

Understanding Mass Transport Processes during Geochemical Characterization of Source Rock and Tight Reservoirs*

Daniel Xia¹, Changrui Gong¹, and Lucia Rodriguez¹

Search and Discovery Article #80734 (2020)**

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¹Apache Corporation, Houston, TX, USA (dnlxia@gmail.com)

Abstract

Geochemical characterizations of source rocks and their contained fluids are essential to the appraisal and development of unconventional resources. Many geochemical and characterization methods, such as pyrolysis, gas desorption, and isotopic measurements on rock or fluid samples, may involve one or more mass transport processes during sample preservation, pretreatment and analyses, including but not limited to Darcy flow, bulk and surface diffusion, and adsorption/desorption. These processes can change oil and gas geochemical fingerprints (ratios between compounds or isotopologues) in the field as well as in the lab. Whether the original hydrocarbon in-place and the geochemical fingerprints of reservoir fluids can be reliably reconstructed through lab measurements requires a quantitative assessment on the impacts from these processes.

This work investigates the sensitivities of various geochemical parameters to different mass transport processes and some geochemical reactions. The following parameters are evaluated: 1) generation and expulsion rates of typical compounds (hydrocarbons, H₂S and heterocyclic aromatics) in geological bodies; 2) hydrocarbon generation and expulsion rates during lab pyrolysis on samples with different sizes; 3) gas isotopic fractionation during the flow in geological bodies and in lab samples; 4) oil compositional fractionation in geological bodies and in lab samples; 5) hydrocarbon loss during coring time and during lab treatments; and 6) collectable hydrocarbon during lab desorption and Rock-Eval pyrolysis.

The results show that the dominating processes controlling geochemical parameters are often different under lab and under geological conditions. These differences make it challenging to restore reservoir fluid properties through lab derived data. The dominating process should be distinguished during geochemical characterization. Correlations between the key parameters of different processes are often vague and not necessarily universal. These uncertainties should be considered when interpreting geochemical data to evaluate the quantity and properties of reservoir hydrocarbons, along with their migration and production from geological bodies.

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Understanding mass transport processes during geochemical characterization of source rock and tight reservoirs

Daniel Xia, Changrui Gong, and Lucia Rodriguez

Apache Corporation

Motivation

- Effects from mass transport processes are common and may interfere geochemical interpretation and source rock characterization

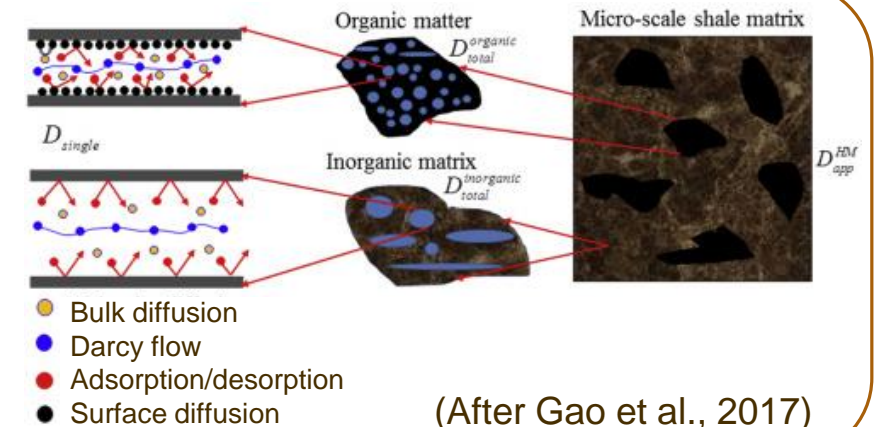
$$[\text{Mass increase with time}] = [\text{Mass increase due to transport}] + [\text{Mass increase due to reaction}]$$

Convection
(Darcy flow)

Diffusion
(bulk and surface)

Desorption,
Adsorption
(Surface)

Generation,
Decomposition



(After Gao et al., 2017)

- The processes are entangled in unconventional plays:
 - Tight rock: slow flow rate
 - Multiple chemical reactions may involve during geological and production time
- Tremendous efforts and misinterpretation can be saved by better understanding mass transport processes

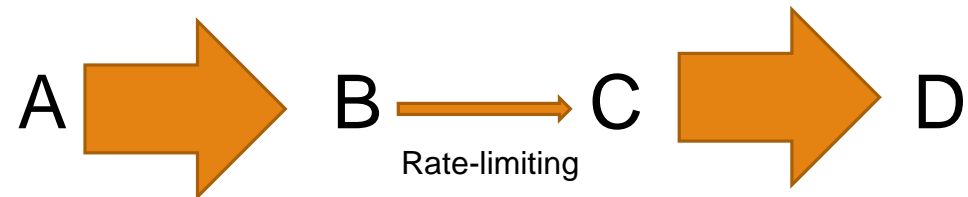
Time scale of processes: Characteristic time

- Characteristic time is “simply a measure of how fast a process will proceed, ... within seconds, hours, days, or weeks” (Morgenroth, 2015)
... or million years, tens of million years in geology
- Calculating characteristic time is semi-quantitative (no difficult numerical simulation)
but effective to recognize governing processes

Parallel processes:
Fast process dominates the change



Sequential (serial) processes:
Slow process limits the rate

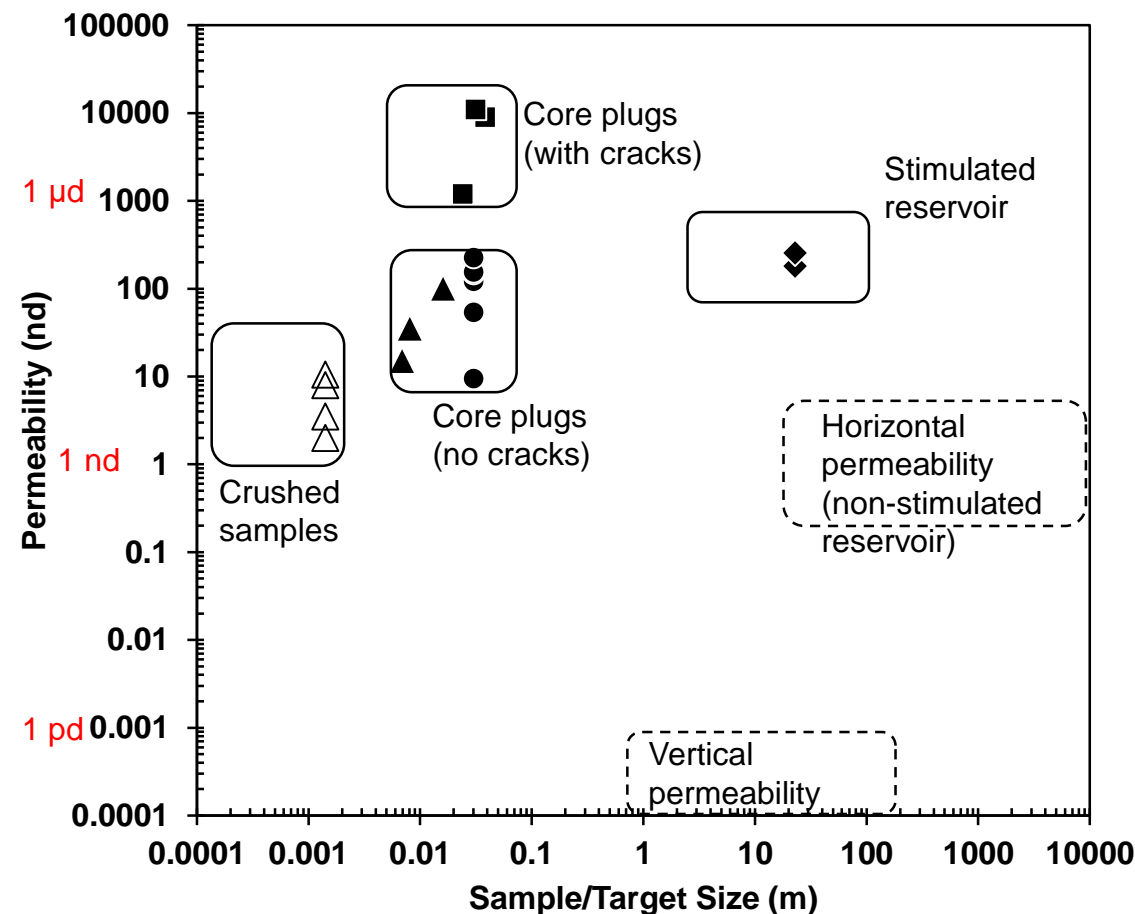


Expression of characteristic time in different processes

Process	Governing equation	Parameters	Characteristic time
Convection	Darcy's Law: $\frac{\partial p}{\partial t} = \frac{\kappa}{\phi \mu c} \nabla^2 p$	Pressure (p), porosity (ϕ), permeability (κ), viscosity (μ), compressibility (c), distance (L)	$\frac{\phi \mu c}{\kappa} L^2$
Diffusion	Fick's Law: $\frac{\partial c}{\partial t} = D \nabla^2 c$	Concentration (c), diffusivity (D), distance (L)	$\frac{L^2}{D}$
Adsorption/Desorption	Wigner-Polanyi Equation: $\frac{\partial \theta}{\partial t} = k_a p(1 - \theta) - k_d \theta$ with $k_a = A_a \exp\left(-\frac{E_a}{RT}\right)$, $k_d = A_d \exp\left(-\frac{E_d}{RT}\right)$	Fractional coverage (θ), frequency factor (A) and activation energy (E) for adsorption and desorption, temperature (T)	$\frac{1}{k_d}$
Chemical reaction	First order kinetic equation most commonly: $\frac{dc}{dt} = -kc$ with $k = A \exp\left(-\frac{E}{RT}\right)$	Concentration (c), frequency factor (A), activation energy (E), temperature (T)	$\frac{1}{k}$

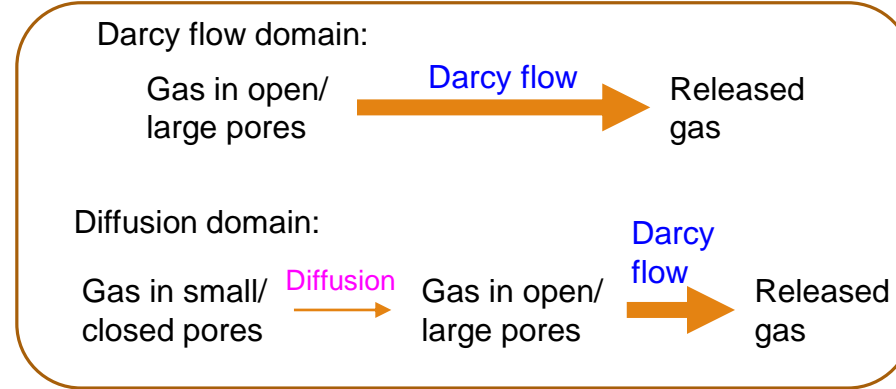
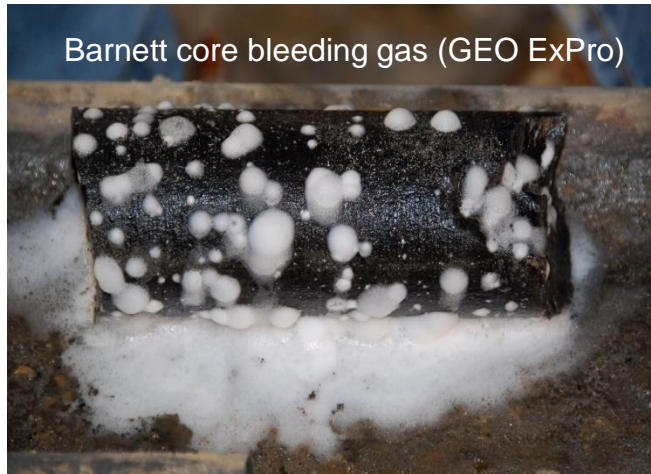
Permeability of shale

- Permeability of shale varies in 8 orders of magnitude depending on
 - Sample/target size
 - Fractures
 - Direction (parallel or perpendicular to lamination)
- Low permeability of shale under geological conditions is confined by the existence of overpressure over tens of millions of years
- Huge variation in characteristic time of Darcy flow

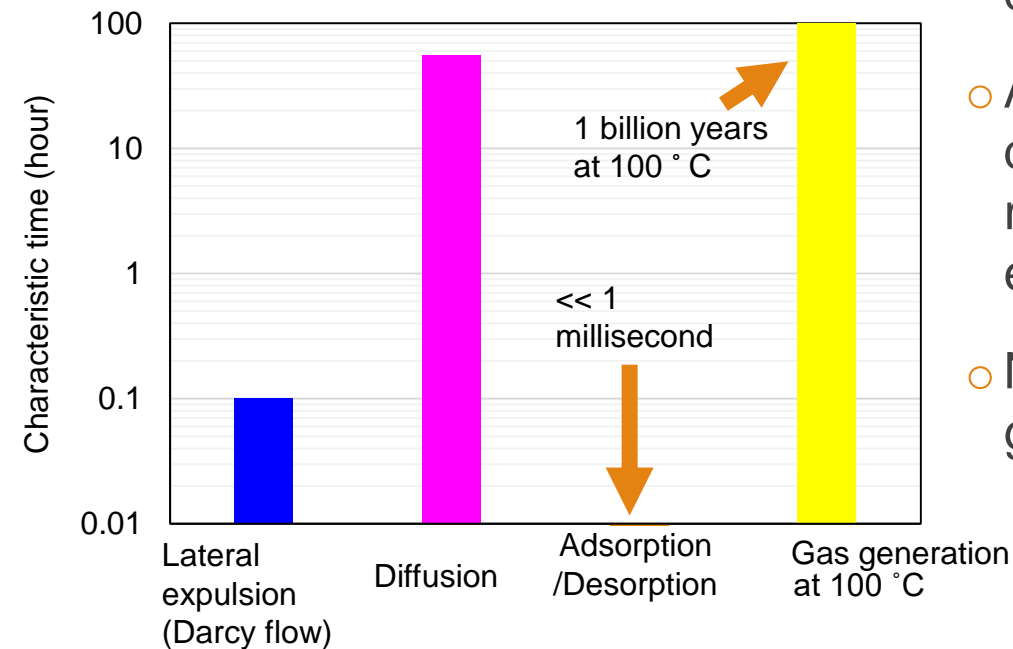
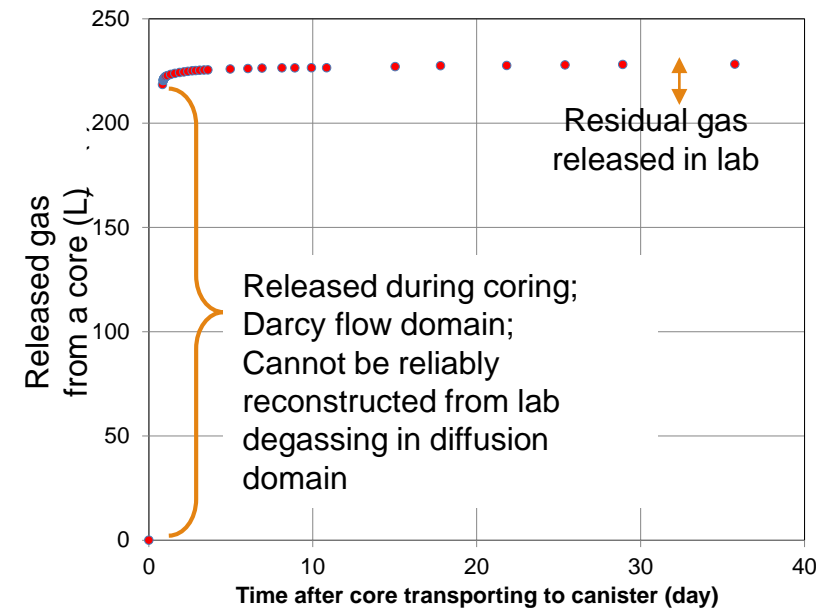


Xia et al. (2020)

Example 1: gas recovery from a core

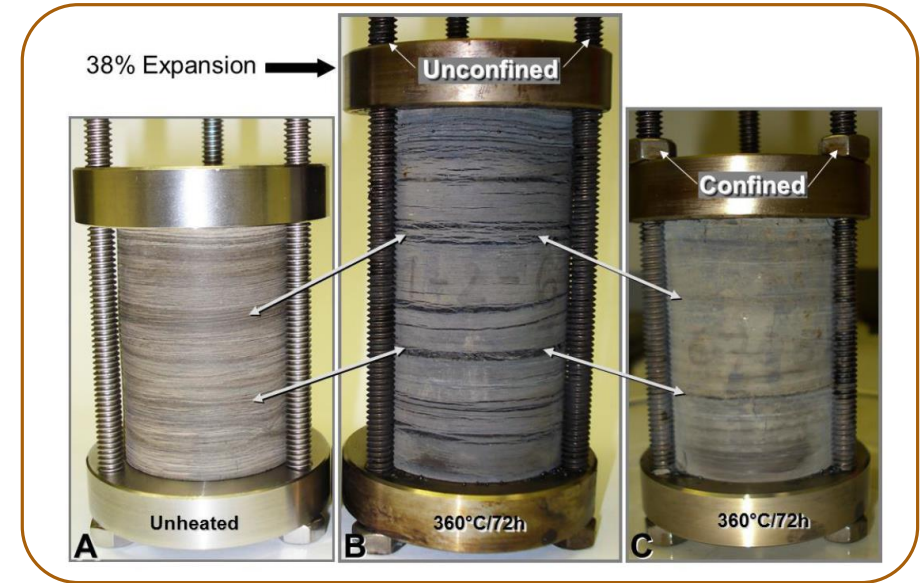


- Gas mainly released directly through convection during coring
- Residual gas (small amount) continue releases during preservation, because diffusion is slow
- Adsorption onto surfaces and desorption from surfaces are rapid, and locally under equilibrium
- Not real-time gas generation from kerogen

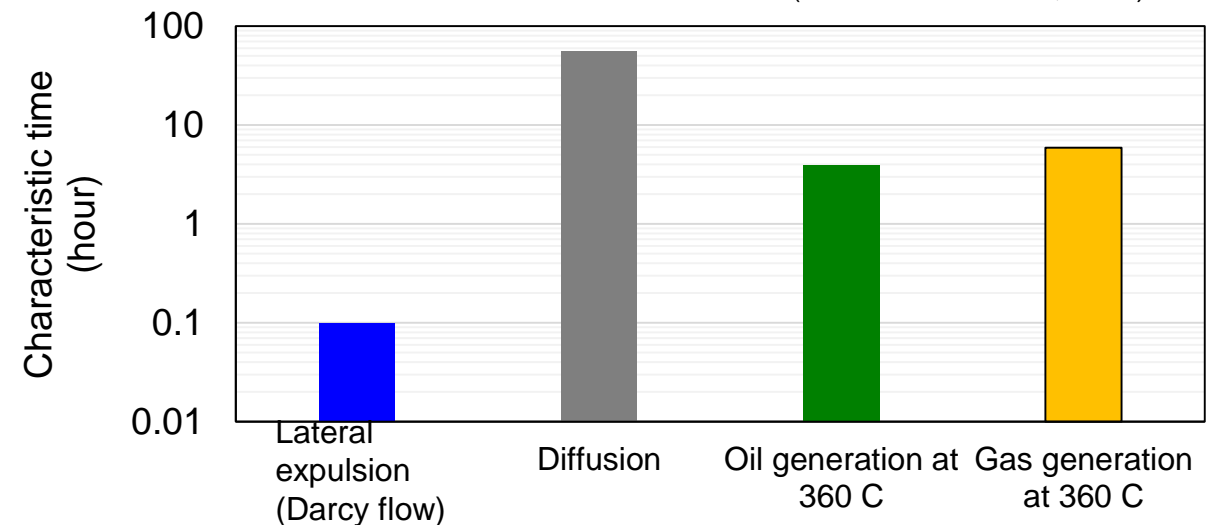


Example 2: oil generation/expulsion during hydro-pyrolysis of a core

- Oil/Gas generation significantly slower than Darcy flow
 - Each generated molecule (in an open pore) is ready to expel
- After pressure equilibrated, Darcy flow stops, and diffusion is slow
 - there is always retained oil, regardless of oil composition
- Retained oil is heavy:
 - Adsorption/desorption equilibrium holds polar compounds on surfaces
 - Large molecules trapped in small pores

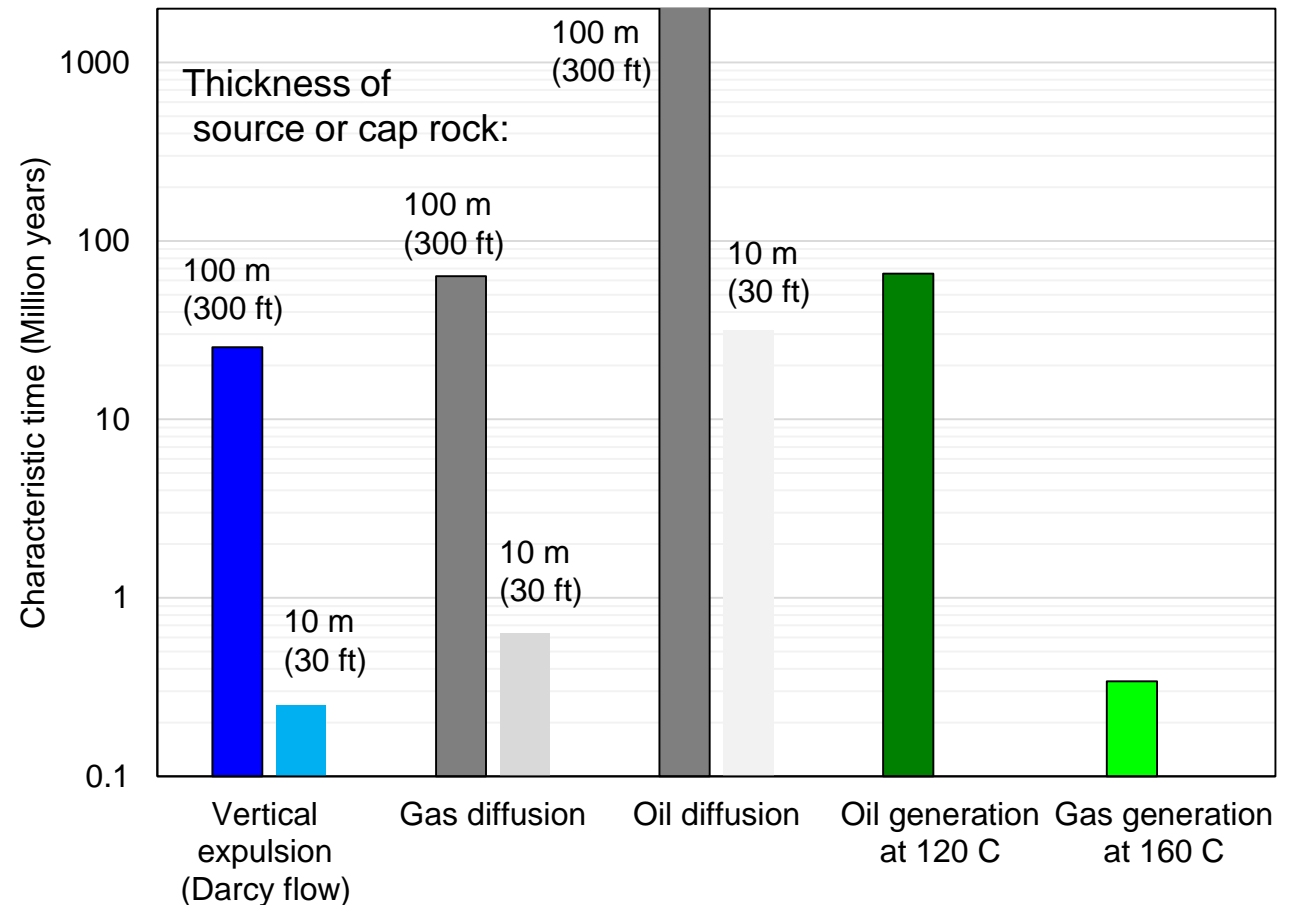


(Lewan and Birdwell, 2013)



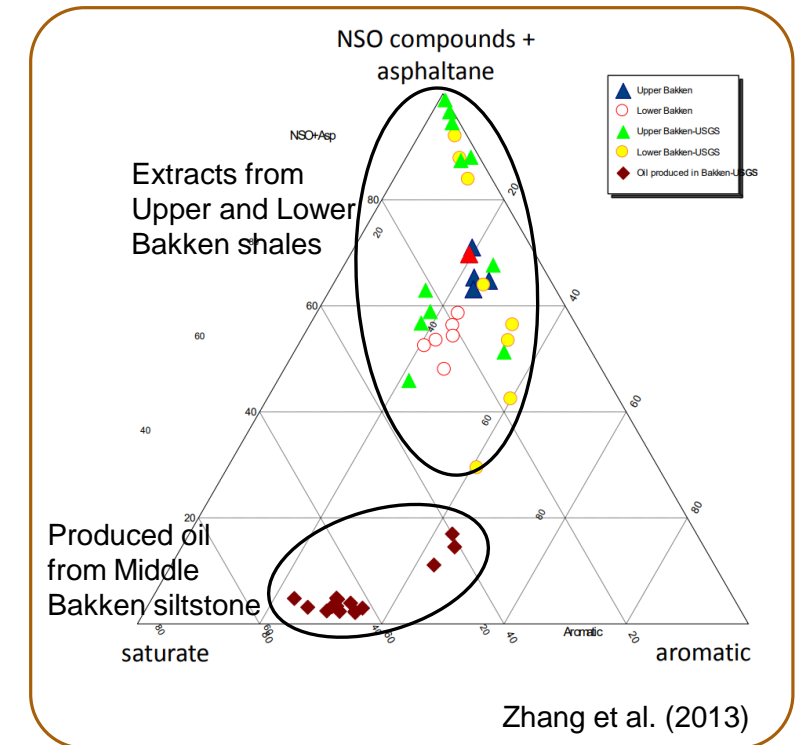
Example 3: Generation/Expulsion under geological conditions

- Oil generation significantly slower than expulsion (despite of an extremely low perm of 1pD)
 - Each generated oil molecule is ready to expel
 - No contribution to overpressure
- Gas generation can be faster than expulsion for a thick source rock or sealing layer
 - May contribute to overpressure
- Contribution of diffusion to oil expulsion significantly lower than Darcy flow
- “Real-time” generation contributing to production is conceptually incorrect



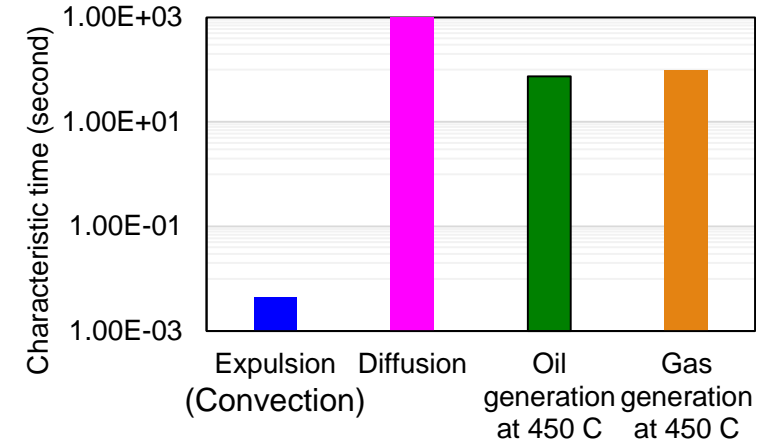
Compositional fractionation during expulsion, migration and production

- Variations of non-polar components is mainly governed by generation (source rock type, thermal maturity) and extent of cumulation (instantaneous vs cumulative), not by the fractionation through mass transport (oil generation is the rate-limiting step)
- Variation of concentration of polar compounds in oil:
 - Partitioning in different phases
 - Selective adsorption on mineral surfaces
 - Selective dissolution in water
 - Polar components saturating the surfaces before migrating
- Reasons of compositional variations (oil fingerprints, gas isotopes) during production:
 - Variation of contributions from different zones
 - Variation in phases due to pressure change

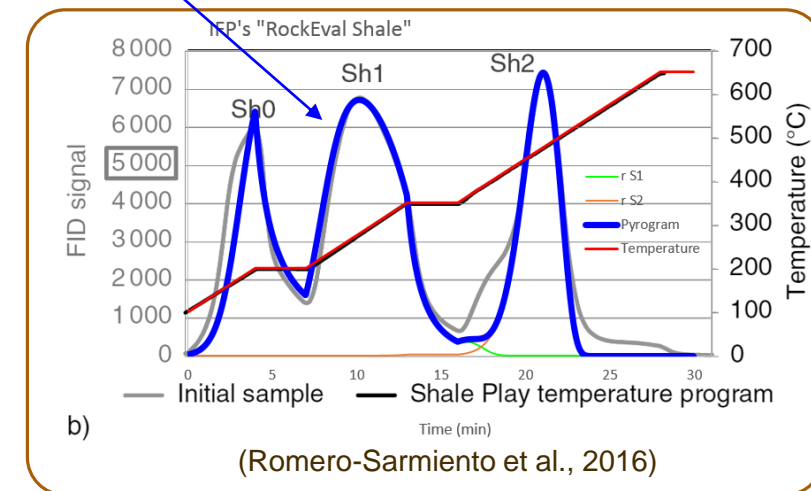
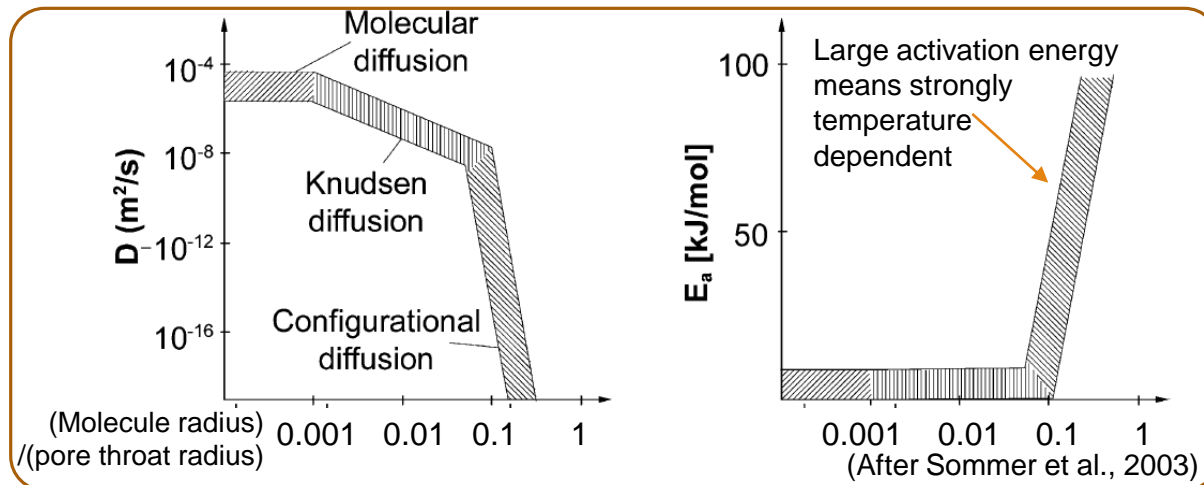


Example 4: S1 peak of Rock-Eval Pyrolysis

- Component of S1 peak
(after majority of hydrocarbon lost during coring, preservation and crushing)
 - Residual oil/gas trapped in closed pores
 - Polar compounds adsorbed on the surfaces
- Release of S1 peak: Diffusion domain
 - Wide peak: broad pore radius distribution; broad molecular size distribution (residual NSO + asphaltene), wide activation energy
 - S1 peak is a measurement on oil diffusion in rock, temperature-dependent, and can be tuned with varying heating ramp

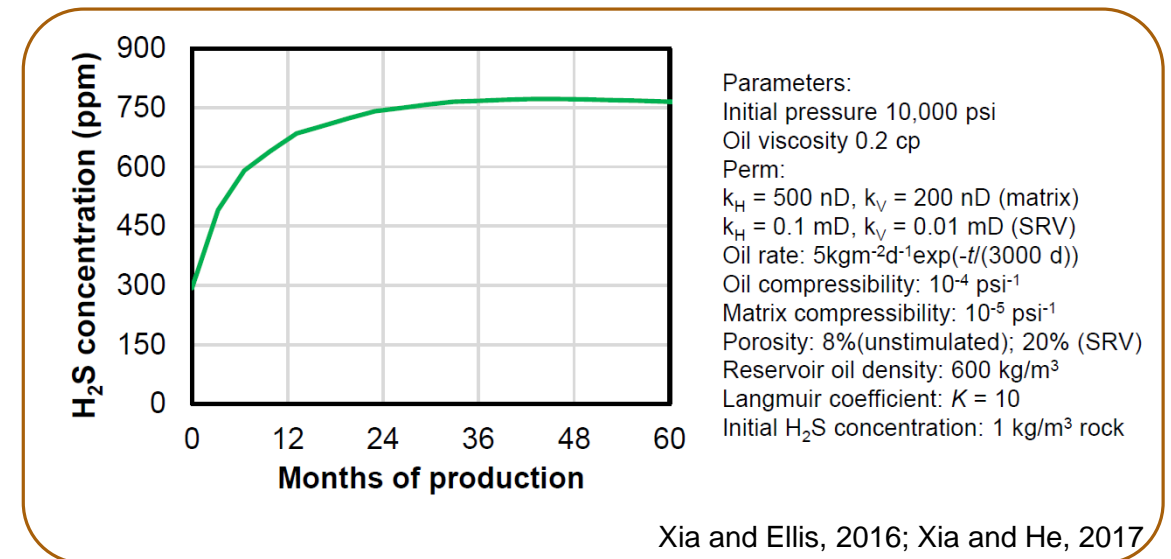
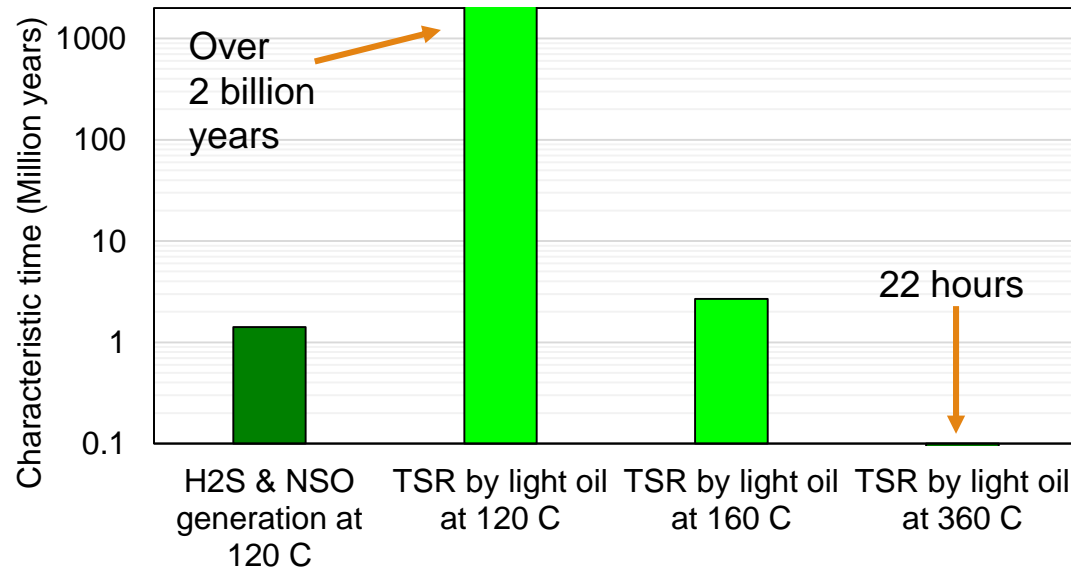


Modeled results (this work):
 S1 peak through diffusion ($A = 10^8 \text{ s}^{-1}$; $E = 93\text{-}121 \text{ kJ/mol}$)
 S2 peak through kerogen cracking ($A = 10^{14} \text{ s}^{-1}$; $E = 226\text{-}231 \text{ kJ/mol}$)



Example 5: H₂S produced with unconventional oil

- “Real-time” H₂S generation during drilling and completion below detection limit
 - Reduction of sulfate (surfactants) in completion fluids not a source of detectable H₂S
 - “Reservoir souring” (biochemical sulfate reduction) requires flooding over years to reach ppm level of H₂S
- H₂S increase during production of horizontal wells:
 - Strong adsorption on fresh fracture surfaces
 - Adsorption/desorption equilibrium shift causes delayed H₂S occurrence and increase during production



Dynamic isotope effect

$$\left[\begin{array}{c} \text{Mass increase} \\ \text{with time} \end{array} \right] = \left[\begin{array}{c} \text{Mass increase} \\ \text{due to transport} \end{array} \right] + \left[\begin{array}{c} \text{Mass increase} \\ \text{due to reaction} \end{array} \right]$$

Convection
(Darcy flow)

Isotopic
fractionation
absents

Diffusion
(bulk and
surface)

Isotopic
fractionation
presents
($^{12}\text{CH}_4$ diffuses
faster than $^{13}\text{CH}_4$)

Desorption,
Adsorption

Isotope fractionation
between free gas phase
and adsorbed phase is
minimal
(typically $< 0.5 \text{ ‰}$ in $\delta^{13}\text{C}$)

$$\begin{cases} \frac{\partial c}{\partial t} = \nabla[u(c + c^*)] + \nabla(D\nabla c) + n_m \frac{\partial \theta}{\partial t} \\ \frac{\partial c^*}{\partial t} = \nabla[u(c + c^*)] + \nabla(D^* \nabla c^*) + n_m \frac{\partial \theta}{\partial t} \end{cases}$$

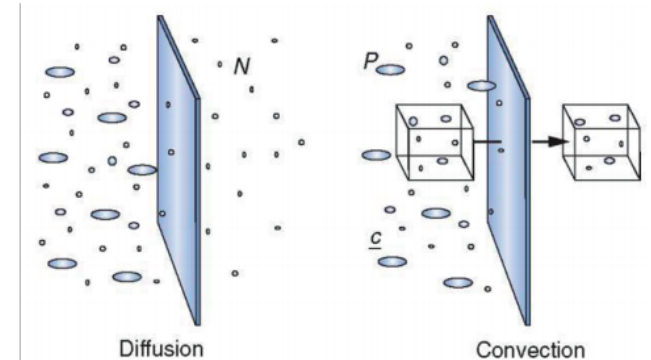


Fig. 1. Diffusion and convection are schematically represented. Diffusion is a movement of a solute with tendency to reach the same concentration on each side of the membrane. Convection occurs when water is driven by either a hydrostatic or an osmotic force across a semipermeable membrane carrying solutes that can pass through membrane pores. Source: Ronco C, Bellomo R, Kellum JA, editors. Critical care nephrology. 2nd ed. Philadelphia: Saunders/Elsevier, 2009.

Example 6: isotopic variations of released gas from rock

- Isotope shift during lab degassing is due to diffusion, not due to “free gas” vs “adsorbed gas”
- The mixing or “deconvolution” calculation is invalid:

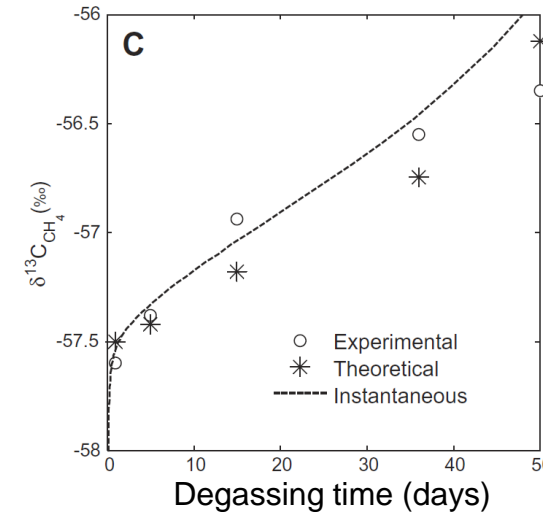
$$\delta^{13}\text{C}_{\text{mix}} = f_{\text{free}} \delta^{13}\text{C}_{\text{free}} + (1 - f_{\text{free}}) \delta^{13}\text{C}_{\text{ads}}$$

$$f_{\text{free}} = (\delta^{13}\text{C}_{\text{mix}} - \delta^{13}\text{C}_{\text{free}}) / (\delta^{13}\text{C}_{\text{mix}} - \delta^{13}\text{C}_{\text{ads}})$$



- Isotope fractionation by diffusion should be considered in the measurement on fluid inclusion samples

- K/T boundary changed from 65 to 66.05 Ma: error due to argon diffusion eliminated during K-Ar and Ar-Ar Dating (Kelley, 2002)



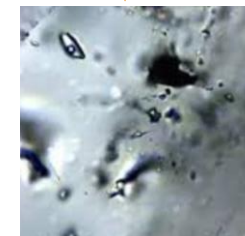
Isotope change due to extent of diffusion, not due to increased contribution of “adsorbed gas” with time

(Xia and Tang, 2012)

Fractionation at shallow burial depth during geological time



Fractionation during sample preparation of fluid inclusions



Summary

- Field and lab test data from unconventional plays may involve multiple geochemical reactions and mass transport processes
 - These processes have large variations in time scale
 - Identifying the dominant or the rate-limiting processes helps to understand geochemical phenomena
 - Key processes should be distinguished
- Avoid overinterpreting artificial effects
- Experiment design:
 - Be cautious of the differences in mass transport between lab and geological conditions
 - Flow domain, flow direction, fluid and pore distributions, temperature, mineral conversion, etc.
 - Separating different processes makes lab simulation more informative

Parameters applied

Parameter		Value
Porosity (ϕ)		0.08
Permeability (κ)	Vertical (geological conditions)	0.1 pD
	Horizontal (in core scale)	100 nD
	Crushed rock	10 nD
Oil viscosity (μ)		0.1 cP
Bulk compressibility (c_t)		1 (GPa) ⁻¹
Diffusivity (D)	Gas	5 $\mu\text{m}^2/\text{s}$
	Oil	0.5 $\mu\text{m}^2/\text{s}$
Frequency factor (A)	Desorption	10 ¹³ s ⁻¹
	Oil generation	1.4 x 10 ¹⁴ s ⁻¹
	Gas generation	3.3 x 10 ¹⁴ s ⁻¹
	TSR by light oil	4.0 x 10 ¹⁴ s ⁻¹
	TSR by gas	6.4 x 10 ¹⁶ s ⁻¹
Activation energy (E)	Desorption (physisorption)	20 – 50 kJ/mol
	Oil generation	53 kcal/mol
	Gas generation	54.6 kcal/mol
	TSR by light oil	56.5 kcal/mol
	TSR by gas	63.2 kcal/mol

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