirs data were regressed between times 0 and 50 months by DED and DED1. The two regressions gave similar curves with high degrees of correlation to the data between these time limits ($R^2 > 0.99$). However, only the DED1 equation predicts the Miller Heirs data beyond 50 months (Figure 8). The DED line fall sharply below the Miller Heirs data. It projects exponential decline while the data describes a largely linear rate of decline beyond 50 months. Figure 8 leaves little doubt about the dimensions of decline in this well. There are clearly three, and DED1 (eq. 9) describes them very well. DED1 is thus a property of Miller Heirs production data and the gas-solid hydrocarbon equilibrium model as Figure 7 so clearly illustrates.

A New light hydrocarbon generation model

Few question the biological pedigree of higher hydrocarbons (biomarkers) in petroleum [3,4]. Their carbon structures are precise fits to the carbon skeletons of bio-precursors. Light hydrocarbons between $C_1$ and about $C_{10}$ are different. They do not resemble biological parents [25], and they display distinctive patterns in composition not seen in the higher hydrocarbons. Methane through butane ($C_1$-$C_4$) are constrained to thermodynamic equilibrium [7,10] and the hexanes and heptanes ($C_6$-$C_7$) display invariant compositions [26,27], for example. A proportionality between ($n$-$C_{n+1}$-$C_7$) and ($n$-$C_{n+1}$-$C_6$), perhaps the highest correlation yet reported for hydrocarbons in crude oils ($R^2 = 0.99$), illustrates their extraordinary compositional order [27].

It is in this context that methane-solid hydrocarbon equilibrium must be weighed. With methane in equilibrium with ethane and propane [7], it should come as no surprise that it would be in equilibrium with the solid hydrocarbons generating it. In fact, there is a strong possibility that all light hydrocarbons form along the same path, with light hydrocarbons and solid hydrocarbons at equilibrium. It is illustrated in a new model for light hydrocarbon generation presented here. The model unifies otherwise disparate elements of light hydrocarbon chemistry: natural gas at thermodynamic equilibrium, invariance in the higher
light hydrocarbons, ingestion, and gas generation during production. It does this by bringing light hydrocarbons and solid hydrocarbons into equilibrium through catalytic intermediates \([C_x]\) and \([\cdots]\):

\[ [C_n] + [\cdots] \leftrightarrow [C_x] \leftrightarrow C_x + [\cdots] \]

\([C_x]\) represents the intermediate shaping product structures and compositions. Metathesis of \([C_x]\) brings \(C_1\) to \(C_4\) to equilibrium \([10]\) and molecular rearrangements of \([C_n]\) bring \(C_5\) to \(C_7\) isomers to invariance \([26,27]\). Ingestion, which links methane to \([C_x]\) and thus to solid hydrocarbons, is the critical step in the proposed methane-solid hydrocarbon equilibrium. Mowry and Fayetteville Shales ingest light hydrocarbons in substantial amounts and with high selectivity. Mowry Shale in argon with open receptors ingest \(C_2-C_4\) hydrocarbons vigorously, and the same shale in methane with pacified receptors totally rejects the same hydrocarbons under the same conditions (Figures 1 and 2). Generation and storage is expressed in the model through:

\[ [C_n] + [\cdots] \leftrightarrow [C_x] \leftrightarrow C_x + [\cdots] \]

It accounts for the linearity in double exponential decay decline curves (Figures 7 & 8). Thus, each component of the general equilibrium model has empirical support.

Most catalytic reactions are reversible, and approach thermodynamic equilibrium over time (residence time). It therefore follows that \(C_1-C_4\) hydrocarbons residing in closed source rocks over geologic time will be at molecular and isotopic thermodynamic equilibrium, and steady state with respect to compositional change. However, once the rock is opened and old hydrocarbons escape, new hydrocarbons will be generated and their residence times can be on the order of hours. \(C_1-C_4\) could then be removed from equilibrium and the \(C_6\) and \(C_7\) hydrocarbons, typically constrained to constant compositions including metastable equilibria \([26-28]\), displaced from these compositions as well. In other words, molecular and isotopic compositions of hydrocarbons generated at steady state can be distinct from hydrocarbons generated at pre-steady state. Our research has focused on hydrocarbons generated at steady state over geologic time. There is less know about pre-steady state because there have been fewer opportunities to find and analyze pre-steady state products. However, we have encountered oils from conventional reservoirs with bizarre \(C_6\) and \(C_7\) distributions consistent with pre-steady state kinetics at the onset of oil generation \([29]\).

Unconventional production from source rocks offers opportunities for finding similar pre-steady state hydrocarbons. Compositions could transition between states in early production, capturing molecular and isotopic biases only rarely seen in conventional reservoirs. The laboratory for finding evidence that transition is in the field, from wells producing oil and gas from source rocks, where the transition might be captured and analyzed.

**Conclusions**

Production rates declining by DED1 is not in itself significant. But, the coincidence of theory and data in Figure 6 is. It implicates gas-solid hydrocarbon equilibria in the production of gas from Fayetteville Shale.

Ingestion gives the hypothesis additional and independent support. First, it is unprecedented. Light hydrocarbons react with solid hydrocarbons in source rocks under conditions where they do not react with ordinary solid hydrocarbons. Methane, perhaps the least reactive hydrocarbon known, disappears in Fayetteville Shale at 100°C leaving no trace of \(CH_4\). It does not emerge in RockEval analysis in the S1 peak at 300°C, but later as some higher hydrocarbon in the S2 peak at 443°C (Table 2). Methane thus becomes part of the solid hydrocarbon ingesting it: \(C_1 + [\cdots] \rightarrow [C_x]\). The reactions between \(C_1-C_4\) hydrocarbons and Mowry Shale at 70°C are equally striking. Adamantanes, like methane in thermal stability and reactivity, become highly reactive on carbon surfaces \([30]\). Solid hydrocarbons in source rocks are not ordinary hydrocarbons. They possess receptors, perhaps catalytic, that react with light hydrocarbons at low temperatures generating solid hydrocarbons of greater mass. The Miller Heirs field data and the ingestion results reported here make a substantial case for methane and solid hydrocarbons in equilibrium in source rocks. The fact that a general equilibrium also accounts for other properties of light hydrocarbons - natural gas at thermodynamic equilibrium and higher hydrocarbons in constant compositions – makes that case even stronger. The capacity of solid hydrocarbons to ingest gas reported here raises the possibility of substantially more gas in shales than analytically apparent, and far more gas in shale deposits than currently recognized.

Only the question of reversibility and perhaps generation remain. Catalysis would seem a given since methane could not react with solid hydrocarbon at 70°C (Table 1) without catalytic assistance. It is, in my view, extremely unlikely that methane could be found in equilibrium with ethane and propane in reservoir rocks \([7]\) and not have been in equilibrium with solid hydrocarbons in source rocks. The Miller Heirs production curve in Figure 7 suggests that it is and that gas generated from solid hydrocarbons sustains production over time (Figure 8). That possibility becomes near certainty should hydrocarbons produced from source rocks transition from steady state to pre-steady state and those produced from conventional reservoirs do not.

**Competing interests**

The author declares that there are no competing interests.

**Acknowledgements**

Author thanks Petroleum Habitats and Worldwide Geochemistry for their generous support.

Received: 4 June 2013 Accepted: 5 December 2013

Published: 12 December 2013
References

1. Evans CR, Rogers MA, Bailey NJL: Evolution and alteration of petroleum in western Canada. Chem Geol 1971, 8:147–170.
2. McNab JG, Smith PV, Betts RL: The evolution of petroleum. Petrol Eng Chem 1952, 44:2556–2563.
3. Tissot BP, Welte DH: Petroleum Formation and Occurrence. New York: Springer, 1984.
4. Hunt JM: Petroleum Geochemistry and Geology. New York: Freeman, 1995.
5. Mango FD: The stability of hydrocarbons under time-temperature conditions of petroleum genesis. Nature 1991, 352:146–148.
6. Mango FD: Methane concentrations in natural gas: the genetic implications. Org Geochem 2001, 32:1283–1287.
7. Mango FD: Natural gas at thermodynamic equilibrium: implications for the origin of natural gas. Geochim Trans 2009, 10:6.
8. Mango FD: Low-temperature gas generation from marine shales. Geochim Trans 2009, 10:3.
9. Mango FD, Jarvie DM: The low-temperature catalytic path to natural gas: wet gas to dry gas over experimental time. Geochim Trans 2009, 10:10.
10. Mango FD, Jarvie DM: Metathesis in the generation of low-temperature gas in marine shales. Geochim Trans 2010, 11:1.
11. Mango FD, Jarvie DM, Herriman E: Natural catalytic activity in a marine shale for generating natural gas. Proc Roy Soc A 2010, 466:3527–3537.
12. Lewan MD, Korarba MJ, Wueckaw D, Iestrzynski A: Evaluating transition-metal catalysis in gas generation from Permian Kupferscheifer by hydrous pyrolysis. Geochim Cosmochim Acta 2008, 72:4069–4093.
13. Parnell J: Native platinum in pyrobitumen from Fonda, New York. Am Mineral 1988, 73:1170–1171.
14. Yen TF: Chemical aspects of metals in native petroleum. In The Role of Trace Metals in Petroleum. Ann Arbor MI: Ann Arbor Science Publishers Inc; 1975:1–30.
15. Pan C, Jiang L, Liu J, Zhang S, Zhu G: The effects of pyrobitumen on oil cracking in confined pyrolysis experiments. Org Geochem 2012, 45:29–47.
16. Alexander R, Berwick LJ, Pierce K: Single carbon surface reactions of 1-octadecene and 2,3,6-trimethylphenol on activated carbon: implications for methane formation in sediments. Org Geochem 2011, 42:540–547.
17. Somorjai GA: Introduction to Surface Chemistry and Catalysis. New York: John Wiley & Sons; 1994:489.
18. Plambeck JA: Introductory University Chemistry (Solutions and Solubility of Gases. 2013. www.chem.ualberta.ca/courses/plambeck/p101/pou82.htm.
19. Pines H: The Chemistry of Catalytic Hydrocarbon Conversions. New York: Academic; 1981:6.
20. Arps JJ: Analysis of decline curves. Trans AIME 1945, 160:228–247.
21. Raghavan R: Behavior of wells completed in multiple producing zones: SPEFE; 1989:219–230.
22. Ferkovich MJ, Works AM, Thrasher TS, Bradley MO: Depletion performance of layered reservoirs without crossflow: SPEFE. 1990.
23. Ilk D, Rushing JA, Perego AD, Blasingame TA: Exponential vs. hyperbolic decline in tight gas sands – Understanding the origin and implications for reserve estimates using Arps’ decline curves, paper SPE 116731 presented 2008 Annual Technical Conference & Exhibition, Denver, CO. 2008.
24. Valko PP, Lee J: A better way to forecast production from unconventional gas wells, paper SPE 134231 presented 2010 Annual Technical Conference & Exhibition, Florence, Italy. 2010.
25. Mango FD: The light hydrocarbons in petroleum: a critical review. Org Geochem 1997, 26:417–440.
26. Mango FD: An invariance in the isoheptanes of petroleum. Science 1987, 237:514–517.
27. Mango FD: The origin of light hydrocarbons. Geochim Cosmochim Acta 2000, 64:1265–1277.
28. Helgeson HC, Knox AM, Owens CE, Shock EI: Petroleum oil field waters, and authigenic mineral assemblages: are they in metastable equilibrium in hydrocarbon reservoirs. Geochim Cosmochim Acta 1993, 57:3295–3339.
29. Mango FD: Pre-steady state kinetics at the onset of oil generation. Org Geochem 1990, 16:41–48.
30. Berwick L, Alexander R, Pierce K: Formation and reactions of alkyl adamantanes in sediments: carbon surface reactions. Org Geochem 2011, 42:752–761.