Experimental Gas Extraction by Rock Crushing: Evidence for Preservation of Methane in Core Samples from the Mudstones of the Eagle Ford Formation and Barnett Shales*

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Abstract

Accurately determining oil-in-place (OIP) and gas-in-place (GIP) is critical for evaluating shale oil and gas plays. Methane is typically stored in nano-size pores in low permeability mudstones, but many of these hydrocarbon-saturated pores may isolate from surrounding mineral matrix. A rock crushing experiment has been devised to test for the presence of gas and condensate in isolated nanopores. We utilize a gas-tight rock crushing cell that can directly introduce released gas to a gas chromatograph after crushing. We have tested this method on mudstones of the Upper Cretaceous Eagle Ford Formation, an emerging oil/gas shale play in the Maverick Basin and the adjacent San Marcos Arch of South Texas.

Five core samples (depths: 4,758ft to 13,608 ft) were collected from the organic matter-rich lower Eagle Ford unit and used in our study. TOC content and Tmax values range from 1.8% to 8.5%, and 428°C to 543°C, respectively. Calculated Ro, based on Tmax, ranges from 0.5% to 2.6%. Hydrogen index (HI) ranges from 741mgHC/g TOC at Ro of 0.5% to 14 mgHC/g TOC at Ro > 1.6%. The large decrease in HI value with increasing thermal maturity results from the transformation of organic matter to oil and gas. CH_2Cl_2 extractable hydrocarbons show that the ratio of the sum of C_8-C_{14} to the sum of C_{15}-C_{32} increases with thermal maturity. The above geochemical observation clearly suggests that oil properties in the organic-rich lower Eagle Ford unit are closely related to thermal maturation of organic matter.

CH_4/CO_2 ratios of gases released during crushing are lower at low thermal maturities and higher at high maturities because more CH_4-rich gas is generated at high maturity levels. CH_4/CO_2 ratios decrease with longer rock crushing time because of the increase in the CO_2-rich adsorbed-gas contribution. Both thermal maturity and gas desorption contribute to changes in CH_4/CO_2 ratio of gas released from rock crushing. However, no obvious compositional fractionation occurs among C_1, C_2 and C_3 during rock crushing. C_1/C_2 and C_2/C_3 ratios remain constant through crushing but greatly increase when the level of thermal maturity is high. Geochemical parameters (C_1/C_2, iC_4/nC_4) of gas released during rock crushing are good indicators of thermal maturation of organic-rich shales. CH_4/CO_2 ratio is a good indicator of free gas and adsorbed gas contributions.

References

Pollastro, R.M., D.M. Jarvie, R.J. Hill, and C.W. Adams, 2007, Geologic framework of the Mississippian Barnett Shale, Barnett-Paleozoic total petroleum system, Bend Arch-Fort Worth Basin, Texas: AAPG Bulletin, v. 91/4, p. 405-436.

Tissot, B.P., and D.H. Welte, 1978, Petroleum formation and occurrence: A new approach to oil and gas exploration: Springer-Verlag, Berlin, Germany, 553 p.

Experimental Gas Extraction by Rock Crushing

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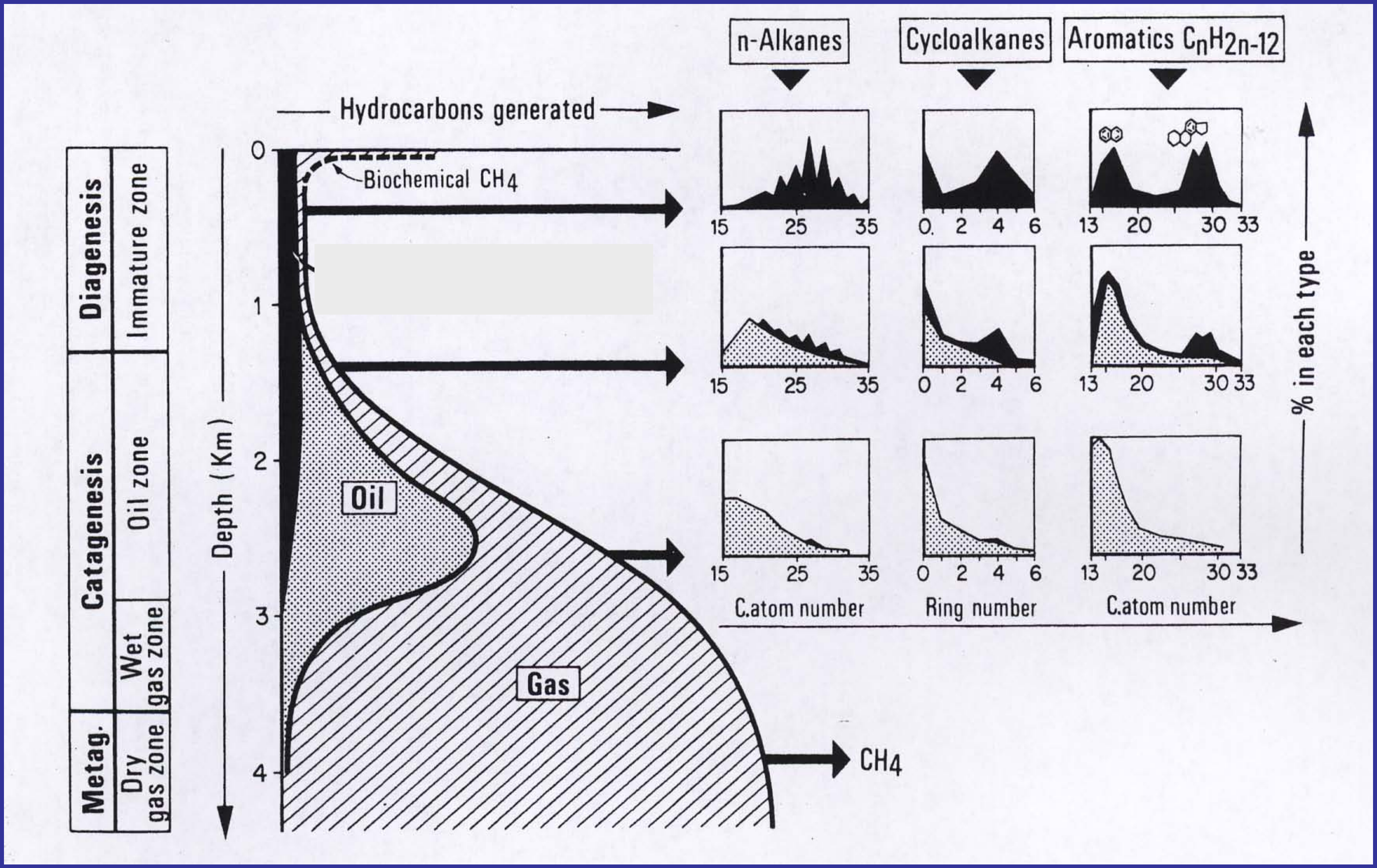
General Scheme of Hydrocarbon Formation with Source Rock Burial



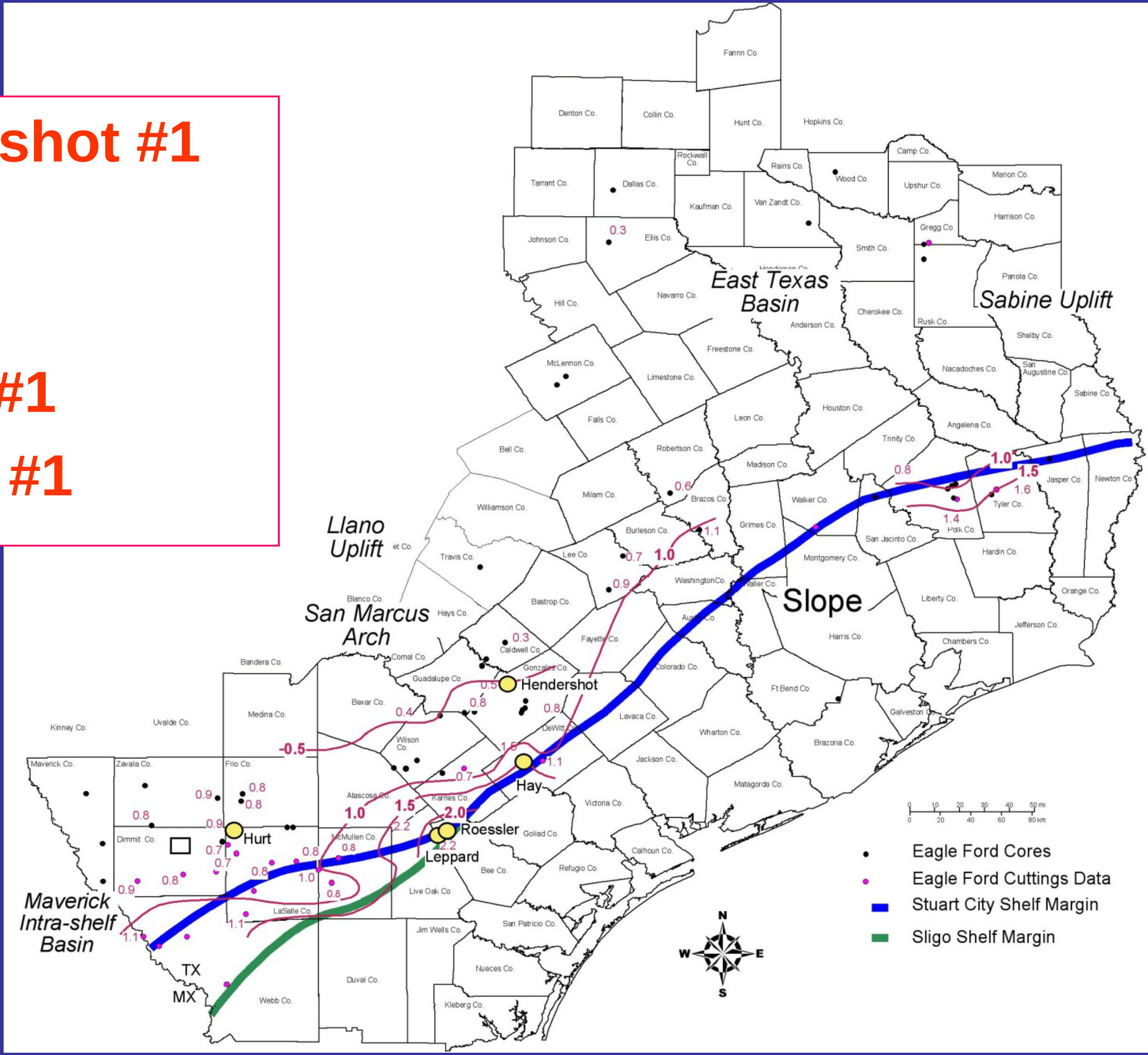
(Tissot and Welte, 1978)

Questions

- What are main controlling factors of gas chemistry in shale gas systems?
- What differences exist between gases produced from kerogen primary cracking and secondary oil cracking?
- What are the main gas storage components: free gas vs. adsorbed gas?
- How does mineral matrix affect gas storage?
- Are major gas storage components predictable by integrating gas chemistry and rock properties?

Eagle Ford Core Gas Data

- **Tesoro Hendershot #1**
- **Getty Hurt #1**
- **Shell Hay #1**
- **Shell Leppard #1**
- **Shell Roessler #1**

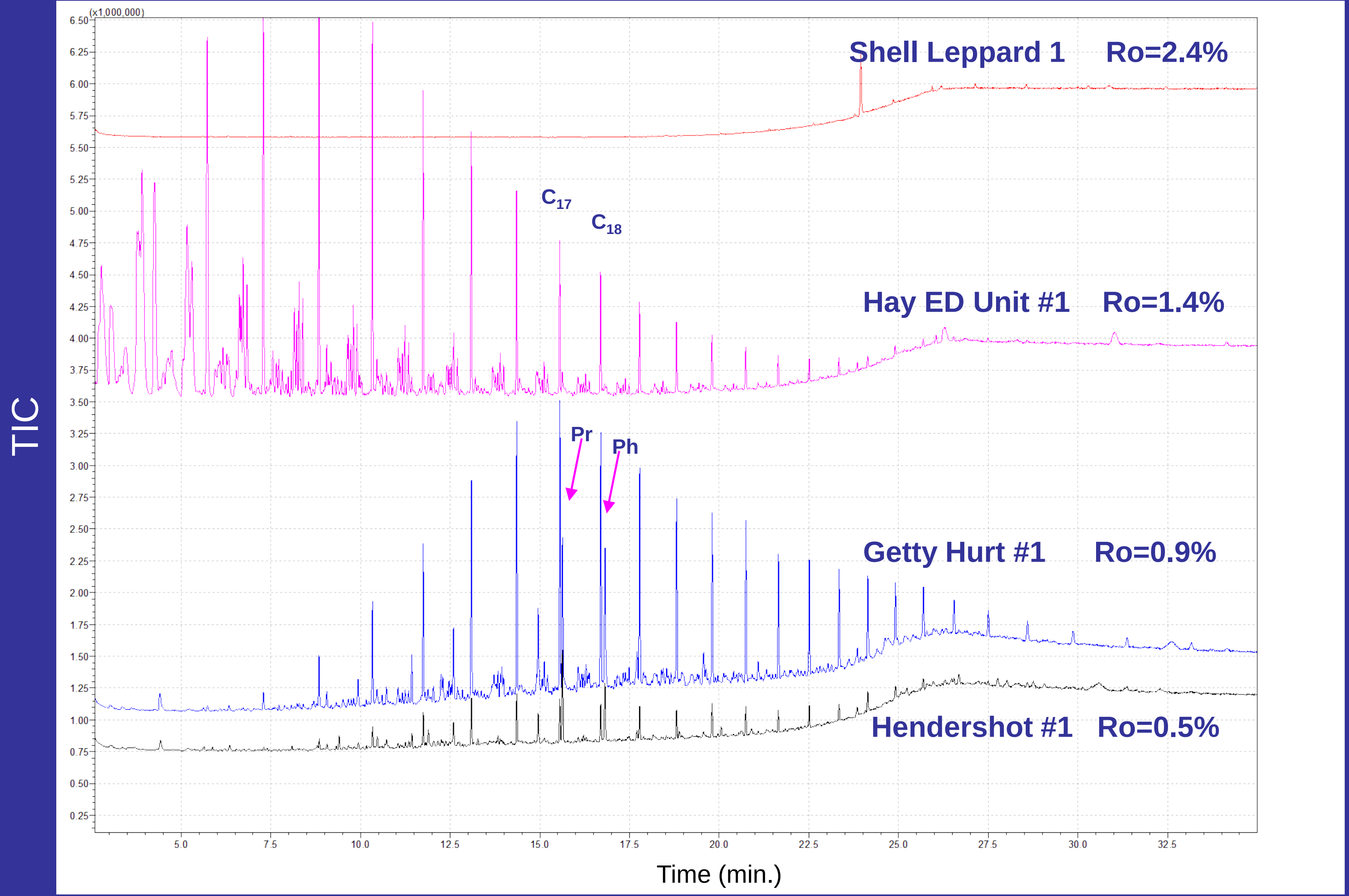


Eagle Ford Core Geochemistry Data

For a Range of Thermal Maturities

Well / parameters	Hendershot #1	Getty Hurt #1	Shell Hay #1		Shell Leppard #1	Shell-Roessler #1
Depth (ft)	4758	7298	13825	13827	13608	13511
TOC	8.5	1.8	5.3	2.26	5.0	4.12
S1	1.8	1.2	1.8	0.83	0.2	0.51
S2	63.2	3.6	1.4	0.72	0.7	0.58
S3	1.0	0.3	0.4	0.32	0.3	0.18
S2/S3	63	12	3.4	2.25	3	3.2
S1/TOC	21	86	33	37	4	12
Tmax (° C)	428	446	475	494	533	543
Ro(%)_calc	0.5	0.9	1.4	1.73	2.4	2.61
HI	741	201	27	32	14	14
OI	12	17	8	14	5	4
PI	0.03	0.25	0.54	0.54	0.24	0.47

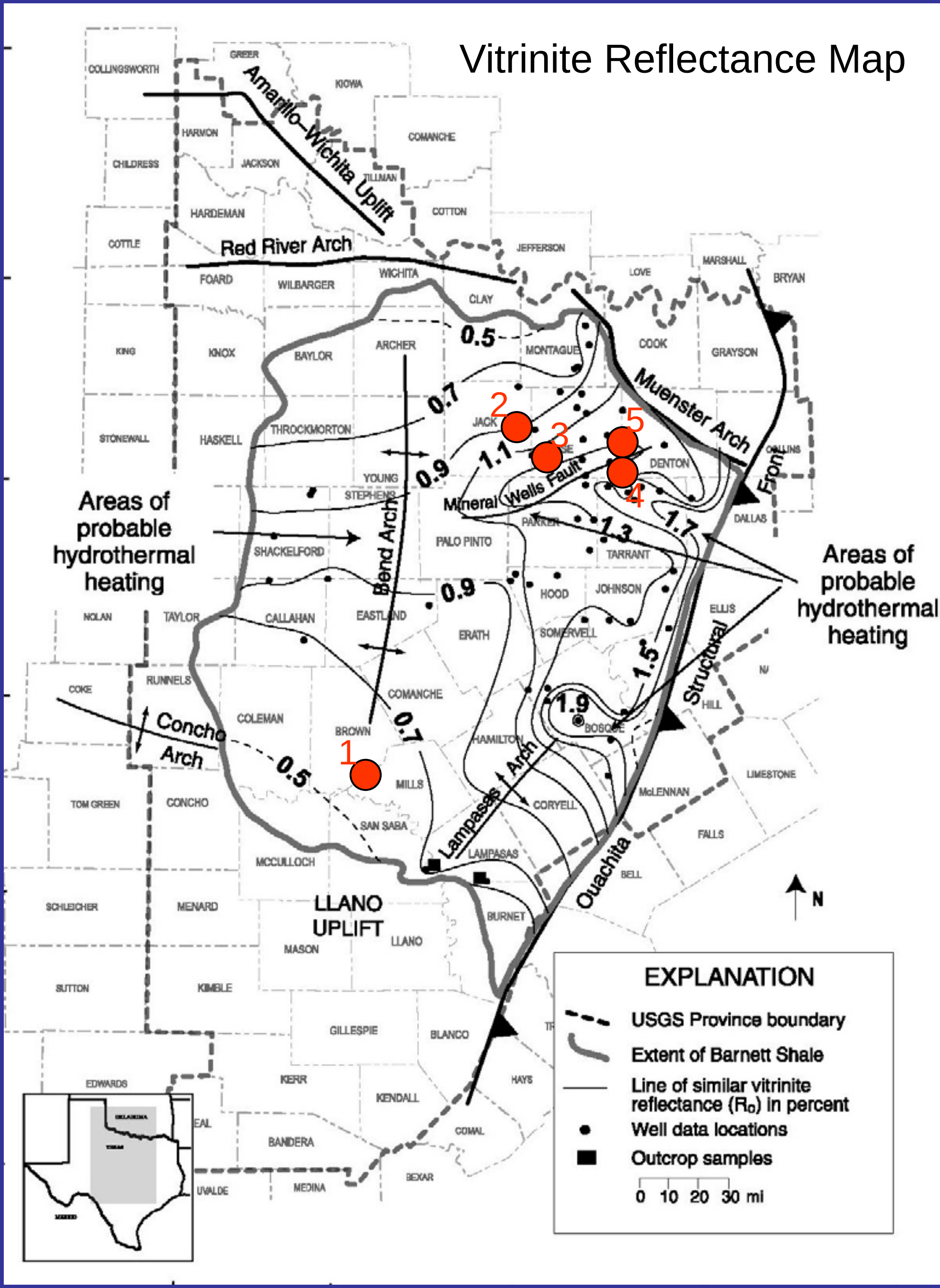
TIC of Solvent Extracts
Eagle Ford Core Samples



Barnett Shale Core Gas Data

Sampled Cores

- 1=Lee C-5-1
- 2=Tarrant #A-3
- 3=Young #2
- 4=Sims #2
- 5=Blakely #1

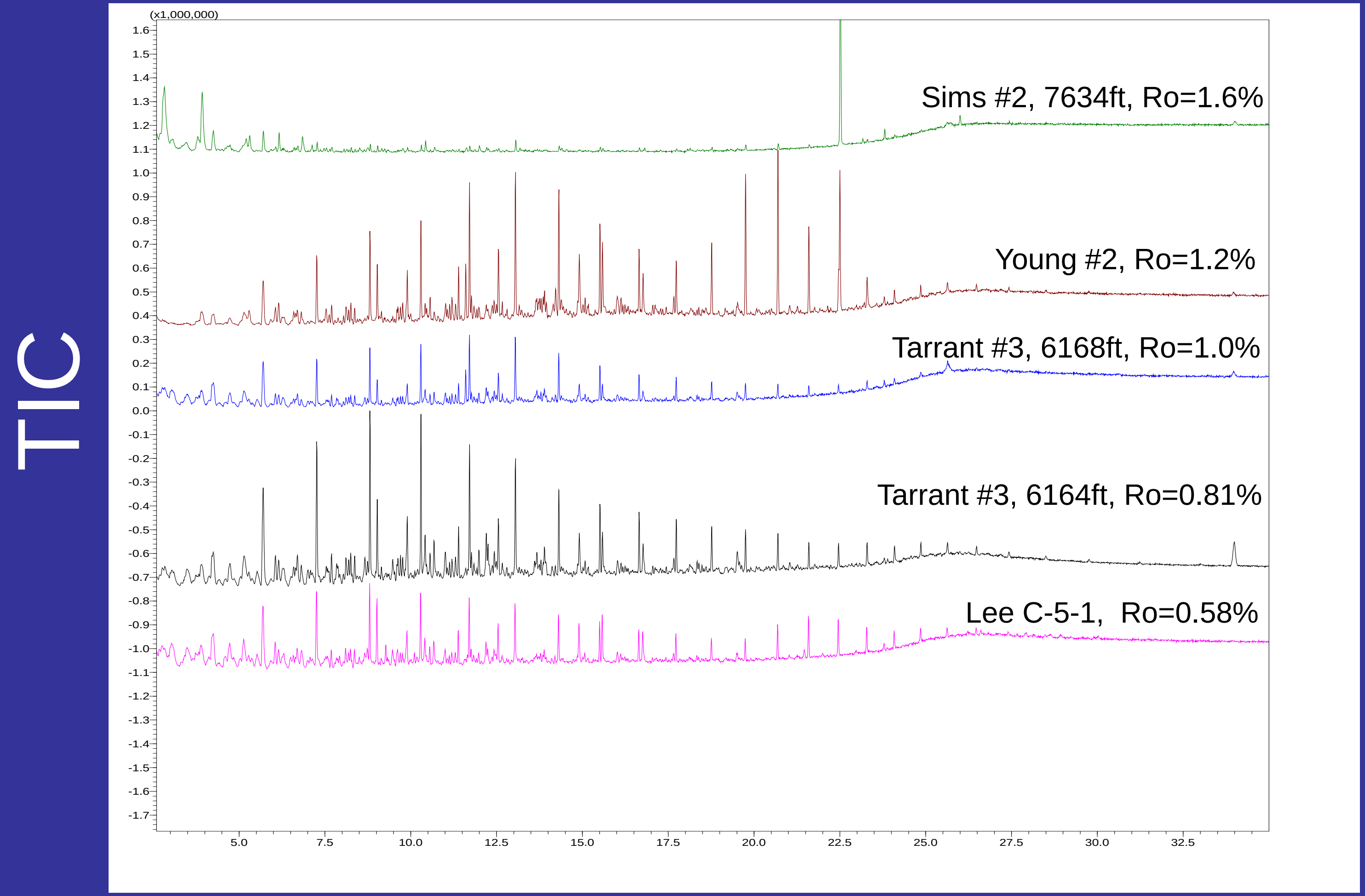


From Pollastro et al, 2007

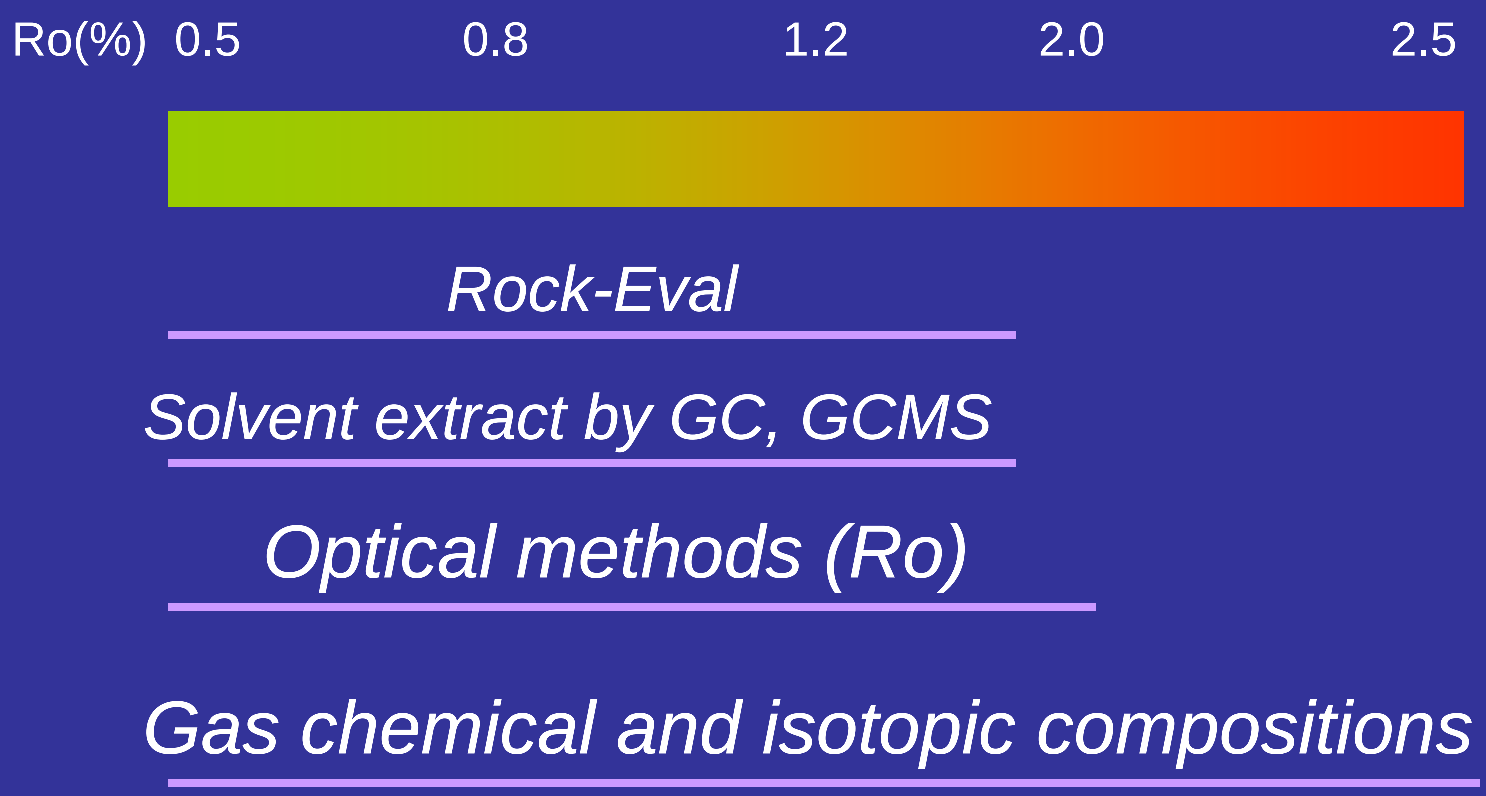
Barnett Core Geochemistry Data
For a Range of Thermal Maturities

Well / parameters	Brown, TX, LeeC-5-1	Jack, TX, Tarrant #A-3		Wise, TX Young #2	Wise, TX Sims #2		Wise, TX, Blakely #1		
Depth (ft)	1250	6164	6168	6918	7634	7742	7112.5	7192	7223
TOC	7.88	7.05	3.27	4.50	3.64	5.99	5.23	6.62	4.14
S1	1.64	4.29	1.50	2.01	0.36	0.35	0.30	0.28	0.37
S2	20.24	14.74	4.07	2.86	1.07	1.7	1.17	1.07	0.74
S3	0.48	0.26	0.32	0.22	0.27	0.16	0.15	0.21	0.21
S2/S3	61	57	13	13	4	10.6	8	5	4
S1/TOC	37	61	46	45	10	6	6	4	9
Tmax (° C)	430	443	455	466	472	510	545	561	518
Ro(%)_calc	0.58(c)	0.81(c)	1.03(c)	1.23(c)	1.61(m)	1.63(m)	1.96(m)	2.01(m)	2.07(m)
HI	551	209	124	64	29	28	22	16	18
OI	9	4	10	5	7	3	3	3	5
PI	0.06	0.23	0.27	0.41	0.25	0.17	0.20	0.21	0.33

TIC of Solvent Extracts from Barnett Shale



Limitation of Methods in Hydrocarbon Characterization of Mudrocks



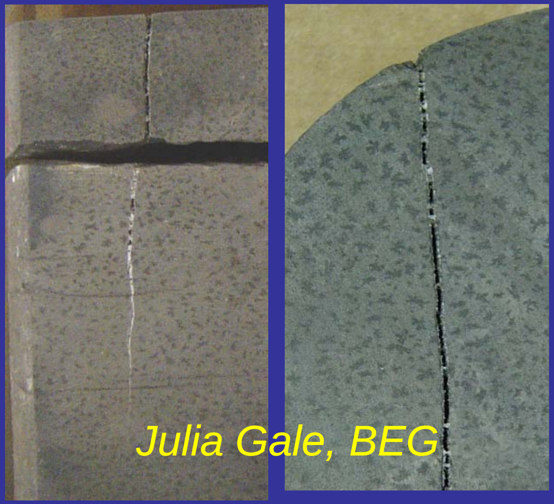
Gas Samples for Shale Gas Studies

- Canister desorption gas
- Mud gas in drilling
- Producing gas in shale gas wells
- Released gas in gas-tight rock crushing
  - Proposed idea and its significance
  - Preliminary gas chemical compositional results from gas-tight rock crushing
  - Potential application

Released Gas in Rock Crushing

- There is a possibility of the presence of isolated pores filled with gases.
- Preserved gas will be released in rock crushing to powder.
- A gas-tight rock crushing cell is critical to test the technique.
- The stainless steel cell from our existing SPEX 8000M Mixer/Mill machine is modified with on-line filter and on/off valve.

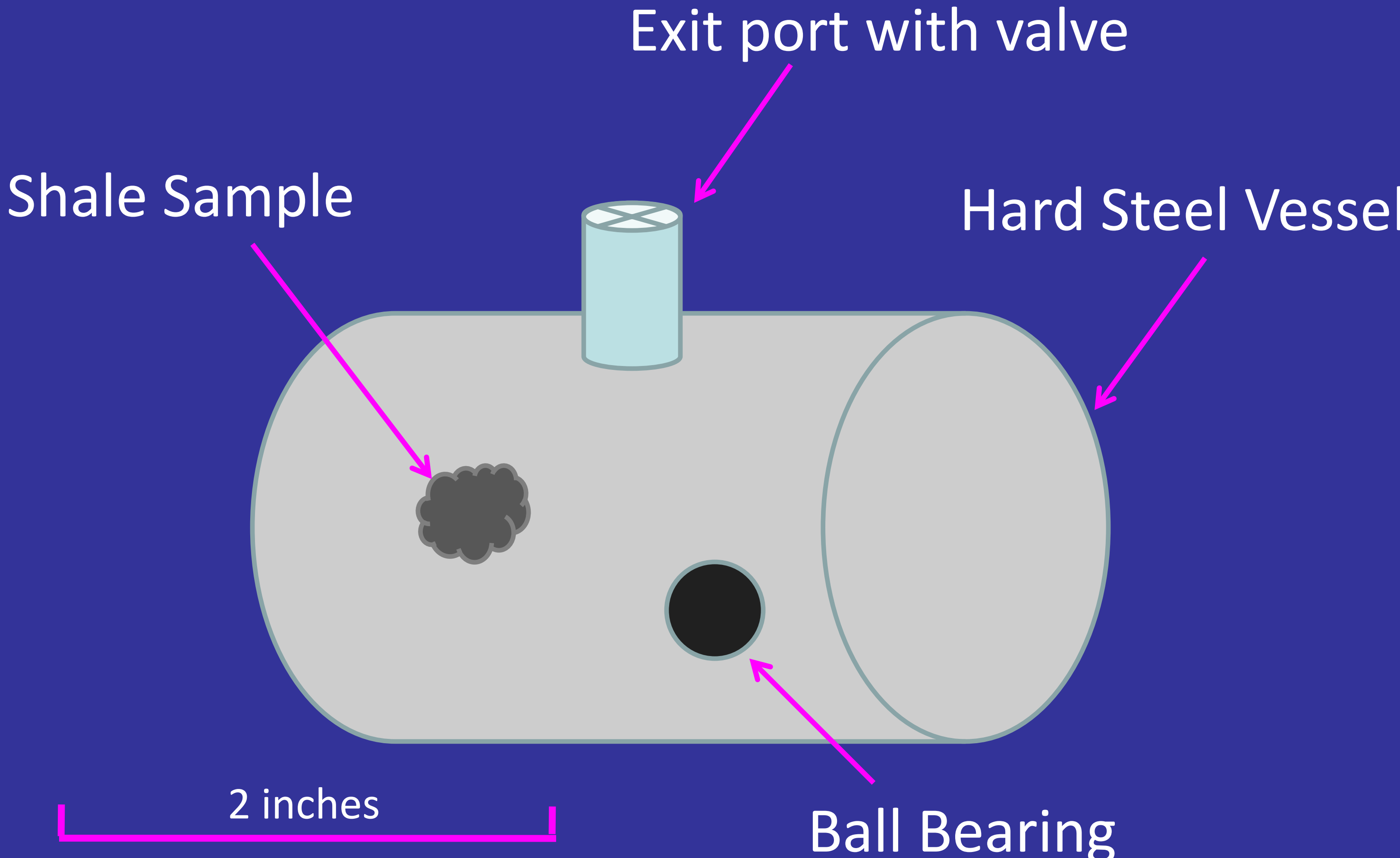
Rob Reed, BEG



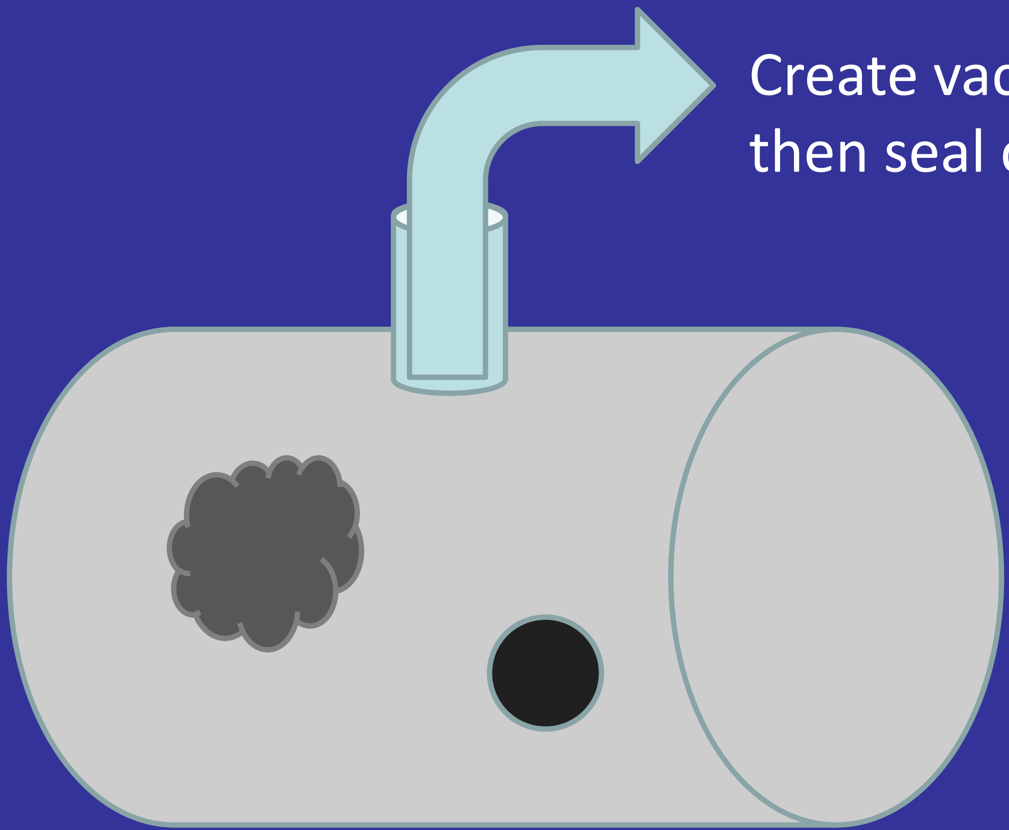
Julia Gale, BEG

Gas-tight Vial for Rock Crushing

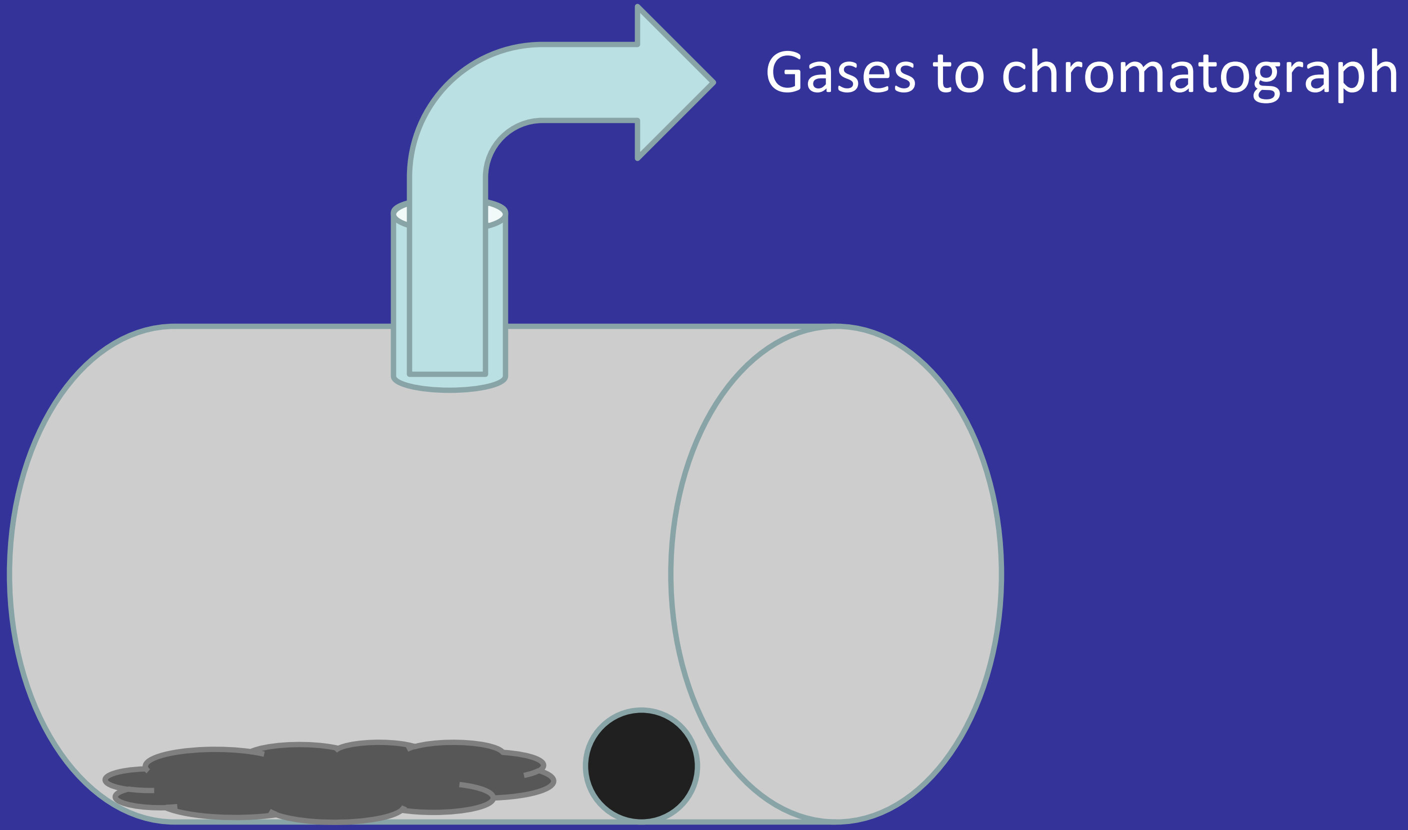
Experimental setup for gas-tight rock crushing



Rock Crushing Process and Gas Recovery



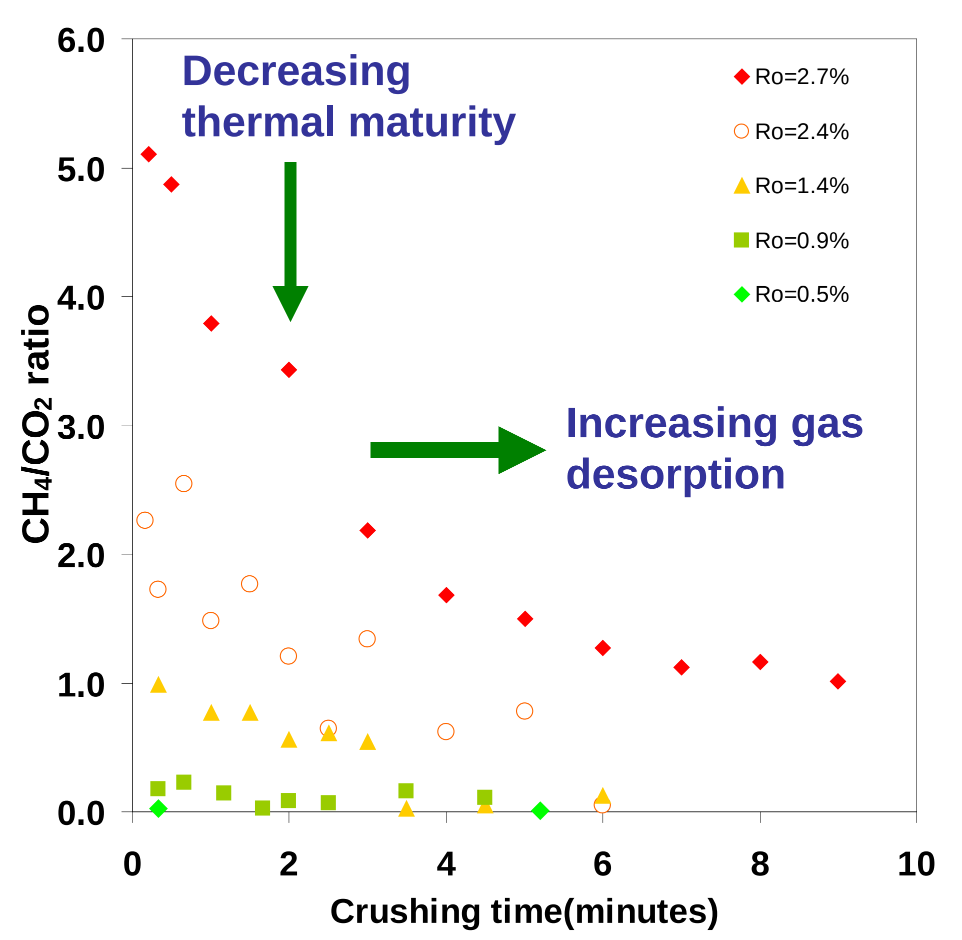
After Crushing, Gas Samples Withdrawn



Effects of Thermal Maturity and Gas Desorption on CH_4/CO_2 Ratio

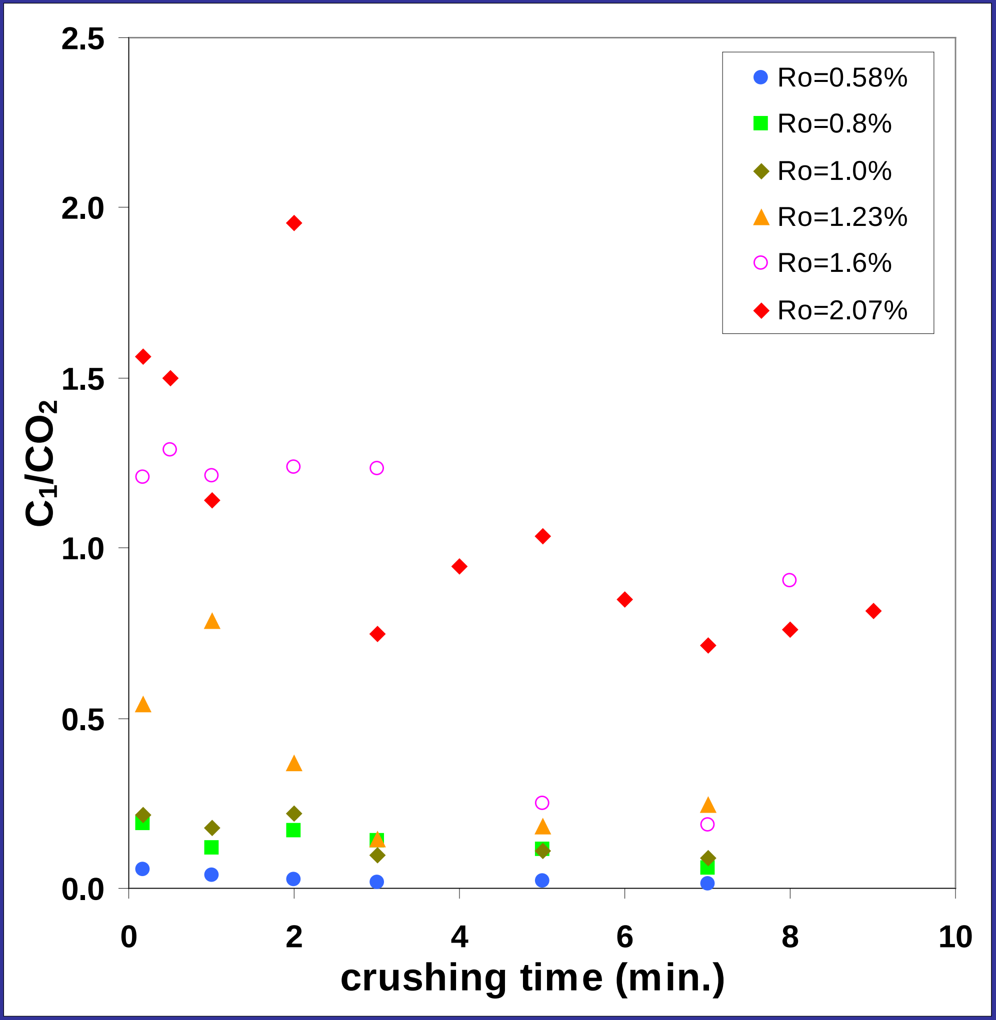
Eagle Ford Rock Crushing Data

- Both thermal maturity and gas desorption contribute to changes in CH_4/CO_2 ratio of released gas from rock crushing.
- CH_4/CO_2 ratios are lower at low thermal maturities because less CH_4-rich gas is generated at low maturity levels.
- CH_4/CO_2 ratios decrease with longer rock crushing time because of increasing CO_2-rich adsorbed gas contribution.



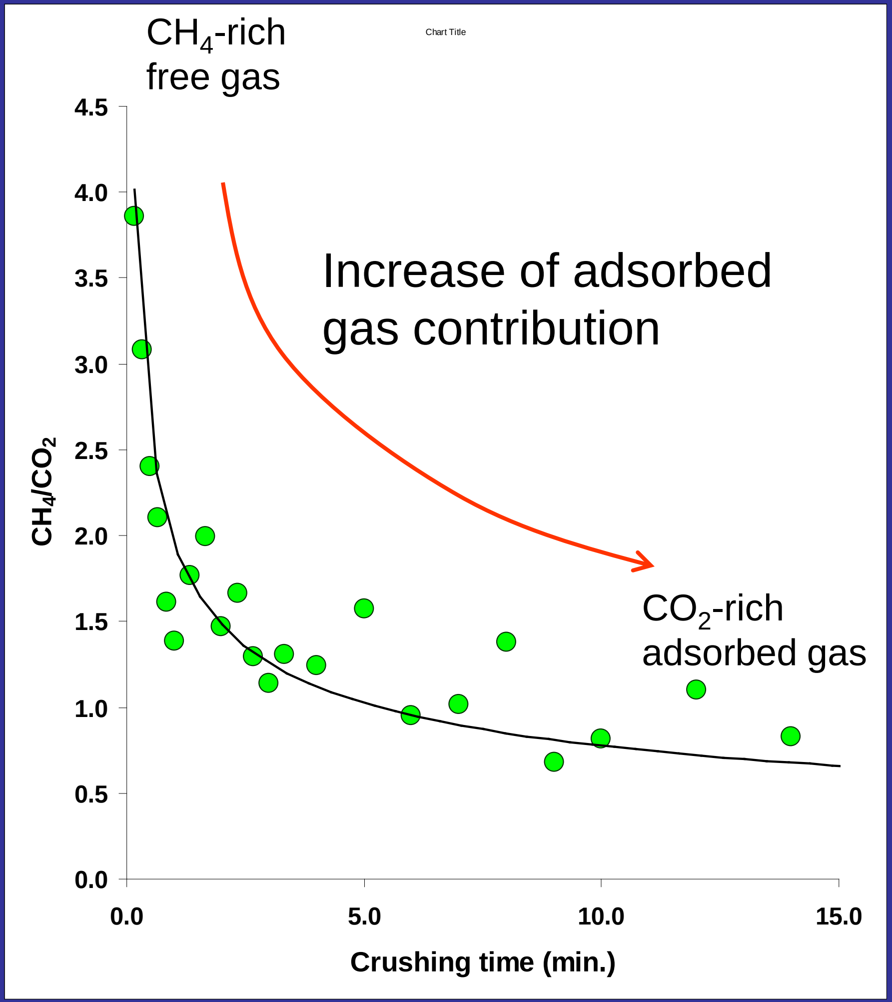
Similar CH_4/CO_2 Ratio Changes are Observed in Barnett Shale Samples

- Similar changes in CH_4/CO_2 ratios are seen in Barnett Shales of various thermal maturity in rock crushing.
- CH_4/CO_2 ratio changes may indicate free gas preservation.



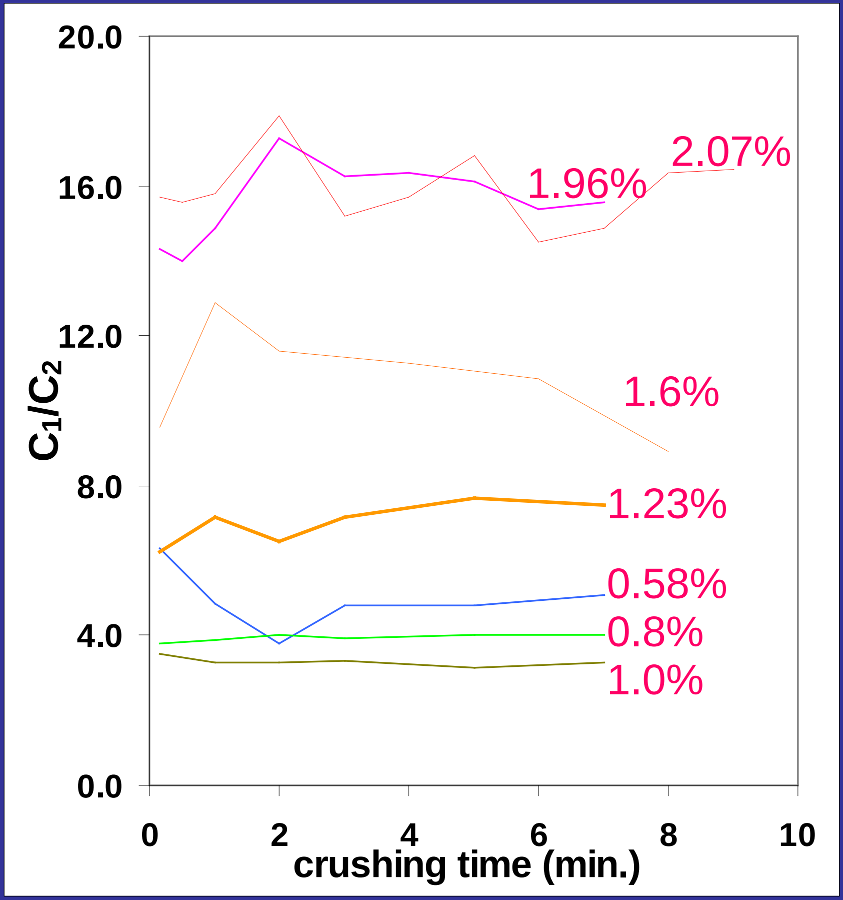
Proposed Mechanism of Gas Releasing in Shales

- CH_4 dominates free gas in the very early stages of rock crushing
- CO_2-rich adsorbed gas is dominant in late stages

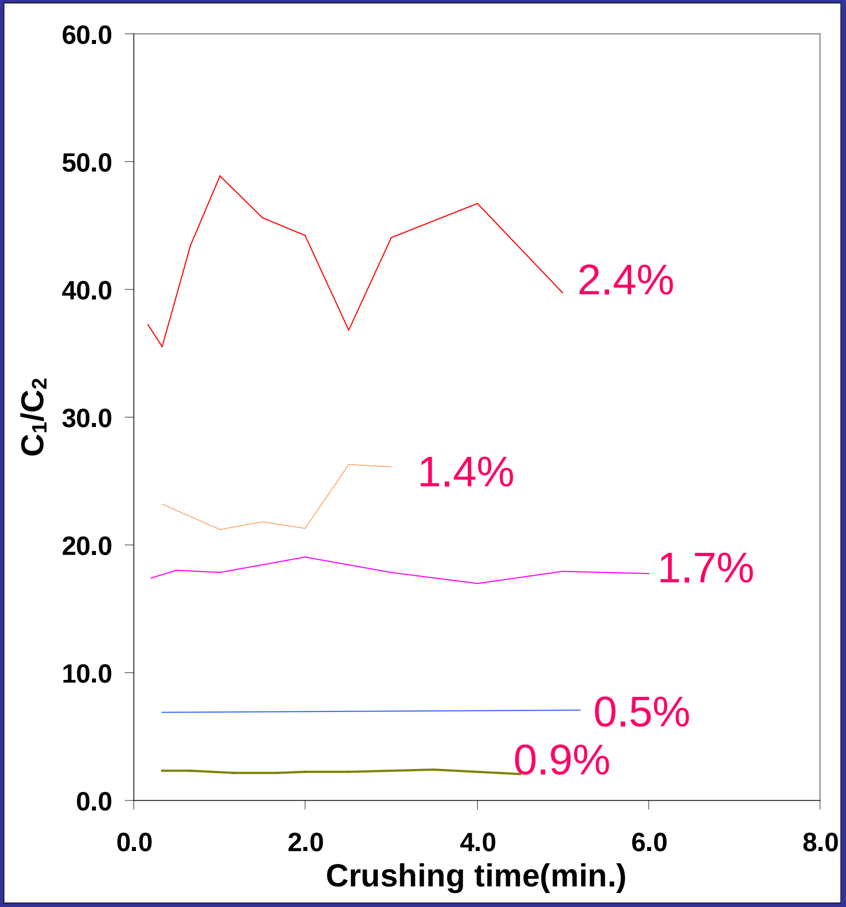


No Obvious Compositional Fractionation Occurs Between C_1 and C_2 in Rock Crushing

Barnett Shale

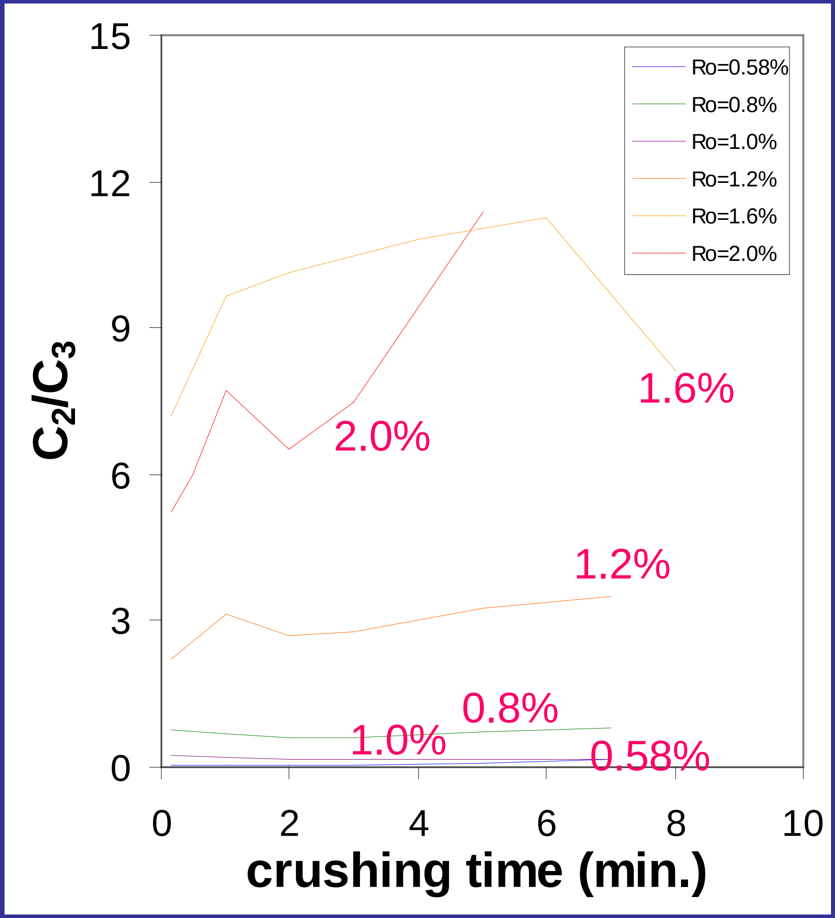


Eagle Ford

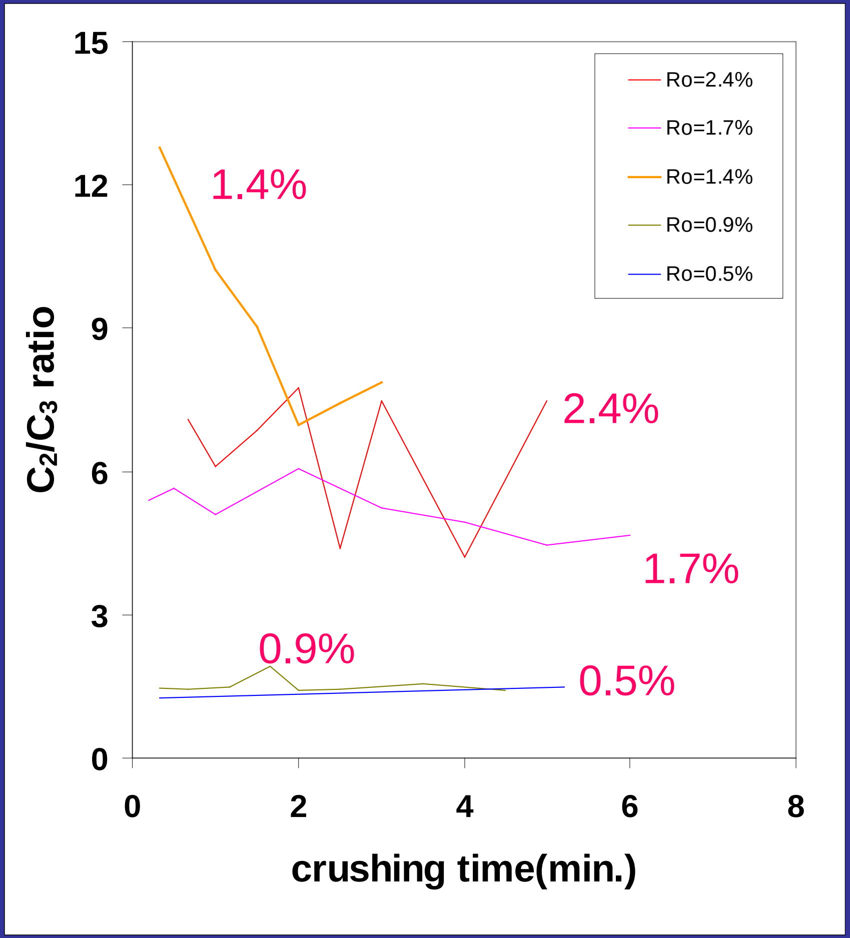


No Obvious Compositional Fractionation Occurs Between C_2 and C_3 in Rock Crushing

Barnett Shale

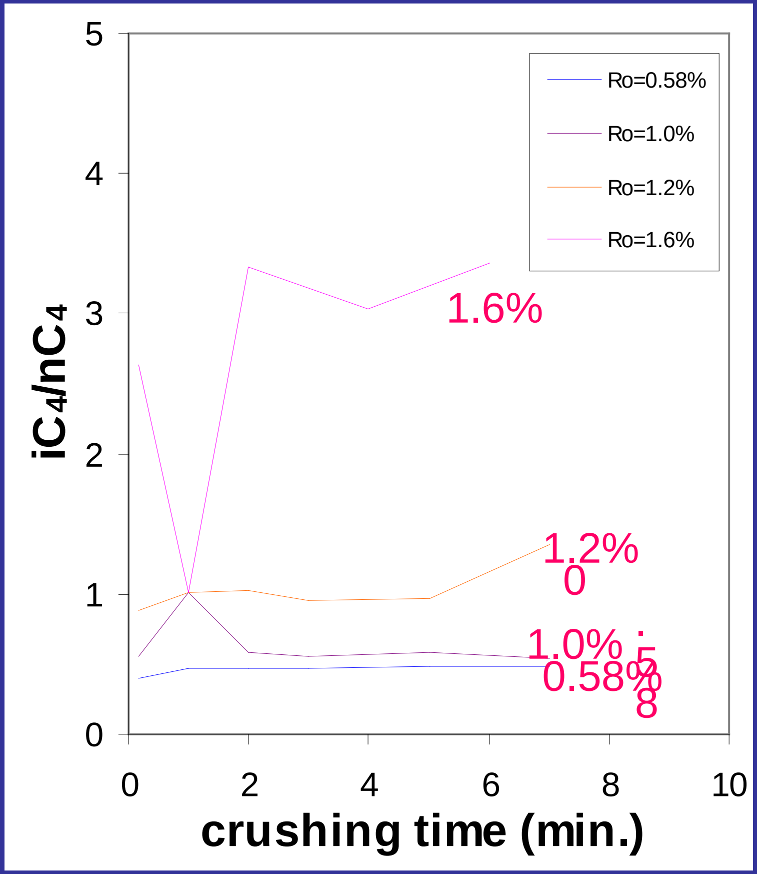


Eagle Ford

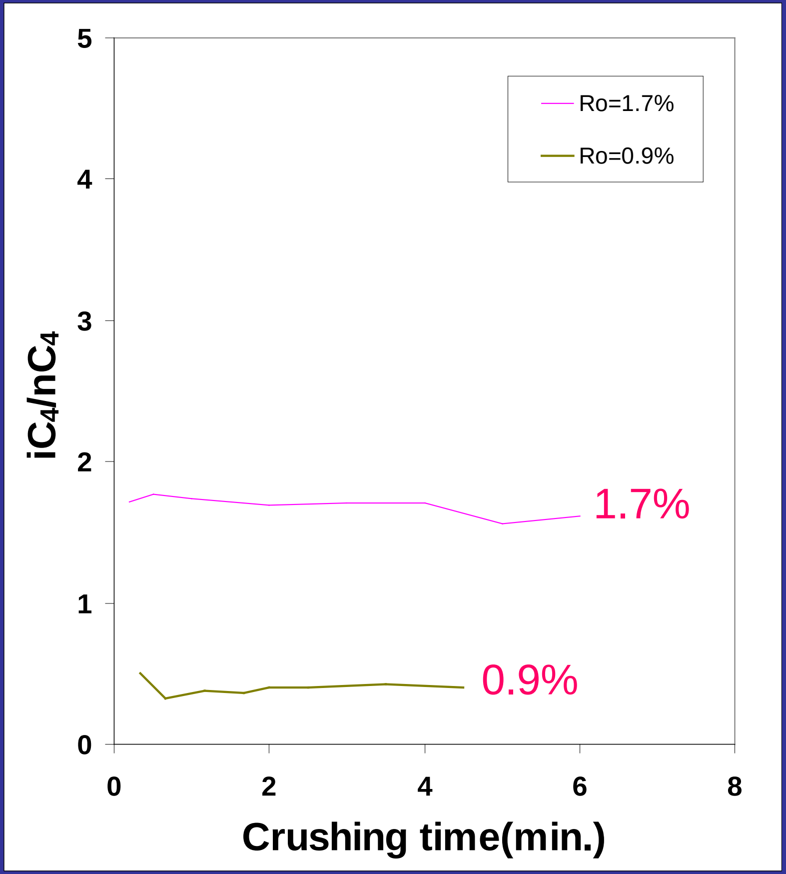


iC_4/nC_4 at Ro ≤1.7%

Barnett Shale

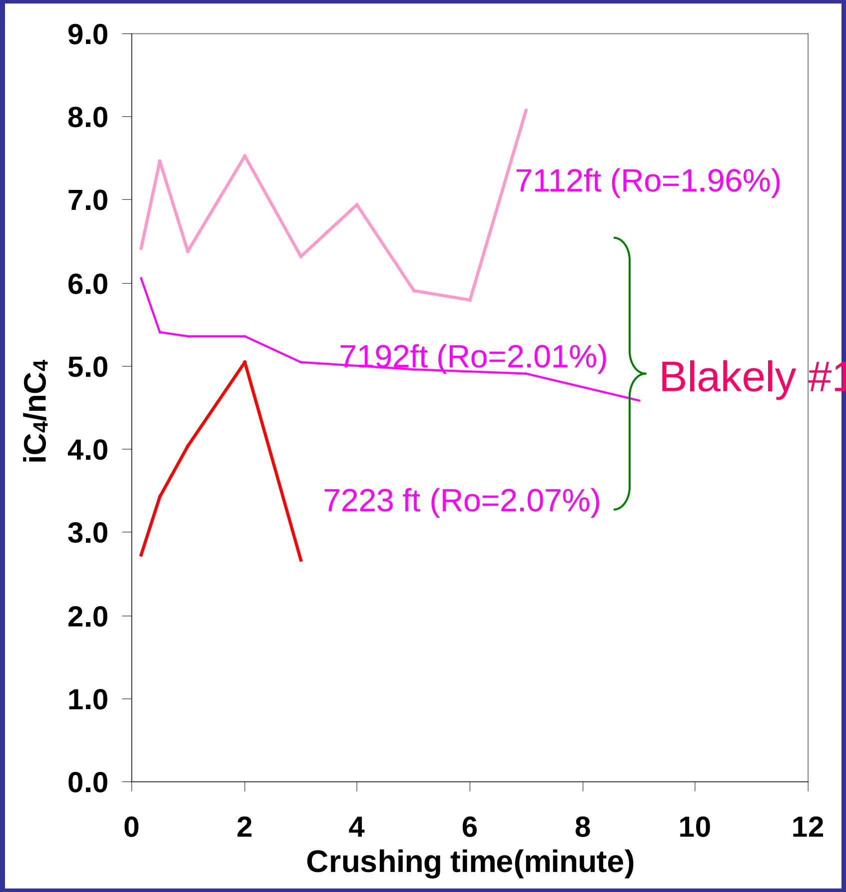


Eagle Ford

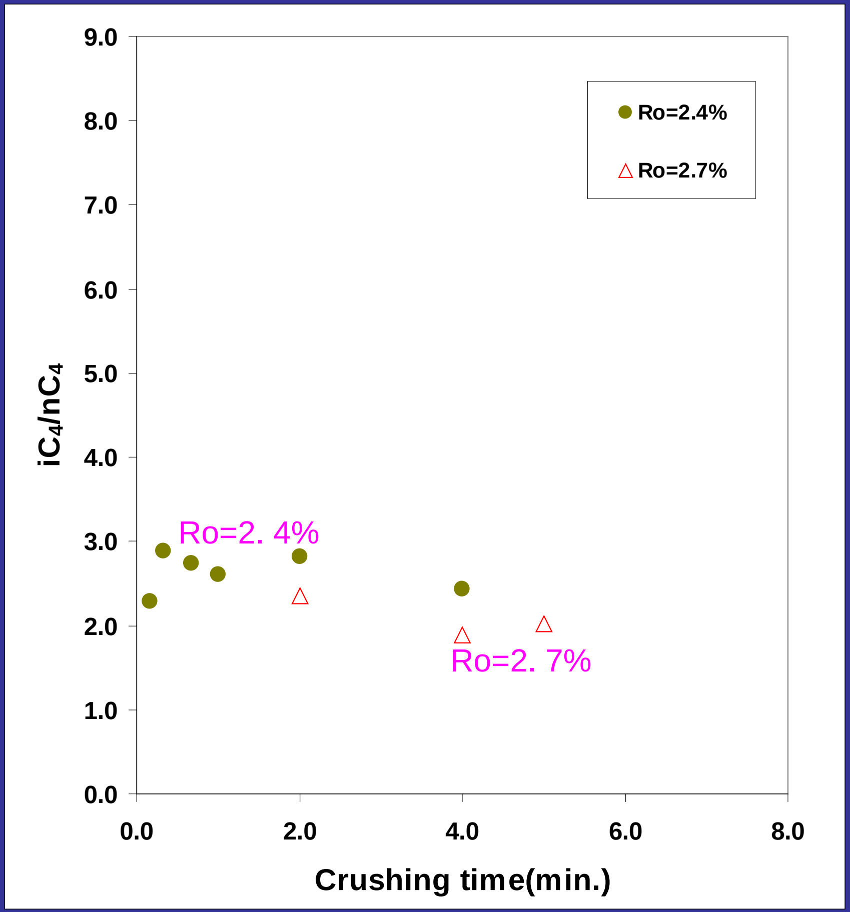


iC_4/nC_4 at Ro > 1.7%

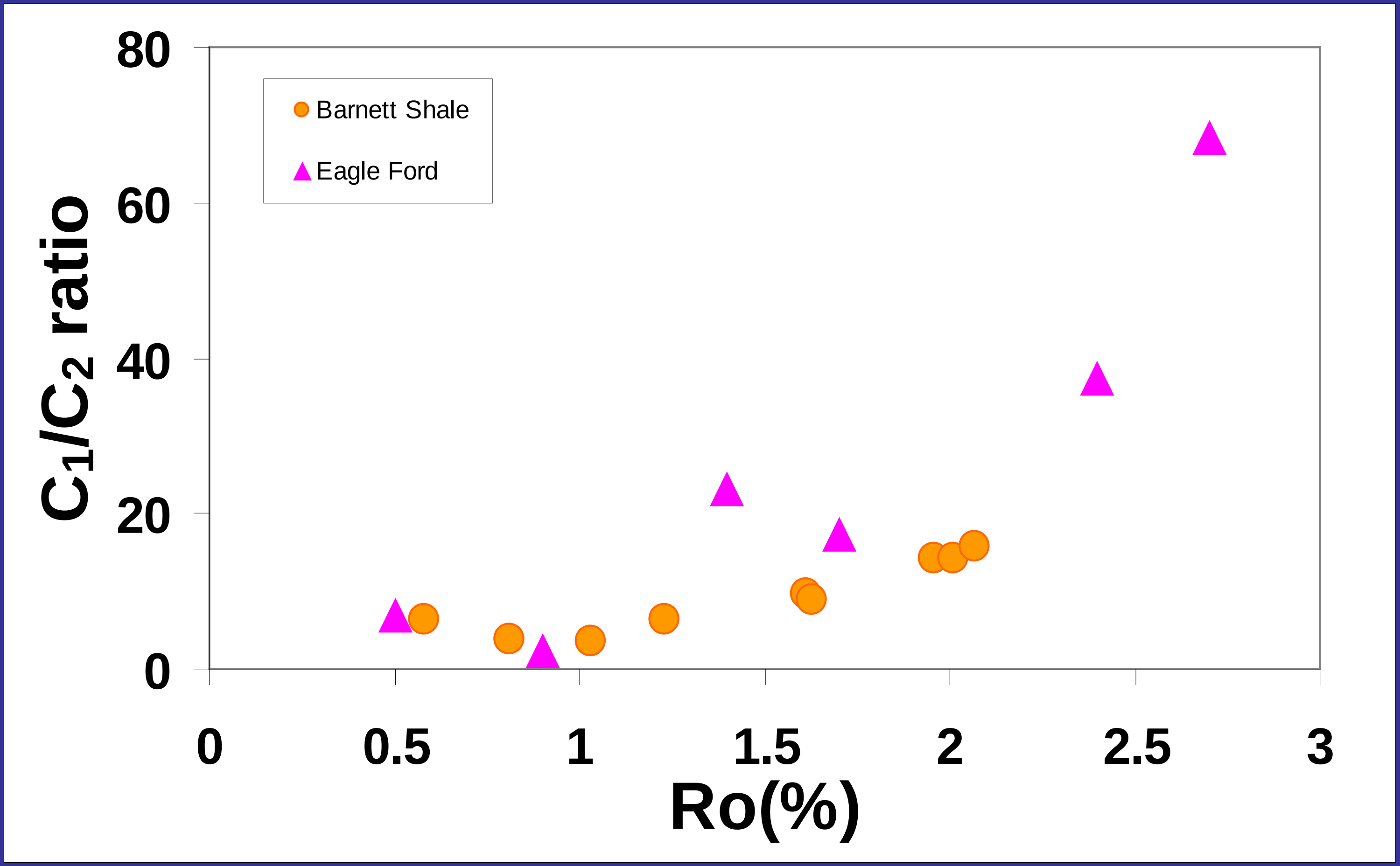
Barnett Shale



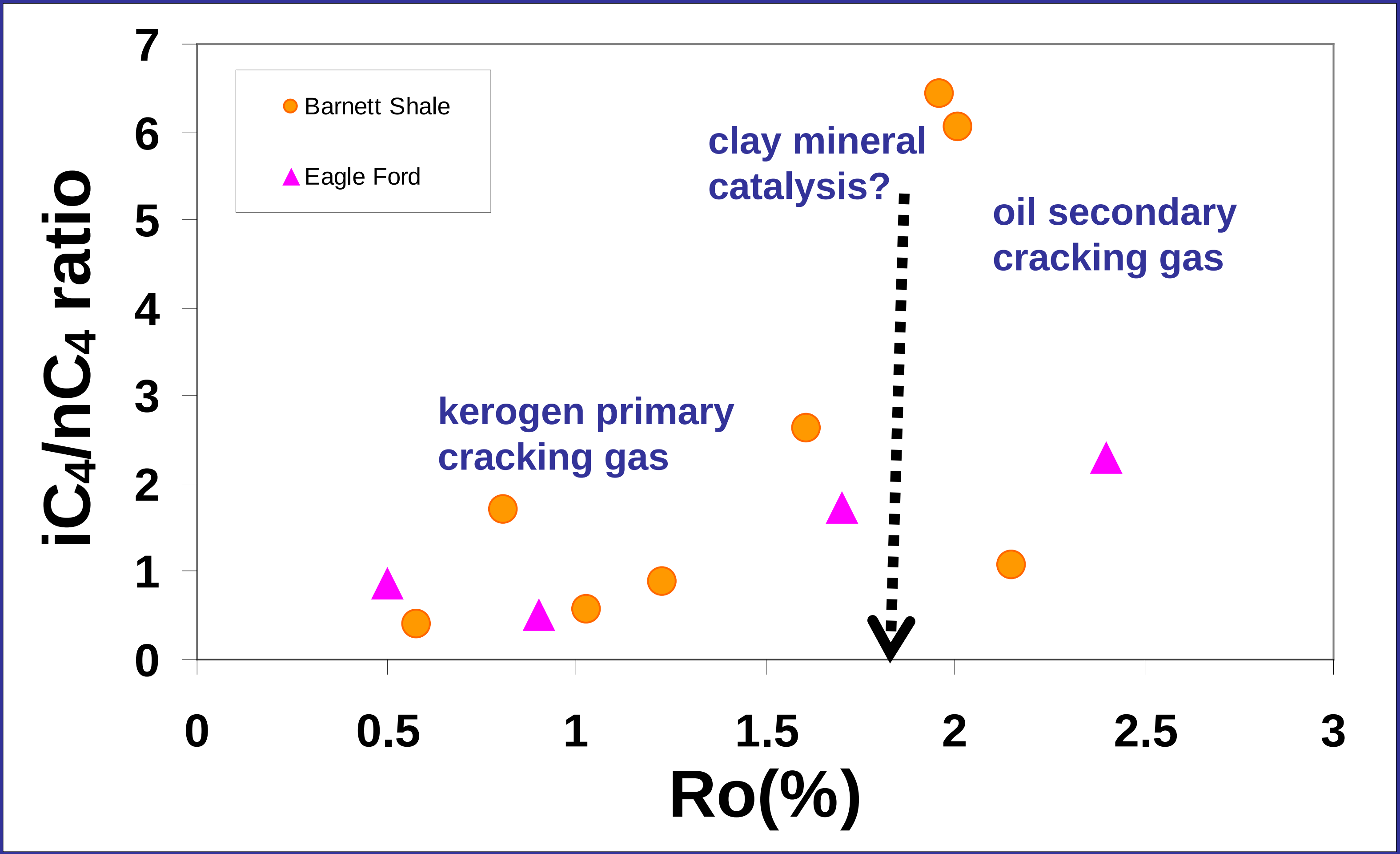
Eagle Ford



Relationship Between Thermal Maturity and C_1/C_2 ratio

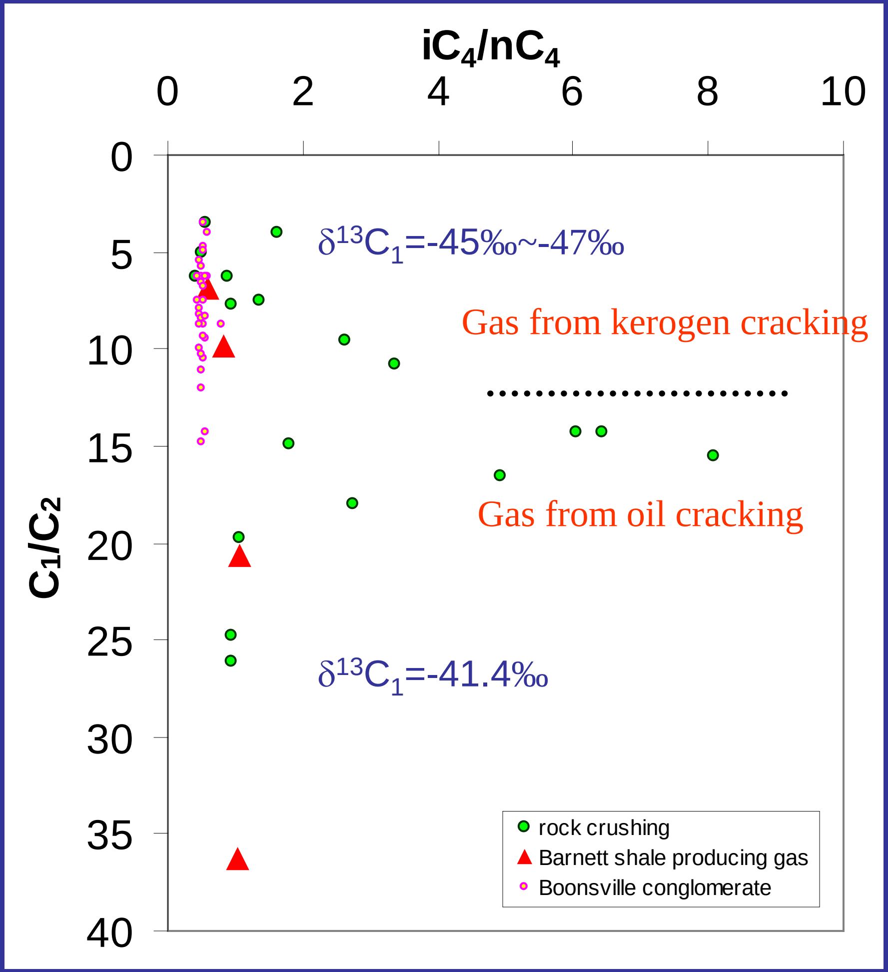


Relationship Between Thermal Maturity and iC_4/nC_4 ratio



Comparison of Gas Chemistry from Rock Crushing Gas and Production Gas

- Gas chemistry data from rock crushing are comparable to those of producing gas in Barnett shale.
- With increasing thermal maturity, iC_4/nC_4 ratio increases first due kerogen cracking to gas, then decreases after oil starts cracking to gas.



Conclusions

- Liquid hydrocarbons characterization in mudstone can provide information about thermal maturation, organic type and depositional environments.
- CH_4/CO_2 ratios from core crushing are controlled by both thermal maturity and gas desorption.
- C_1/C_2 and C_2/C_3 are good indicators of thermal maturation of organic-rich shales.
- The role of clay mineral catalysis in oil cracking to gas needs to be investigated.
- Quantified released gas amount in rock crushing and gas isotope compositional measurement need to be addressed.

Acknowledgements

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