Evolution of Vitrinite Reflectance Models*

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Abstract

Vitrinite reflectance is a standard method for measuring the thermal maturity of sedimentary rocks and kinetic models of vitrinite reflectance commonly used to constrain paleothermal histories in basin and petroleum system modeling. EASY%Ro is a one such kinetic model. EASY%Ro is based on the concept that reflectance is related to the chemical composition of vitrinite phytoclasts. It was derived from an earlier model, Vitrimat, which modeled the compositional evolution of vitrinite based on both laboratory experiments and natural maturation trends. EASY%Ro uses distributions of activation energies that spread the maturation reactions over a wide range of thermal exposure. A variety of alternatives to EASY%Ro has been proposed, including unpublished versions that use fewer second-order reactions to speed computation and extend the predictions to higher reflectance. Some workers have proposed models based on single first-order reactions and power-law reaction models. Others have proposed models that take into account suppression of reflectance by co-generated oil and overpressure within petroleum source rocks. The objectives of this paper are to review these models and supporting observations in order to assess the reliability of EASY%Ro and how modifications might improve reliability of the method.

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Evolution of Vitrinite Reflectance Models

AAPG Annual Convention and Exhibition 2016, Calgary, Alberta, Canada, June 19-22, 2016

Presented by Alan K. Burnham, Kenneth E. Peters, Oliver Schenk

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Statement of Importance

Vitrinite reflectance is one of the most important parameters used to calibrate paleothermal histories

All models of vitrinite reflectance are approximations that require validation at the time-temperature conditions of application

Numerous variations of Arrhenius-based models are available

Which is the most reliable, and why?

Genetic relationships among vitrinite reflectance models

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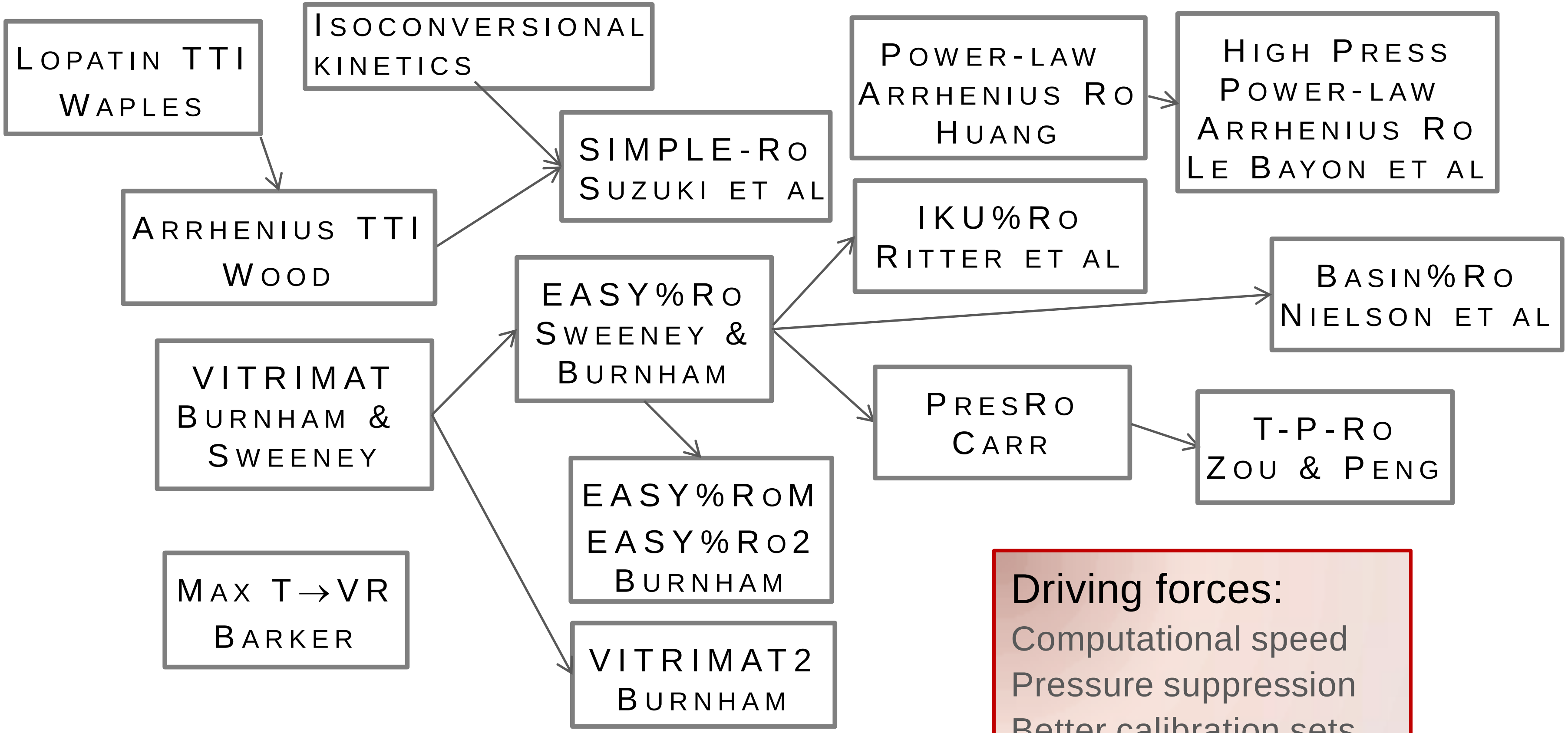

Driving forces:

Computational speed

Pressure suppression

Better calibration sets

Complex materials require a reactivity distribution

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Various approaches:

Isoconversional

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[f(\alpha)A_\alpha] - E_\alpha/RT_{\alpha,i}$$

Power law in time

$$\alpha = kt^n$$

≈ Gamma distribution in *A*

Pseudo nth-order reaction

$$\frac{d\alpha}{dt} = k(1-\alpha)^n$$

≈ Gamma distribution in *A*
≈ power law in *t*

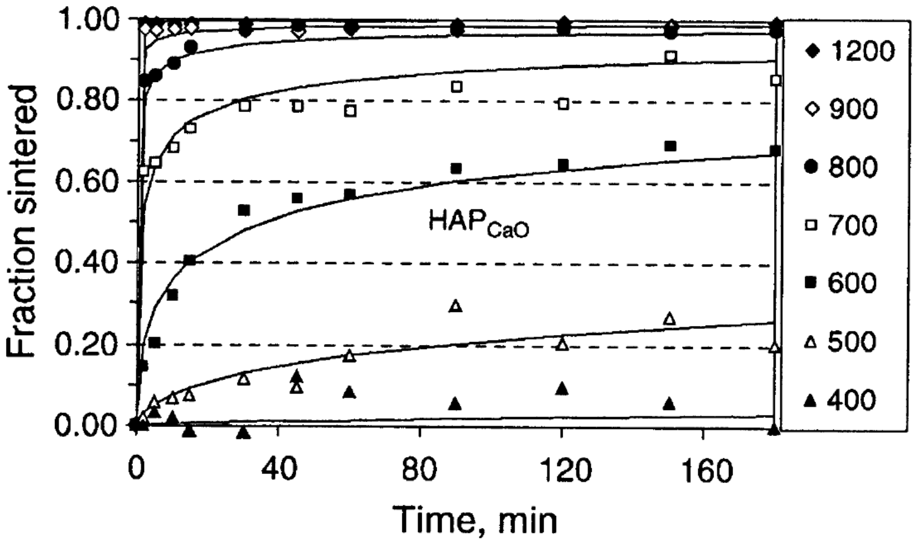
Continuous E distributions

Gaussian, Weibull, etc.

Discrete distributions

E only and *E* with ln(*A*)=*a*+*bE*

SINTERING OF HYDROXY APATITE
NTH-ORDER GAUSSIAN E DISTRIBUTION
BURNHAM, CHEM. ENG. J. 108. 46-50 (2005)



Reaction order interpreted as distribution of diffusion lengths
E distribution interpreted as range of diffusion energy barriers

EASY%Ro is a simplified model calibrated to the atomic H/C correlation of VITRIMAT

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VITRIMAT elemental balance equations and reflectance correlations

correction

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

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

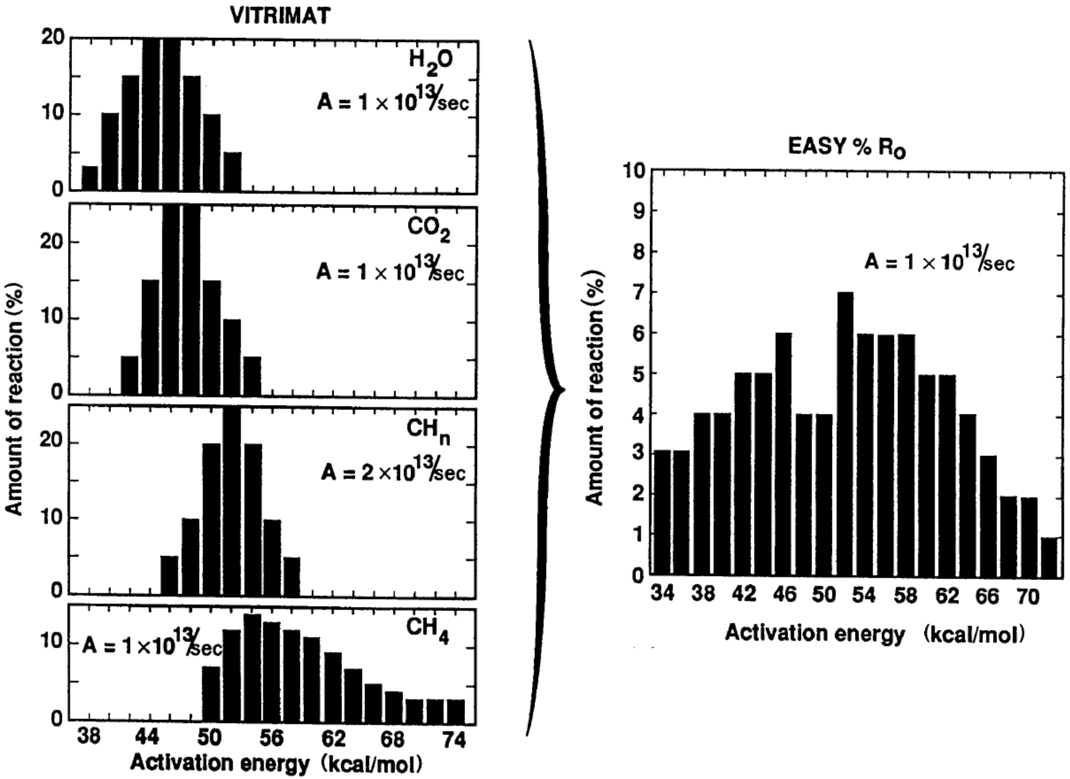
$$H/C = (x - ny\alpha f_\alpha - n\gamma f_\gamma - 4\delta f_\delta)/(1 - y\beta f_\beta/2 - \gamma f_\gamma - \delta f_\delta)$$

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

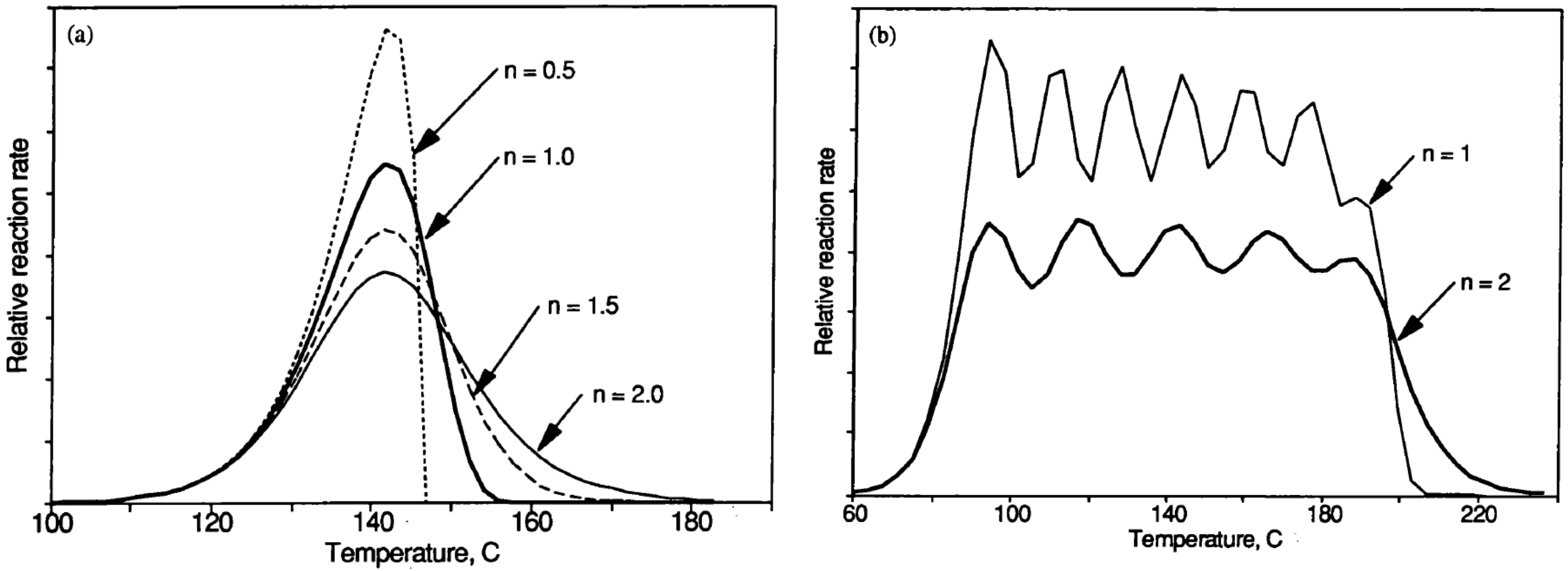
α = fraction of initial O eliminated as H_2O
β = fraction of initial O eliminated as CO_2
γ = fraction of initial C eliminated as CHn
δ = fraction of initial C eliminated as CH_4
f_i = fraction of species i generated
$wt\%\ C = 1200/[12 + (H/C) + 16(O/C)] - 1.5$

$$\%Ro = 12\exp(-3.3(H/C)] - 16(O/C)$$

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



Pseudo nth-order reactions reduce the number of required energy channels



Vitrimat2 simplified the reaction network

- Used pseudo-2^{nd}-order reactions
- (same energy distribution for CO_2 and H_2O; no oil)
- 30% less computer time than Easy%Ro while still matching the van Krevelen diagram

Vitrinite reflection is often "suppressed" in source rock intervals

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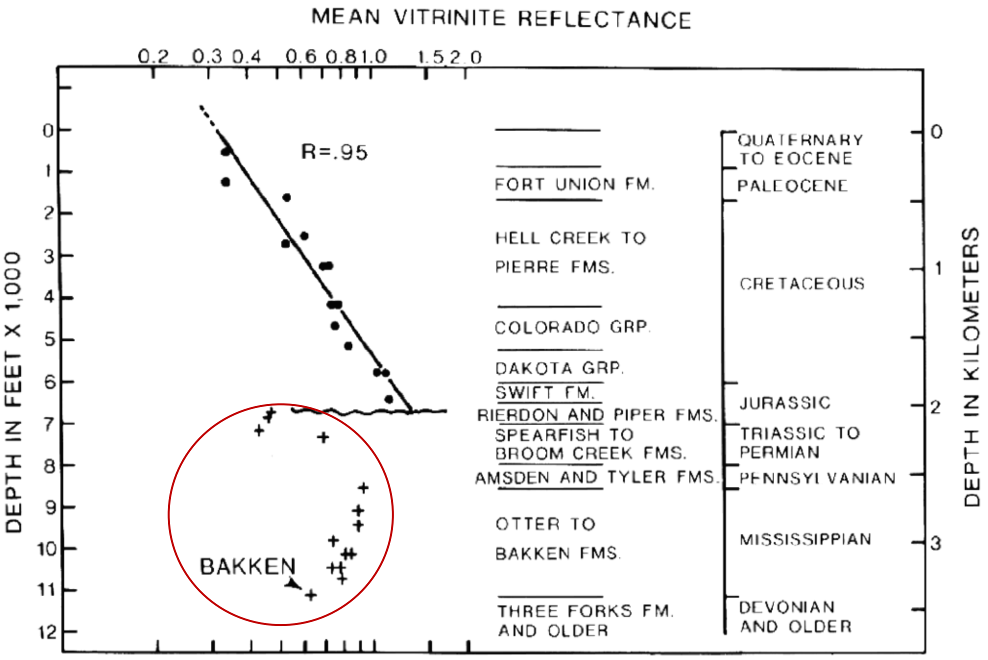
- Is it due to overpressuring in the generating interval?
  - Experimental studies indicate that pressure can be important, but probably not enough
- Is it because of interaction of vitrinite interaction with bitumen?
  - Extraction does not significantly affect reflectance, so interaction is not as simple as swelling (Barker et al., 2007)
- Is it due to different kinds of vitrinite?
  - Laboratory data suggests it can be



Price and Barker, J. Petr. Geol. (1985)

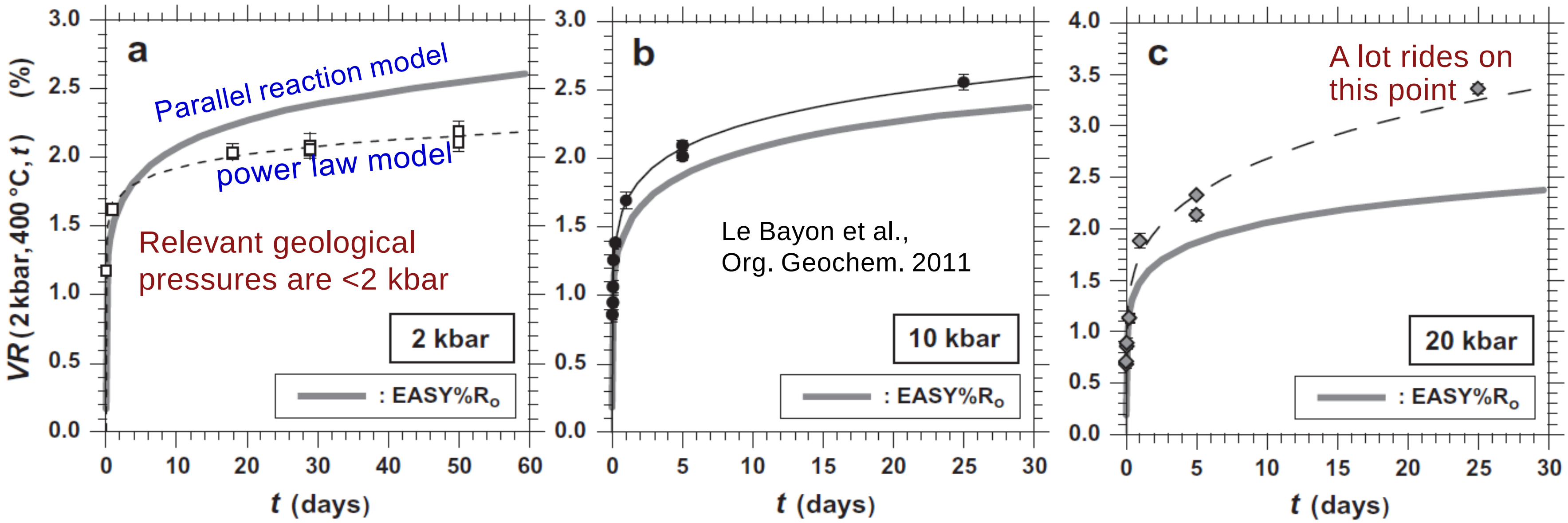
Pressure effects are present, but small and inconsistent at geological pressures

Huang (1996) found a large difference between open and closed pyrolysis but little difference between 0.5 and 2 kbar

Landais et al. (1994) found little effect between 0.5 and 4 kbar

Uguna (2012) found pressure slightly inhibited reflectance between 0.2 and 0.9 kbar

Della Torre (1997) and Le Bayon et al. (2011) found either inhibition or acceleration of reflectance increases depending on the pressure and reflectance range



Hydrous and confined pyrolysis experiments say source is more important than pressure

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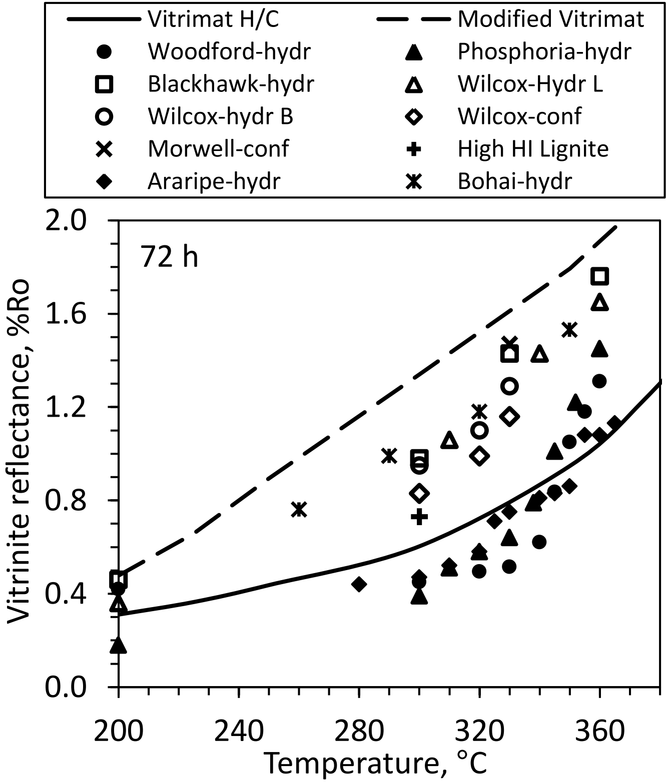
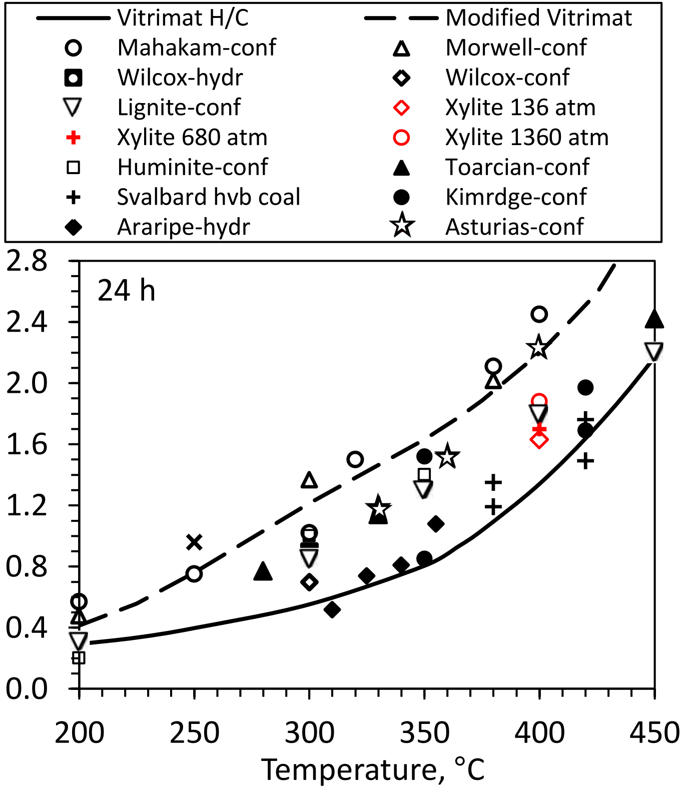
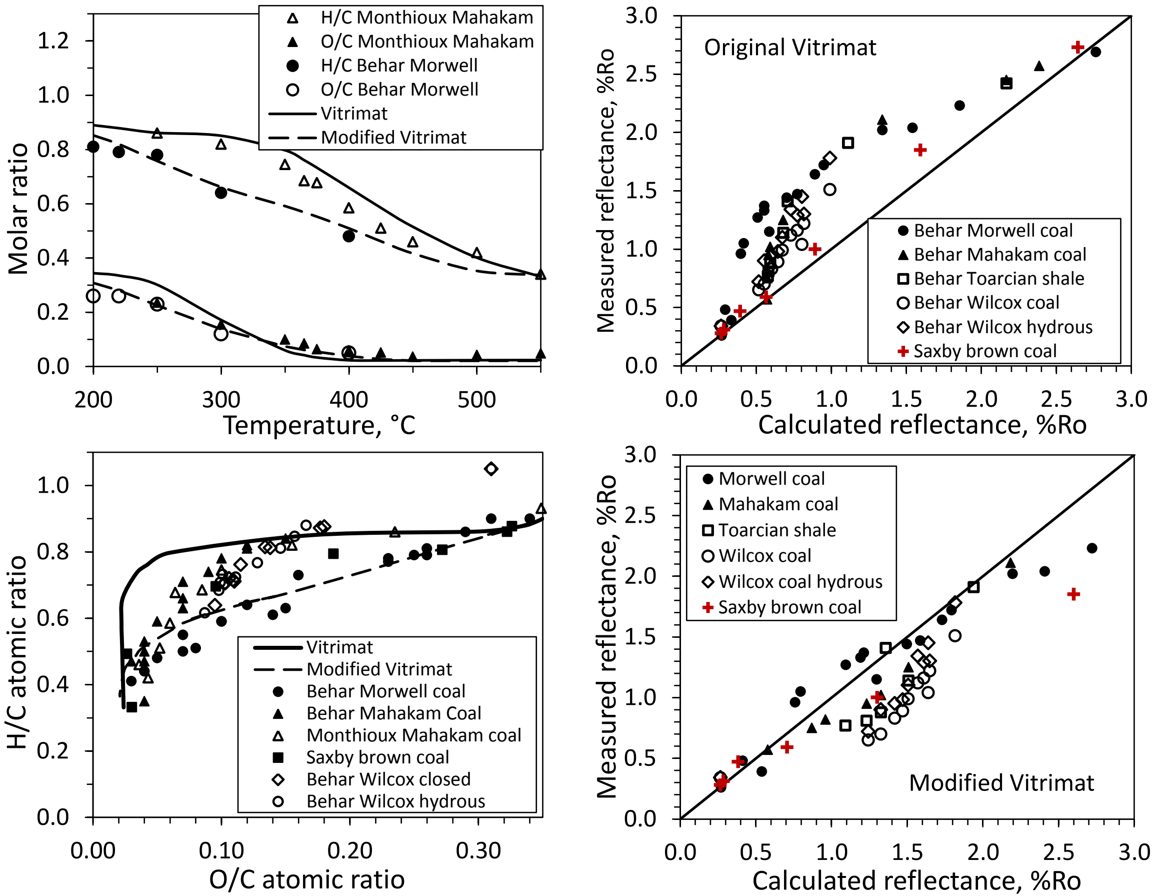


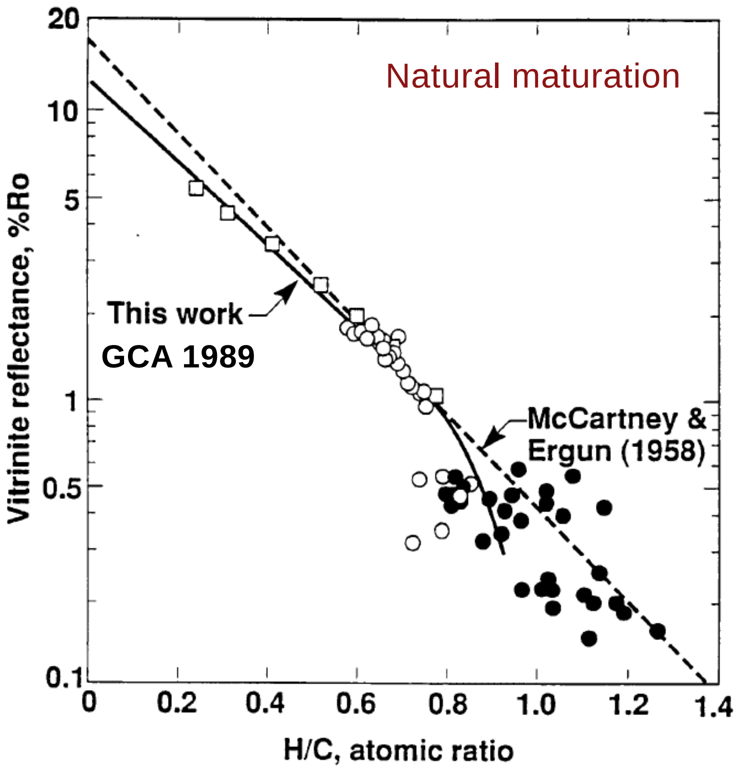


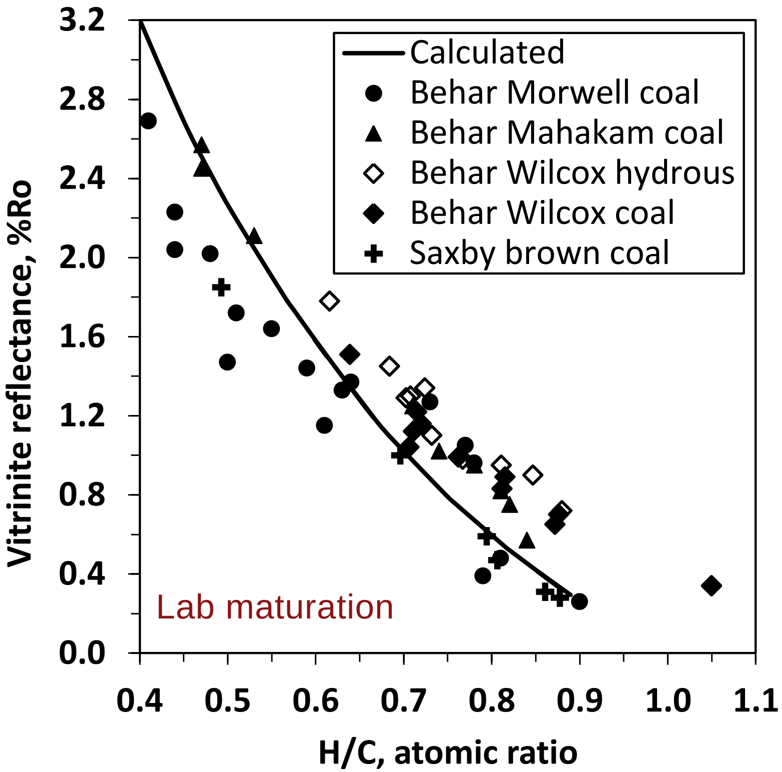
Coal samples tend to have higher reflectance for the same pyrolysis conditions

Variations in oxygen elimination kinetics were explored through Vitrimat modifications

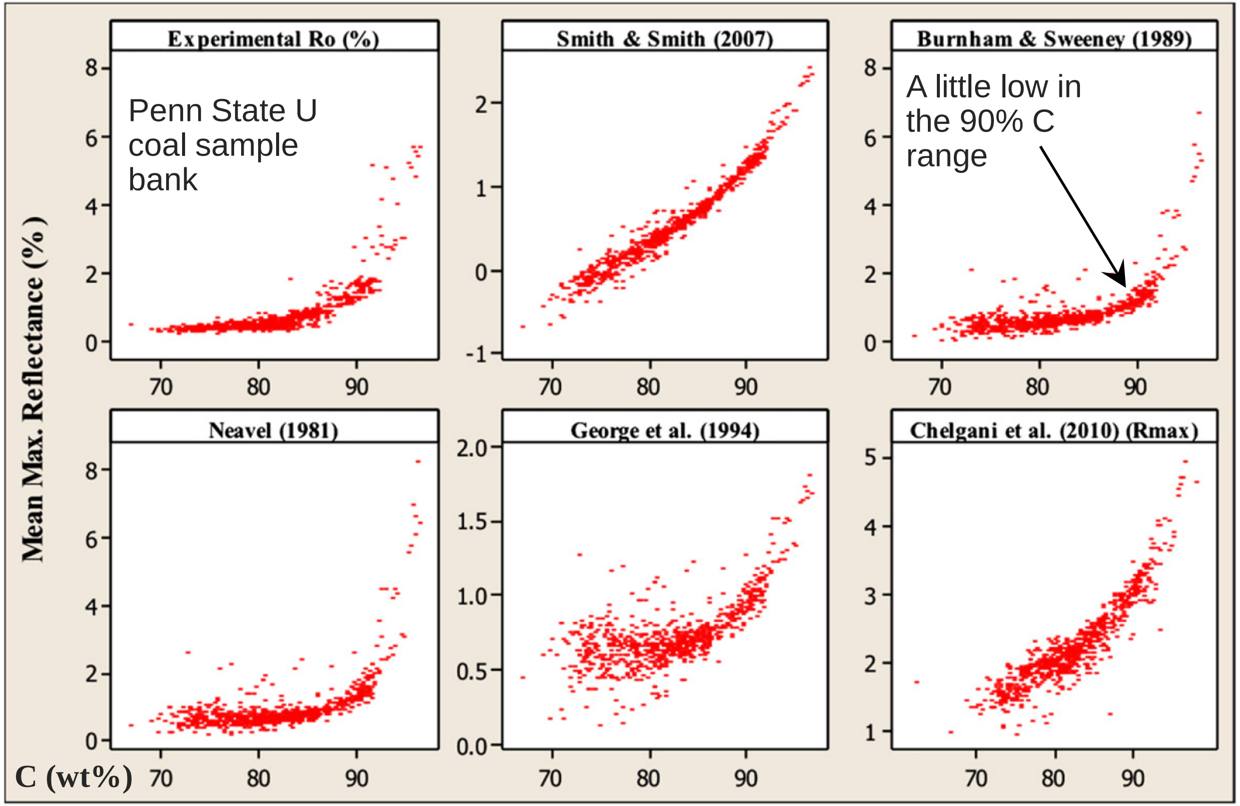


Potential improvements should also consider the compositional relationship to reflectance





Vitrimat correlations are the best overall in the literature, but some improvements are still warranted



Mathews et al., Fuel Processing Technology (2014)

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

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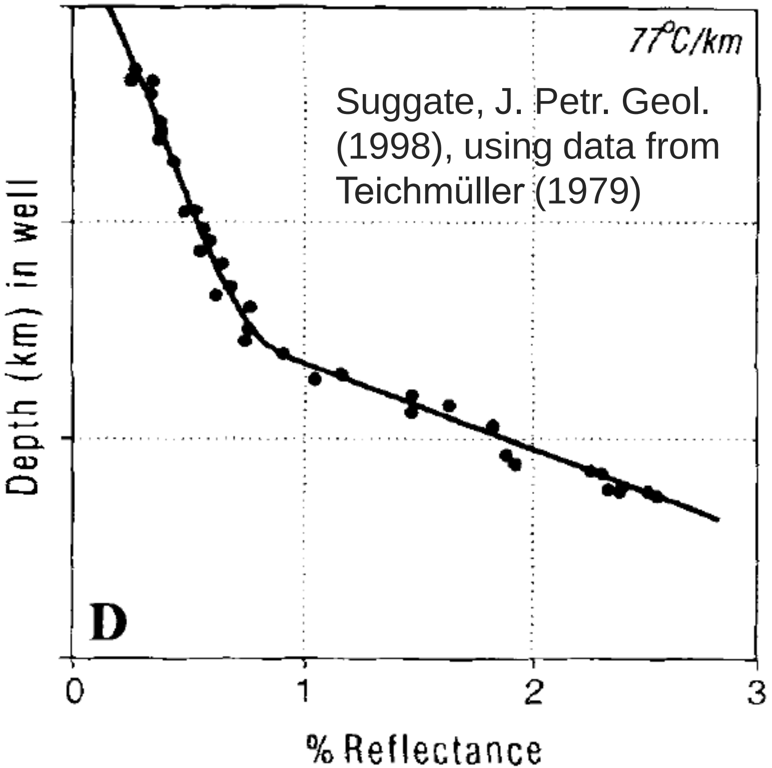

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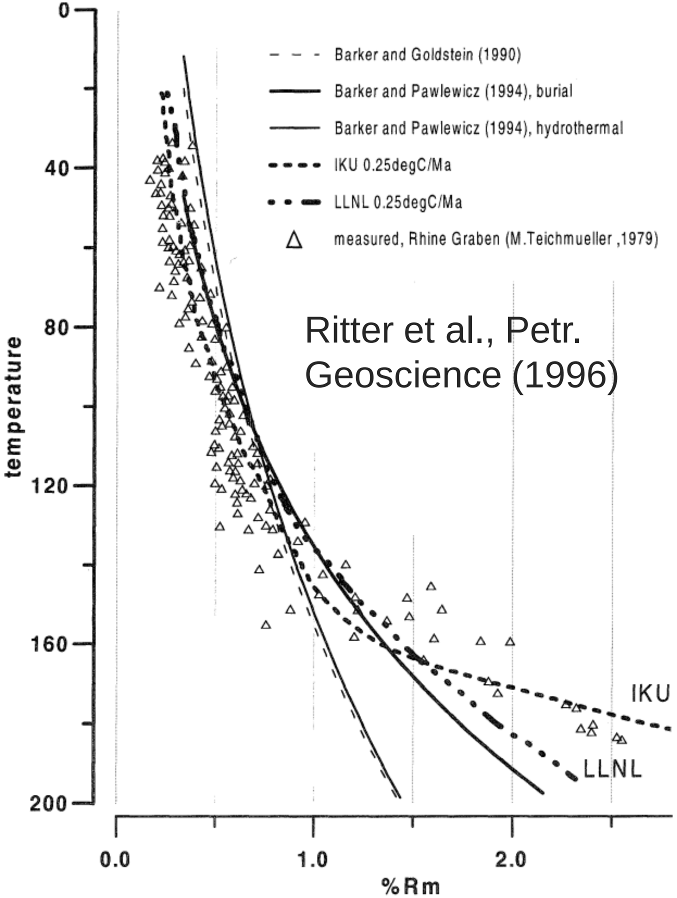
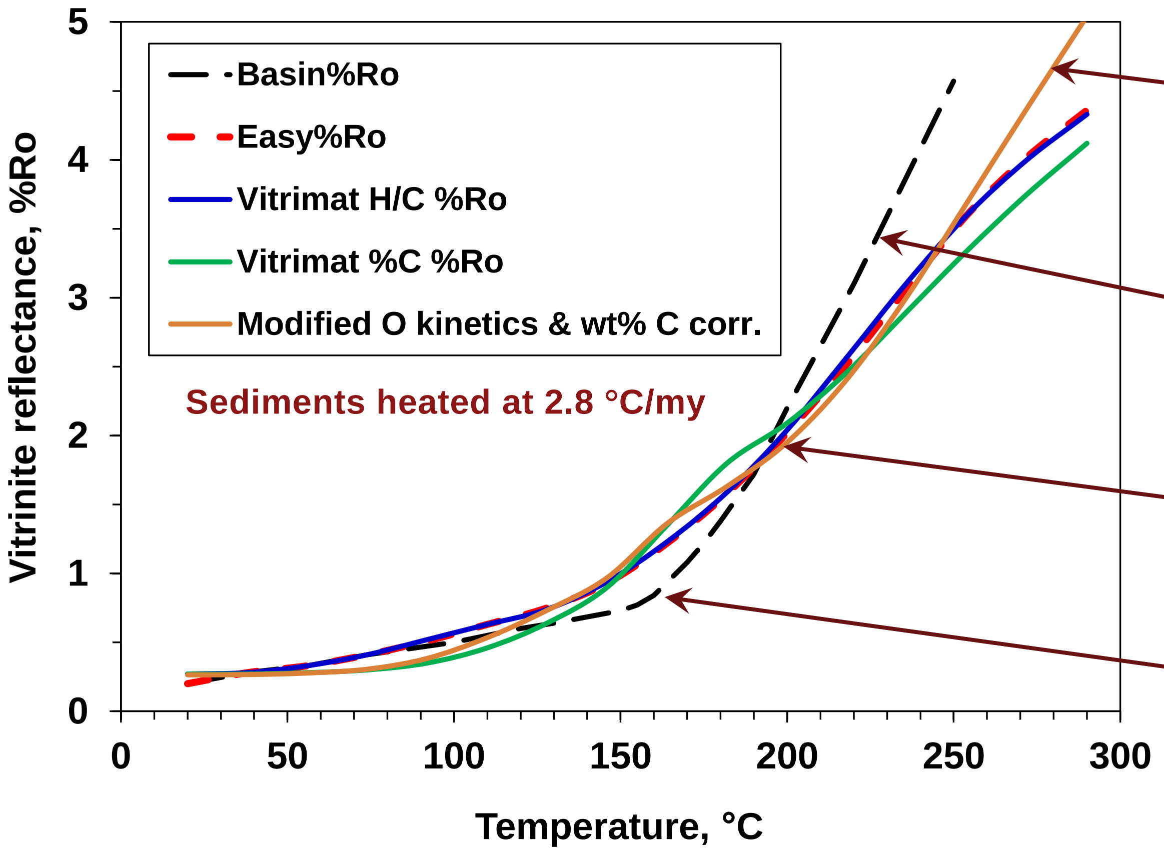


Ritter et al., Petr. Geoscience (1996)

Nielsen et al. (2016) propose Basin%Ro as an improved calibration of Easy%Ro



Easy to modify Vitrimat parameters to increase %Ro at high maturity —if warranted

Basin%Ro rises faster at high maturity

All agree at ~2% Ro

Sharper kink in the oil generation window

Temperature calibration for Aurora-1 well, Alaska North Slope

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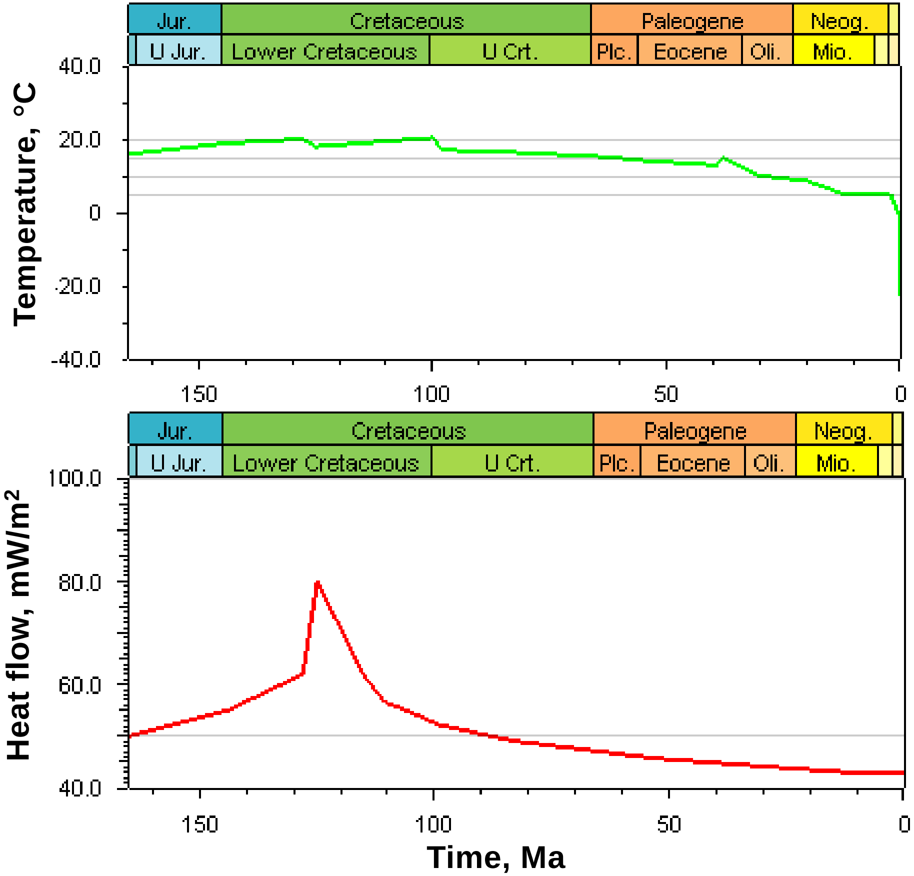

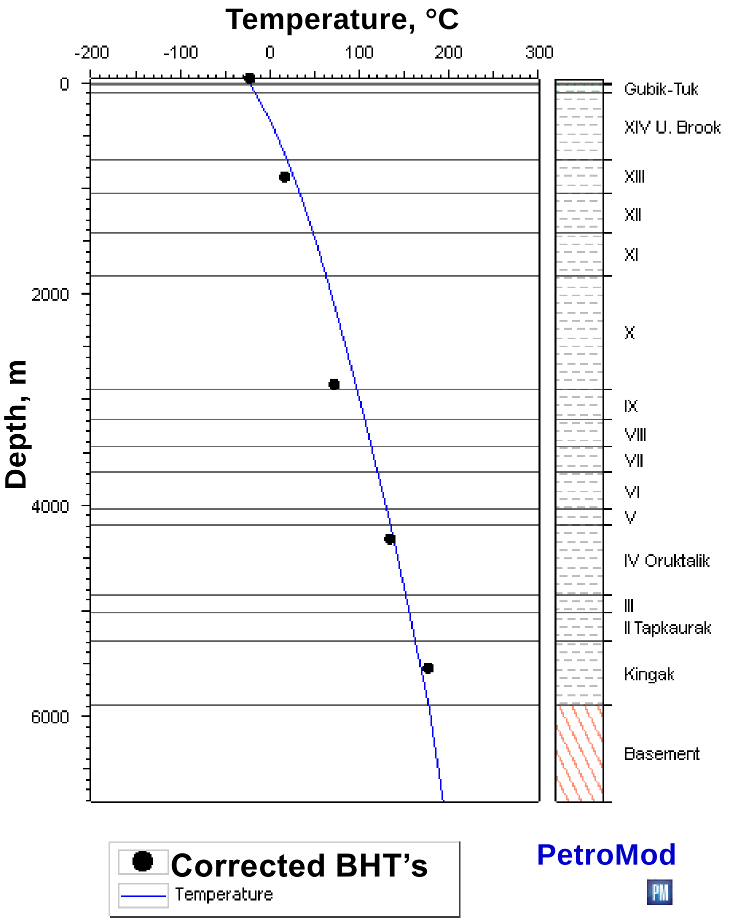

PetroMod

Basin%Ro agrees better with measurements and predicts slightly different source rock maturities

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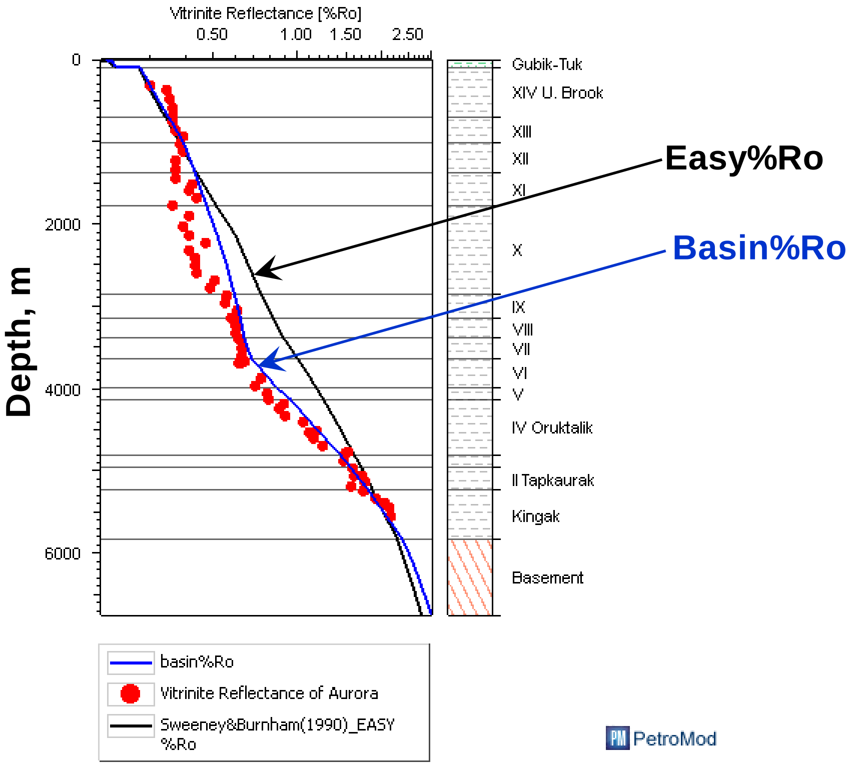

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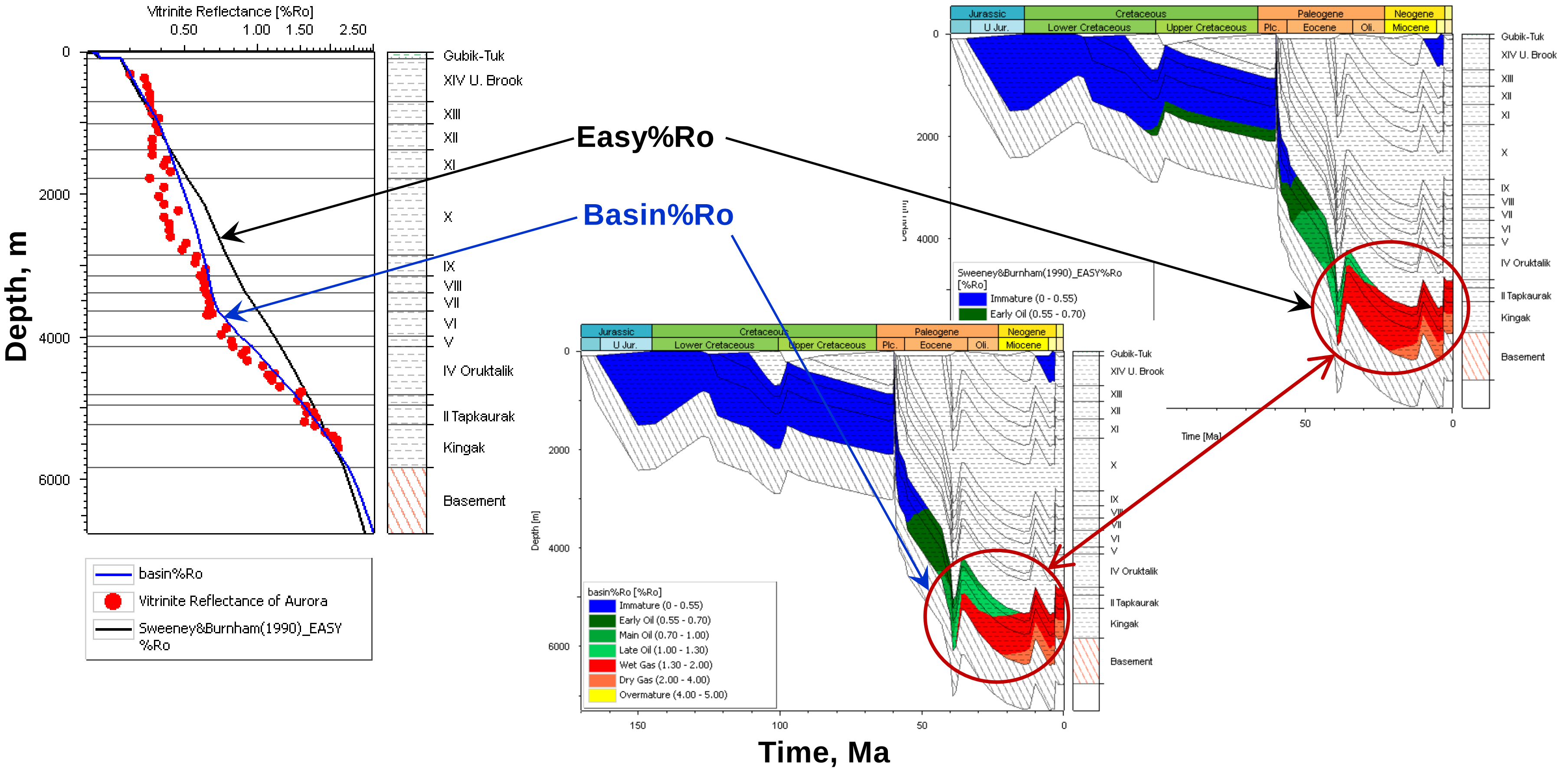

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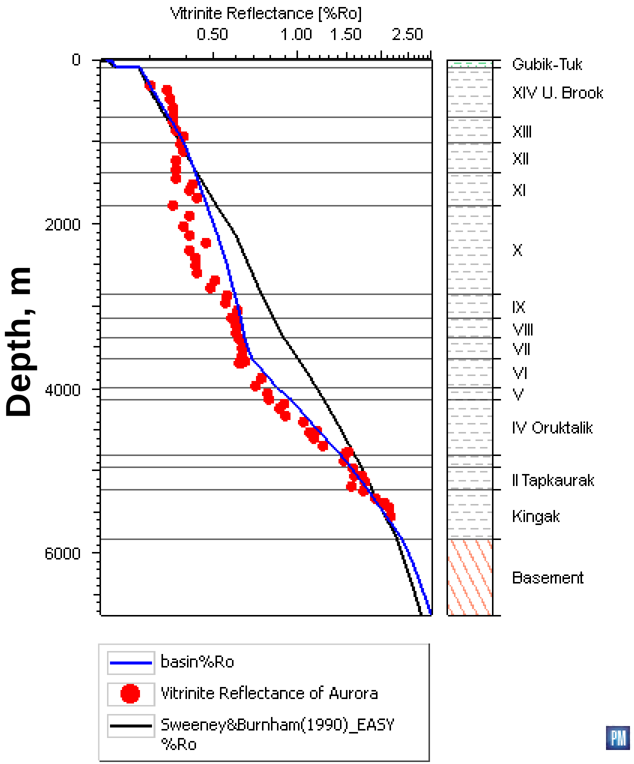

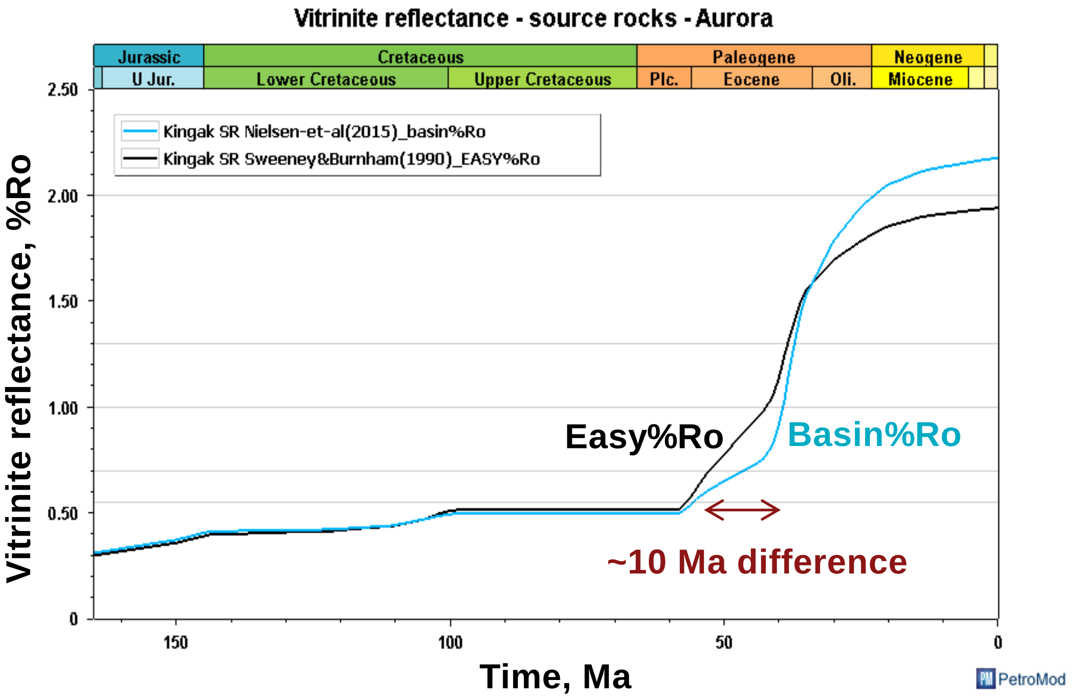

The best model is yet to come

Nielsen et al (2015) correctly observe that Easy%Ro agrees better with high-pressure experiments

- Due to the greater weight given to them by Burnham and Sweeney

Even so, %Easy%Ro could use some improvement for agreement with laboratory experiments

- Preliminary calculations suggest a frequency factor of $1x10^{14}$ s^{-1} would provide a better simultaneous match with lab and geo data

However, scatter in laboratory experiment indicates there are significant differences among vitrinites in different samples

- Almost certainly a different calibration will be required for vitrinite in coals and oil prone organic matter
- Each type has at least ±0.1%Ro variation among different workers for similar organic matter

Summary

Numerous vitrinite reflectance kinetic models have been developed to address various issues

- Computational time
- Effects of pressure
- Vitrinite suppression

Computational speed can be enhanced by using fewer second-order reactions

Much more good calibration data is available now compared to the late 1980s

Vitrinite reflectance versus depth (temperature, maturity) has a sharper dog-leg than calculated by Vitrimat H/C and Easy%Ro

Vitrinite suppression is more likely due to differences in deposition conditions and maceral interactions than pressure

ACKNOWLEDGEMENTS

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