Guidelines for Kinetic Input to Basin and Petroleum System Models*

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Abstract

Accurate kinetic parameters for the thermal decomposition of source-rock kerogen to oil and gas are needed for reliable computerized basin and petroleum system models (BPSM). This article provides guidelines for the use of kinetic parameters in BPSM based on data from 81 worldwide source rocks containing types I, II, IIS, II/III, and III kerogen plus calibrated model results for several exploration wells, such as the Aurora-1 well, North Slope Alaska.

(1) Kerogen type as defined by Rock-Eval pyrolysis hydrogen index of thermally immature source rock is not linked to kinetic response. For example, the kinetics for type II kerogen from one basin may be unlike those in another. (2) Kinetic parameters measured on thermally immature equivalents of the source rock in the study area are recommended. Use default kerogen kinetics with caution when appropriate samples are unavailable. (3) Descriptions of depositional environment are generally insufficient to define kerogen type or kinetic response. For example, lacustrine source rock from one basin can contain various kerogen types, each having different kinetic parameters. (4) Kerogen kinetics can vary laterally and vertically in source rock. If possible, confirm kinetic variations by measurements. (5) Hydrous and single-ramp programmed pyrolysis kinetics are not recommended because they may not adequately assess the discrete activation energy distribution of the source rock kerogen. Multiple-ramp kinetics are recommended where both the activation energy (E_a) and frequency factor (A) are optimized by the

kinetic software. (6) Kinetic uncertainty can be described by the 1-2-3 rule. Because of the Arrhenius compensation law, a 1°C error in the measurement of E_a is compensated by a twofold adjustment of the frequency factor in order to maintain the same calculated laboratory pyrolysis reaction rate. When such erroneous kinetics are extrapolated to geologic time, the corresponding error in predicted temperature is ~3°C. Assuming a universal Ea of 1×10^{14}/sec rather than optimizing both E_a and A can result in temperature errors of 20°C or more when extrapolated to geologic time. (7) Easy%Ro may be less accurate than Basin%Ro for calibration of BPSM. Basin%Ro more accurately replicates the dogleg in vitrinite reflectance versus depth that is commonly observed at depths corresponding to ~0.7 to 1.0% Ro, where hydrogen index decreases due to kerogen transformation after being approximately uniform at lower maturity.

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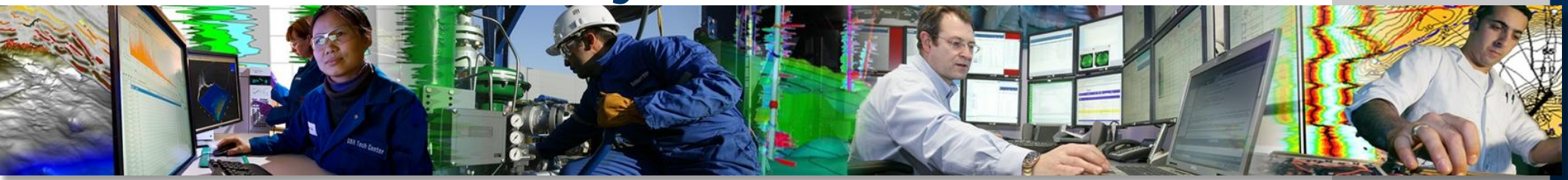
Geochemistry/Petroleum Systems: Basin Modeling and Geochemistry Along the Value Chain
Tuesday April 4, 2017

April 4, 2017
Houston, TX

Guidelines for Kinetic Input to Basin and Petroleum System Models



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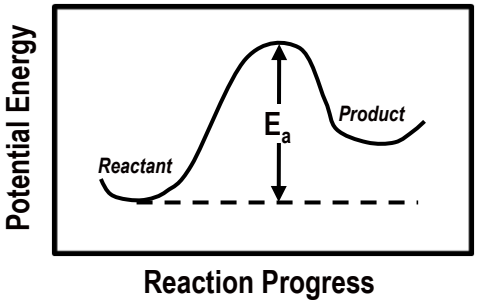


Purpose of the Presentation

This talk provides guidelines for the use of chemical reaction kinetics to model petroleum generation from kerogen in source rocks. The main goal is to identify 'best practice' for measuring/using kinetic parameters.

Kerogen – insoluble particulate organic matter that consists of macerals derived from different organisms

Preview of Conclusions

- **Kerogen type is *only weakly* linked to kinetic response, i.e., avoid inferring kinetics from (1) Rock-Eval hydrogen index, and (2) source-rock depositional environment.**
- **Describe kinetics by a discrete activation energy (E_a) distribution and corresponding frequency factor (A) rather than a single E_a and A or a distribution of E_a and fixed A.**
- **Use 'default' kinetics as a last resort. Measured kinetics may not account for lateral/vertical organofacies variations.**
- **Alternative vitrinite kinetics may be more reliable than Easy%R_o to calibrate basin and petroleum system models.**

"Discrete Activation Energy Models": *One* Frequency Factor

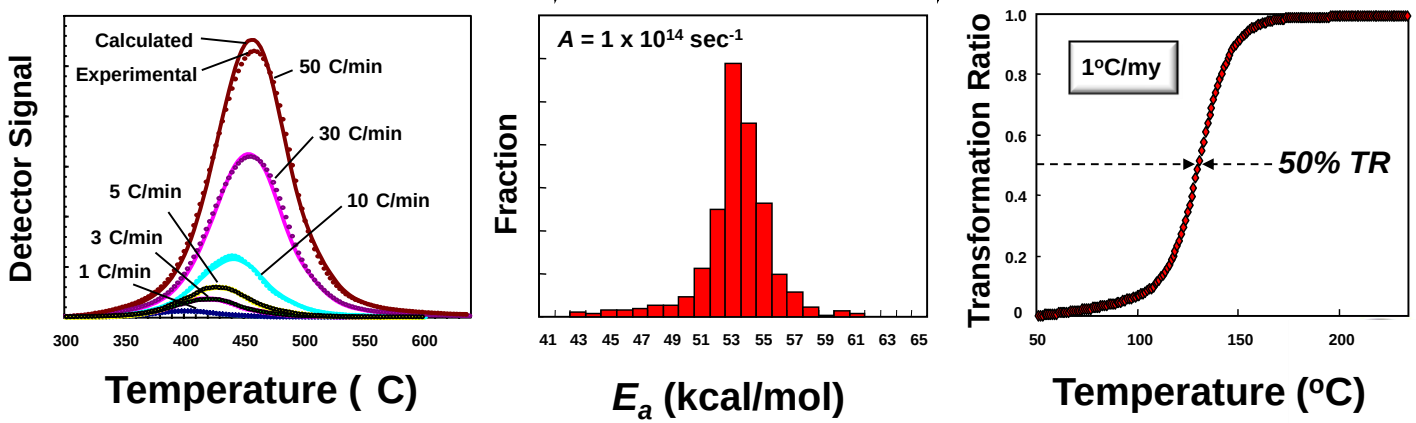
$$k = Ae^{-E_a/RT}$$ ***Arrhenius equation***

k = Arrhenius rate constant (kerogen to oil and gas)

***A* = frequency factor (e.g., vibrational frequency of bonds broken)**

E_a = activation energy, R = gas constant, *T* = temperature

Programmed Pyrolysis → ***Optimization*** → ***Geologic Conditions***



Presenter's notes: **Discrete activation energy (DAE) modeling** is mathematically an ill-posed problem (Sundararaman et al., 1992) that requires optimization of the calculated parameters. The "compensation law" shows that a wide range of E_a and A combinations can satisfy the Arrhenius equation for the laboratory rate constant, but extrapolation of incorrect E_a and A to geologic time can result in incorrect temperature predictions. DAE uses a single frequency factor (A) for all possible activation energies associated with the

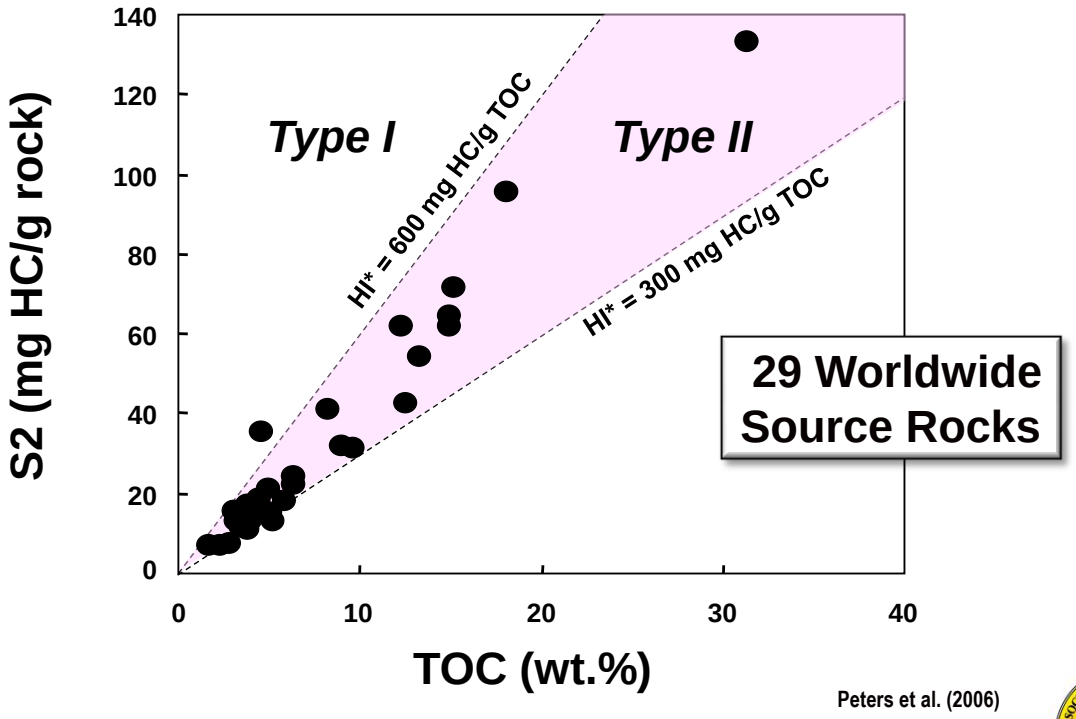
(Presenter's notes continued on next slide)

discrete distribution. *A* can be optimized by the Kinetics05 software or it can be an assumed, universal value. Use of one value for *A* can lead to erroneous results, especially for organic matter associated with a very broad activation energy distribution, i.e., type III kerogens. For robust solutions, the pyrolysis experiments must include three or more widely differing heating rates using an energy spacing of 1 kcal/mol or less. Optimization involves minimizing a nonlinear error function for E_a and A.

The Arrhenius equation states that reaction rate increases exponentially with temperature, so that a 10°C rise in T causes the reaction rate to double. However, the rate of increase slows with increasing T, so that at 200°C the rate increases by a factor of only 1.4 for a 10°C rise in T (Robert, 1988).

- Two parameters characterize rate behavior of a reaction in the Arrhenius equation:
  - ✓ E_a, activation energy
  - ✓ A, pre-exponential factor

Examine Kinetics for a Global Collection of Type II Kerogens

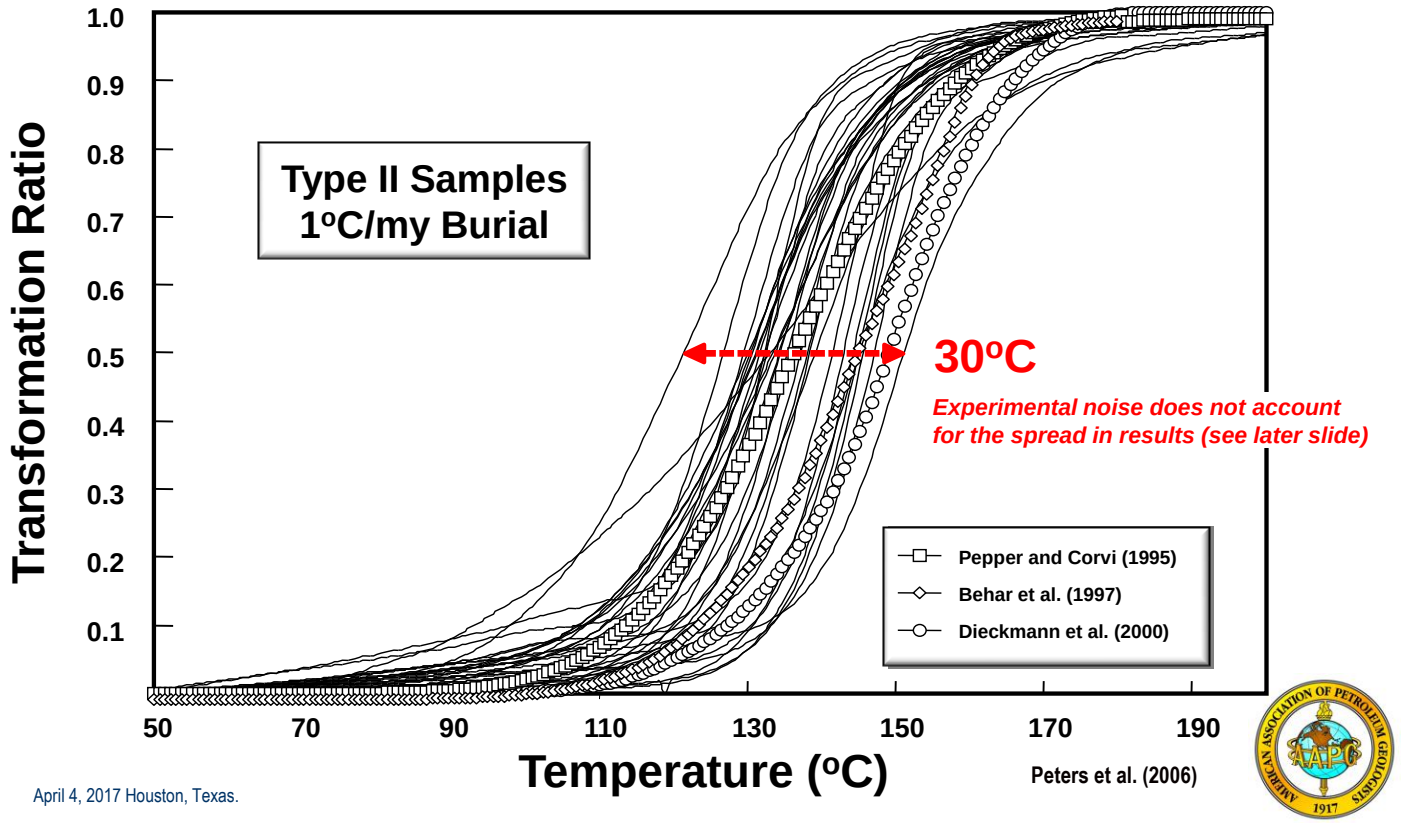


Peters et al. (2006)

*HI = Rock-Eval hydrogen index = 100 x S2/TOC

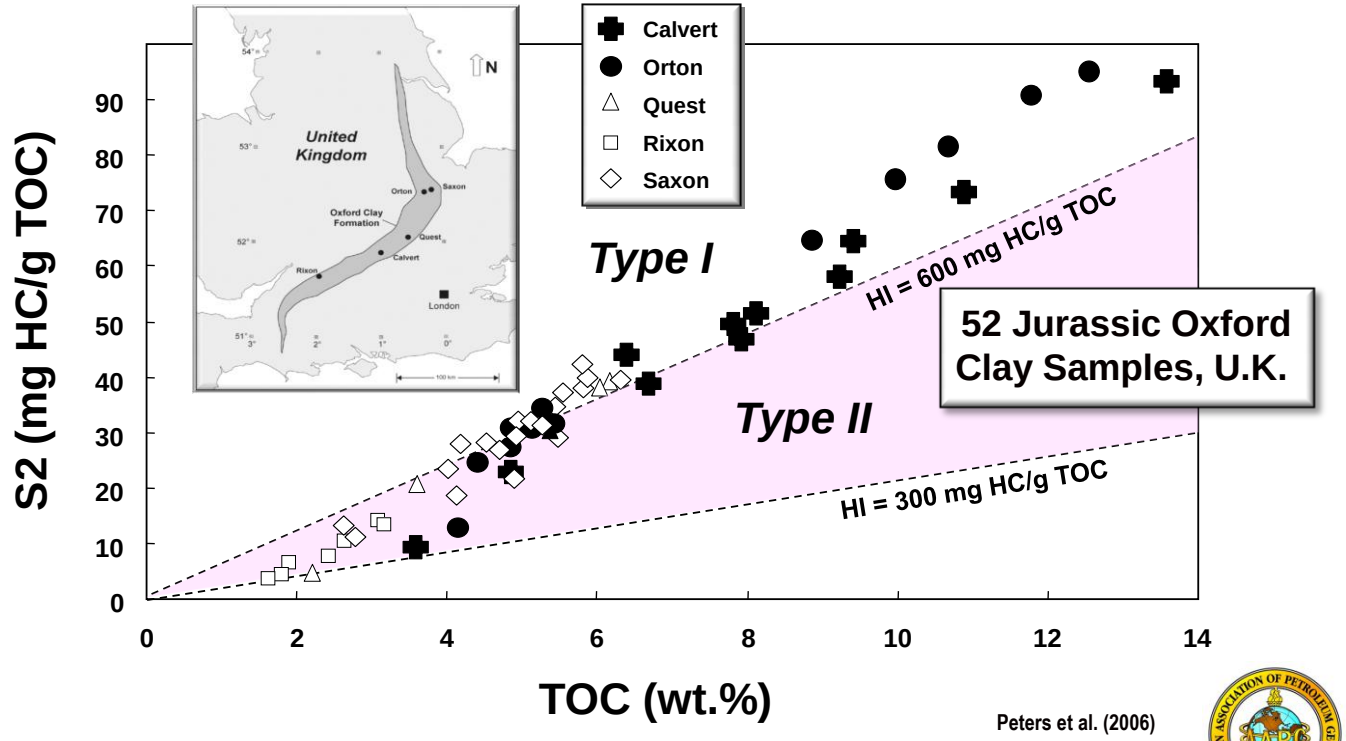
Presenter's notes: Samples from 29 marine source rocks worldwide that contain mainly type II kerogen (HI = 230-786 mg HC/g TOC) were subjected to open-system programmed pyrolysis to determine activation energy distributions for petroleum generation. Assuming a burial heating rate of 1$_o$C/m.y. for each measured activation energy distribution, the calculated average temperature for 50% fractional conversion of the kerogen in the samples to petroleum is ~136$_o$C $\pm$7$_o$C, but the range spans ~30$_o$C (~121$_o$-151$_o$C).

Does Kerogen Type (HI) Indicate Kinetic Response? No!



Presenter's notes: Calculated fractional conversions based on an assumed heating rate of 1°C/m.y. for 29 worldwide petroleum source rocks that contain mainly type II kerogen. The range of calculated temperatures at 50% fractional conversion of kerogen to petroleum is 30°C (range 121°-151°C). Circled numbers indicate four curves for the corresponding samples in previous figure. The calculated fractional conversions for three common "default" type II kerogens are included for comparison.

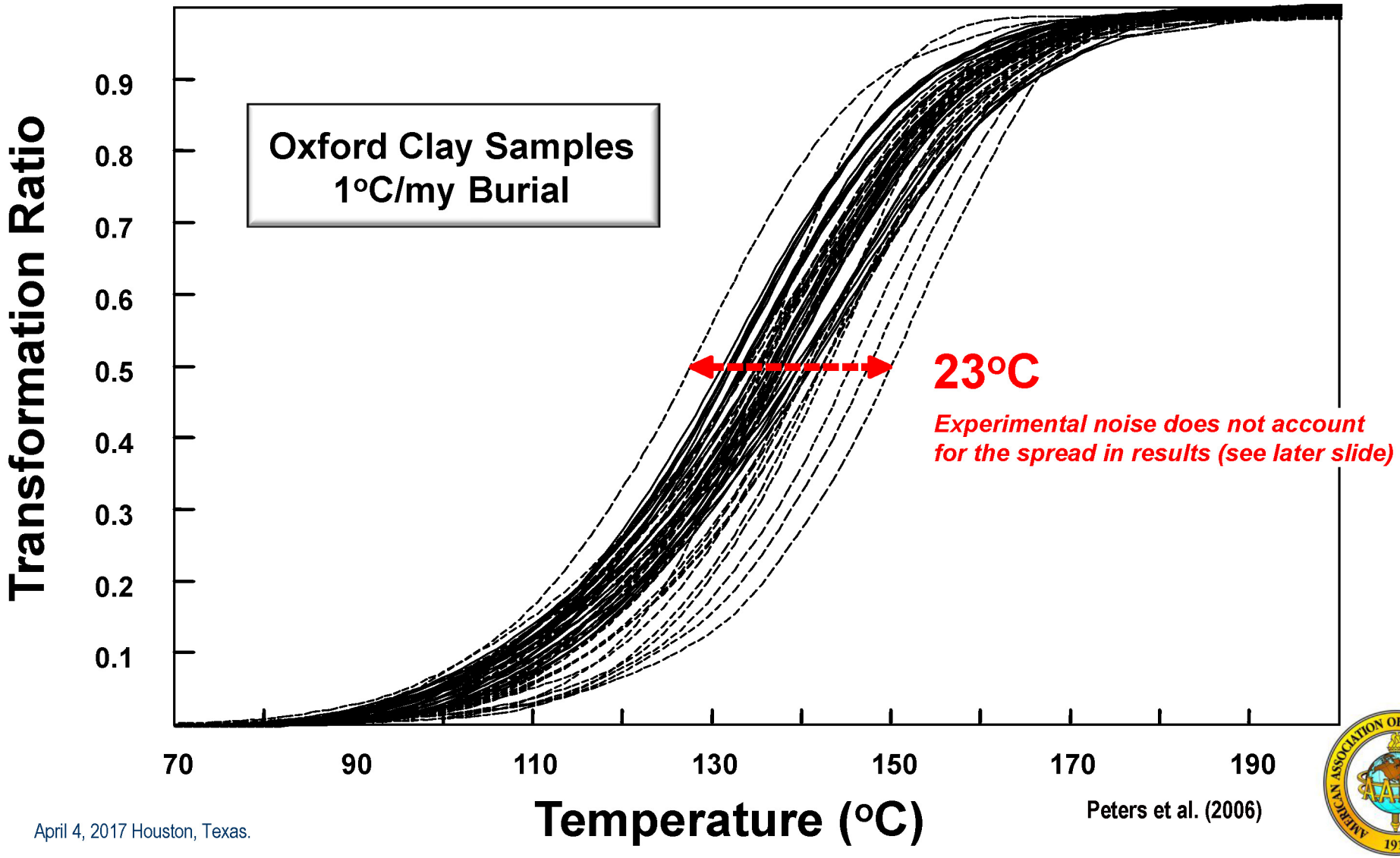
Examine Kinetics for Samples Within One Source Rock



Peters et al. (2006)

Presenter's notes: Total organic carbon (TOC, wt.%) versus Rock-Eval pyrolysis S2 (mg hydrocarbon/g rock) for 52 samples of unweathered Jurassic Oxford Clay Formation source rock collected from five sites in the United Kingdom. Many samples from the Quest, Rixon, and Saxon sites (open symbols) contain <6 wt.% TOC and oil-prone type II kerogen, while many samples from the Calvert and Orton sites (solid symbols) contain >6 wt.% TOC and very oil-prone type I kerogen.

Are Kinetics Uniform Within One Source Rock? No!



Peters et al. (2006)

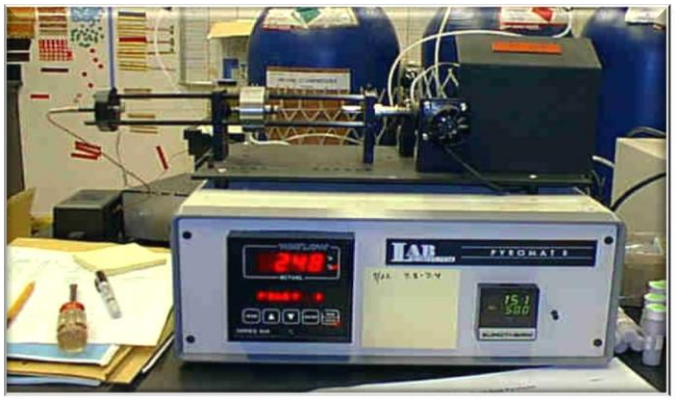
Some Recommend "Single-Ramp" Kinetics with a Fixed *A*

- **Single-ramp kinetics at 25°C/min (e.g., Waples et al., 2010) use a *fixed, universal* value of *A*.**
- **Single-ramp is faster and cheaper than multiple-ramp kinetics and can be used on archived pyrolysis data.**
- **Multiple-ramp kinetics optimize *both* E_a and *A*: Pyromat II® ramps = 1, 3, 5, 10, 30, and 50°C/min**

Is Single-Ramp Better than Multiple-Ramp Kinetics? No!

- **Compare reliability of various combinations of open-system pyrolysis ramps to determine the kinetics of petroleum generation for 52 global source rocks.**
- **Is single-ramp kinetics using a fixed *A* (1 x 10^{14} sec^{-1}) more reliable than multiple-ramp kinetics where *both* E_a and *A* are optimized?**

Laboratory Pyrolysis

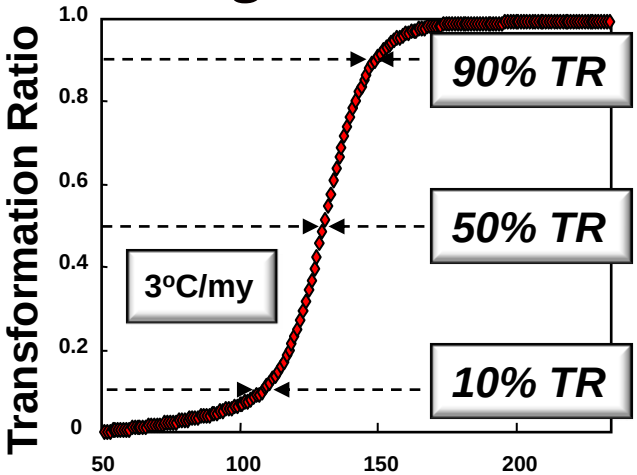


Pyromat II® Micropyrolysis

Optimization

Kinetics05® Software

Geologic Conditions



Temperature (ºC)

16 Single-Ramp Replicates Give 'Best' E_a of 0.28 Kcal/mole

Bellagio Road outcrop (Type II)
$A_{fixed} = 1 \times 10^{14}\ sec^{-1}$

	T_{max}* °C	Mean E_a, kcal/mole	Geologic Extrapolation Assuming 3°C/my: Temp °C at 10% TR†	Temp °C at 50% TR†	Temp °C at 90% TR†
Average	449.3	53.54	112.0	137.3	163.7
Minimum	447.8	52.97	105.2	135.8	160.4
Maximum	452.1	53.87	115.0	138.4	168.2
Std. Dev.	1.3	0.28	2.3	0.8	2.2

*T_{max} as measured using Pyromat II
†TR = transformation ratio (extent of conversion of kerogen to petroleum)

Fixed *A* Introduces ~20°C Error in Extrapolated Temperature

1-2-3 Rule: 1 kcal/mol error doubles A and yields ~3°C error in geologic extrapolation of temperature

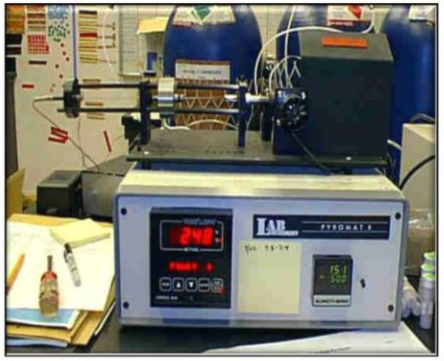
Range *A* for 52 kerogens = 10^{12} to 10^{16} sec^{-1}
Assume a fixed *A* of 1 x 10^{14} sec^{-1}

$10^{14}/10^{12} = 100$
$Log_2 100 = 6.65$ (i.e., *A* doubles 6.65 times)
6.65 x 3°C/my ~ 20°C error

Heating-Rate Ratio (R_r) = Maximum / Minimum Ramp

- Pyromat II® Ramps = 1, 3, 5, 10, 30, and 50°C/min
- Therefore, R_r of 1 is a single-ramp experiment (fixed *A*).
- R_r of 50 consists of all 50/1 multi-ramp experiments (optimized *A*):

Pyromat II™

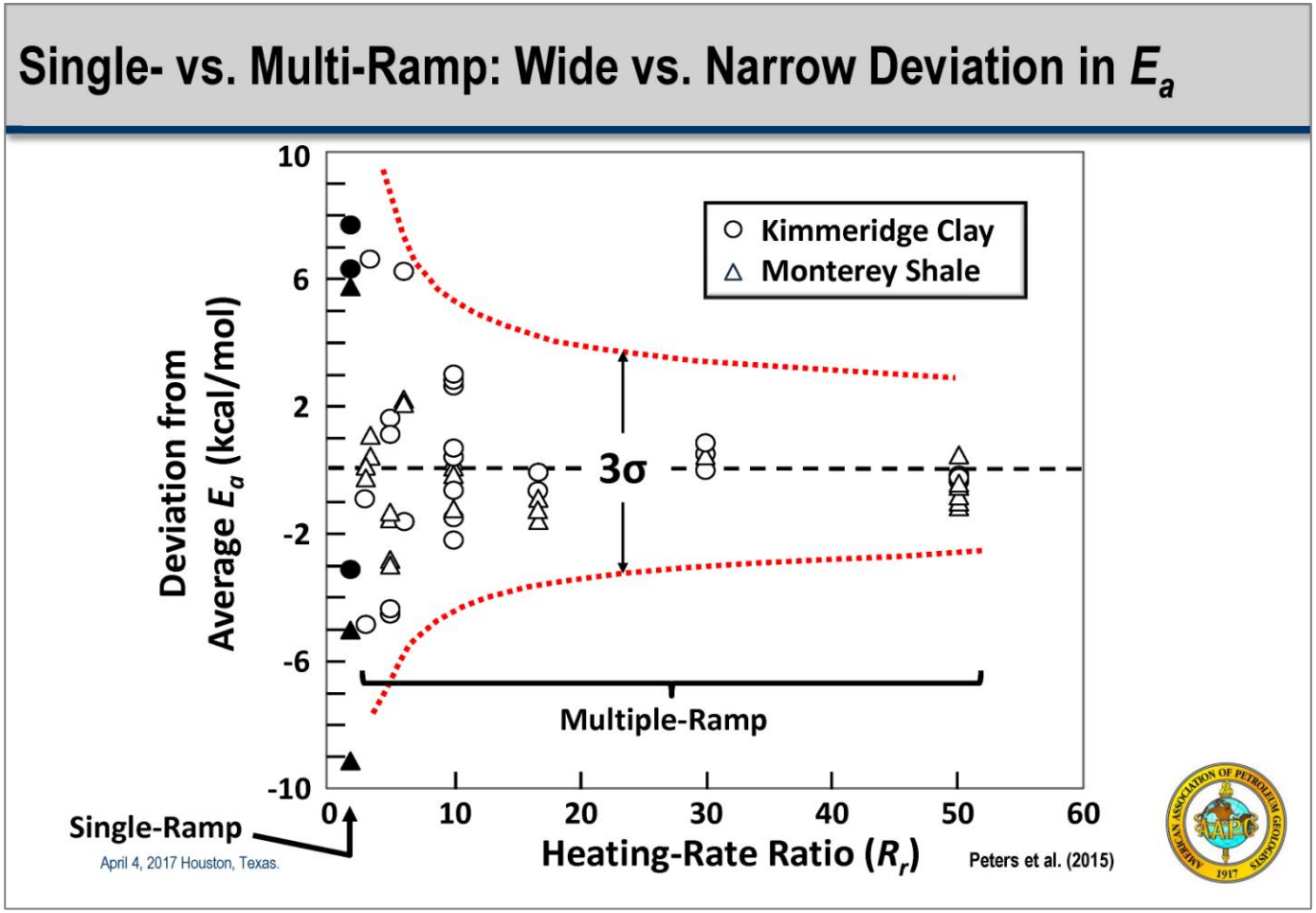


1,50
1,3,50
1,5,50
1,10,50
1,3,5,50
1,5,10,50
1,10,30,50
1,3,5,10,30,50

°C/min

April 4, 2017 Houston, Texas.

Presenter's notes: Deviation from average activation energy (E_a) versus heating-rate ratio (R_r = maximum divided by minimum rate) for samples from the Kimmeridge Clay and Monterey Shale (type II and IIS kerogen, respectively). Optimized kinetic parameters were calculated from one (solid symbols) or combinations of two to six heating rate experiments (open symbols) in the range 1, 3, 5, 10, 30, 50°C/min. When R_r is low, the variability of E_a (and the corresponding frequency factor, *A*) is large. For heating R_r >16, the variability of E_a becomes relatively small. Dotted lines represent the temperature error (3) in E_a calculated from the standard deviation for the 16 Bellagio Road measurements as a function of R_r



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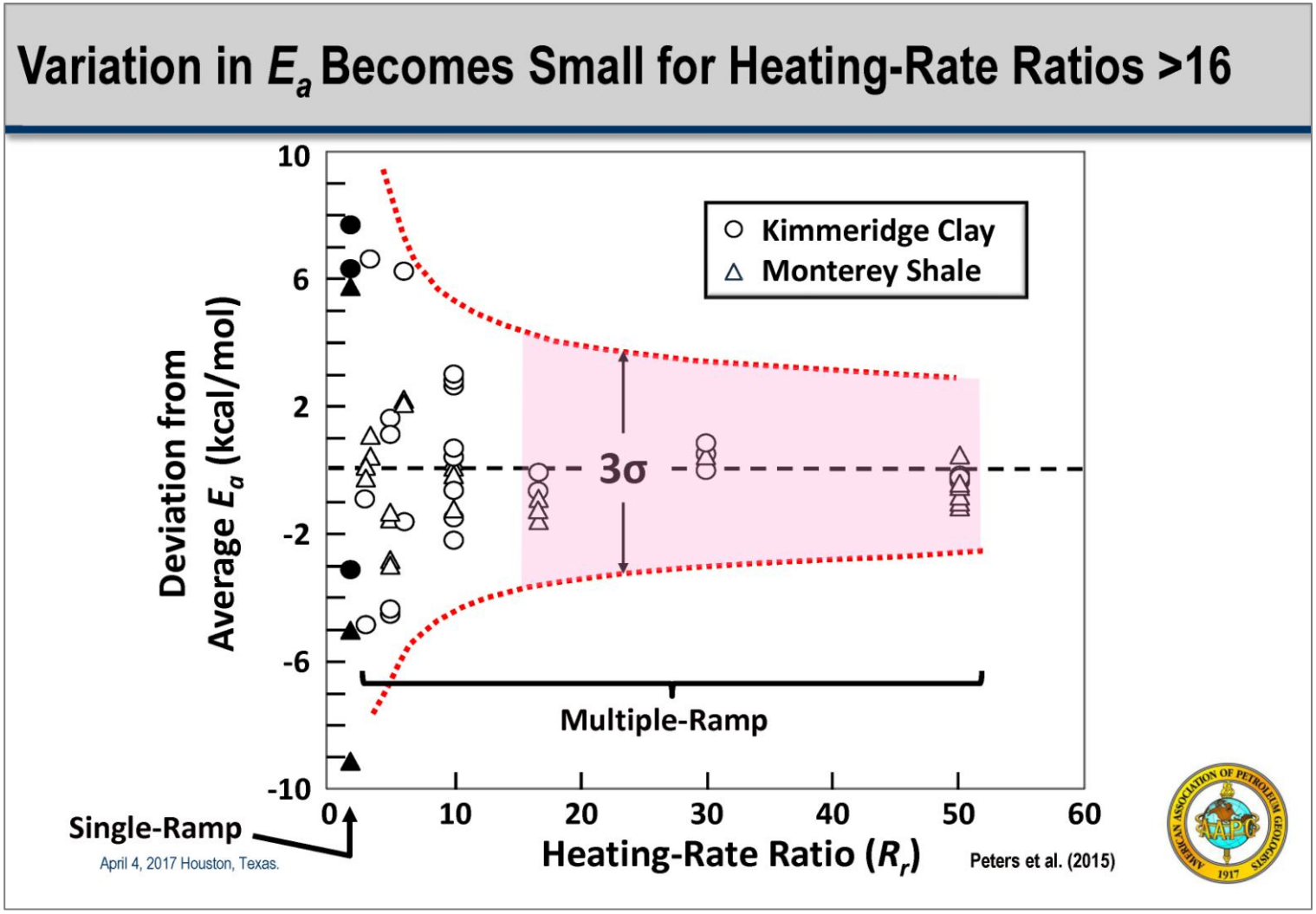
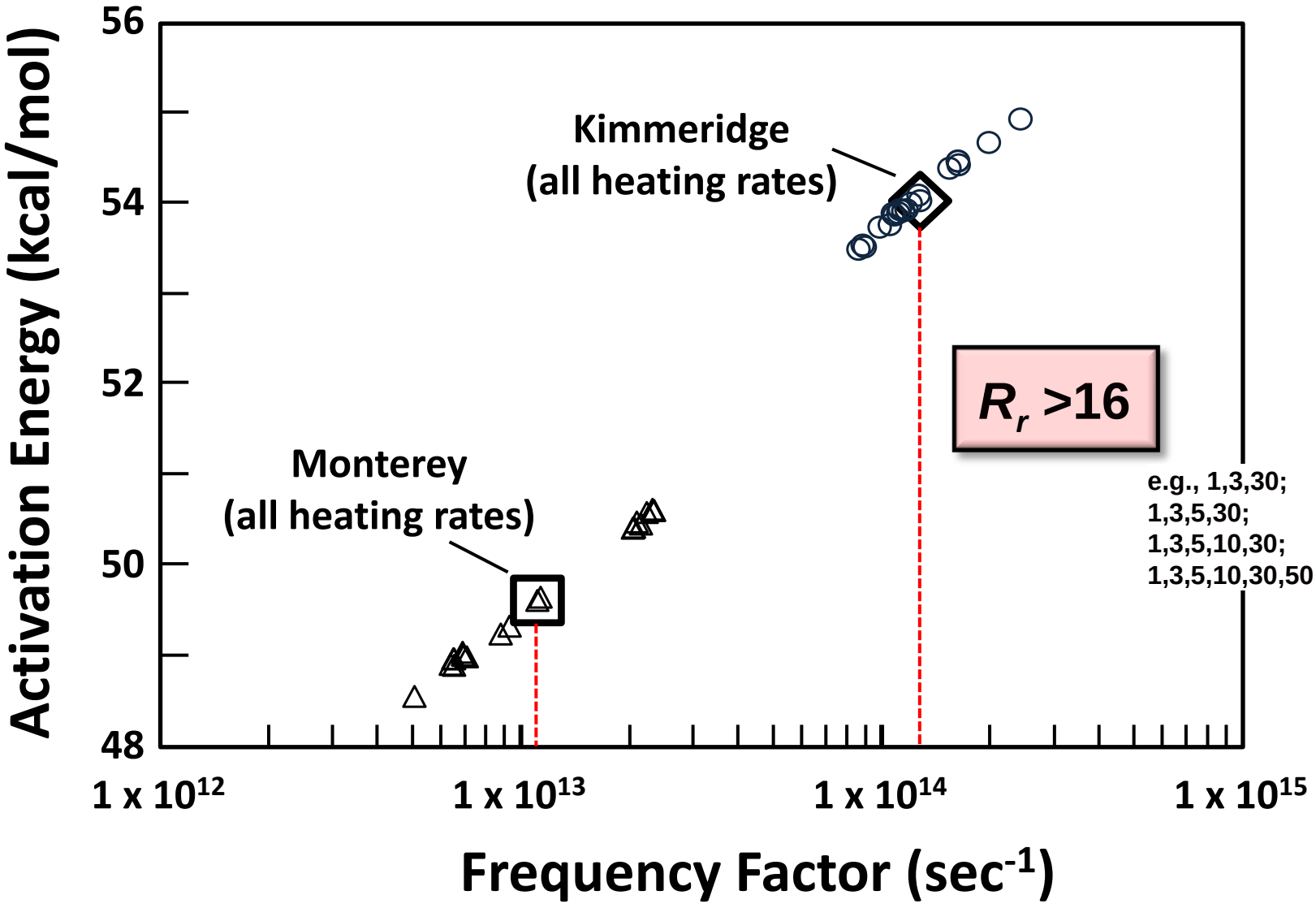
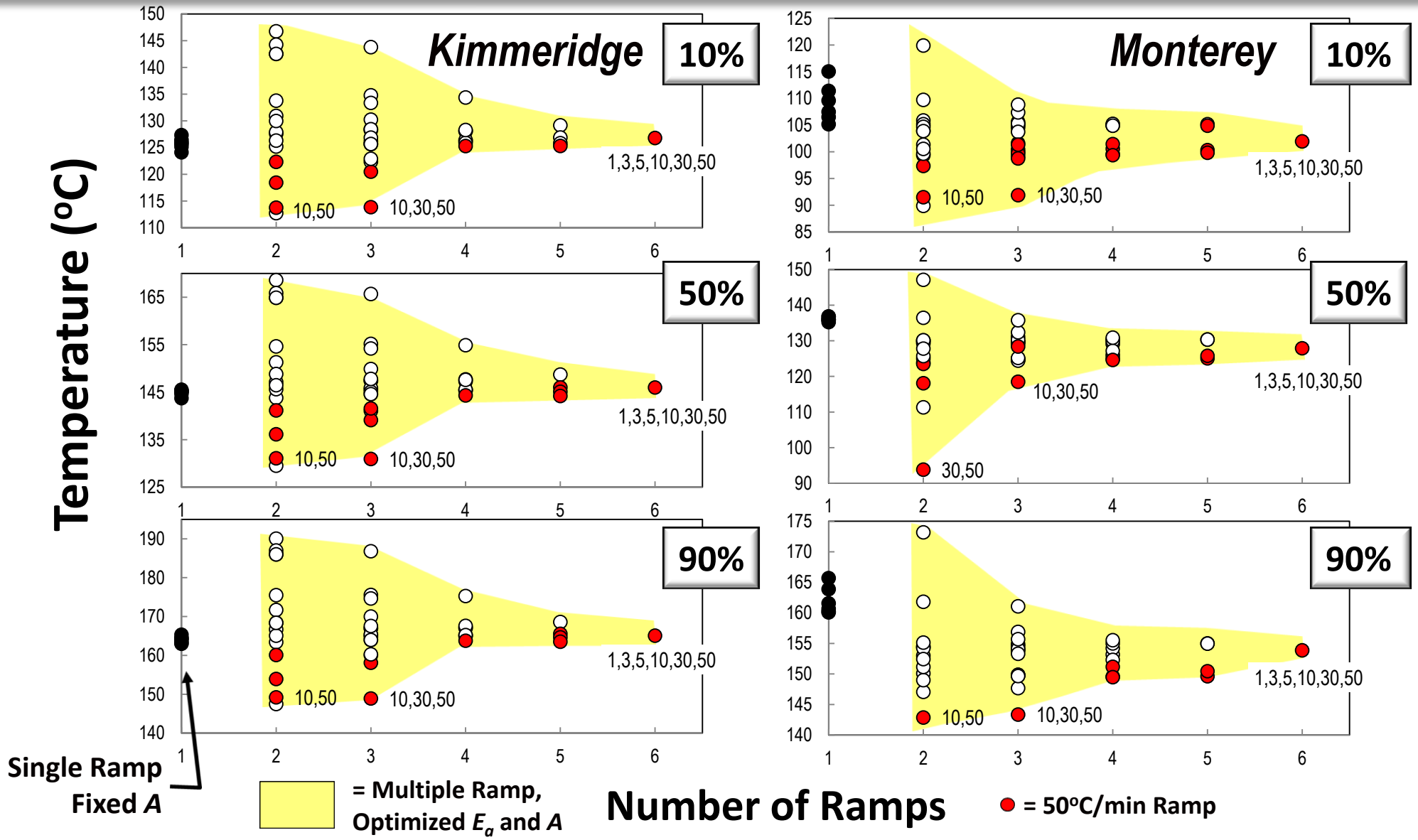


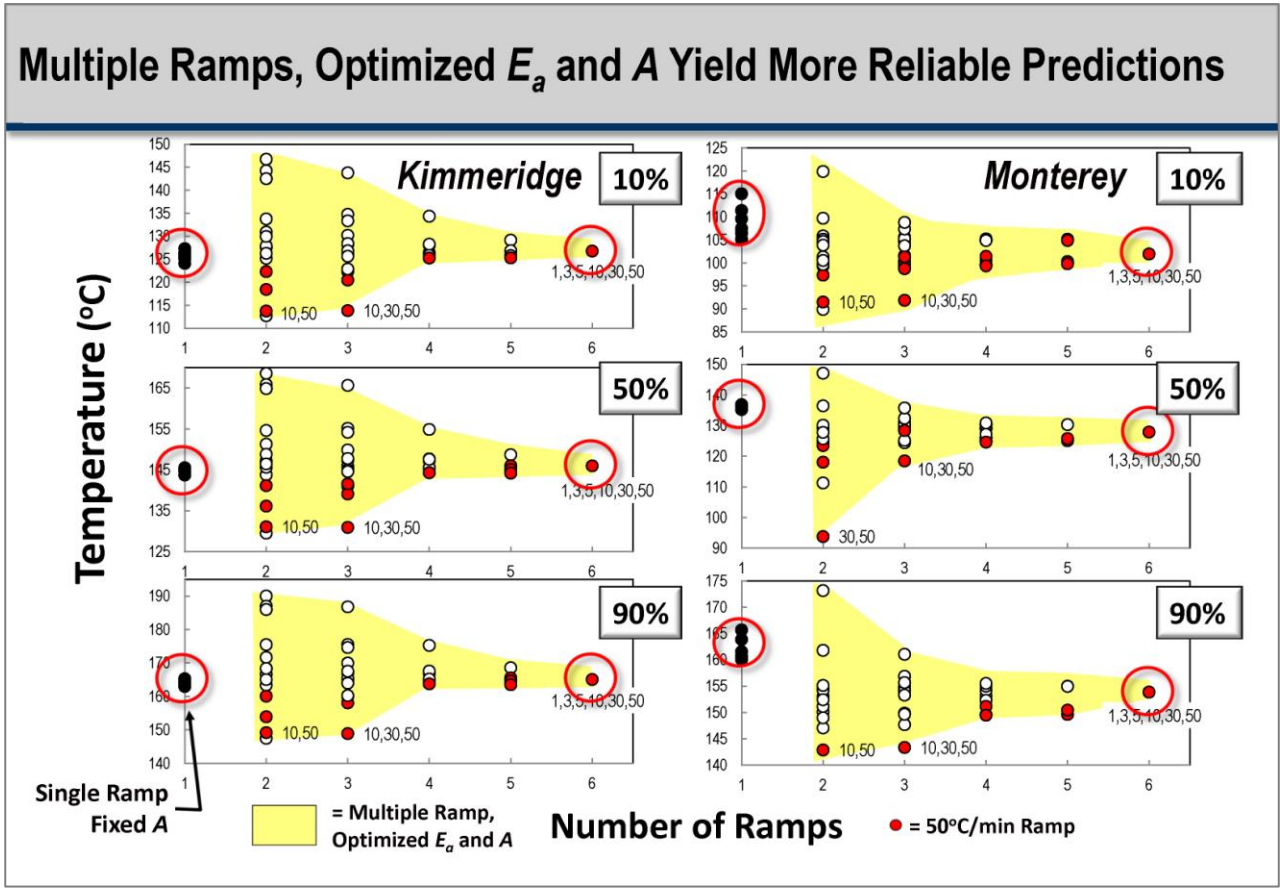
Presenter's notes: Plot of optimized frequency factor-activation energy (A-E_a) pairs for heating-rate ratios, R_r >16 shows that differences in the mean A and E_a are real and not a measurement artifact. The Kimmeridge Clay and Monterey Shale kinetic parameters do not overlap, and the average frequency factor for the two samples based on all combinations two to six heating rates (1, 3, 5, 10, 30, 50$_o$C/min; Table 3) differs by factor of ~10.

Differing E_a and A are Real and Not Measurement Artifacts



More Ramps Focus Predicted Temperature and Transformation Ratio



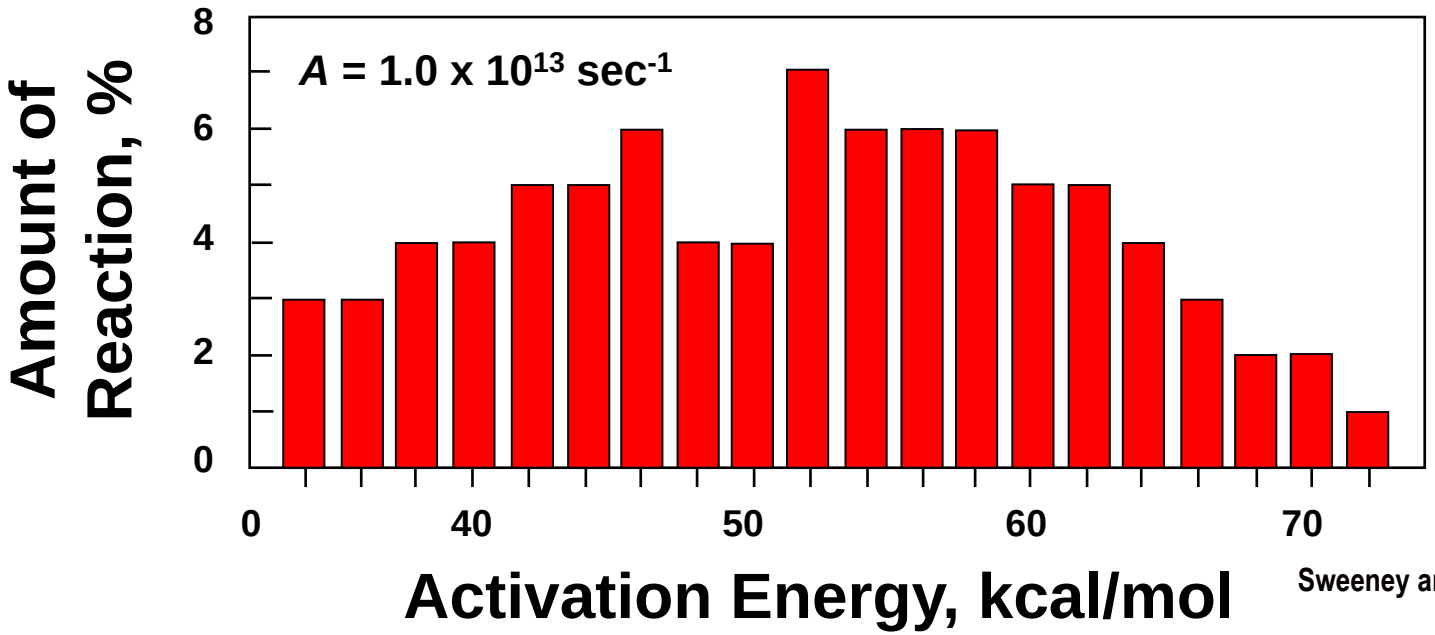


Presenter's notes: The distribution of activation energies and value of the frequency factor for the maturation of vitrinite are not well constrained. For this reason, R_o measurements should always be compared with other paleotemperature estimates.

Presenter's notes: 21
Pre-exponentials:
Easy%R_o: 1 x 10^{13}/sec
Easy%R_oDL: 2 x 10^{14}/sec (DL = dogleg)
Basin%R_o: 9.696 x 10^{12}/sec (almost the same as Easy%Ro)

Is Easy%R_o Best to Calculate Vitrinite Reflectance? Maybe Not!

- **Global vitrinite maturation is described by:**

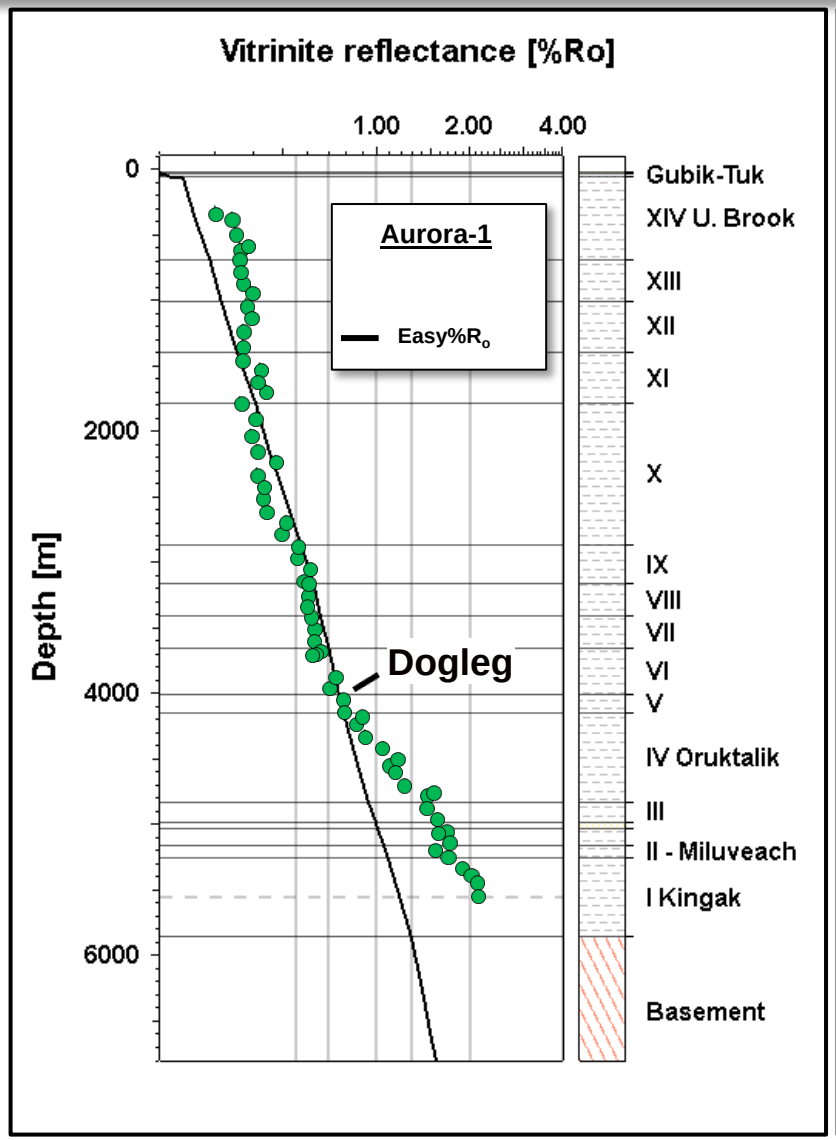


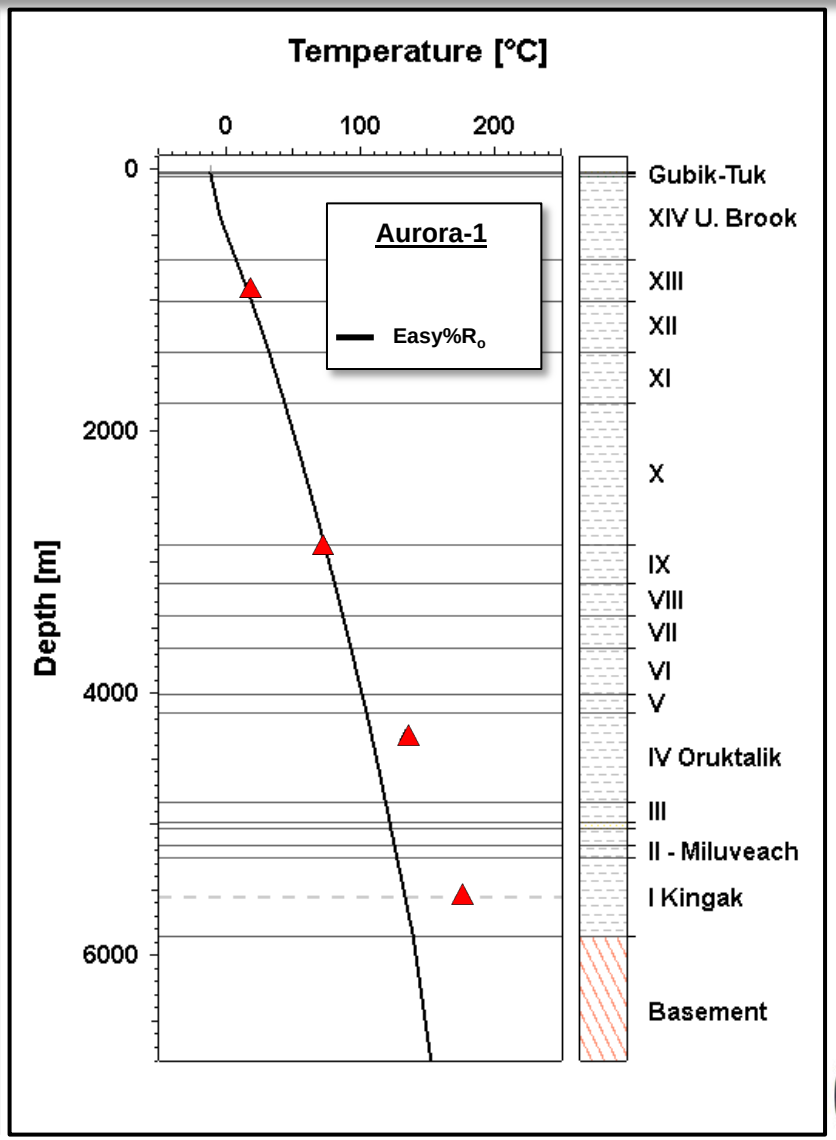
Sweeney and Burnham (1990)

- **Reflectance is related to total conversion by:**

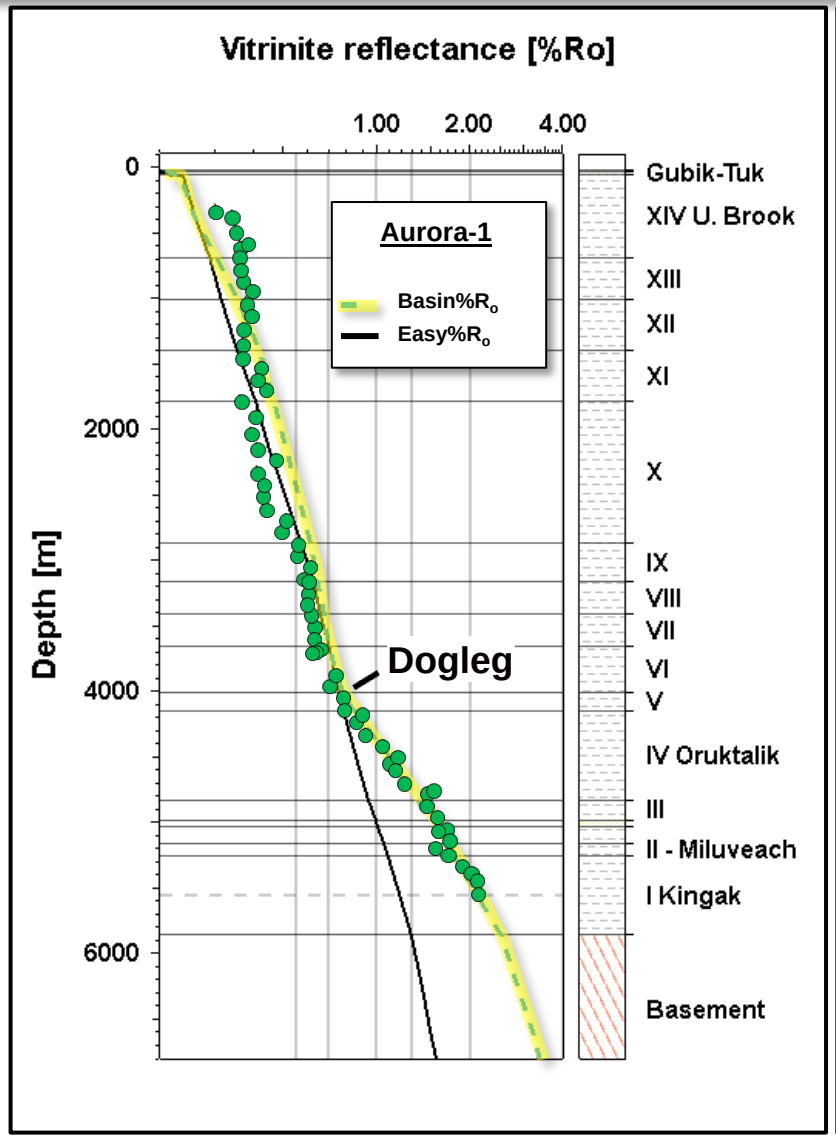
$$\%R_o = \exp(-1.6 + 3.7 * \text{fractional conversion})$$

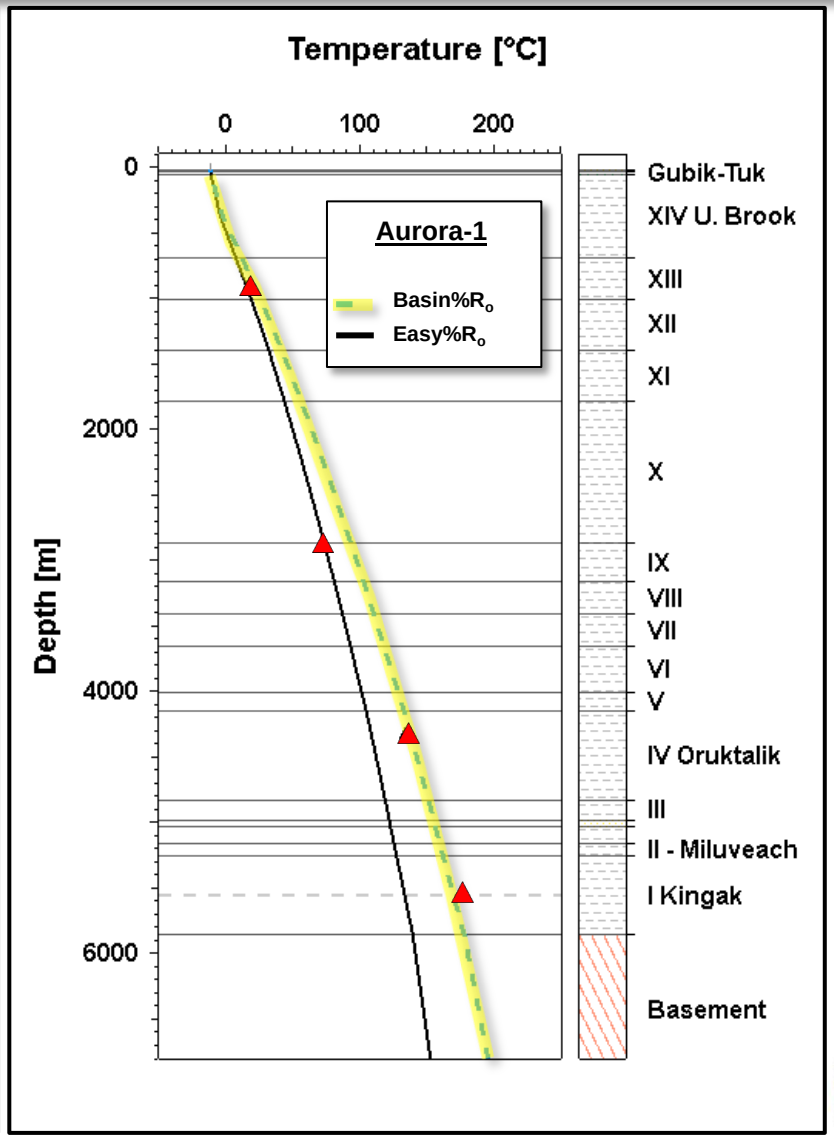
EasyR$_o$ Does Not Calibrate R$_o$ Below the Dogleg at 4000 m



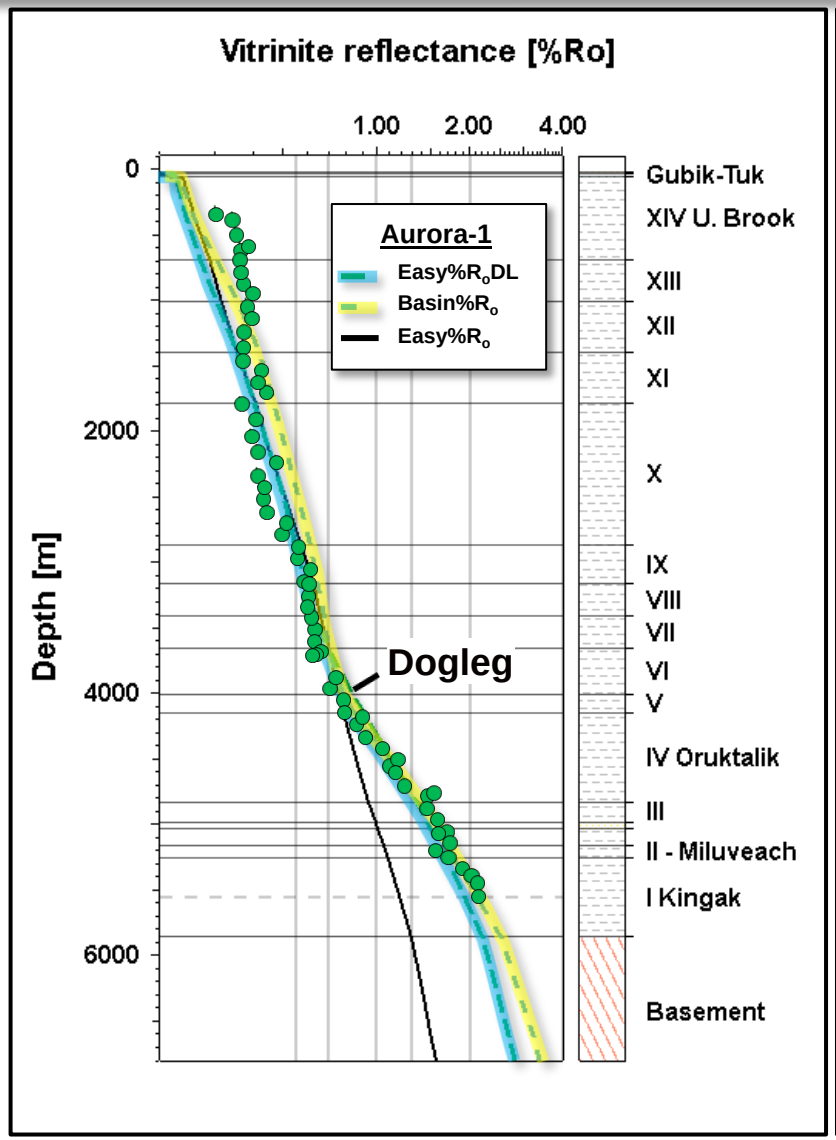


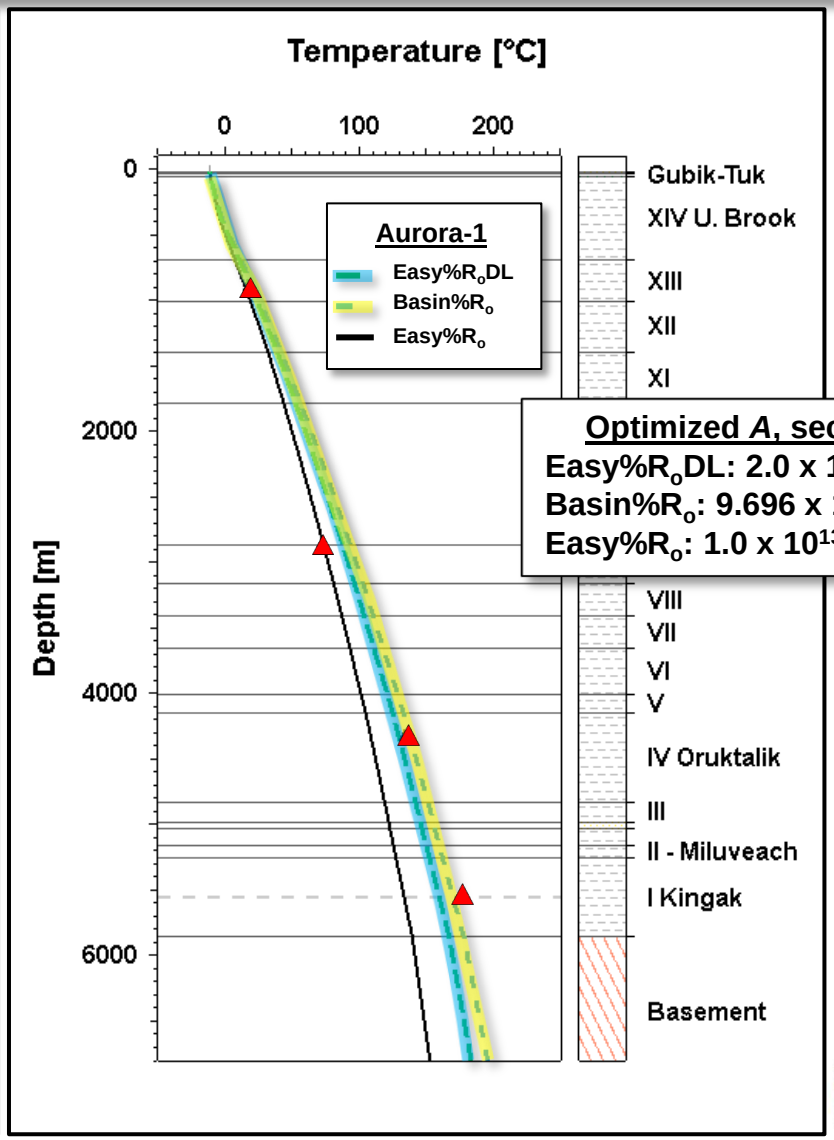
Basin%R_o Better Replicates the Dogleg and Deeper R_o Data





EasyR$_o$ May be Less Reliable Than Basin%R$_o$ and Basin%R$_o$DL





Summary of Conclusions (I)

- **Kerogen type is *only weakly* linked to kinetic response, i.e., *if possible*, do not infer kinetics from Rock-Eval HI or depositional environment, avoid 'default' kinetics.**
- **Kerogen kinetics are best described by a discrete activation energy (E_a) distribution and corresponding frequency factor (A).**
- **Measured kinetics on thermally immature equivalents of the active source rock may not adequately account for lateral/vertical organofacies variations.**
- **Single-ramp pyrolysis *can* yield kinetic results that are inconsistent with those from multiple-ramp experiments.**

Presenter's notes: Neither single- nor multiple-ramp discrete E_a distribution models are reliable for kerogens with narrow E_a ranges where nucleation-growth models are needed.

Summary of Conclusions (II)

- **Adoption of fixed *A* of 1 x 10^{14} sec^{-1} can result in error of up to ~20°C in geologic temperature extrapolation.**
- **Pyrolysis ramps >30°C/min can be too fast for good kinetic fit because of thermal lag; minimize sample and thermocouple size, optimize thermocouple orientation.**
- **20- to 30-fold variation in heating rate using at least three ramps is recommended (e.g., 1, 5, 25°C/min or 1, 3,10, 25°C/min) with replicates at highest and lowest rates.**
- **Easy%R_o may be less reliable than other calibration methods, such as Basin%R_o or Easy%R_oDL.**