Geological Openness Effect on the Chemical and Carbon Isotopic Signatures of Shale Gas: Implications from the Stepwise Pyrolysis Bitumen*

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Search and Discovery Article #41901 (2016)**
Posted September 26, 2016

*Adapted from oral presentation given at AAPG Annual Convention & Exhibition, Calgary, Alberta, Canada, June 19-22, 2016

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Abstract

Earlier studies have revealed that part of shale gas is derived from the cracking of residual oils, and one line of evidence of this process is the presence of abundant pyrobitumen in mature and over-mature gas shales. Many experiments have been carried out to investigate the chemical and carbon isotopic signatures of oil cracking gas in a closed or confined system, but most of the results failed to fully explain the characteristics of shale gas that is usually much drier and characterized with relatively heavier methane carbon isotopes than the pyrolysate gas. In fact, the shale system is probably not a completely closed or confined system when the shale gas is being generated, and therefore the shale gas could be released periodically with the natural fracturing of shales induced by gas generation. This overpressure fracturing has been recorded by the fluid inclusions of gas in some gas shales. From this point of view, the shale gas today may be considered as the residual part of more abundant gas generated in shales. Therefore, it is necessary to carry out experiments that can match the geological conditions as much as possible.

In this study, we performed a series of closed and stepwise experiments on a low mature bitumen (Rb=0.8%) using sealed gold tube method to investigate how the experimental openness affected the chemical composition of pyrolysates, the methane yield and its carbon isotope. The closed experiment shows that most of the ethane and propane is generated before the maturity level of EasyRo 2.3% and 1.7%, respectively. In the stepwise experiments, the residual bitumen samples that have been artificially depleted of ethane and propane potentials, were pyrolyzed again to imitate the regeneration of gas after shale fracturing and subsequent gas loss, and to investigate the late methane potential and its carbon isotopic composition without the influence of ethane and propane. The results show that there is still a maximum methane potential of about 70-102 mL/g bitumen, and the methane carbon isotopic values are 3-5‰ heavier than those in the closed system and are much closer to the carbon isotopes of methane in shale gases. These results imply that (1) the cracking of wet gases in a closed system will produce isotopically lighter methane than the cracking of residual bitumen itself, and (2) the shale gas today is only the residual part of gas generated in shales after its migration into conventional reservoirs.

Selected References

Hill, R.H., Y. Tang, and I.R. Kaplan, 2003, Insights into oil cracking based on laboratory experiments: Organic Geochemistry, v. 34, p. 1651-1672.

Rooney, M.A., G.E. Claypool, and H.M. Chung, 1995, Modeling thermogenic gas generation using carbon isotope ratios of natural gas hydrocarbon: Chemical Geology, v. 126, p. 219-232.

Zumberge, J., K. Ferworn, and S. Brown, 2012, Isotopic reversal (‘rollover’) in shale gases produced from the Mississippian Barnett and Fayetteville formations: Mar. Pet. Geol., v. 31, p. 43-52.

Geological Openness Effect on the Chemical and Carbon Isotopic Signatures of Shale Gas: Implications from Stepwise Pyrolysis of a Low Mature Bitumen Sample

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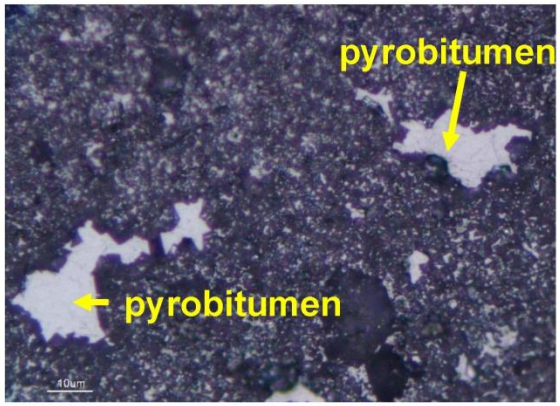
June 22, 2016 Calgary, Canada

Outline

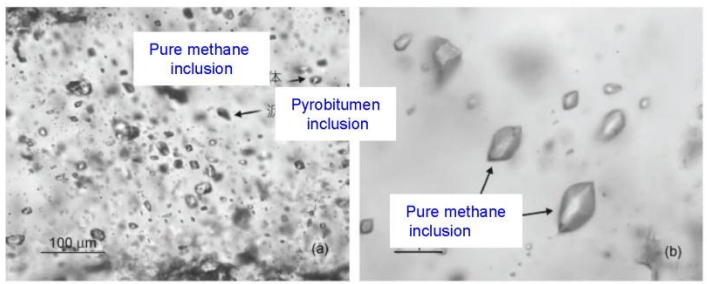
- Why geological openness and why bitumen?
- Stepwise pyrolysis experiments
- What can we learn?
  - Gas potential
  - Chemical and isotopic signatures
  - Geological implications
- Summary

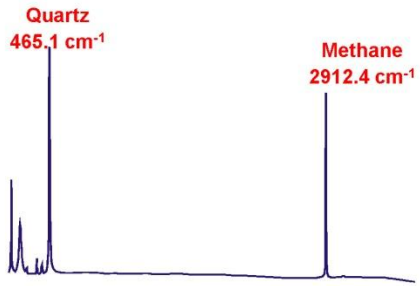
Why geological openness?

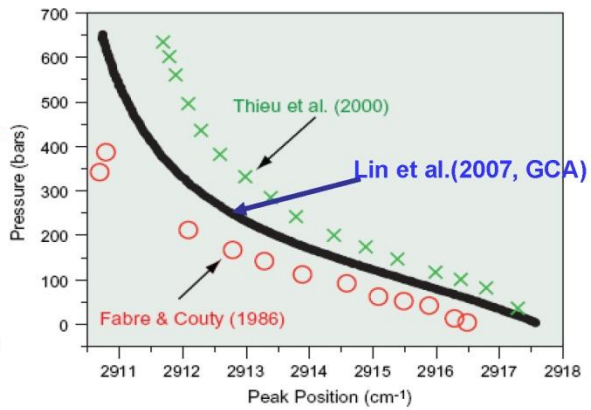


- **Retained oil (bitumen) cracking**
- **Residual kerogen cracking**

Oil (or kerogen) cracking generates overpressure that may naturally fracture shales



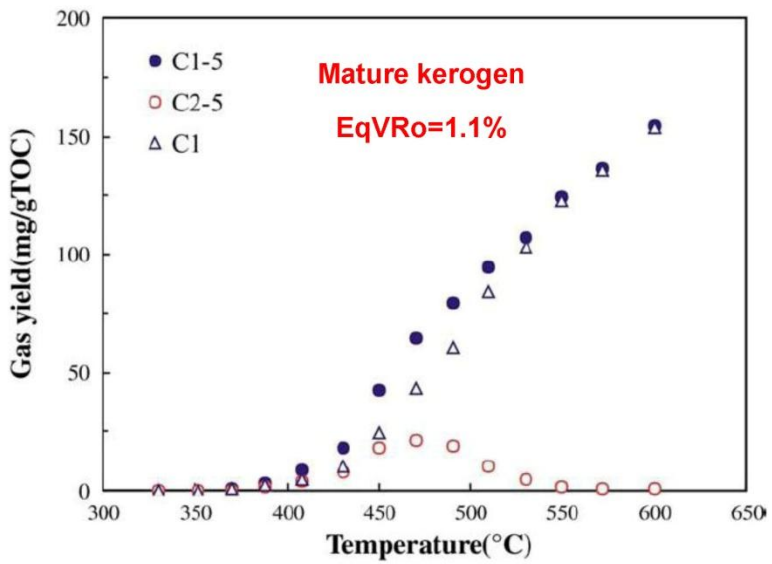


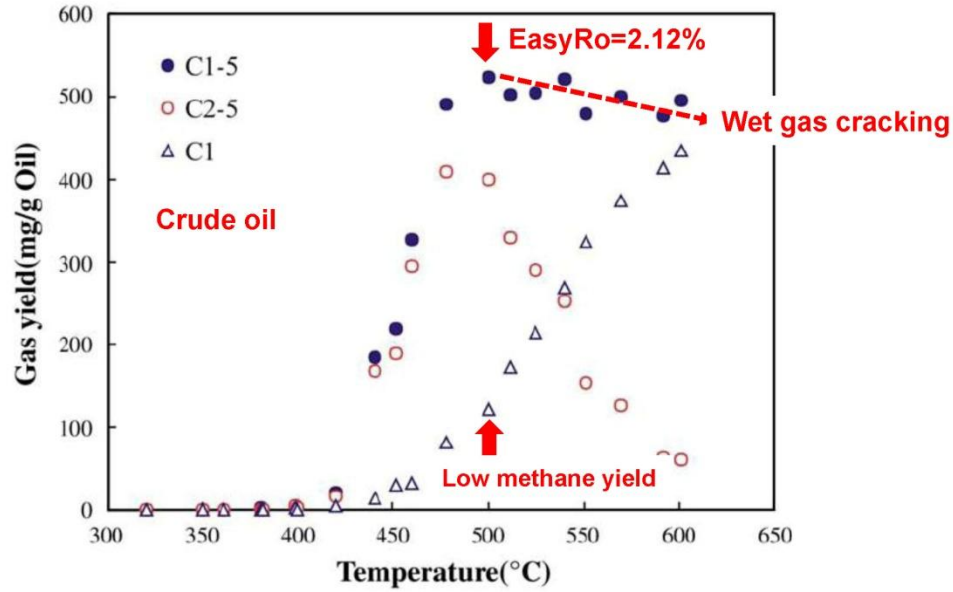


Presenter's notes: Overpressure by oil cracking can be recorded by pure methane inclusion. The Raman shift has been used to infer the density or internal pressure of methane in fluid inclusion.

Why geological openness?

How different are the gases from kerogen and oil cracking?



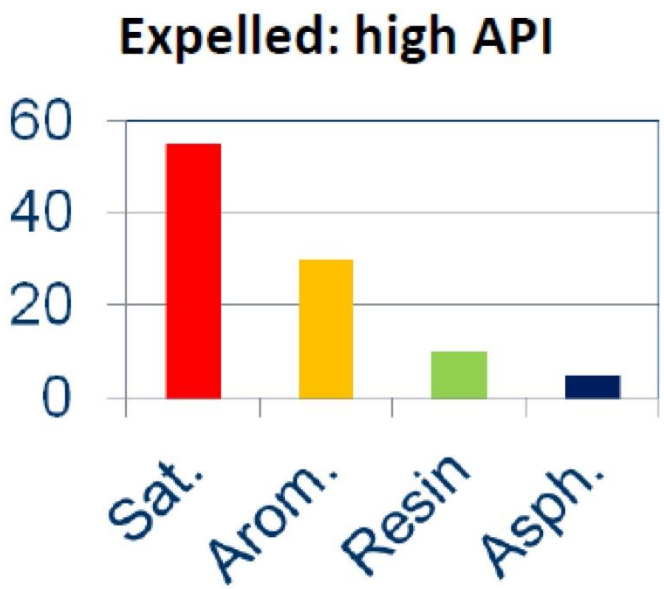


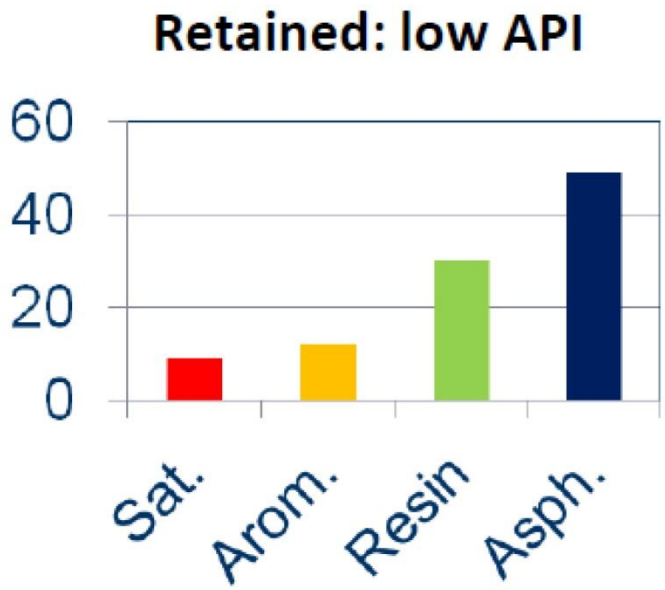
For confined or closed geological systems:

- **Kerogen cracking gas is much wetter than oil cracking gas**
- **Wet gas contribution to late methane is more profound for oil cracking gas**

Presenter's notes: Most methane from oil cracking is derived from the secondary of wet gases at highly maturity level. Without wet gas contribution, late methane from oil cracking might be very low.

Why bitumen?

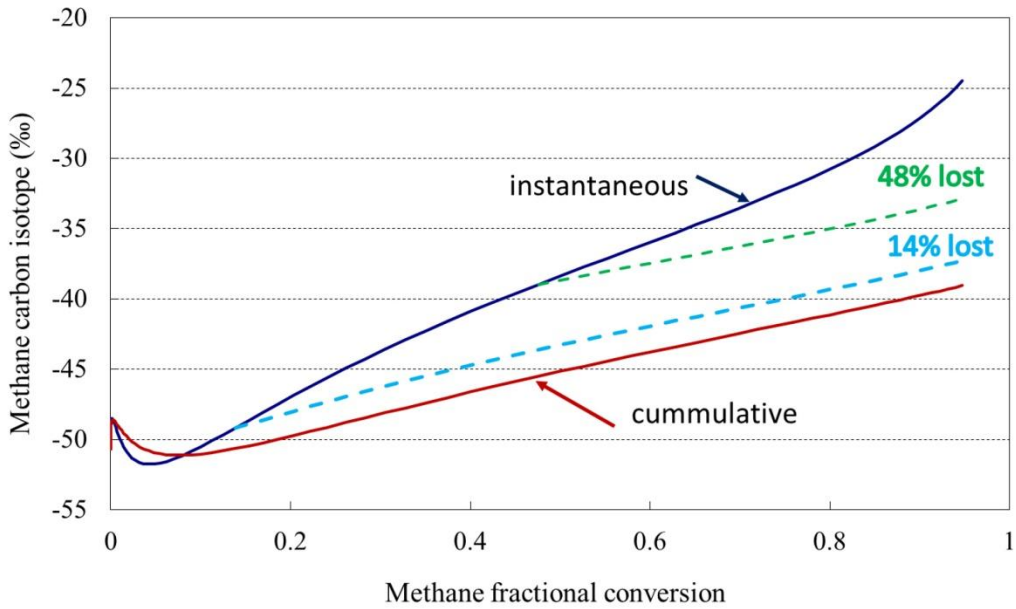




Oil cracking gas in shales might be largely sourced from resin and asphaltene fractions

Presenter's notes: Primary migration of oils out of shales leaves the retained oil more asphaltene riched than the oils accumulated in conventional reservoirs.

The state of the art



Conventional Rooney's model for partially trapped methane carbon isotope (Rooney et al., 1995, Chemical Geology)

This model requires:

- **Consistent methane source**
- **Absolutely open systems**

For a real geological system

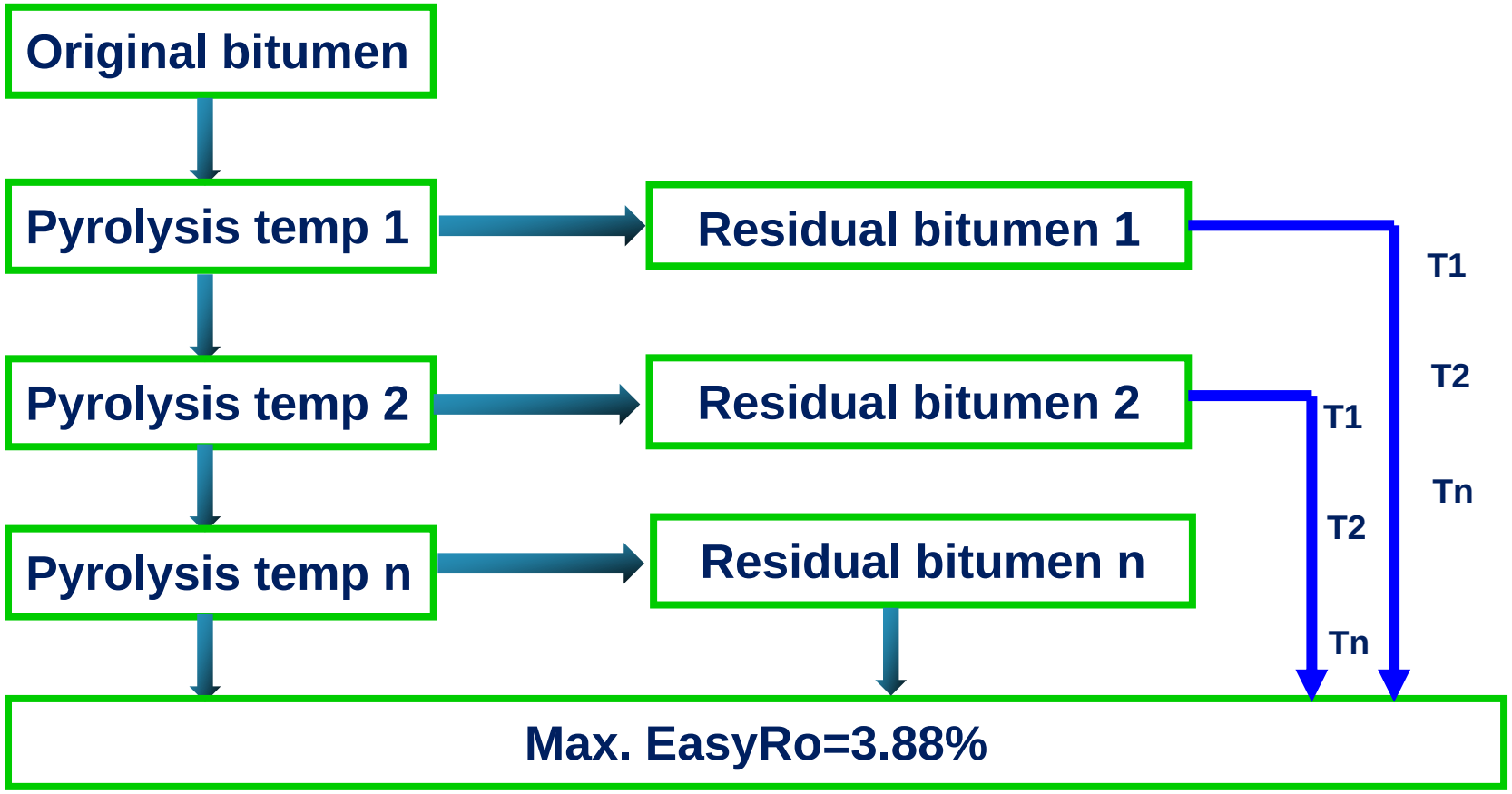
- **pulsed expulsion of gases**
- **Inconsistent methane source, i.e., bitumen itself and generated heavy hydrocarbons including wet gases**

Presenter's notes: Conventionally, carbon isotopic composition for partially trapped methane is estimated from the Rooney model on the basis of mass balance. This model, however, applies well to a simple situation where the methane is generated from a single source. For methane from oil cracking gas, its source is very complex, and the methane carbon isotope for partially trapped methane may be significantly distorted using the Rooney model.

Experimental design

Bitumen sample

TOC: 80.9%; EqvRo≈0.8; stable carbon isotope: -35.7‰

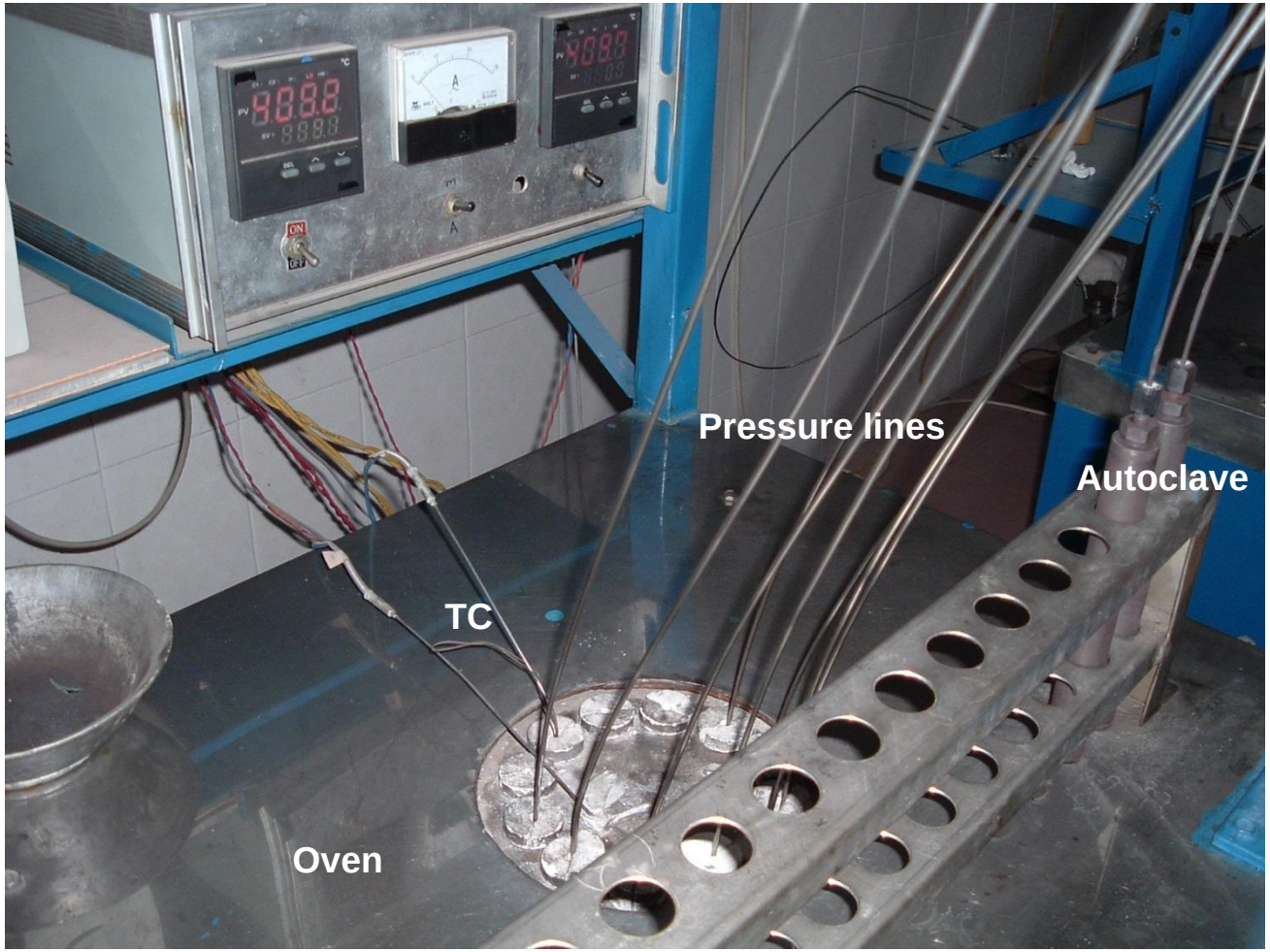


Pyrolysis Temp (ºC)	EasyRo (%)
Original	0.80
480	1.81
500	2.12
510	2.30
530	2.65
600	3.88

Pyrolysis program:

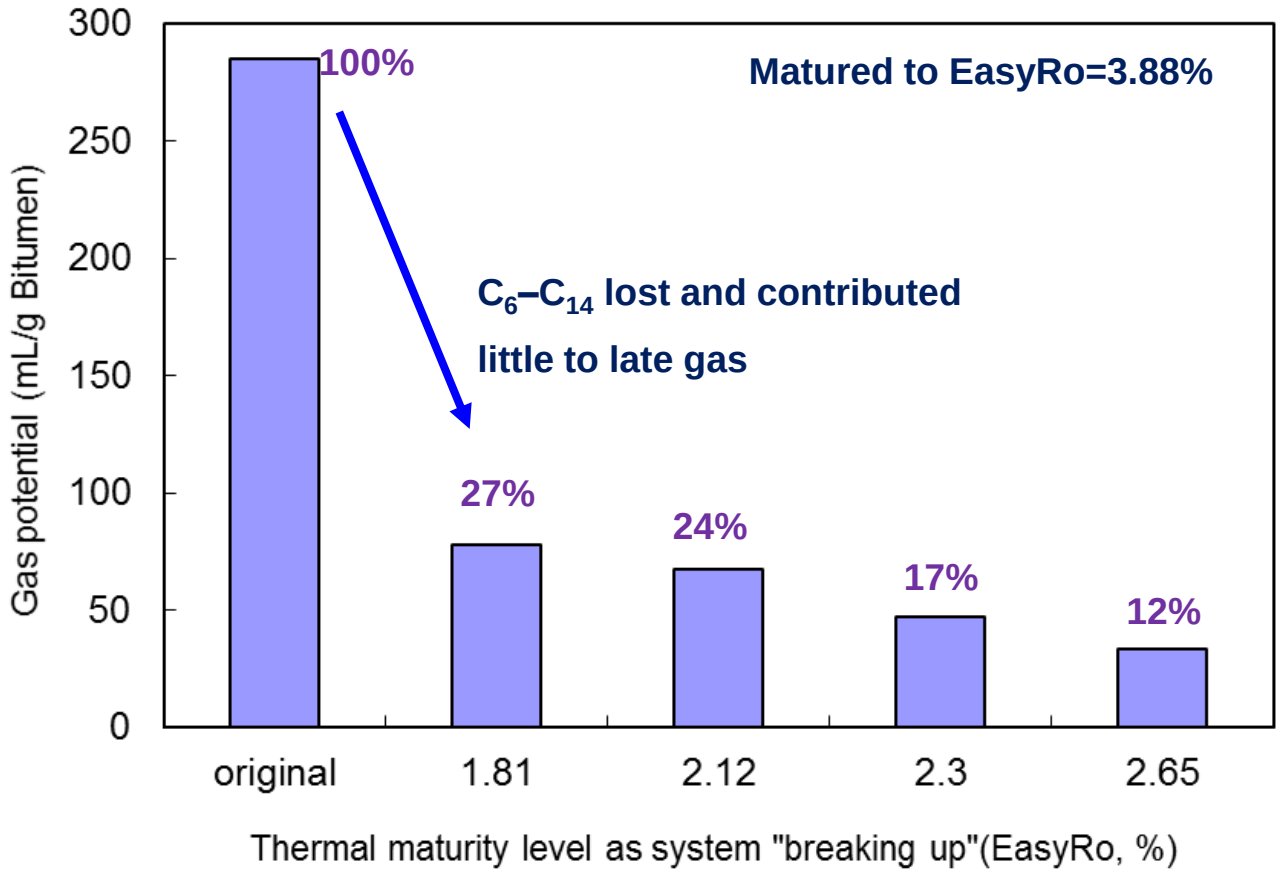
- **12 h from room temperature to 200 ºC;**
- **20 ºC/h from 200 ºC to 600 ºC**

Experimental setup



Gas potential

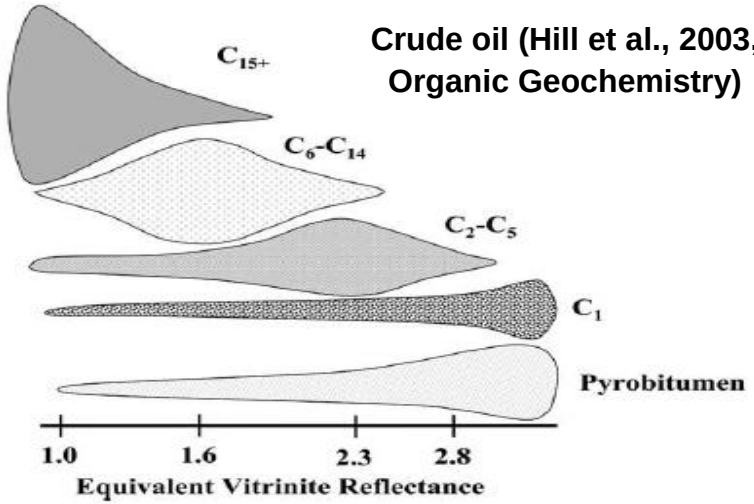
Comparison of intermittently open and constantly confined systems



Geological openness affects TOC/bitumen criteria for potential gas shales!

Comparison of gas potential:

- **1 wt.% for cumulative gas**
- **8 wt.% for partially trapped gas after EasyRo=2.65%**

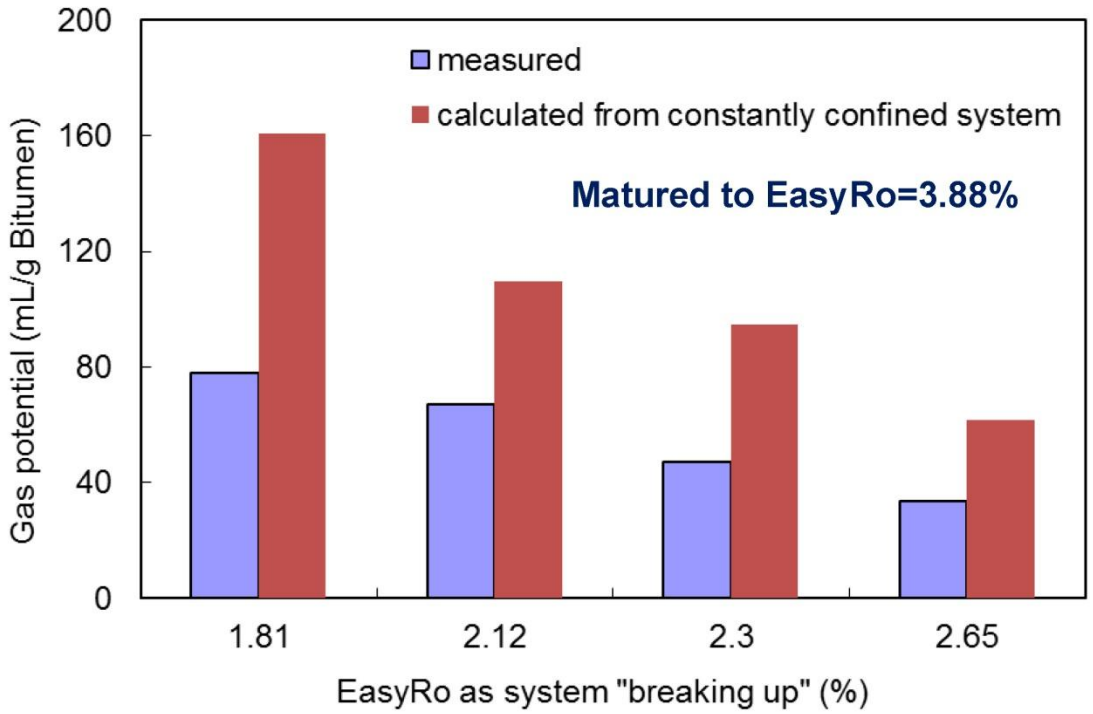


Crude oil (Hill et al., 2003, Organic Geochemistry)

Gas potential is calculated as the total volume of C_1–C_5 at STP conditions (0 ºC and 1 atm)

Gas potential

Pitfalls from a constantly confined system for an intermittently open system

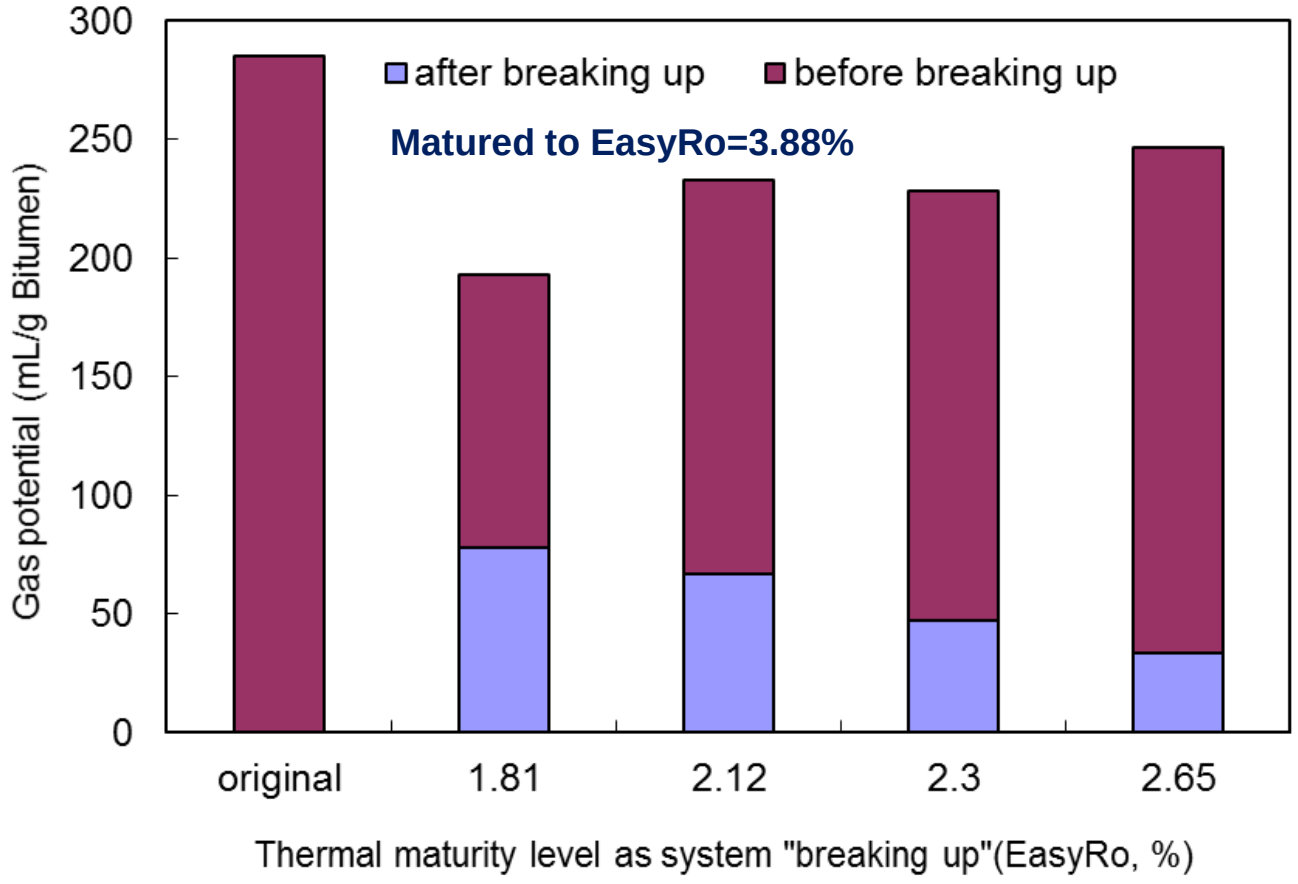


Gas potential could be significantly overestimated by extrapolating data from a constantly confined system to an intermittently open system!

Presenter's notes: Using data from a constantly confined system to estimate gas potential for an intermittently open system could overestimate the gas potential

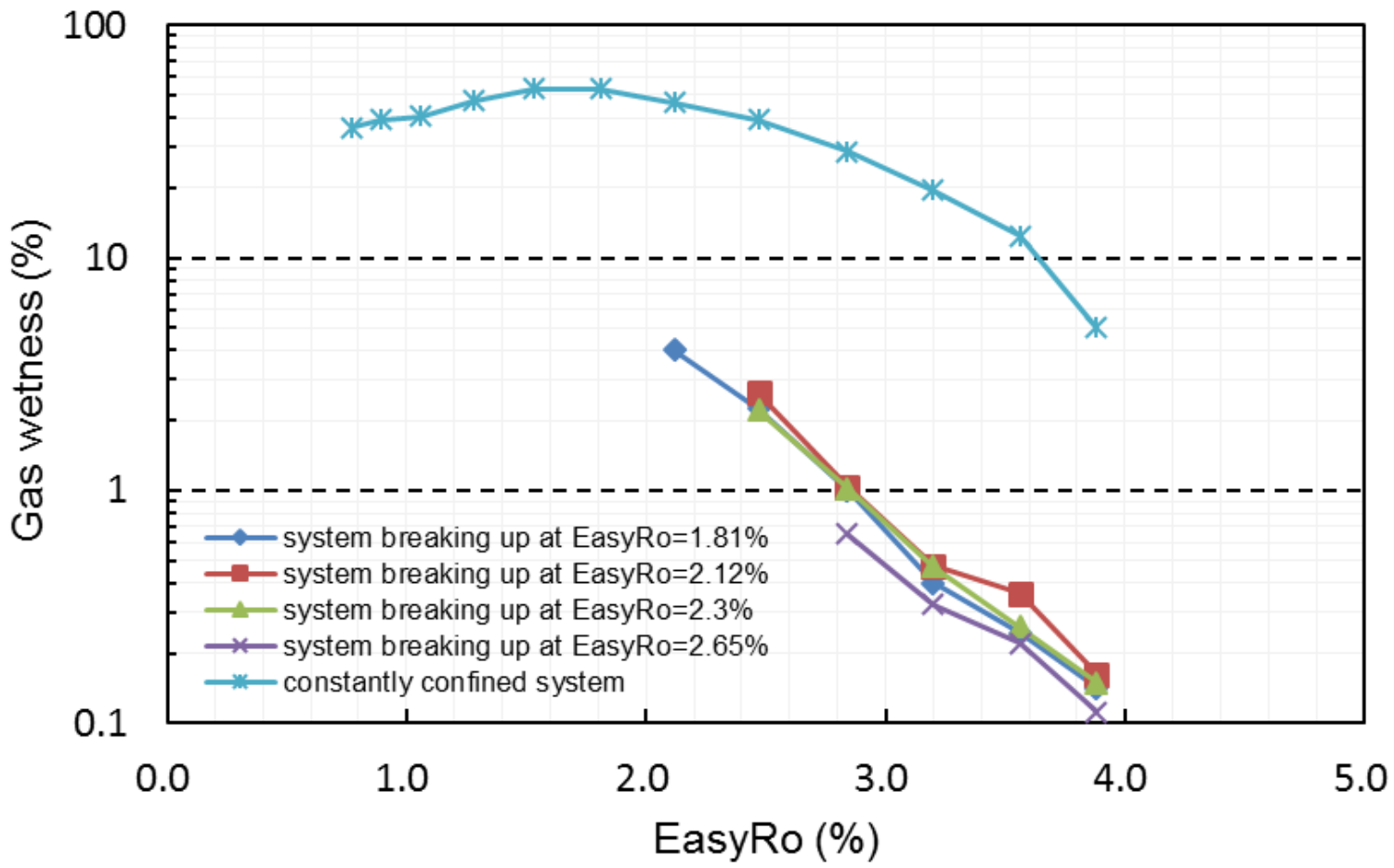
Gas potential

Mass balance for an intermittently open system



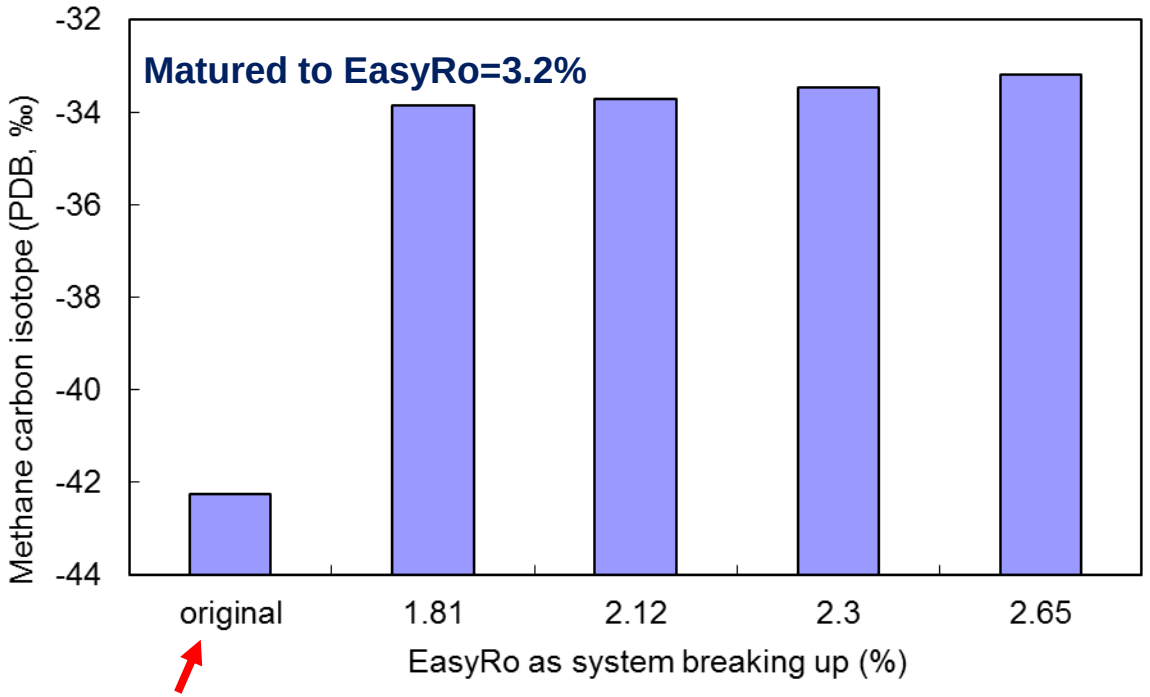
With system breaking up, the total gas volume generated from bitumen never exceeds that from a constantly confined system when the bitumen reached to the same thermal maturity level!

Chemical composition

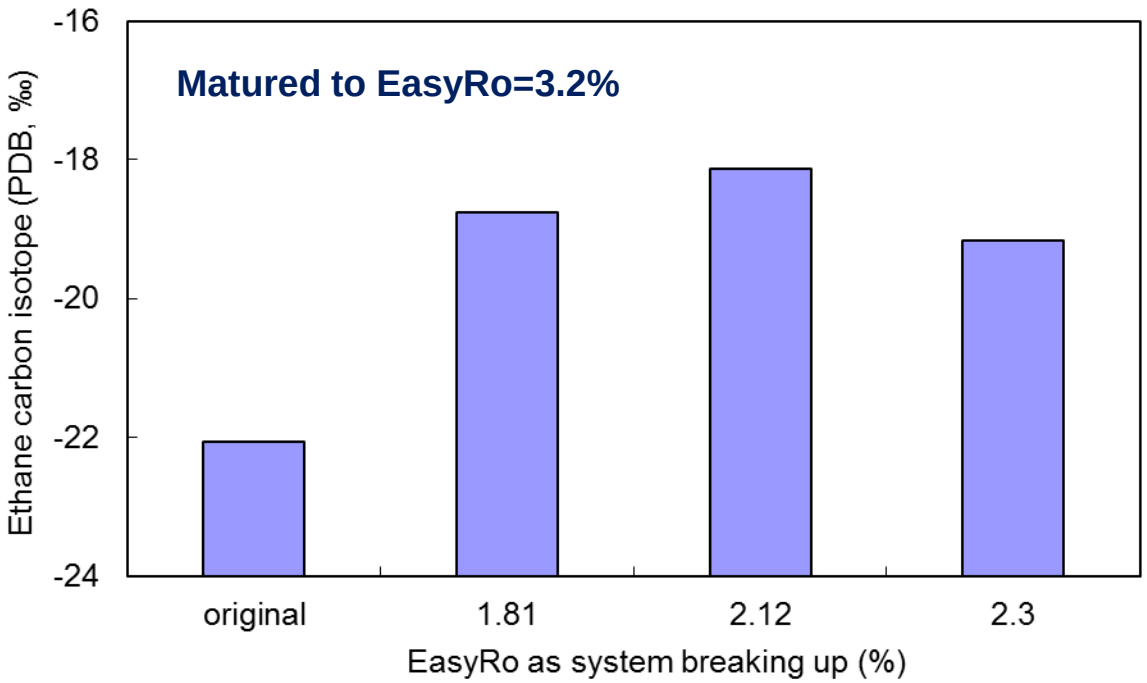


Late gas from bitumen itself rather than wet gas cracking is dry with gas wetness values comparable to those observed for natural gases in thermally over-mature shales!

Stable carbon isotopes

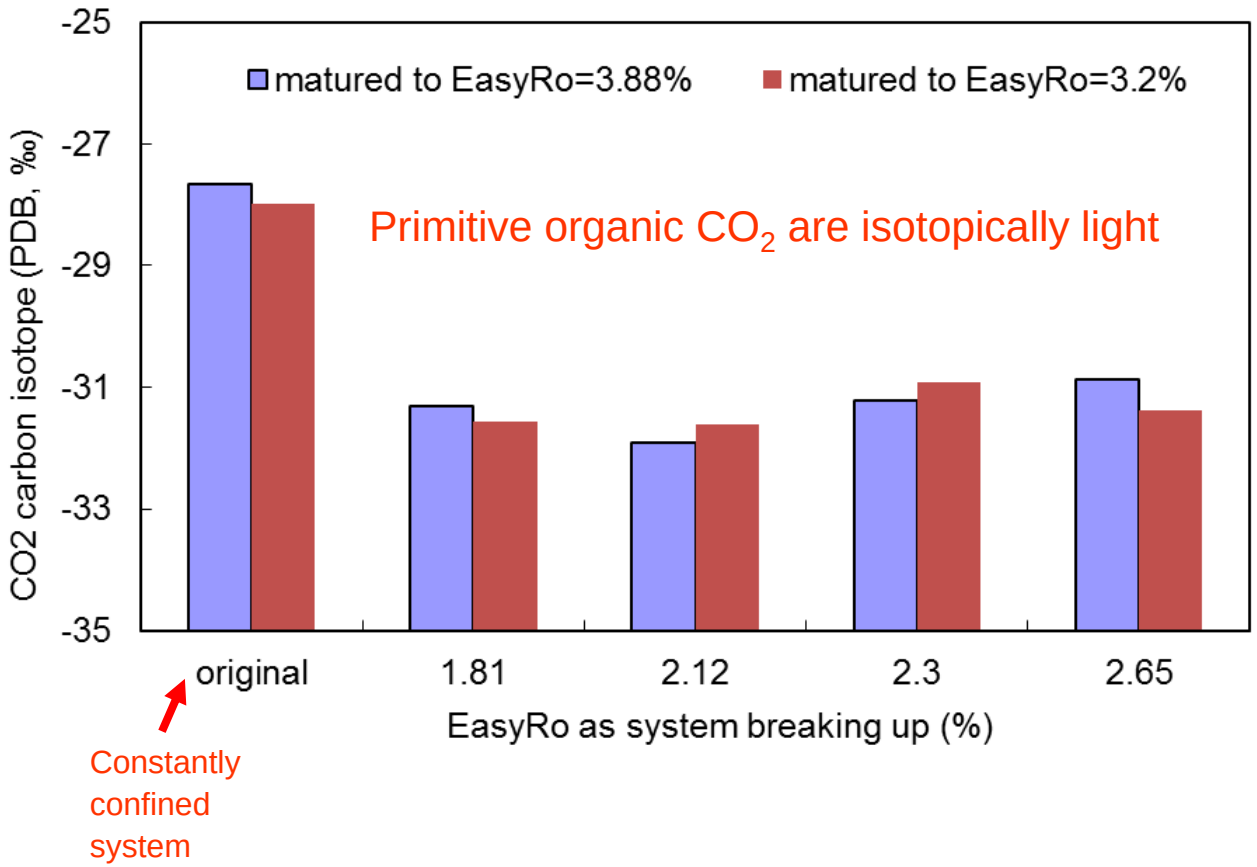


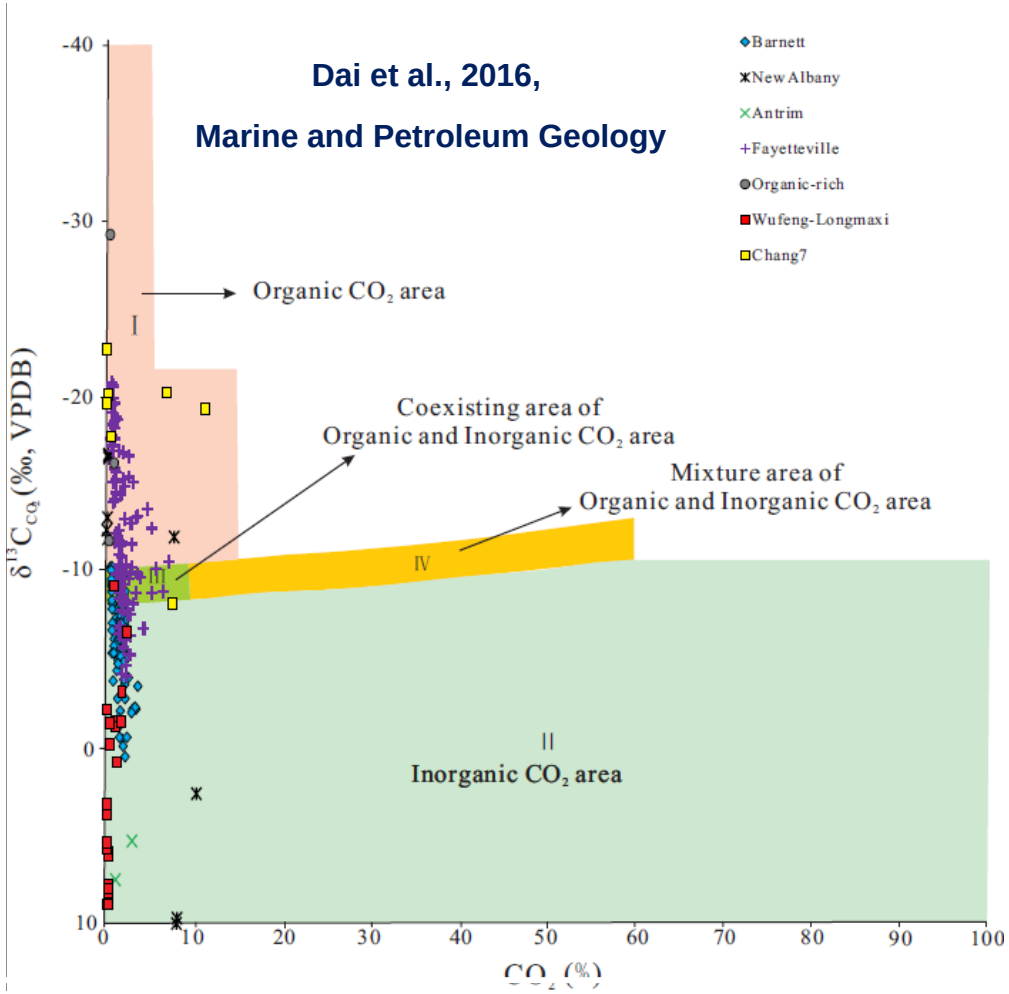
Constantly confined system



Trapping efficiency significantly affects methane and ethane carbon isotopes, but no reversals were observed!

Stable carbon isotopes





CO_2 in natural shale gas may have been involved in reactions to form isotopically light ethane

(Tang et al., 2011; Zumberge et al., 2012)

Geological implications

Methane carbon isotope fractionation at EasyRo = 3.88%

in a constantly confined system for various gas sources

Organic type	Bulk $\delta^{13}C$ (‰)	$\delta^{13}C_1$ (‰) *	Difference (‰)
Marine whole oil	-28.6	-34.8	6.2
Saturates	-28.5	-35.5	7
Aromatics	-28.3	-32.2	3.9
Asphaltenes	-28.4	-33.1	4.7
Solid bitumen	-35.7	-38.7	3
Mature type II kerogen	-30.4	-31.5	1.1

***: matured to EasyRo = 3.88% in a constantly confined system**

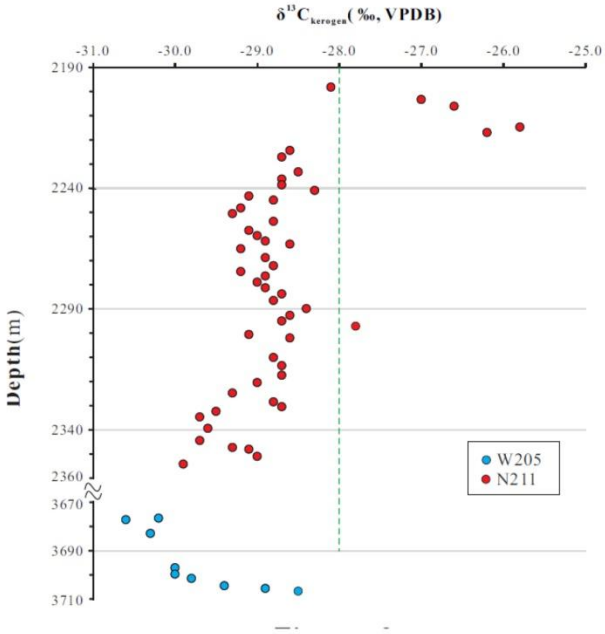
Methane carbon isotopes are expected to be variably lighter than the bulk carbon isotopes of their parent sources.

Geological implications

Very heavy methane carbon isotope values for oil/bitumen cracking gas

Sample	Depth (m)	EqVRo (%)	CH_4 (%)	C_2H_6 (%)	C_3H_8 (%)	CO_2 (%)	N_2 (%)	$\delta^{13}C_1$ (‰)	$\delta^{13}C_2$ (‰)	$\delta^{13}C_3$ (‰)
Ning201-H1	2745		99.12	0.5	0.01	0.04	0.3	-27	-34.3	
Ning201-H1	2745		99.04	0.54		0.4	0	-27.8	-34.1	
Ning211	2313-2341	3.2	98.53	0.32	0.03	0.91	0.17	-28.4	-33.8	-36.2
NingH2-1	2790		99.07	0.42	0.1	0	0.4	-28.7	-33.8	-35.4
NingH2-2	2586		99.28	0.47	0.01	0	0.23	-28.9	-34	
NingH2-3	2503		98.62	0.42	0.01	0.59	0.37	-31.3	-34.2	-35.5
NingH2-4	2568		99.15	0.44	0.01	0	0.4	-28.4	-33.8	
Zhao104	2117.5	3.3	99.25	0.52	0.01	0.07	0.15	-26.7	-31.7	-33.1
YSL1-1H	2002-2028	3.2	99.45	0.47	0.01	0.01	0.03	-27.4	-31.6	-33.2

Dai et al., 2016, Marine and Petroleum Geology

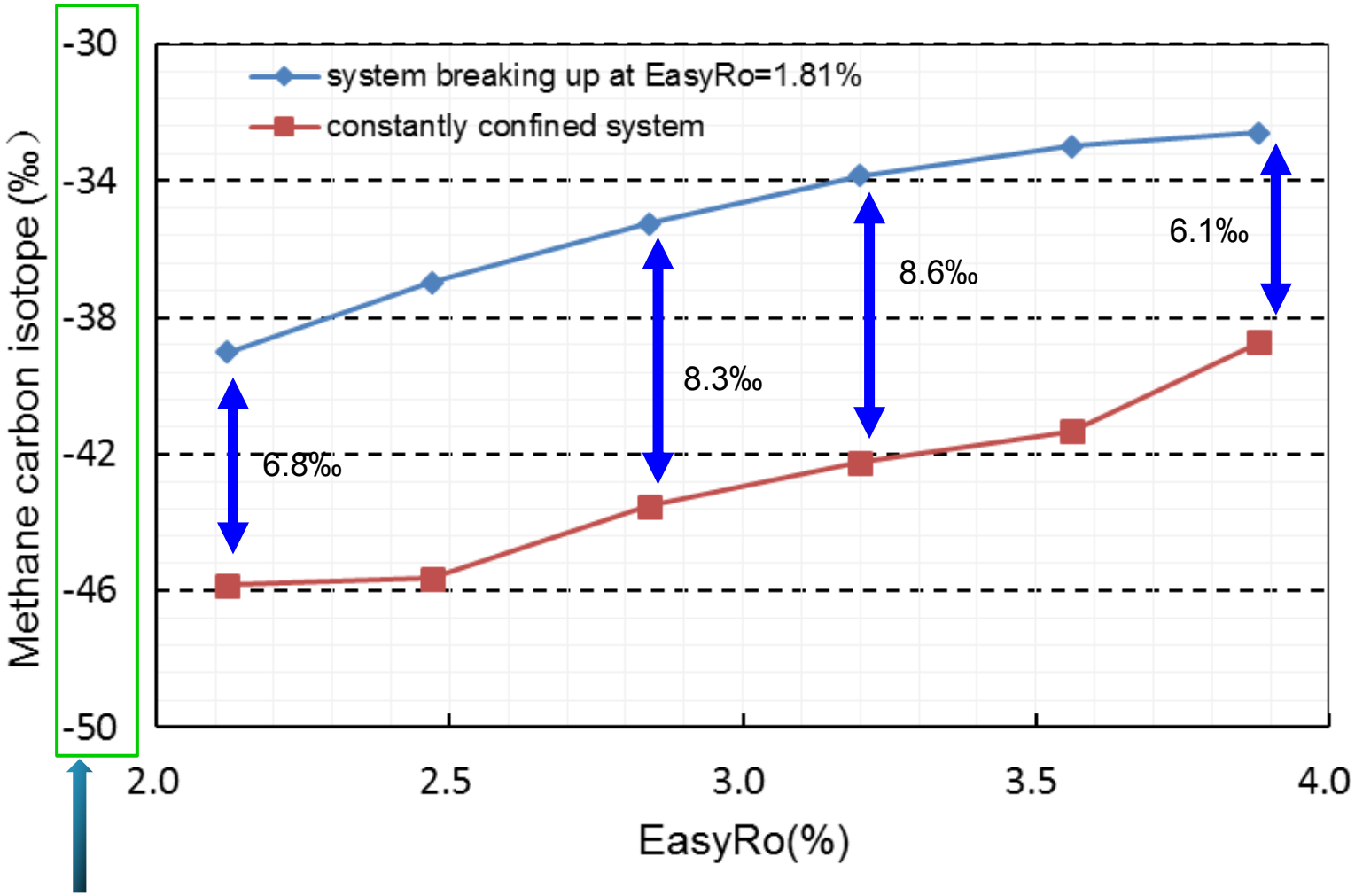


Shale gases with very high maturity were not generated in a constantly confined system

Presenter's notes: Compared with the carbon isotopes of kerogen, the carbon isotopes for methane are abnormally heavy, indicating they are partially trapped or are regenerated from residual bitumen with very high thermal maturity.

Geological implications

Very heavy methane carbon isotope values for oil/bitumen cracking gas

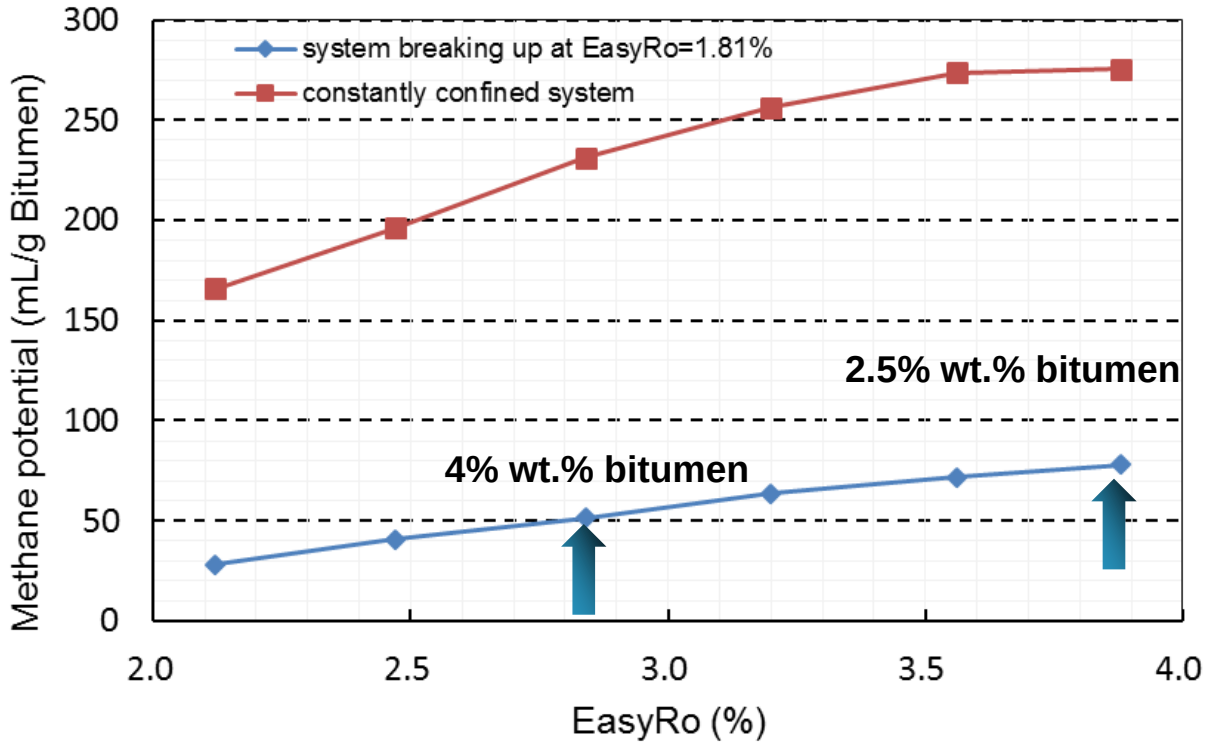


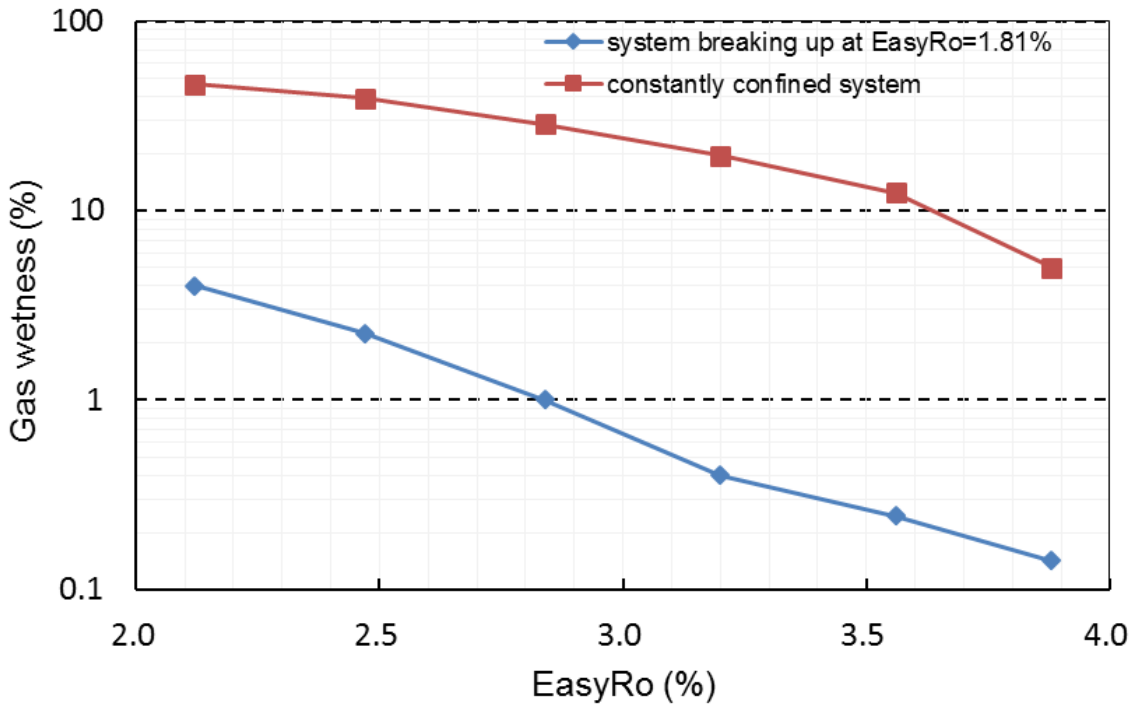
System breaking up might lead to much heavier methane carbon isotopes than a constantly confined system!

Values may be variable depending on specific parent sources!

Geological implications

Sufficient gas potential can also be achieved even if system breaks up at a high maturity level





A higher but not impossible bitumen or TOC content is needed to reach a minimum gas content of 2 m^3/ton for industrial production

The gas wetness values are comparable to those observed for naturally produced shale gas

Summary

- For an intermittently open shale reservoirs, a higher TOC content is required to generate sufficient dry gas with isotopically heavy methane, but no carbon isotopic reversals were observed during pyrolysis experiments.

- Primitive organic CO_2 generated in pyrolysis experiments are isotopically lighter than the CO_2 in natural shale gases, confirming that CO_2 -involved reactions to form isotopically light ethane or butane that leads to carbon isotope reversals (Tang et al., 2011; Zumberge et al., 2012) ;

- Specific pyrolysis experiments are recommended for given shale gas plays to fully understand their shale gas potential and geochemical characteristics.


Thanks for your time!
Any questions?