Evolution of Vitrinite Reflectance Models
Understanding the fundamentals

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Norwegian Petroleum Directorate
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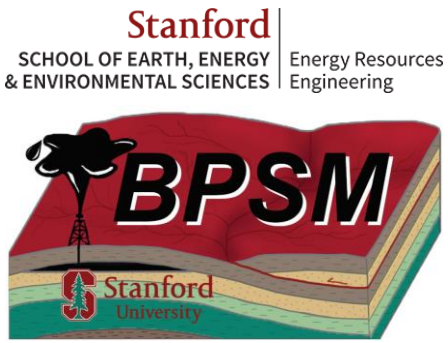

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BPSM is evolving

Now stands for **B**asin **P**rocesses and **S**ubsurface **M**odeling

Expanded scope includes carbon sequestration, gas hydrates, carbonate models, pore-pressure prediction, integrated workflows, and other basin-scale subsurface processes

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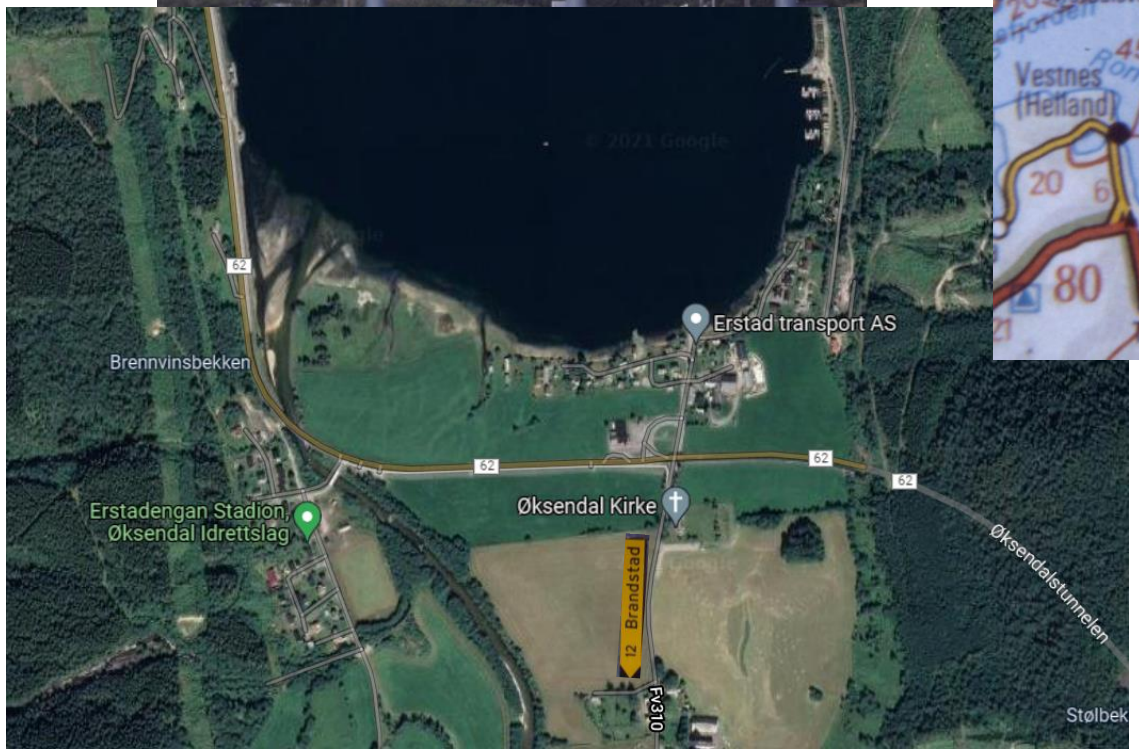
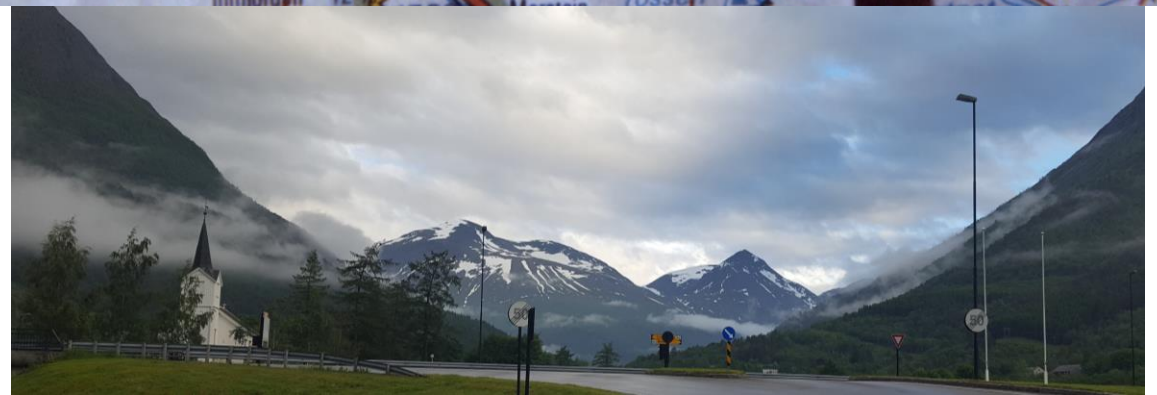
My Mother's side comes from Brandstad, Norway

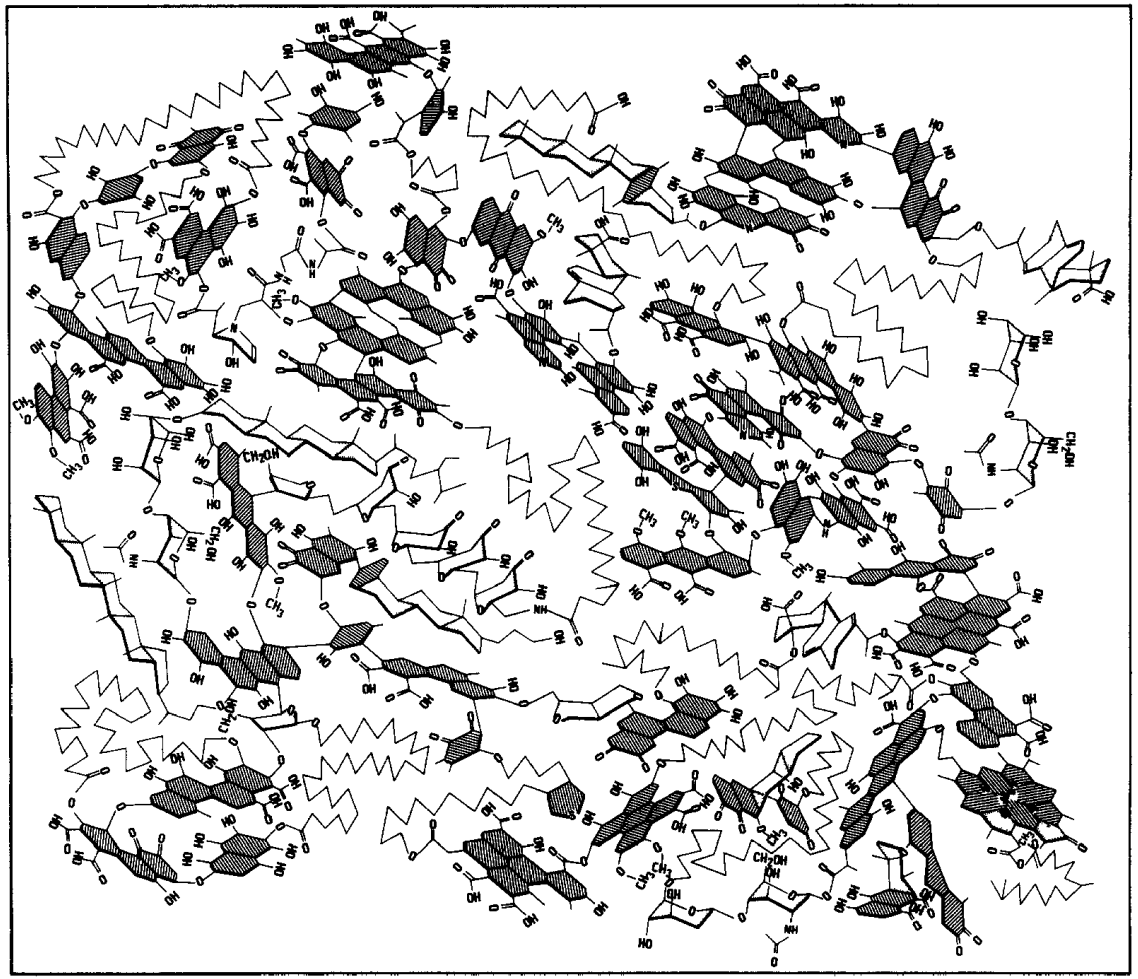




All organic matter becomes more aromatic and anisotropic with burial and maturation

Behar and Vandenbrouke, Org. Geochem., 1987

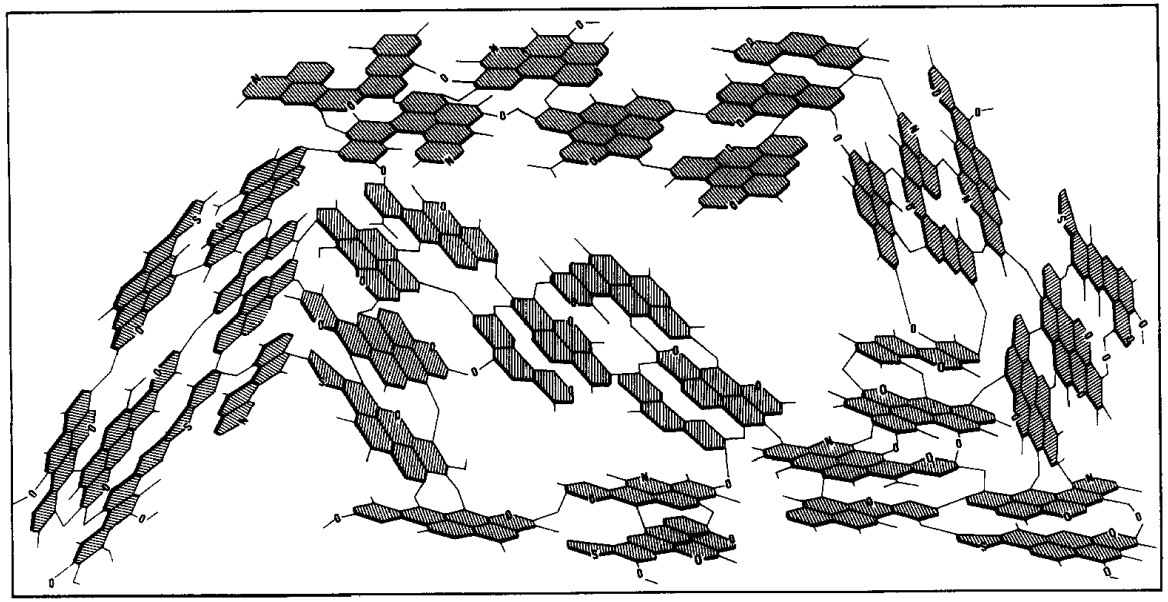
STRUCTURE III-a : H/C = 1,06 O/C = 0,281 MW = 26 176



Reflectance is related to refractive and absorptive indices of the material (Fresnel-Beer eq.)

Absorptive indices are dominated by the size and orientation of aromatic rings (Schuyer et al., Trans. Faraday Soc. 1953)

STRUCTURE III-c : H/C = 0,67 O/C = 0,059 MW = 13 226



Models of vitrinite reflectance range in sophistication

Simple correlations with temperature

Example:

Barker's geothermometer

Global kinetics that correlate with reflectance; may have pressure dependence

Examples:

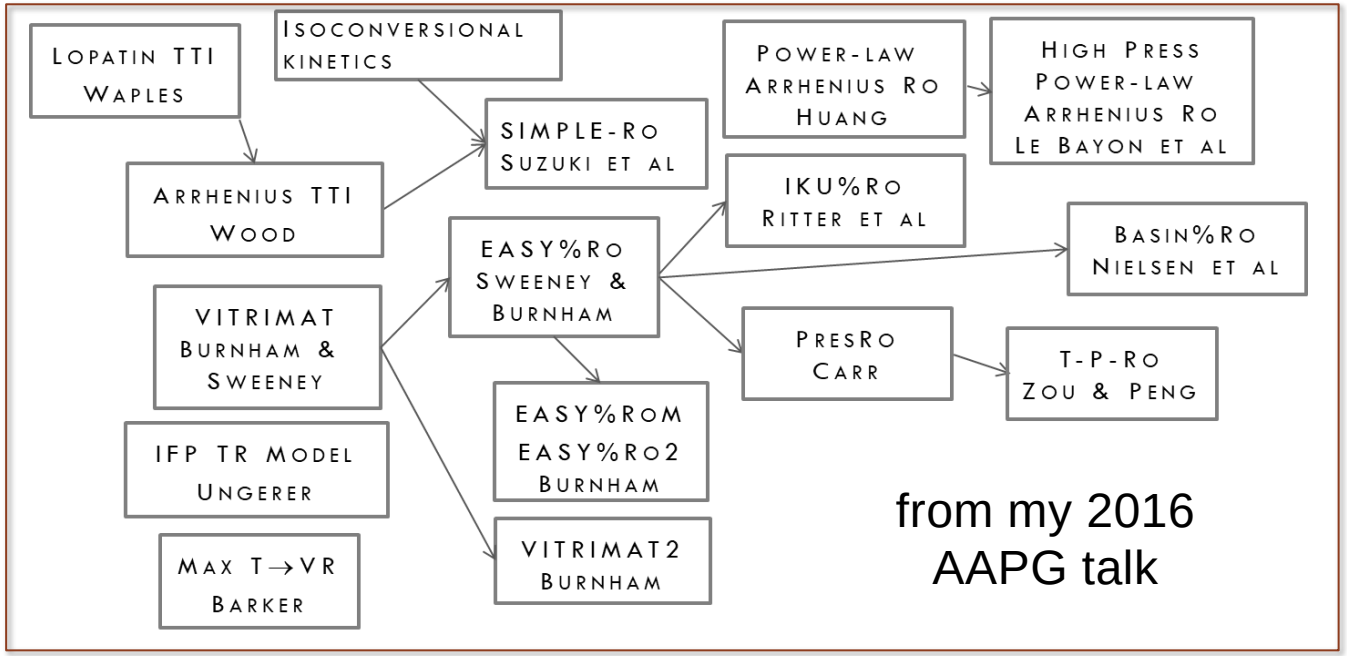
TTI

Easy%RoX

Calculate molecular composition and relate to reflectance

Example:

Vitrimat



from my 2016 AAPG talk

My Takeaway Advice

1. Don't use Easy%R_o anymore—it has some serious weaknesses
   a) My preference is Easy%R_oV for basin modeling; Easy%R_oB for bitumen when no vitrinite is available

2. The Easy%R_o family of models were developed to reduce computation time, which is not as important with today's computers; using 2nd-order reactions is just as effective

3. The Vitrimat approach is more rigorous and adaptable to various kinds of organic matter

4. Most vitrinite reflectance suppression is due to misidentification of vitrinite, but true suppression can exist in sapropelic shales

Relating reflectance to fundamental optical properties came in the 1950s

(1866?)

Fresnel-(Lambert) law:

$$\%R_o = \frac{(n-n_o)^2+(nk)^2}{(n+n_o)^2+(nk)^2} \times 100\%$$

n = refractive index
n_o = refractive index of immersion oil
k = absorption coefficient
l = thickness
λ = wavelength
ρ = number density
α = polarizability

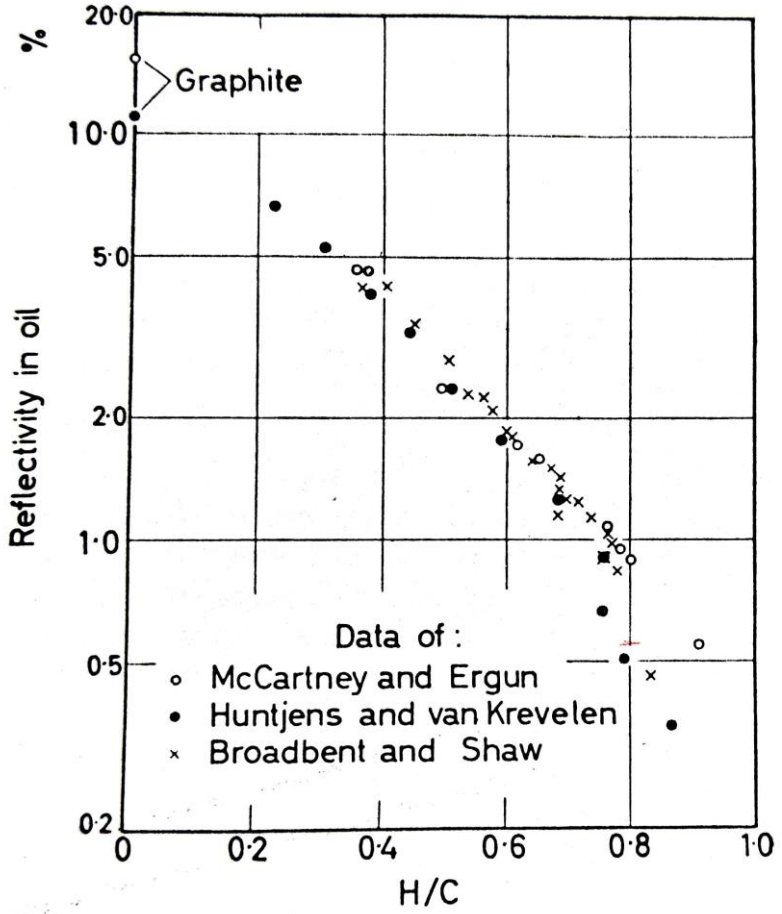
(1869-1878)

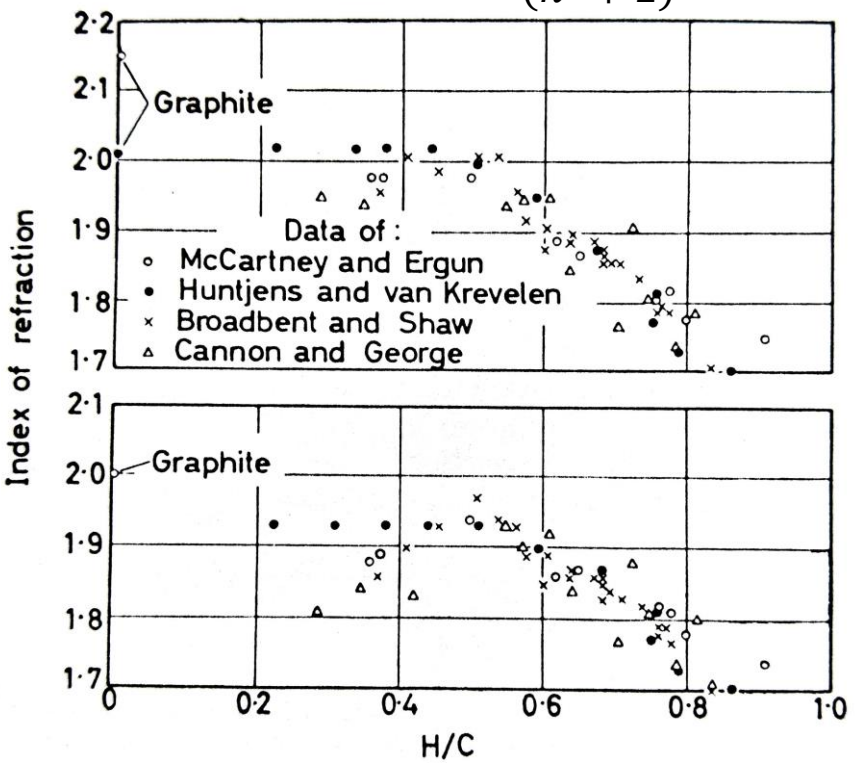
Lorentz-Lorenz eq: $\frac{(n^2-1)}{(n^2+2)} = \rho\alpha$

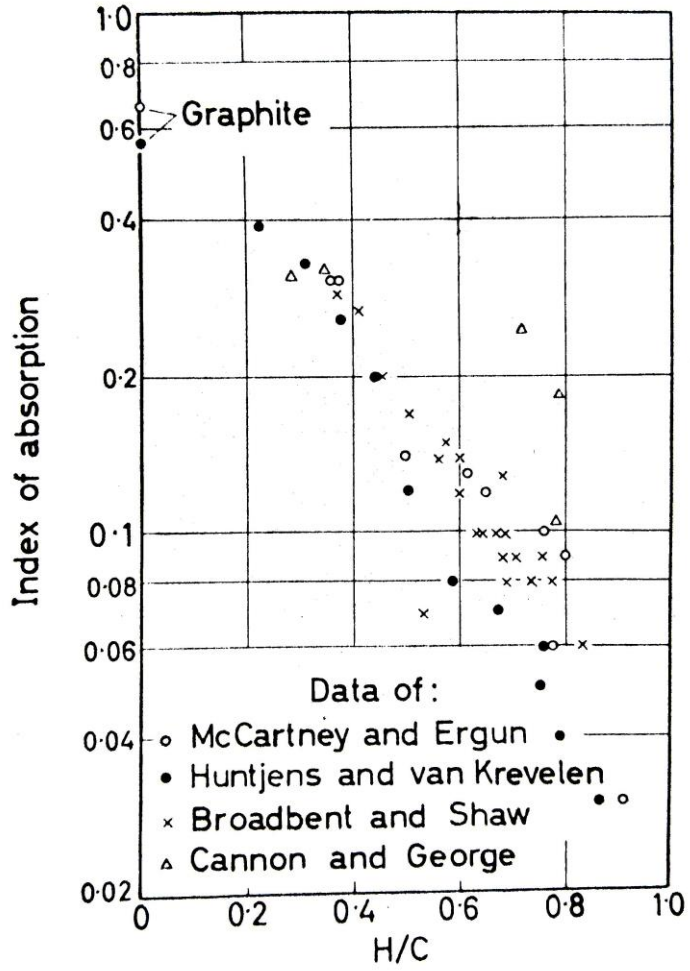
(1729-1852)

Lambert-Beer law:

$$I = I_0 exp(-4\pi(nk)l/\lambda)$$



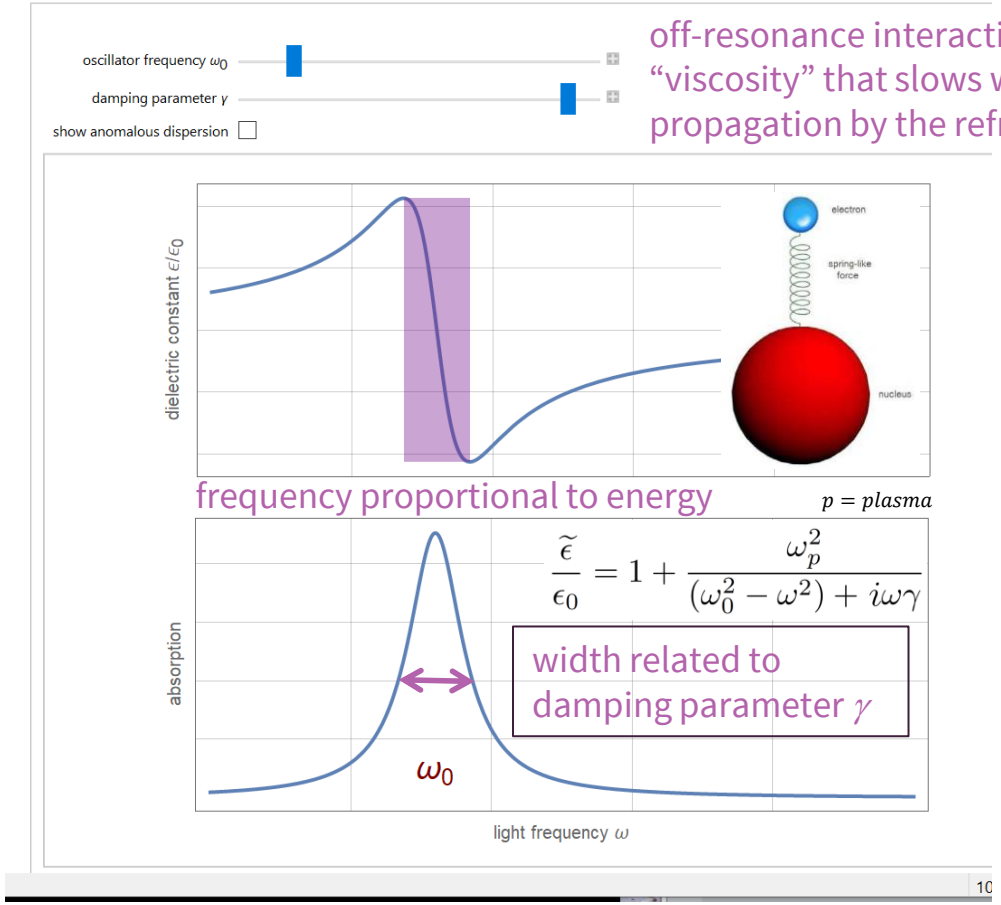




Refractive index has contributions from localized and delocalized electrons (n^* is a complex number: $n^* = n \pm ik$)

Wolfram Demonstrations Project demonstrations.wolfram

Drude-Lorentz Model for Dispersion in Dielectrics: localized electrons



off-resonance interaction causes "viscosity" that slows wave propagation by the refractive index

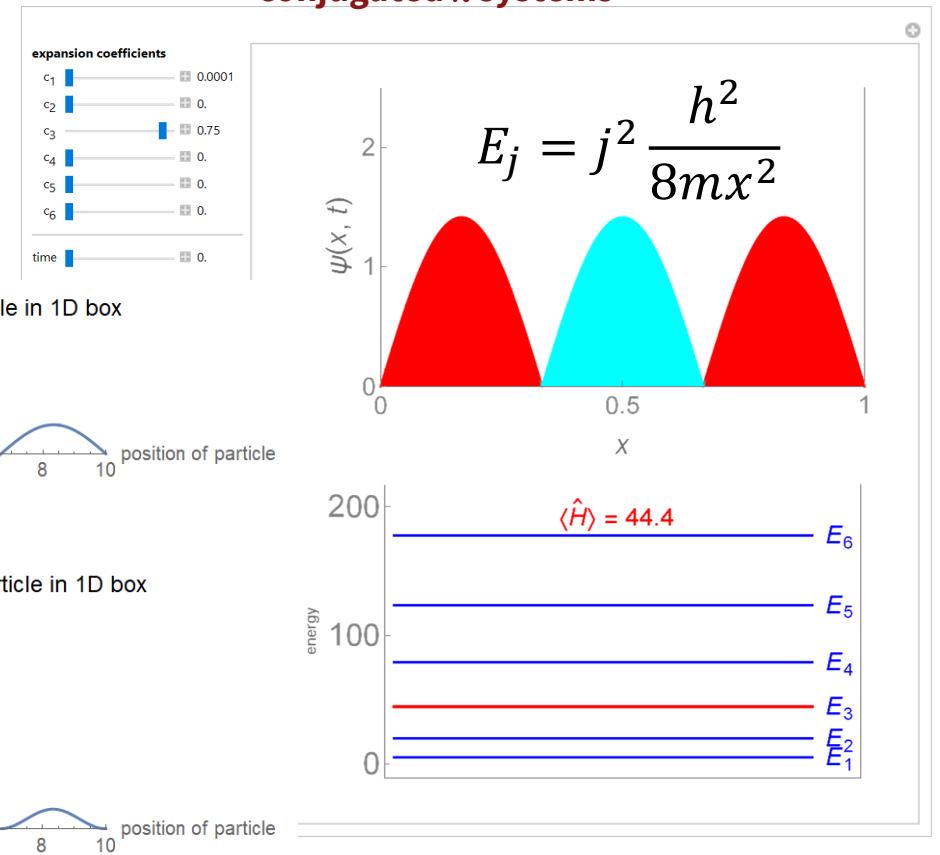
frequency proportional to energy

$p = plasma$

width related to damping parameter γ

Wolfram Demonstrations Project demonstrations.wolfram.com »

Time-Dependent Superposition of Particle-in-a-Box Eigenstates: delocalized electrons in conjugated π systems



1D energy in atomic units: 0.01125

Localized electron contributions to the refractive index can be estimated by group additivity rules

Refractive index is determined by the number densities of C, H, N, S, and O

- More precisely, the number densities of atoms with different hybridizations
- Van Krevelen (2009) cites group additivity rules in his book, Properties of Polymers: Their correlation with chemical structure; their numerical estimation and prediction from additive group contributions.

To a first approximation:

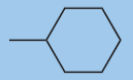
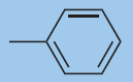
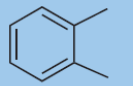
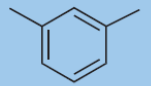
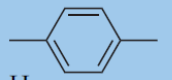
C=2.8; H=1.0; N=2.8; S=8.0; O=1.8

- Eliminating H and O increases the polarizability density
- PVAc=1.47, PE=1.49, PS=1.59

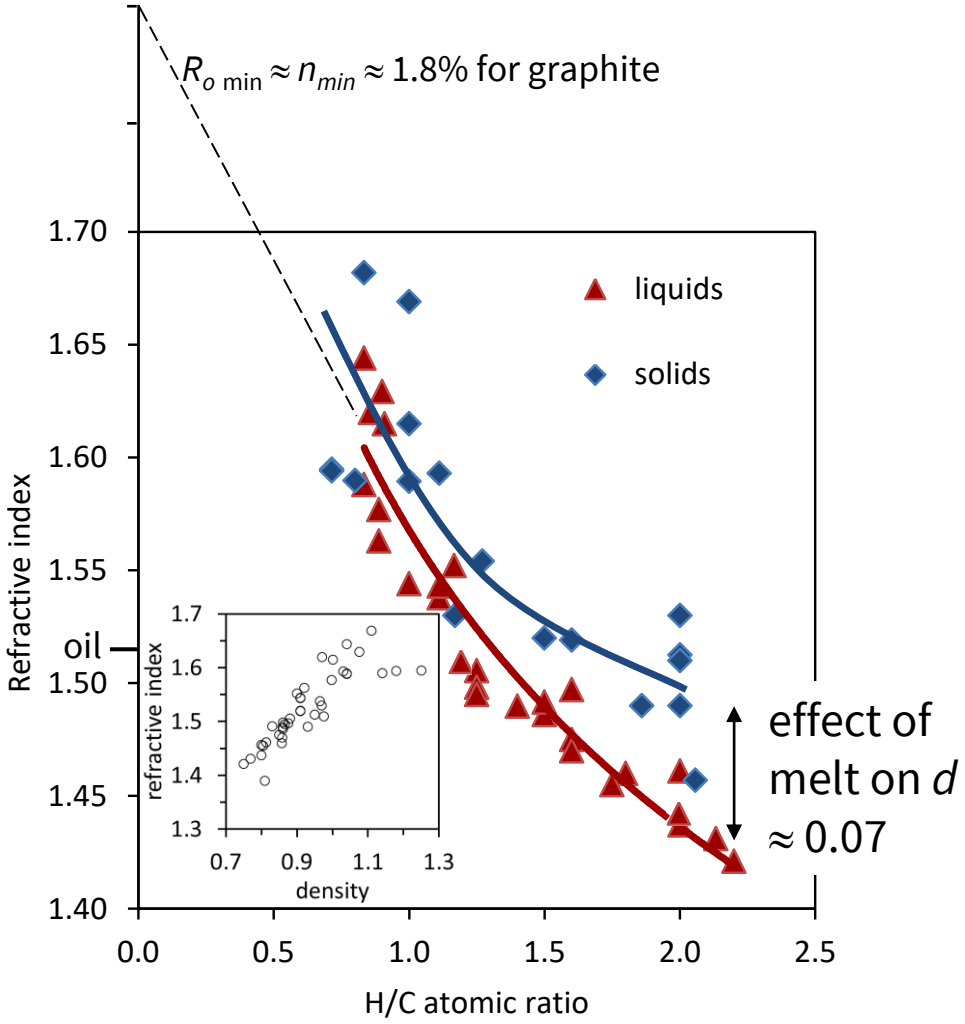
Group contributions to the molar refraction version of the Lorentz-Lorenz eq.

$$\mathbf{R}_{LL} = \frac{n^2 - 1}{n^2 + 2}\frac{\mathbf{M}}{\rho} \qquad n = \left(\frac{1 + 2\frac{\mathbf{R}_{LL}}{\mathbf{V}}}{1 - \frac{\mathbf{R}_{LL}}{\mathbf{V}}}\right)^{1/2}$$

Group contributions in 10^{-6} m^3/mol to the molar refraction ($\lambda = 589$ nm)

$-CH_3$	General		5.644
	Attached to benzene ring		5.47
$-CH_2-$	General		4.649
	Attached to benzene ring		4.50
>CH–	General		3.616
	Attached to benzene ring		3.52
>C<	General		2.580
	Attached to benzene ring		2.29
	Cyclohexyl	n=1.43	26.686
	Phenyl	n=1.50	25.51
	*o*-Phenylene		24.72
	*m*-Phenylene		25.00
	*p*-Phenylene		25.03
H_{ar}	Average value		0.59
–O–	Methyl ethers		1.587
	Higher ethers		1.641
	Attached to benzene ring		1.77
	Acetals		1.63
–OH	Primary alcohol		2.551
	Secondary alcohol		2.458
	Tertiary alcohol		2.453
	Phenol		2.27
>C = O	Methyl ketone		4.787
	Higher ketones		4.533
	Attached to benzene ring		5.09
–CH = O	General		5.83
–COOH	General		7.212
–COO–	Methyl esters		6.237
	Ethyl esters		6.375
	Higher esters		6.206
	Attached to benzene ring		6.71
	Acetates		6.306
–OCOO–	Methyl carbonates		7.75
	Higher carbonates		7.74
$-NH_2$	General		4.355
	Attached to benzene ring		4.89
>NH	General		3.585
	Attached to benzene ring		4.53
>N–	General		2.803
	Attached to benzene ring		4.05
–CONH–	General		7.23
	Attached to benzene ring		8.5
–C≡N			5.528
$-NO_2$			6.662
–SH	Primary		8.845
	Secondary		8.79
	Tertiary		9.27
–S–	Methyl sulphide		7.92
	Higher sulphides		8.07
–SS–			16.17

Consider the various contributions to hydrocarbons, diamond, and graphite



Diamond (tetrahedral C)

n = **2.42** (greater than mature kerogen~1.8)

d = 3.52 g/cm^3

R_o ~ 6%

Anthracite (polyaromatic rings)

$n_{max} \approx 2.01$, $n_{min} \approx 1.93$

d = 1.5 g/cm^3

$R_o \approx 4\%$ and H/C ≈ 0.3

Graphite

n_{max} = 2.15, n_{min} = **1.81**

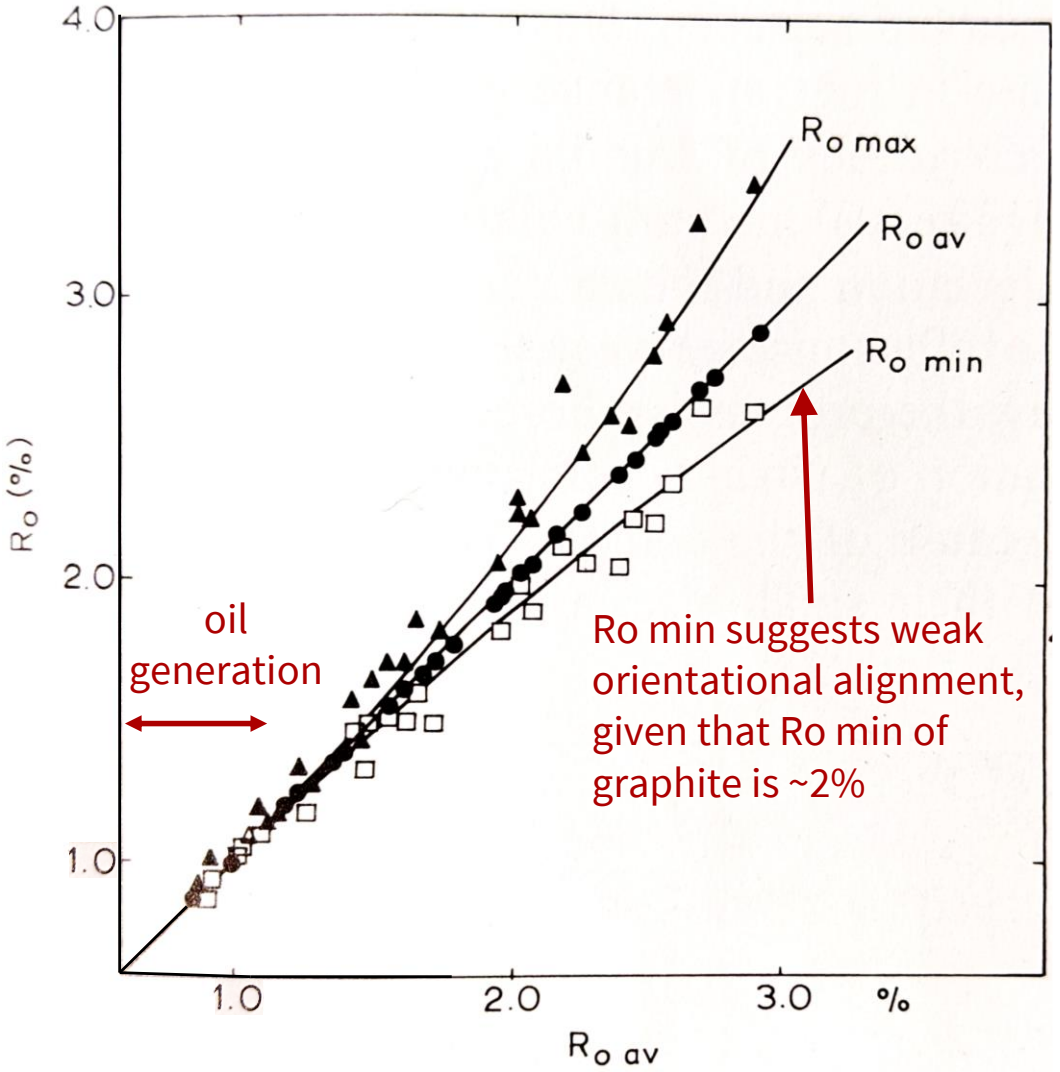
k_{max} = 0.66, k_{min} = 0.0

d = 2.26 g/cm^3

$R_{o\ max}$ = 15.6% and $R_{o\ min} \approx 2\%$

indicates that the primary contribution to reflectance is the absorptive term parallel to the aromatic ring

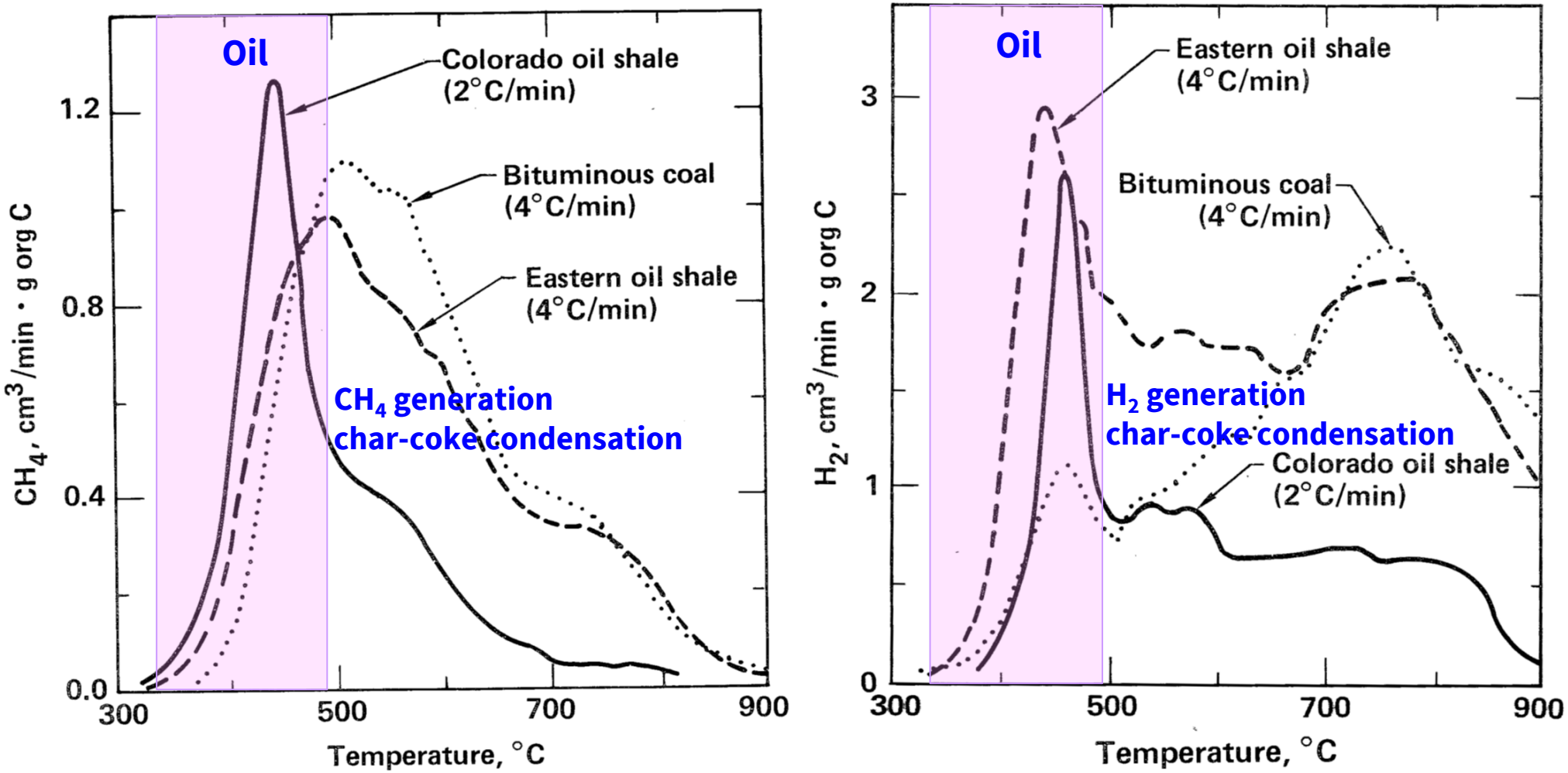
Anisotropy starts above 1.0%Ro and is not clearly significant until 1.5%Ro (H/C ~ 0.6), after the oil is generated



Sharkey & McCartney, 1981

quoted by Mukhopadhyay, 1992

LLNL work around 1980 shows that ring condensation occurs mainly after oil components are generated



Ring condensation provides long π-bond resonance lengths for broader and stronger optical absorption

Elemental balance equations and original correlations derived for the original Vitrimat (GCA 1989)

$$CH_xO_y \rightarrow C_{1-b-c-d}H_{x-2a-nc-4d}O_{y-a-2b} + a\,H_2O + b\,CO_2 + c\,CH_n + d\,CH_4$$

$$\delta = [x - 2y\alpha - n\gamma - \chi(1 - y\beta/2 - \gamma)]/(4 - \chi)$$

$$H/C = (x - ny\alpha f_\alpha - n\gamma f_\gamma - 4\delta f_\delta)/(1 - y\beta f_\beta/2 - \gamma f_\gamma - \delta f_\delta)$$

$$O/C = y(1 - \alpha f_\alpha - \beta f_\beta)/(1 - y\beta f_\beta/2 - \gamma f_\gamma - \delta f_\delta)$$

α = fraction of initial O eliminated as H_2O
β = fraction of initial O eliminated as CO_2
γ = fraction of initial C eliminated as CH_n
δ = fraction of initial C eliminated as CH_4
f_i = fraction of species i generated
$wt\%\ C = 1200/[12 + (H/C) + 16(O/C)] - 1.5$

$$\%Ro = 12\exp(-3.3(H/C)] - (O/C)$$

$$\%Ro = \exp(-1.25 + 4.5\Delta + 300\Delta^5 + 1.6 \times 10^8\Delta^{15})$$

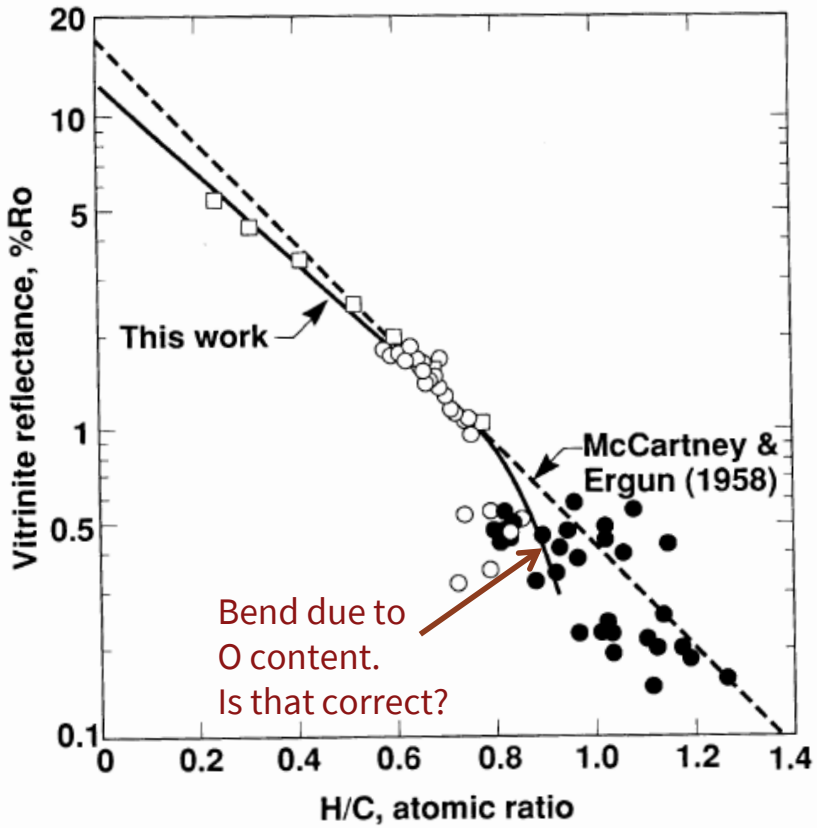
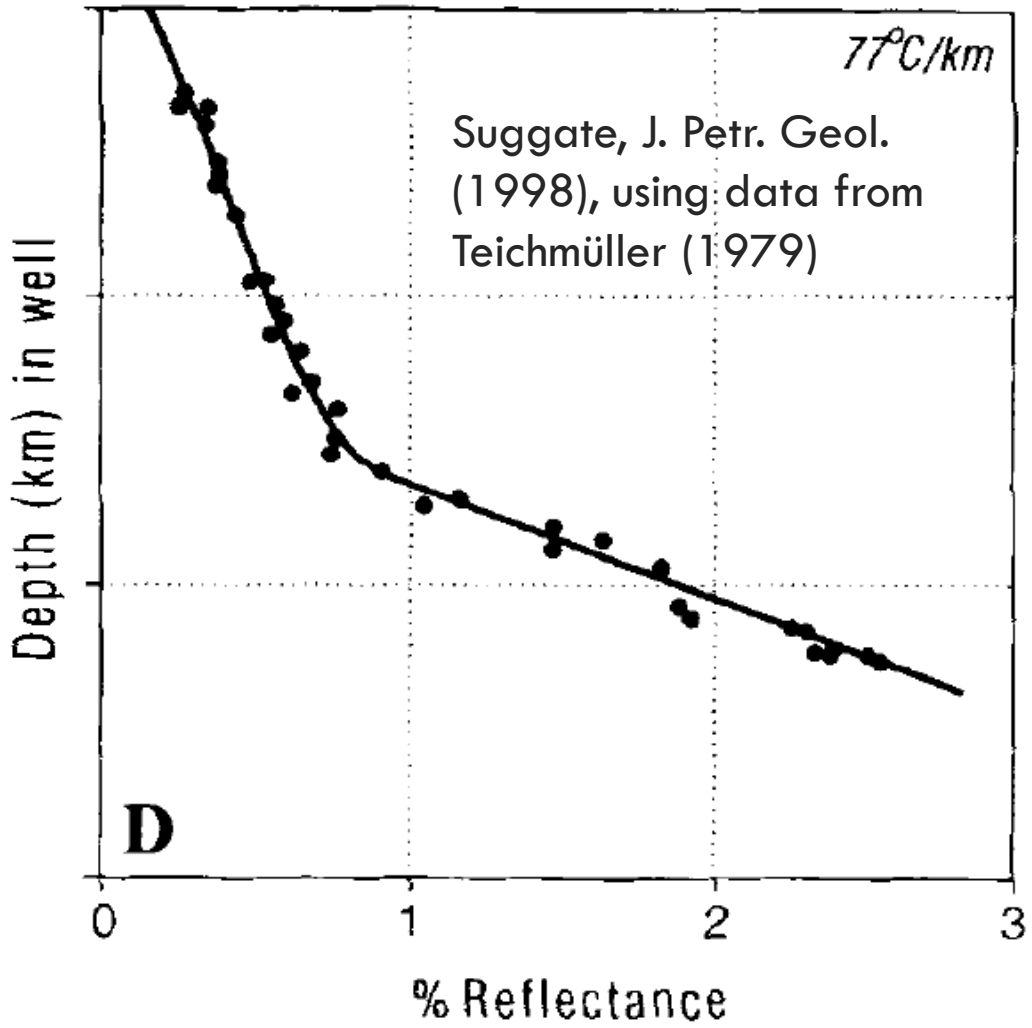
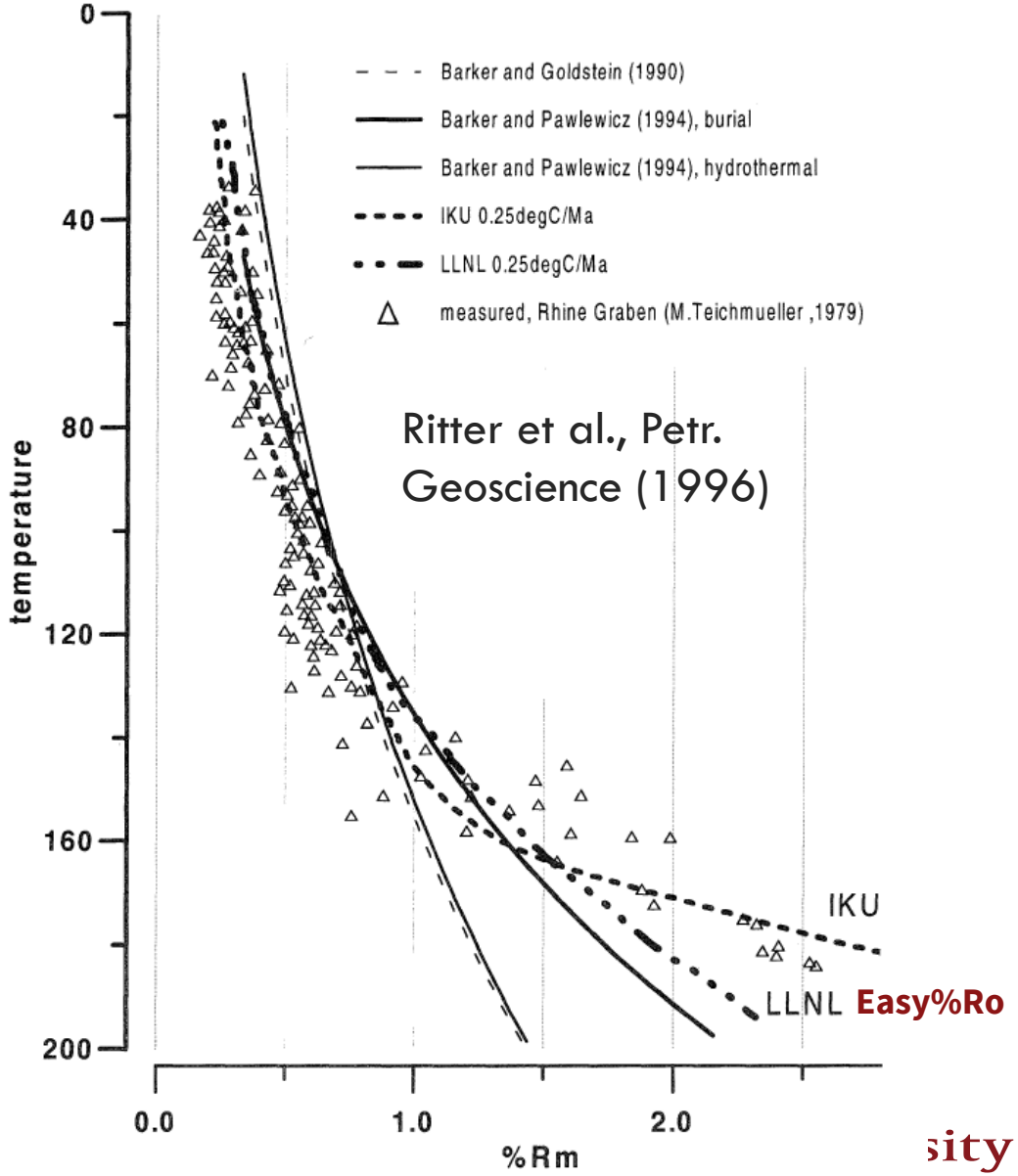


FIG. 1. Comparison of vitrinite reflectance data (MCCARTNEY and TEICHMÜLLER, 1972) to that calculated with Eqns. (1) and (2). The symbols retain their original meaning: ❑, ● European vitrinites; ○ U.S. coals.

Multiple workers have noted a dogleg shape not captured by Easy%Ro





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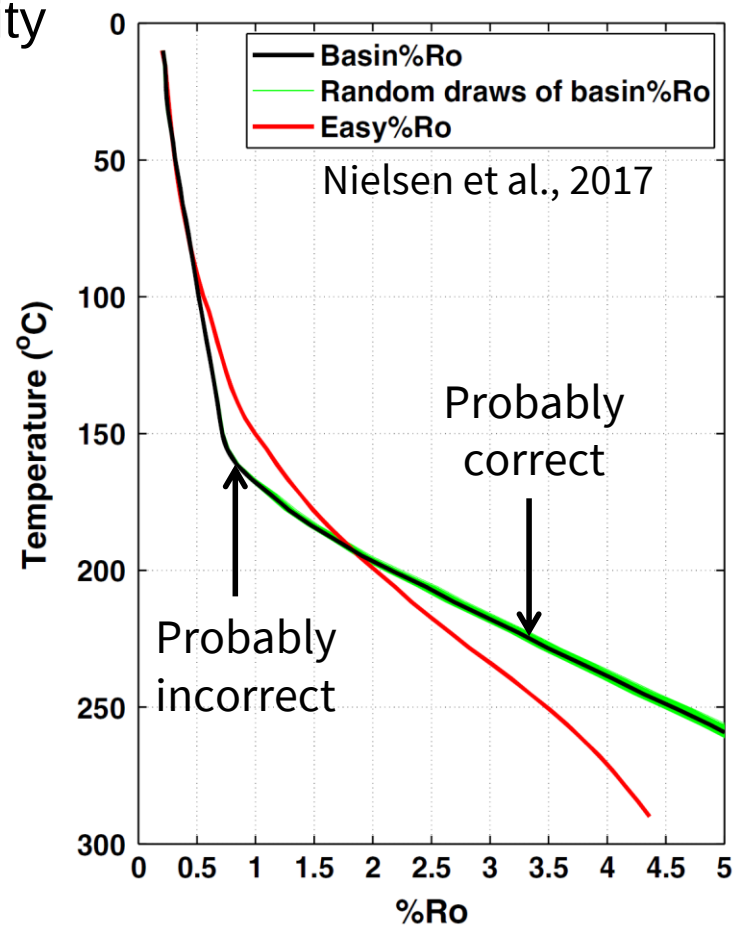
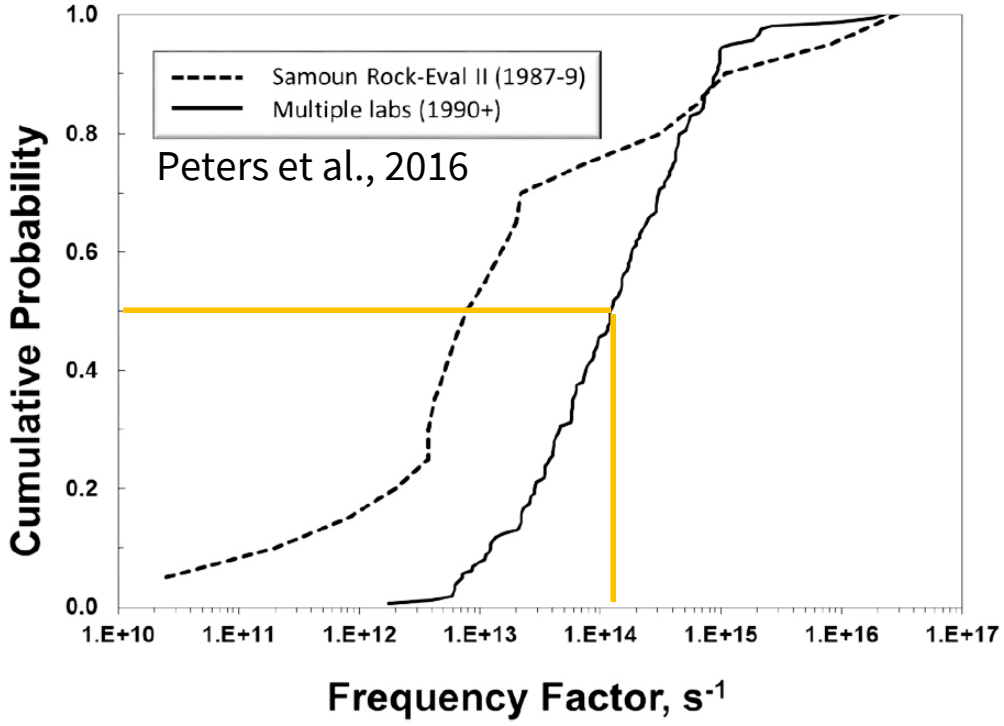
Motivation for updating Vitrimat (and Easy%Ro)

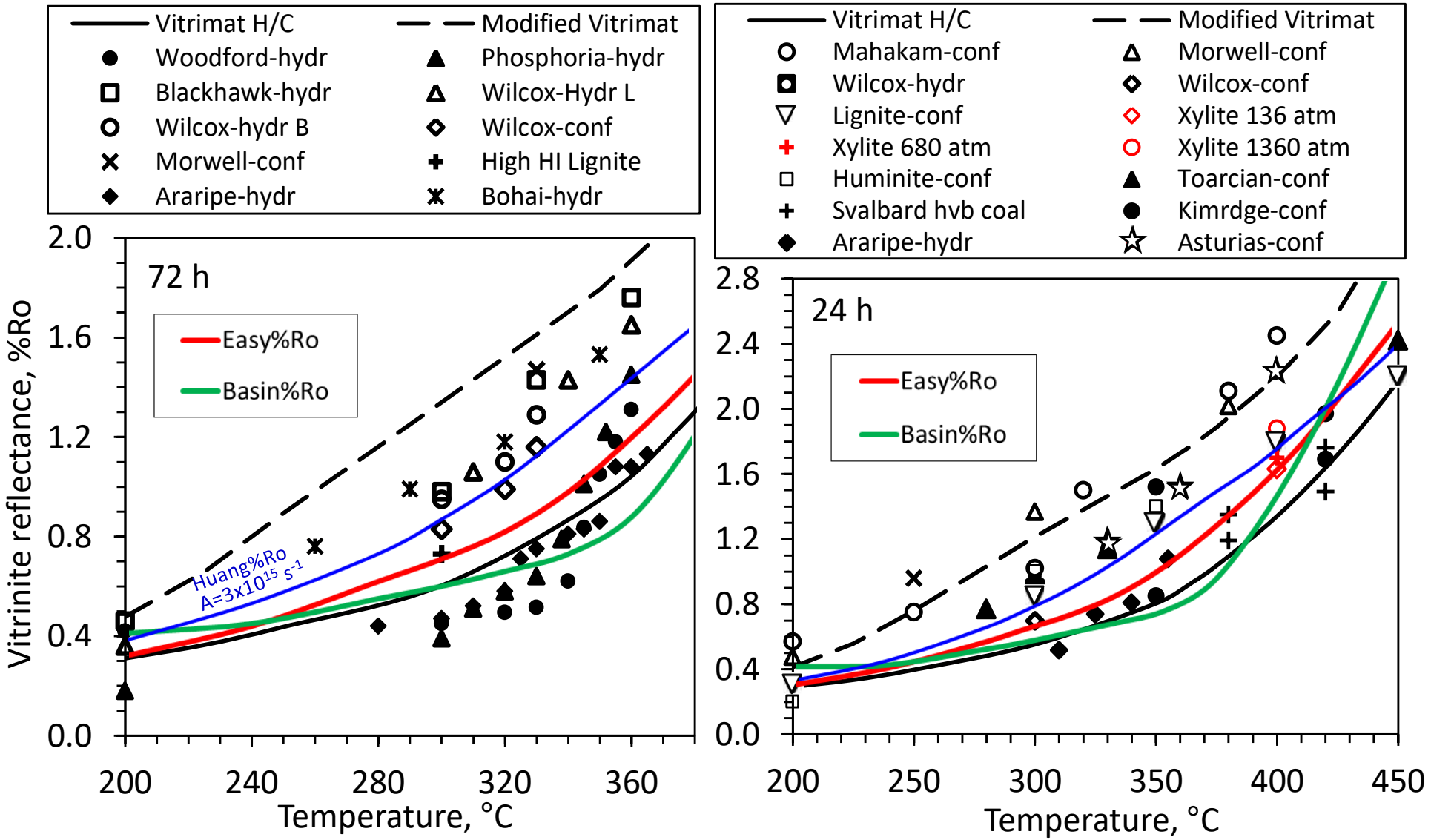
- Several authors, most recently Nielsen et al. (2017), have indicated that Easy%R_o does not increase fast enough at high maturity



- Kinetic studies in the 1990s and later indicate that the most probable frequency factor for kerogen conversion is about 2×10^{14} s^{-1} instead of 1×10^{13} s^{-1} assumed for Vitrimat 1989



Basin%Ro does not work well at laboratory time scales for humic coals—worse than Easy%Ro



Easy%R_oDL was a step on the road to improvement but still did not match laboratory data very well

Original Vitrimat

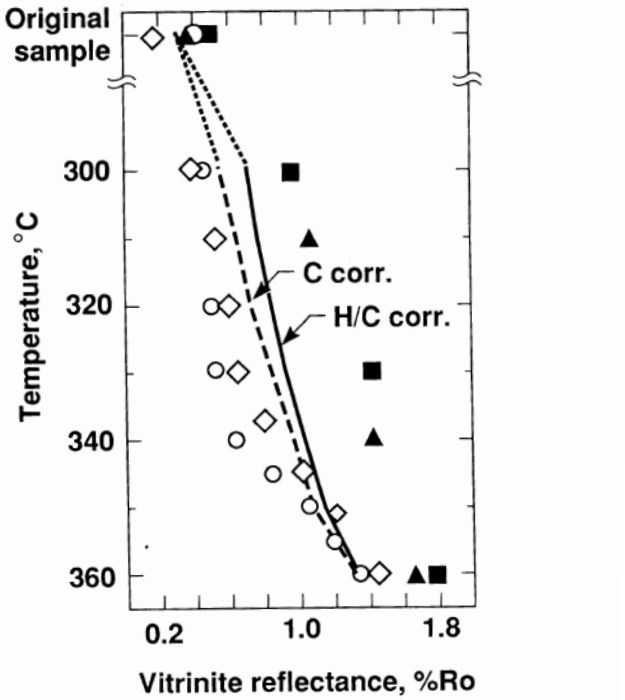
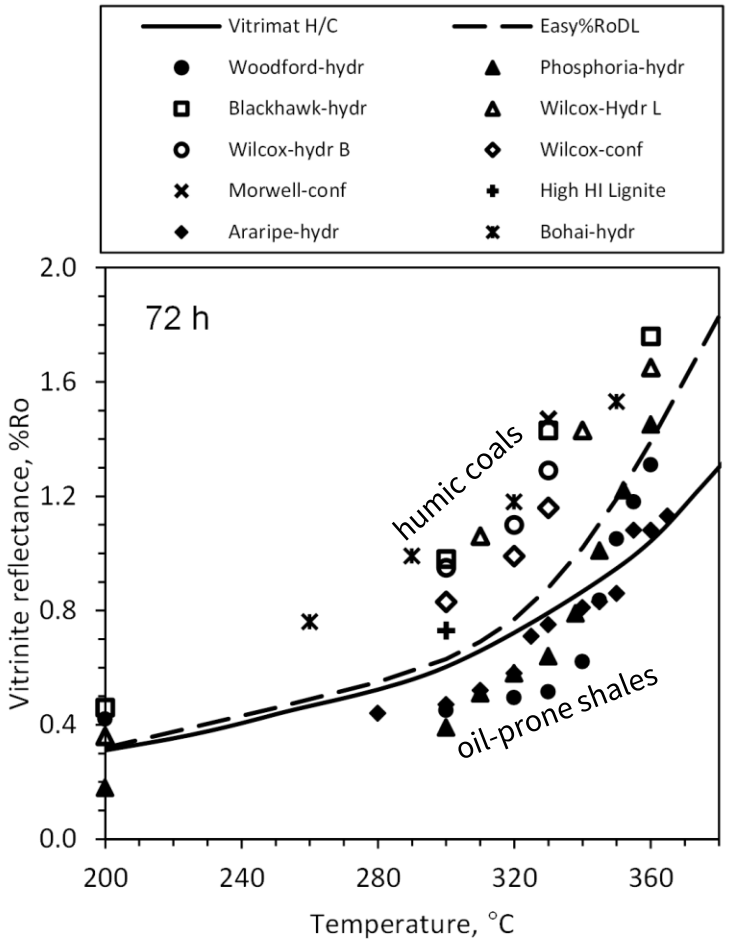
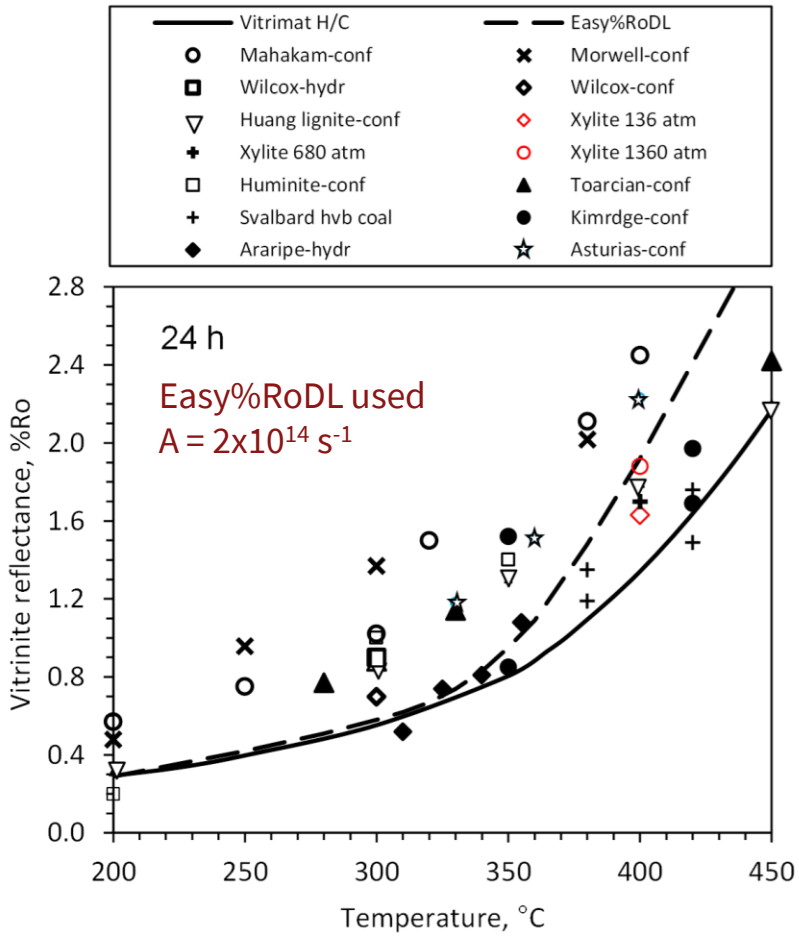


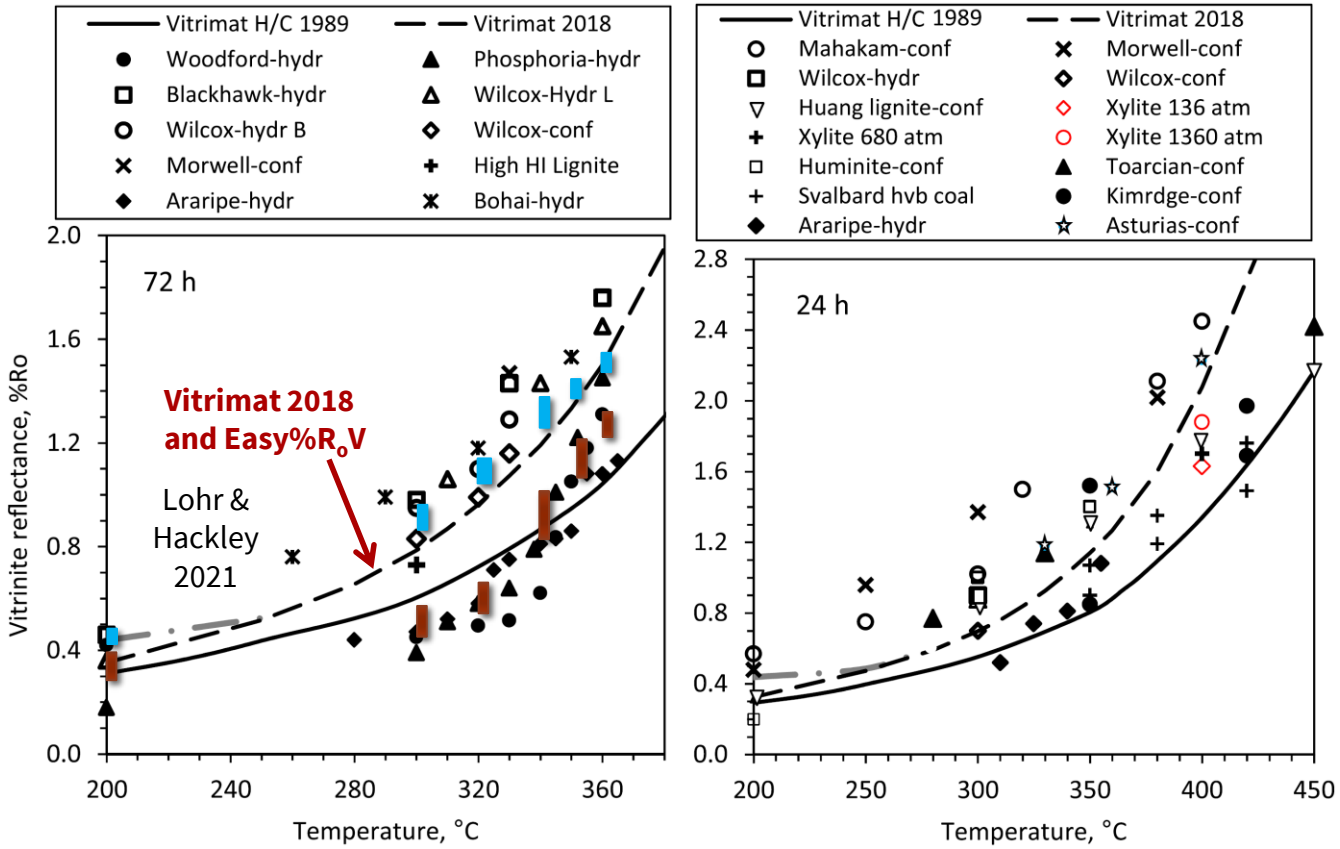
FIG. 9. Vitrinite reflectance data of LEWAN (1985) for hydrous pyrolysis of Phosphoria (◇) and Woodford (○) shales and Wilcox Fairfield (▲) and Blackhawk coals (■) compared to our model calculations (72 h at indicated temperature).

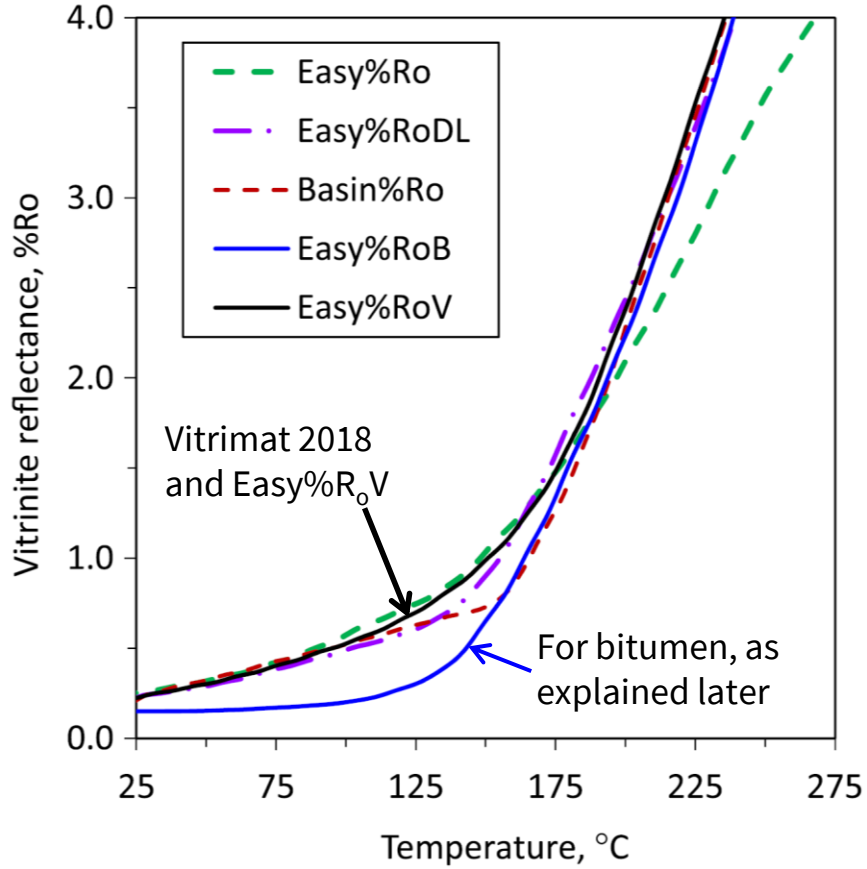




Better agreement at high reflectance, but reflectance still too low compared to coals during early maturation

After trying lots of options, I found better simultaneous agreement with lab data using $A=1\times10^{15}$ s^{-1}





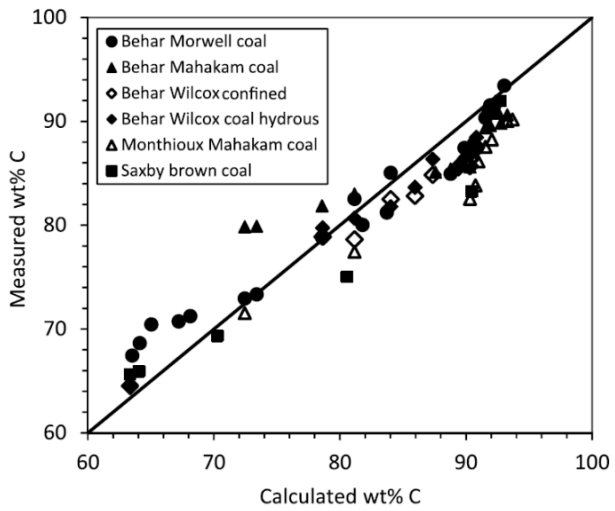
Comparison of various reflectance models for geological heating at 2 °C/Myr.

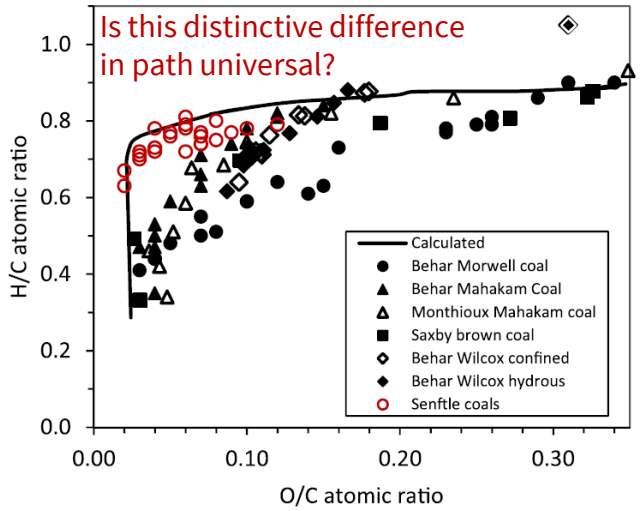
Vitrimat 2018: Burnham, *Org. Geochem.* 131, 50-59 (2019)

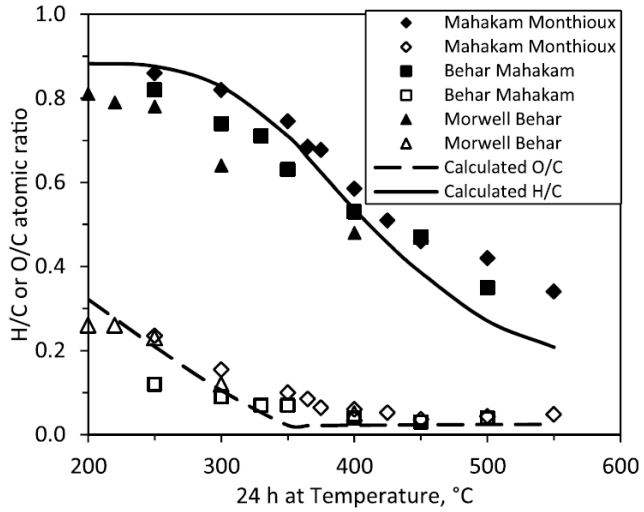
Developed with support from Total S. A.

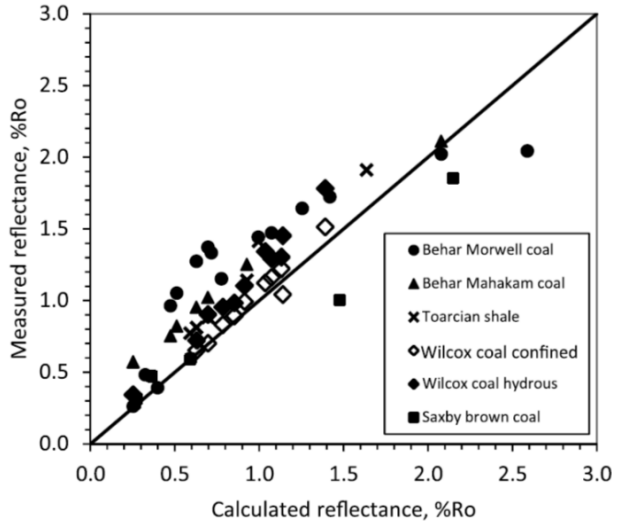
Stanford University

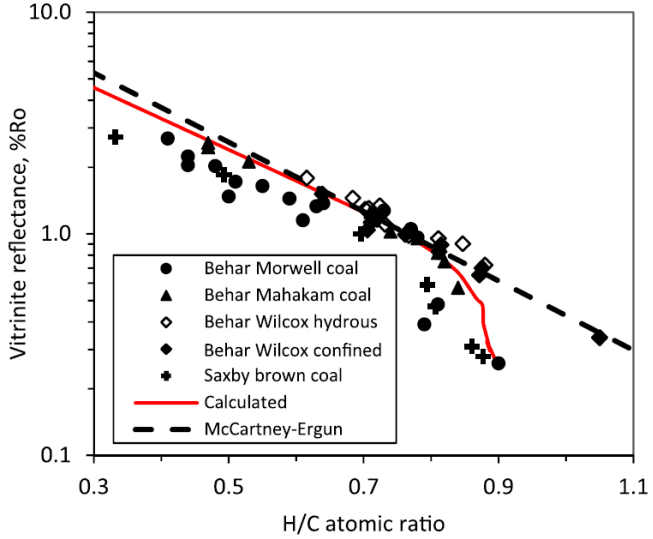
Vitrimat 2018 was also calibrated against more compositional data than the original Vitrimat

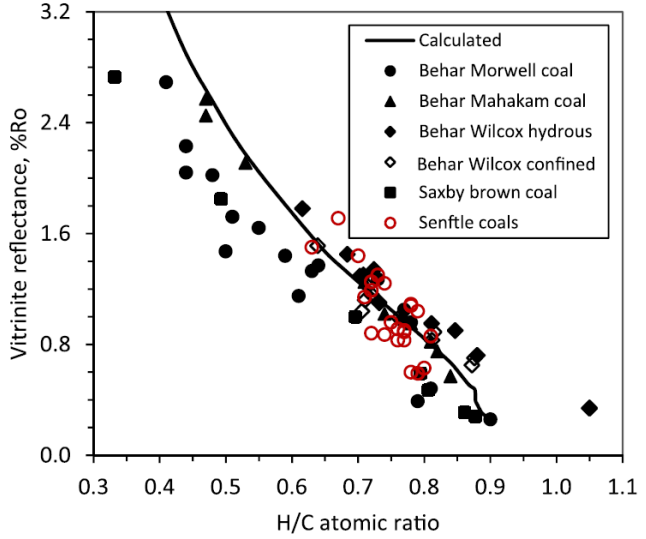






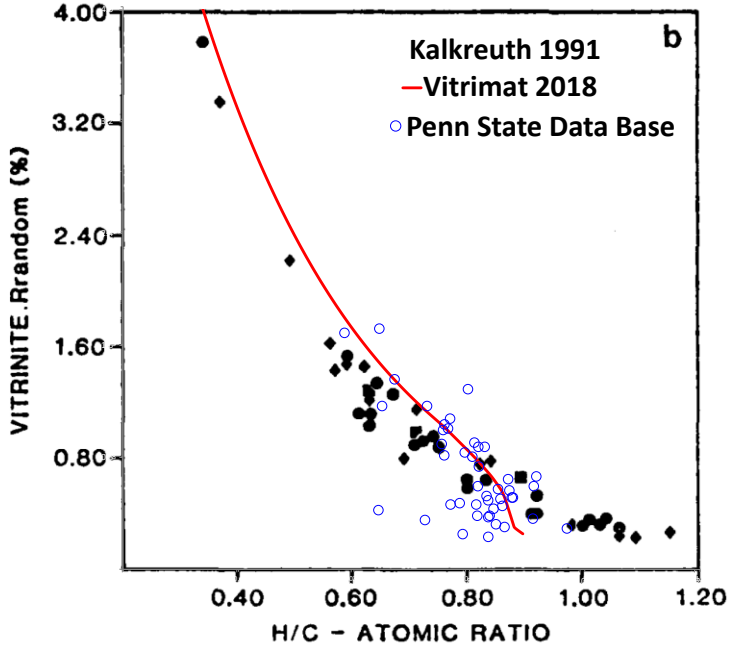


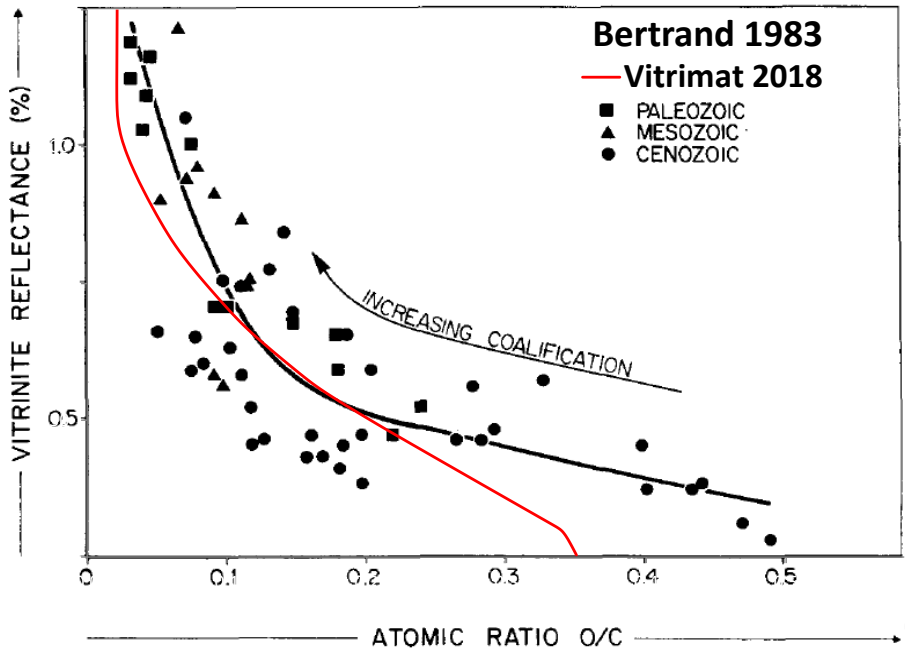


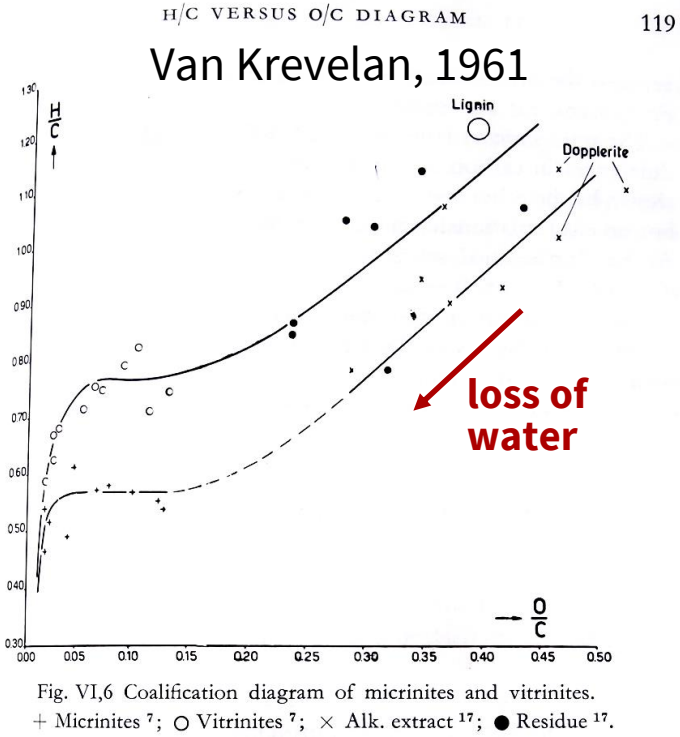


Additional comparisons have been made since

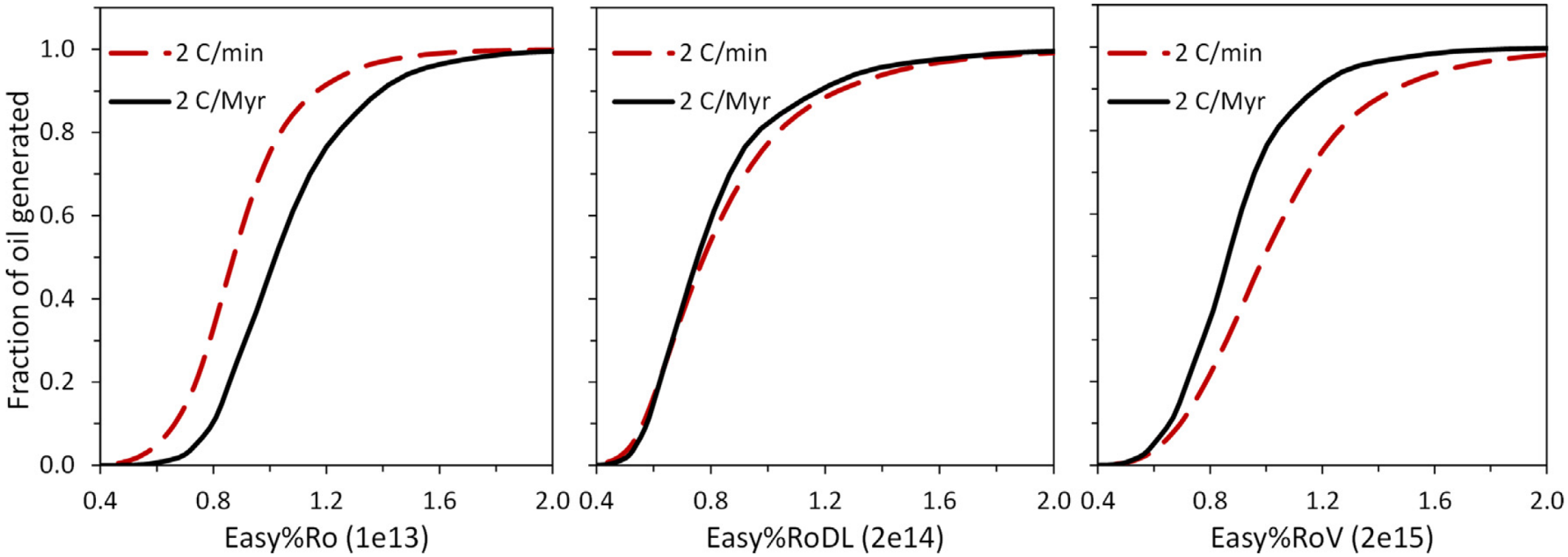
- More optimization of the Vitrimat CO_2 and H_2O kinetics at low maturity may be warranted
- Faster water release kinetics during diagenesis are needed to match diagenesis
- These would have a minor effect on calculated reflectance during and after the oil window



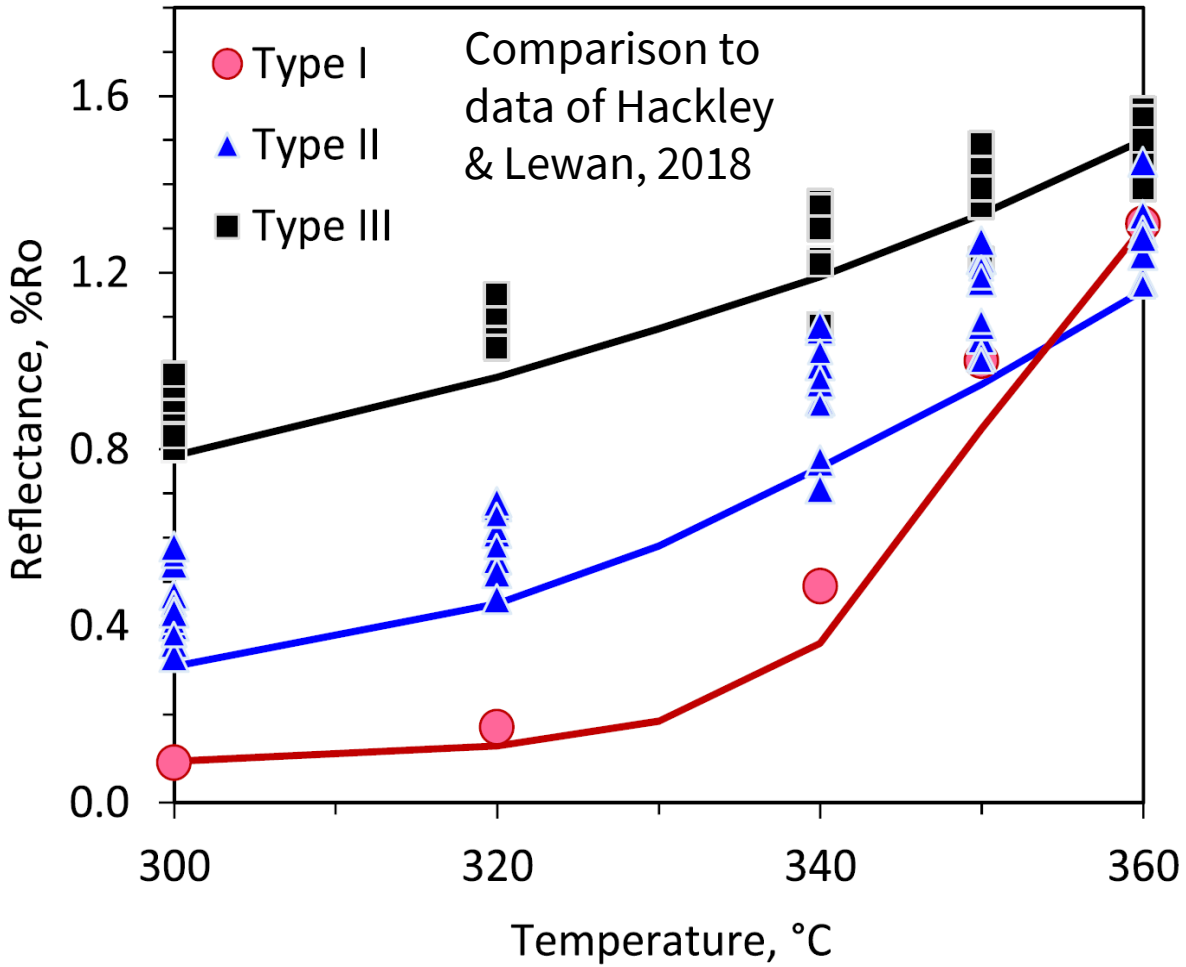


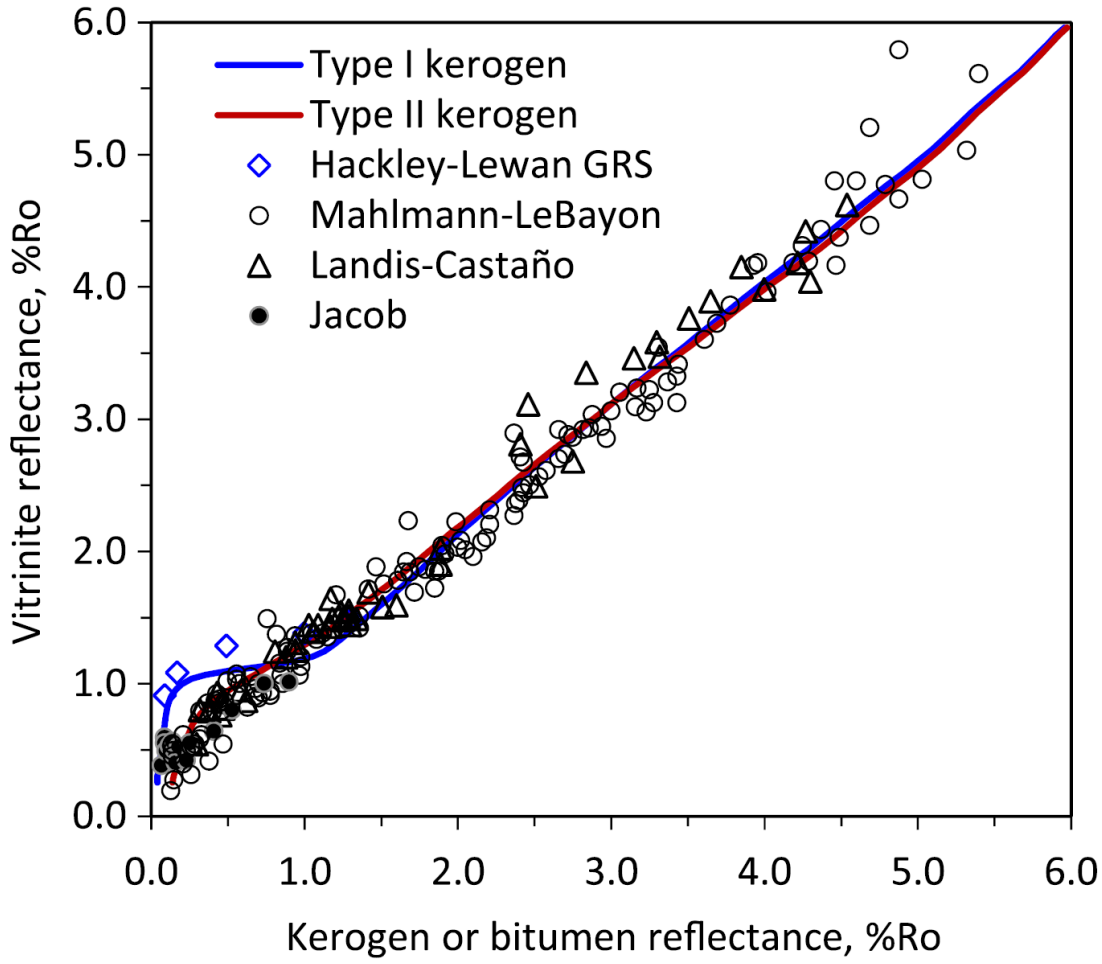


An open question is the whether the relationship between oil generation and vitrinite reflectance is exactly the same in nature and in the laboratory



The Vitrimat 2018 algorithms can be used with any sedimentary organic matter

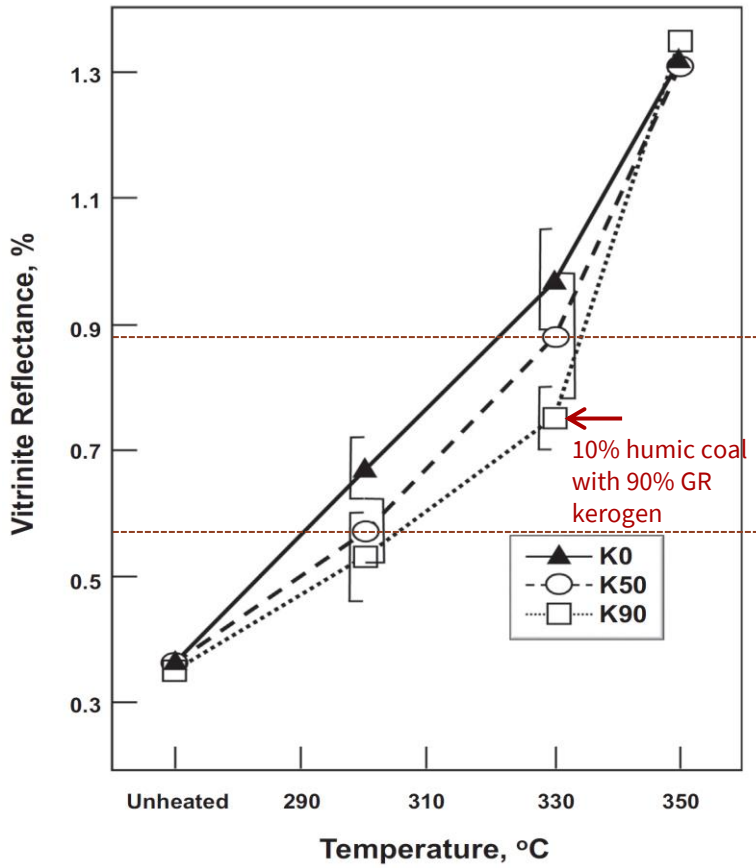


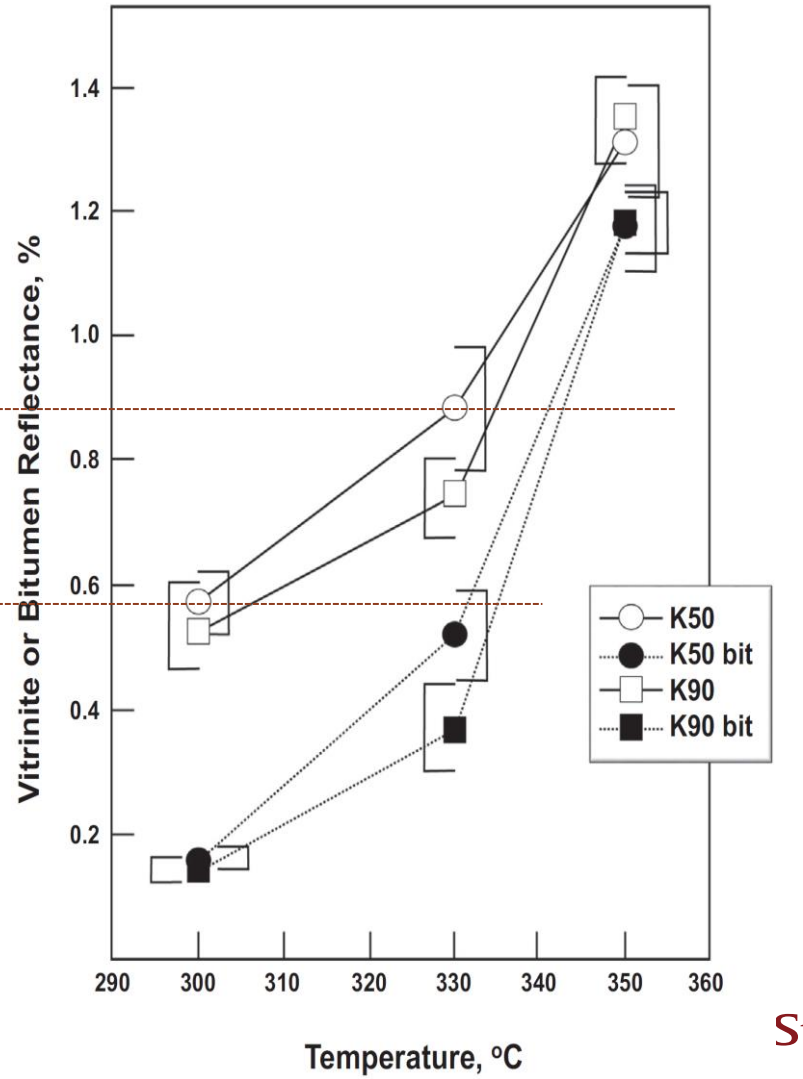


Type II kerogen is very similar to reported values for bitumen

Vitrinite reflectance suppression is real

- Demonstrated using HP of mixtures by Peters et al. (*Org. Geochem*., 2018)
- Suppression tends to disappear by VR = 1.3 $\%R_o$
- VR and BR merge above 1.4 $\%R_o$





Summary

- Vitrinite reflectance increases due to a combination of densification and aromatic condensation reactions
  - The anisotropy of graphite helps put them in perspective
- Evidence is strong that Easy%R_o underestimates VR at high maturities
- Easy%R_oDL and Easy%R_oV have a sharper dogleg near the end of oil generation
  - Corresponds to the onset of aromatic condensation reactions
- Easy%R_oV is derived from Vitrimat 2018,which is based on a higher frequency factor
- Vitrimat 2018 also inspired Easy%R_oB for bitumen reflectance
- Vitrinite suppression is real, so vitrinite in oil-prone shales is misleading