**Geochemistry Seals the Deal: Data to Support Your Ideas***

Chris Laughrey¹

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¹Weatherford Laboratories, Golden, Colorado (christopher.laughrey@WeatherfordLabs.com)

Abstract

This presentation provides a brief survey and review of the principal tools of petroleum geochemistry and suggests how they can be integrated with geology, geophysics, and petroleum engineering to reduce risk in petroleum exploration and development. This review is followed by the presentation of selected examples of recent data that illustrate 1) the interpretive resolution of conflicting data, 2) challenges to popular emerging paradigms regarding organic porosity, kerogen types, and thermal maturity, and 3) new ideas concerning productive hydrocarbon floors in deep basin settings.

Selected References


Jarvie, D.M., J.D. Burgess, A. Morelos, R.K. Olson, P.A. Mariotti, and R. Lindsey, 2001, Permian Basin petroleum systems investigations: Inferences from oil geochemistry and source rocks: AAPG Midcontinent Section Meeting, Amarillo, Texas:


Also referenced

Geochemistry Seals the Deal

Data to support your ideas

Christopher D. Laughrey
christopher.laughrey@WeatherfordLabs.com
How this deal was sealed...

Data to support your ideas...
Petroleum geochemistry is the application of chemical principals to the study of the origin, migration, accumulation, and alteration of petroleum (oil and gas) and the use of this knowledge in exploring for and recovering petroleum (Hunt, 1996).

This presentation:

- Briefly survey and review the principal tools of petroleum geochemistry and state how they can be integrated with geology, geophysics, and petroleum engineering to reduce risk in petroleum exploration and development.
- Present selected examples of recent data that illustrate:
  1) the interpretive resolution of conflicting results;
  2) new ideas concerning productive hydrocarbon floors in deep basin settings.
Exploration Risk (Hunt, 1996)

- The probability of spending exploration funds without economic success.
- Reducing risk depends on finding a *trap* and on determining how high the probability is that petroleum has migrated from a *mature source rock* into that trap and has not escaped or been destroyed.
- Successful exploration depends upon:
  - The existence of a trap (structure, reservoir, seal)
  - The accumulation of a petroleum charge (source, maturation, migration to the trap, timing)
  - Preservation of the entrapped petroleum (thermal history, meteoric water invasion)
- The probability of success is the product of the probabilities of all three of these factors.
Essential Elements and Processes of a Petroleum System

• **Essential Elements:**
  - A *petroleum source rock*
  - A petroleum reservoir rock
  - A seal rock
  - An overburden rock

• **Essential Processes:**
  - Trap formation
  - *Generation, migration, and accumulation of petroleum*
The Geochemist’s Toolbox

Basic methods for assessing source rocks

- Direct TOC measurement
- Indirect TOC measurement:
  - Geophysical approach
- Microscopy techniques:
  - The nature of organic matter – macerals and associated minerals
  - Fluorescence microscopy and the quality/thermal maturity of organic matter
  - Vitrinite reflectance and thermal maturity
  - Scanning electron microscopy and organic porosity
- Programmed pyrolysis:
  - Rock-Eval
  - New instruments

Characterization of oil and gas: the geochemical approach

- Hydrocarbons
- NSO compounds
- Molecular fossils (biomarkers)
- Advanced analytical procedures:
  - The SARA separation
  - Gas chromatography
  - Gas chromatography – Mass spectroscopy
  - Isotope analysis
  - Source rock kinetics
  - Hydrous pyrolysis
Essential Elements: The Petroleum Source Rock

Initial Screening

- Organic richness (quantity):
  - Generative potential
- Type of organic matter and expected product (quality):
  - Kerogen type
- Thermal maturity:
  - Maturation
  - Generation

Detailed studies

- Advanced organic matter typing and thermal maturity assessment
- Problem solving for conflicting geochemical screening data
- Oil – oil and oil – source correlations
- Gas – source correlations
- Kinetics
Initial Screening

Generative Potential

WOODFORD: TOC = 2.22 – 11.3; S1 = 1.7 – 10; S2 = 3.3 – 21.4

12,750 TOC wt.%

S1 mg/g

(S1/TOC) 100 = 28 - 143

12,960

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Initial Screening

Kerogen Type and Expelled Product

WOODFORD: HI = 129 – 215; Mean OI = 3.2

- 82 – 96 % Liptinite
- 1 – 11% SHC
- 2 – 4% Inertinite
- 1 – 4% Vitrinite

Burruss and Hatch, 1989

Kerogen Type and Expelled Product

WOODFORD: HI = 129 – 215; Tmax = 441° - 461°C

- Immature
- Type I: oil-prone, usually lacustrine
- Type II: oil-prone, usually marine
- Type III: gas-prone
- Postmature

Dry Gas Window

Oil Window

Coalslate - Wet Gas Zone

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Thoughts on Kerogen “Types”

- For practical purposes kerogens are classified into so-called “types” that reflect their elemental composition (H/C, O/C, and S/C atomic ratios) when they are immature.
- Historically three “types” are defined according to specific reference series:
  - TYPE I: Eocene Green River Formation, Utah, USA
  - TYPE II: Lower Toarcian shales of western Europe
  - Type III: Miocene of the Mahakam delta, Indonesia
- Based on this classification, a kerogen is assigned to a type by matching its location on a Van Krevelen diagram with these three reference series.
- “The commonly accepted relationship between Type I and lacustrine kerogen, Type II and marine kerogen, and Type III and land plant kerogen may be misleading and should only be used as a practical guideline rather than a deterministic rule” (Huc, 2013, p.73).
Initial Screening

Thermal Maturity

WOODFORD: HI = 129 – 215; Ro = 0.77 - 1.14% (av. = 0.95%)

WOODFORD: PI = 0.13 – 0.48; Tmax = 441° - 461°C

VRo = 0.85 – 0.97%
%VR_{o(calculated)} = (0.0180)(T_{max}) – 7.16 \quad (Jarvie \ et \ al., \ 2001)

Weatherford T_{max} - R_{o} Correlation Woodford & Barnett in OK & TX

T_{max} - R_{o} correlation for Woodford and Barnett in Oklahoma and Texas Basins. All pyrolysis data on RE II; petrographers Wayne Knowles and Jack Burgess. Only samples with S2>0.5 mg/g and w/o spikes in pyrogram. The full form of the equation is:

\[ R_{o}(\%) = (0.01867 \pm 0.00063) \times T_{max} - (7.306 \pm 0.284). \]

based upon 245 Ro-Tmax pairs. Uncertainties are 1 sigma.
Initial Screening

- Reconstruction of original source-rock generative potential and hydrocarbon yields (see Peters and others, 2007):
  - The transformation ratio of the Woodford Shale in this well is 0.7866; 78.7% of the petroleum generation process is complete.
  - The original average TOC before generation and expulsion was 8.99%.
  - The estimated original mean S2 was 44.95 mg HC/g rock (984.4 bbls oil/acre-ft.)
  - The Woodford has generated 34.9 mg HC/g rock (764 bbls oil/acre-ft.)
  - Expulsion Efficiency = 85.8%
Initial Screening: Niobrara (PRB)

TOTAL OIL = (S1\text{whole} - S1\text{extracted}) + (S2\text{whole} - S2\text{extracted})

TOTAL OIL = (5.70 - 0.14) + (28.18 - 22.37)

TOTAL OIL = 11.07 mg oil/g rock (242.4 barrels of oil/acre-ft.)

See Jarvie, 2012
Initial Screening: Niobrara (PRB)

Total Oil = ($S_{1\text{whole rock}} - S_{1\text{extracted rock}}) + (S_{2\text{whole rock}} - S_{2\text{extracted rock}})$

- Jarvie, 2012
Bar graph of S1 and Total Oil values (y-axis in mg hydrocarbon/g rock) for 20 samples collected from the Niobrara Fm in PRB. S1 values are red. Total Oil samples are blue. S1 ranges from 0.74 to 6.85 mg hydrocarbon/g rock (16.2 to 150 bbls of oil/acre-ft.), and averages 3.85 mg hydrocarbon/g rock (84.3 bbl oil/acre-ft.). Total Oil ranges from 1.8 to 20.76 mg HC/g rock (39.4 to 455 barrels of oil/acre-ft.), and averages 9.07 mg HC/g rock (198.6 barrels of oil/acre-ft.).
Essential Processes: Petroleum Generation

1. Kerogen: Insoluble organic solid

2. Char/Pyrobitumen: Insoluble organic solid

3. Bitumen: Soluble organic tar

4. Crude Oil: Hydrocarbon-rich liquid

5. Natural Gas: Hydrocarbon-rich gas

6. Hydrogen Sulfide: Non-hydrocarbon-rich gas

Immature

Mature

Over mature

Courtesy Michael Lewan, USGS
Kerogen Type Determines Timing/Rates of Conversion

%Ro

0.40

0.60

0.75

0.95

1.10

1.30

1.50

0.40

0.60

0.75

0.95

1.10

1.30

1.50

Tmax (°C)

420

430

440

450

460

470

480

Type II-OS

Type II

Type III

Type I
Type I lacustrine kerogen

- TOC 4.84wt. %
- S1 = 5.08 mg HC/g rock
- S2 = 57.30 mg HC/g rock (1254.9 bbls oil/acre-ft.)
- Tmax = 451°C
- HI = 1184 28727.8
- PI = 0.08

MODEL USED: Gaussian
CALCULATED RESULTS USING 3.3°C/million years MODEL:
- COMPUTED ONSET (10% TR) TEMPERATURE (°C): 145
- COMPUTED ONSET (10% TR) %Ro VALUE: 0.90
- COMPUTED PEAK GENERATION TEMPERATURE (°C): 159
- COMPUTED PEAK GENERATION %Ro VALUE: 1.13
Source Rock Kinetics

Type II marine kerogen

- TOC = 4.37 wt. %
- S1 = 0.25 mg HC/g rock
- S2 = 33.06 mg HC/g rock (724 bbls oil/acre-ft.)
- T_{max} = 429°C
- HI = 756 mg/g TOC
- S2/S3 = 27.8
- PI = 0.01

MODEL USED: Gaussian

CALCULATED RESULTS USING 3.3°C/million years MODEL:
- COMPUTED ONSET (10% TR) TEMPERATURE (°C): 122
- COMPUTED ONSET (10% TR) %Ro VALUE: 0.70
- COMPUTED PEAK GENERATION TEMPERATURE (°C): 142
- COMPUTED PEAK GENERATION %Ro VALUE: 0.87
Essential Processes: Modeling Hydrocarbon Generation and Migration

KINETICS DATA GRAPHICAL REPORT SUMMARY

DISTRIBUTION OF ACTIVATION ENERGIES

TDC (%): 100
MODEL USED: Gaussian
CALCULATED RESULTS USING 3.3°C/million years MODEL:
- COMPUTED ONSET (10% TR) TEMPERATURE (°C): 122
- COMPUTED ONSET (10% TR) %Ro VALUE: 0.70
- COMPUTED PEAK GENERATION TEMPERATURE (°C): 142
- COMPUTED PEAK GENERATION %Ro VALUE: 0.87

Weatherford Labs
Pyrolysis Methods for Petroleum Generation

Rock-Eval
open-system w/o water

Micro Scale Sealed Vessel (MSSV)
closed-system w/o water

Hydrous Pyrolysis
closed-system w/ water

Courtesy Michael Lewan, USGS
Hydrous Pyrolysis and Rock-Eval/SRA Differences

Hydrous Pyrolysis
Expelled Oil

Rock Eval Pyrolysis
FID Volatiles

Generated Gas
Water

Oil
200 - 500g Crushed Source Rock (0.5 - 2.0 cm)

Carrier Gas
Volatilized HCs

To FID Detector

Electronic signal of volatilized hydrocarbons

S2

Time (min)

FID Response

20-50 mg Powdered Source Rock (< 25 μm)

Experimental Products

Courtesy Michael Lewan, USGS

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Product Composition

Natural System

Saturate HCs

100%

Hydrous Pyrolysis

Saturate HCs

100%

Aromatic HCs

100%

Polars (NSOs, resins + asphaltenes)

100%

Aromatic HCs

100%

Polars (NSOs, resins + asphaltenes)

100%

Crude Oil

Expelled Oil

Bitumen

Bitumen

Courtesy Michael Lewan, USGS
Essential Processes

Migration
- Primary migration (expulsion)
- Secondary migration
- Tertiary migration ("dysmigration")
- Drainage and migration patterns:
  - Lateral drainage
  - Vertical drainage
  - Tracking petroleum from source to trap: Molecular Descriptors

Accumulation
- Trap formation
- Reservoir in-filling history
- Compartments and permeability barriers
- In-reservoir bitumen
- Hydrocarbon alteration processes:
  - Biodegradation
  - Thermal cracking
  - TSR
  - Water washing
  - Evaporative fractionation and gas washing
  - Thermodynamic disequilibrium and deasphalting
Hydrogen Sulfide and Nitrogen in Trenton/Point Pleasant Reservoir, PA

- Wolpert #1 well, Bradford County, PA
  - 0.51 mole percent $\text{H}_2\text{S}$
  - 14.14 mole percent $\text{N}_2$
- Limits to deeper Ordovician gas?

From Patchen and others, 2007
What is the Source of the H₂S?

- δ³⁴S = 14.7 permil
- Stable isotope composition suggests a sulfate source for the H₂S:
  - Dissolved sulfate in brine
  - Anhydrite
- H₂S formed in the reservoir at high temperatures (> 140°C) through thermochemical sulfate reduction (TSR)
What is the Source of the Nitrogen?

- $\delta^{15}N_2 = 0.4$ permil
  - Deep crust or mantle source
  - Further constrained by noble gas data:
    - No fractionation due to diffusion
    - Highly mature organic matter source; possibly metamorphic

- Nitrogen concentration increased at the expense of hydrocarbons destroyed by TSR
Essential Processes: Accumulation

- Assessing reservoir fluid composition
- Production monitoring and allocation
- Flow insurance and organic deposits:
  - Asphaltenes
  - Pyrobitumen
  - Diamondoids
  - Paraffins
Selected Examples of Recent Data

• The interpretive resolution of conflicting laboratory results:
  – Thermal maturity interpretation – Niobrara Formation, DJ basin
  – Microbial and thermogenic gas – Colorado Group, Alberta

• New implications concerning productive hydrocarbon floors in deep basins – Marcellus Formation, Appalachian basin
Thermal Maturity Interpretation – Niobrara Formation, DJ Basin

T_{\text{max}} = 439^\circ C \text{ (early mature)}

VR_0 = 0.58\%

VR_0 = 0.87\%
Thermal Maturity Interpretation – Niobrara Formation, DJ Basin

\[ T_{\text{max}} = 438°C \] (early mature)

Primary alginite

Recycled alginite

FID Response
Thermal Maturity Interpretation – Niobrara Formation, DJ Basin

PRIMARY KEROGEN:
TAI of yellow to pale orange alga (arrow) = 2.5 – 2.6 ($VR_o$e $\sim$ 0.5 – 0.6%)
$T_{max} = 441^\circ C$ (RE6)

RECYCLED KEROGEN:
TAI of dark orange to light brown spore (arrow) = 2.7 – 2.9 ($VR_o$e $\sim$ 0.7 – 0.9%)
$T_{max} = 440^\circ C$ (RE6)
“...the essence of proper intelligence [is] the embrace of contradiction.” (Colum McCann, 2013)

 Thermal Maturity Interpretation – Niobrara Fm, D J Basin

$T_{\text{max}} = 430^\circ C$ (thermally immature with respect to oil generation)

Mean $VR_o = 0.92\%$

“And the recognition of complexity [is] to be balanced against the need for simplicity”
Microbial and Thermogenic Gases, Cretaceous Colorado Group, Alberta
Microbial and Thermogenic Gases, Cretaceous Colorado Group, Alberta

Average %R₀ = 0.38

Recycled/Oxid. Vitrinite
Microbial and Thermogenic Gases, Cretaceous Colorado Group, Alberta

Colorado shows residual structure and is, in this case, faulted due to the underlying channel.

Upper Mannville Channel shows substantial drape from differential compaction.
Productive Hydrocarbon Floors in Deep Basins

Approximate %VR_o = 3.0 in Pennsylvanian Strata (Levine and Davis, 1989): Marcellus “Line of Death”?
The Marcellus Formation in NE PA Produces Natural Gas From Post-Mature Marine Mudrocks

Conodont Alteration Index

From Repetski and others, 2008, USGS SI Map 3006
The Marcellus Formation in NE PA Produces Natural Gas From Post-Mature Marine Mudrocks

8850 ft. Mean VR_o = 4.60%

8250 ft. Mean VR_o = 4.61%:
Dark grey to black amorphous kerogen consistent with vitrinite reflectance data (ca. 4-5% Ro)

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Organic porosity

Late Mature: $V_{R_o} = 1.1\%$

Postmature: $V_{R_o} = 3.0\%$

Courtesy Bill Zagorski, Range Resources
Lower Marcellus Pressure Core: GIP = 329.03 scf/ton

CUMULATIVE DEGASSING VOLUME (% OF TOTAL)

1 ft. canister sample (9:57)

PC-2 canister (9:00 – 20:35)

Crushed sample gas

δ¹³C₁ of mud and production gases

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Production and Mud Gas Geochemistry

\[ \delta^{13}C_{\text{kerogen}} = -28.8\% \]
What must geoscientists understand about the geochemistry of petroleum?

- What is the composition of petroleum?
- How does it originate?
- How does it migrate in the subsurface?
- How does it change with depth, temperature, and pressure?
- How can we use such knowledge to help us find and produce commercial accumulations of petroleum?
What are the questions?

- Are petroleum source rocks present in the basin? If so, where?
- Are the potential source rocks oil or gas prone, or both?
  - What was the depositional environment of the source rock (e.g., deltaic or marine)?
  - Under what environmental conditions (salinity, water temperature and depth, redox conditions) were these rocks deposited?
- Has oil or gas been generated?
- Where was the petroleum generated?
- When was the petroleum generated?
- Where are the migration pathways for the oil and/or gas?
- Was the timing for migration optimum for entrapment, considering the basin’s depositional and structural history?

From Merrill, 1991, p. xiii
Questions...and time for lunch
Essential Reading


