Petroleum Generation Kinetics: Single- Versus Multiple-Heating Ramp Open-System Pyrolysis*

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Abstract

Some recent publications promote one-run, open-system pyrolysis experiments using a single heating rate (ramp) and fixed frequency factor to determine the petroleum generation kinetics of source rock samples because they are faster, less expensive, and presumably yield results similar to those from multiple-ramp experiments. The purpose of this work is to compare the efficiency of various combinations of open-system pyrolysis heating rates to determine the kinetics of petroleum generation. Pyromat II® open-system micropyrolysis experiments were conducted on a large number of drill cuttings samples from a worldwide collection of source rocks at one or more of the following heating rates: 1, 3, 5, 10, 30, and 50°C/min. The resulting pyrolyzate peaks were processed using Kinetics05® software to derive chemical rate models. Although some one-ramp pyrolysis experiments using a fixed frequency factor of $1 \times 10^{14} sec^{-1}$ indeed yield kinetic results similar to those from multiple-ramp experiments using floating frequency factors, the data illustrate that one-ramp kinetics are generally unreliable. The precision of kinetic results, as measured by calculated temperatures at 10, 30, and 90% transformation ratio, increases with the number of pyrolysis heating ramps in the range 1 to 50°C/min. However, the accuracy of these temperature predictions is unclear. The data show that kinetic results based on three different pyrolysis temperature ramps closely approximate those determined from six runs, provided that that the three temperature ramps span an appropriate range of heating rates. However, temperature ramps of 30 and 50°C/min appear to be too fast to obtain a good kinetic fit because of delayed heat transfer between the thermocouple and the sample. At least three pyrolysis ramps are recommended, such as 1, 3, and 10°C/min or 1, 3, 5, and 10°C/min. Delayed heat transfer between the thermocouple and sample may even affect these comparatively slow heating rate experiments. These conclusions do not address the more fundamental question as to whether discrete kinetic models based on open-system pyrolysis are sufficiently accurate for use in basin simulators.

Selected References

Braun, R.L., A.K. Burnham, J.G. Reynolds, and J.E. Clarkson, 1991, Pyrolysis kinetics for lacustrine and marine source rocks by programmed micropyrolysis: Energy & Fuels, v. 5, p. 192-204.

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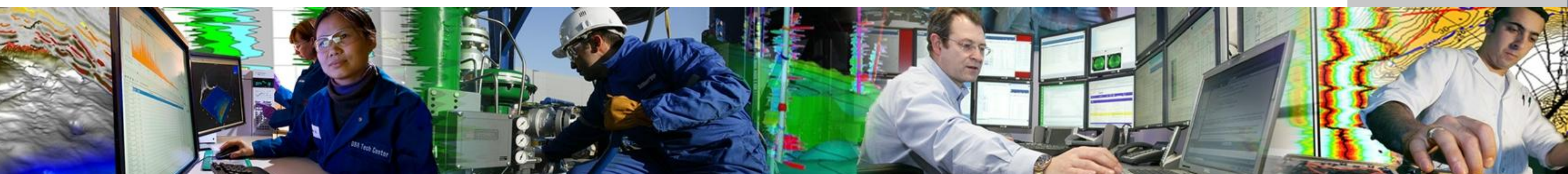

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“Discrete Activation Energy Models”: *One* Frequency Factor

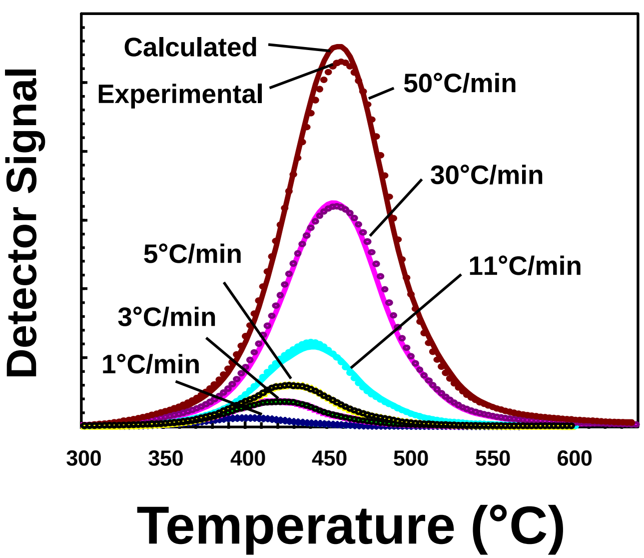
$$k = Ae^{-E_a/RT}$$

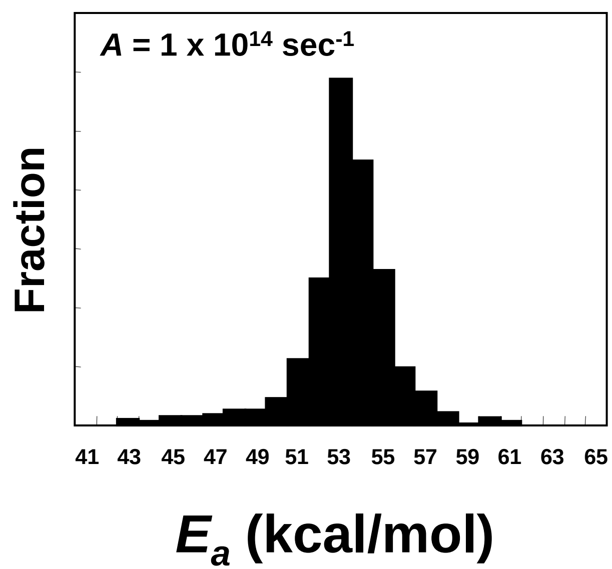
k = Arrhenius rate constant (kerogen to oil and gas)

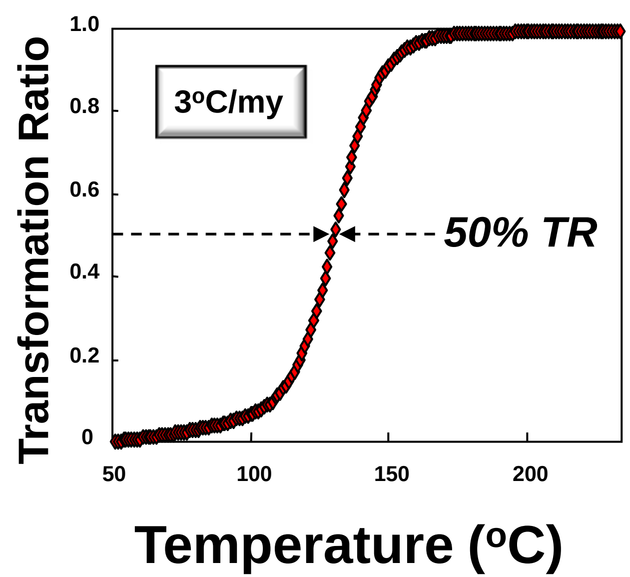
A = frequency factor (e.g., vibrational frequency of bonds broken)

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

Laboratory Pyrolysis → ***Optimization*** → ***Geologic Conditions***







Recent Papers Recommend "Single-Ramp Kinetics"

- **Single-ramp kinetics (Waples et al., 2002, 2010), Waples and Nowaczewski (2014) use a *fixed, universal 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**

Purpose of the Kinetic Study

- **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* (1×10^{14} sec^{-1}) more reliable than multiple-ramp kinetics where *both* E_a and *A* are optimized?**

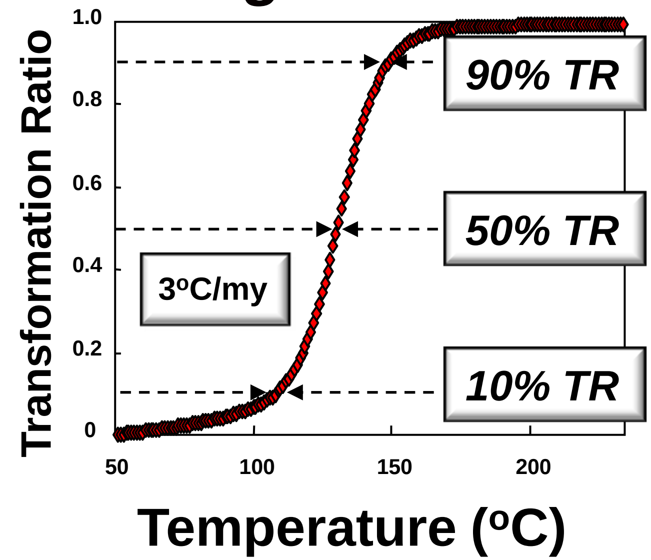
Laboratory Pyrolysis

Pyromat II® Micropyrolysis

Optimization

Kinetics05® Software

Geologic Conditions



Assessment of Single-Ramp Kinetics Involves Three Factors

1) Are there real differences in frequency factors (*A*) for petroleum generation from kerogen in source rocks?
2) Are the differences in *A* large enough to significantly impact extrapolation of temperatures to geologic conditions (e.g., at different transformation ratios)?
3) What experimental conditions are required to answer questions 1 and 2?

Arrhenius Equation Expressed Relative to Reference Values

$$k = Ae^{-E_a/RT}$$

$$k_1 = A_1e^{-E_1/RT} \qquad k_2 = A_2e^{-E_2/RT}$$

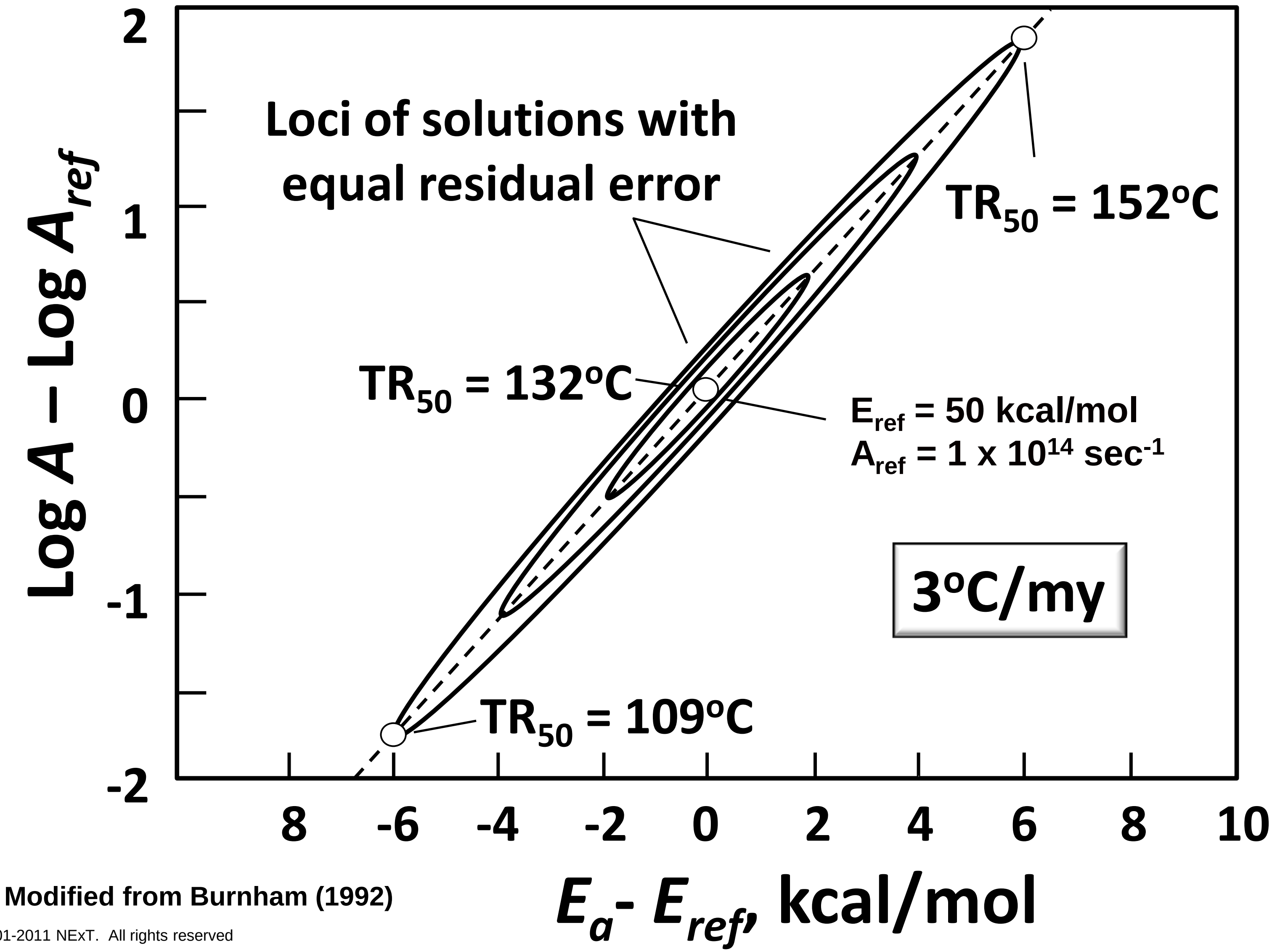
Pick T so that $k_1 = k_2$

$$A_1e^{-E_1/RT} = A_2e^{-E_2/RT}$$

$$Ln\ A_1/A_2 = (E_1 - E_2)/RT$$

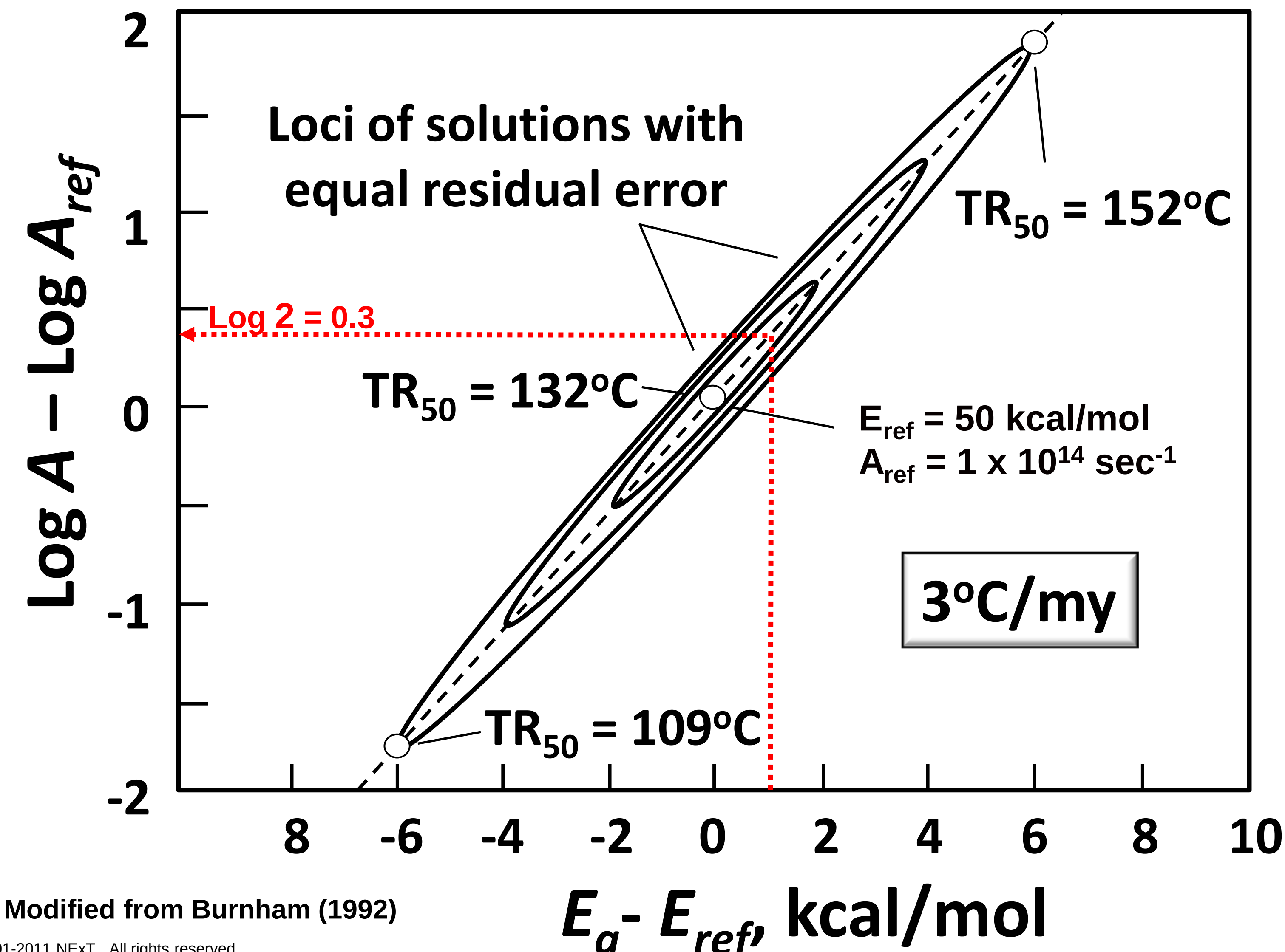
$$\text{Log } A - \text{Log } A_{ref} = (E_a - E_{ref})/2.303RT$$

Compensation Law: Lab Predictions Deviate at Geologic Heating Rates



Modified from Burnham (1992)

1 Kcal/mol Error in E_a is *Compensated* by 2-Fold Change in *A*



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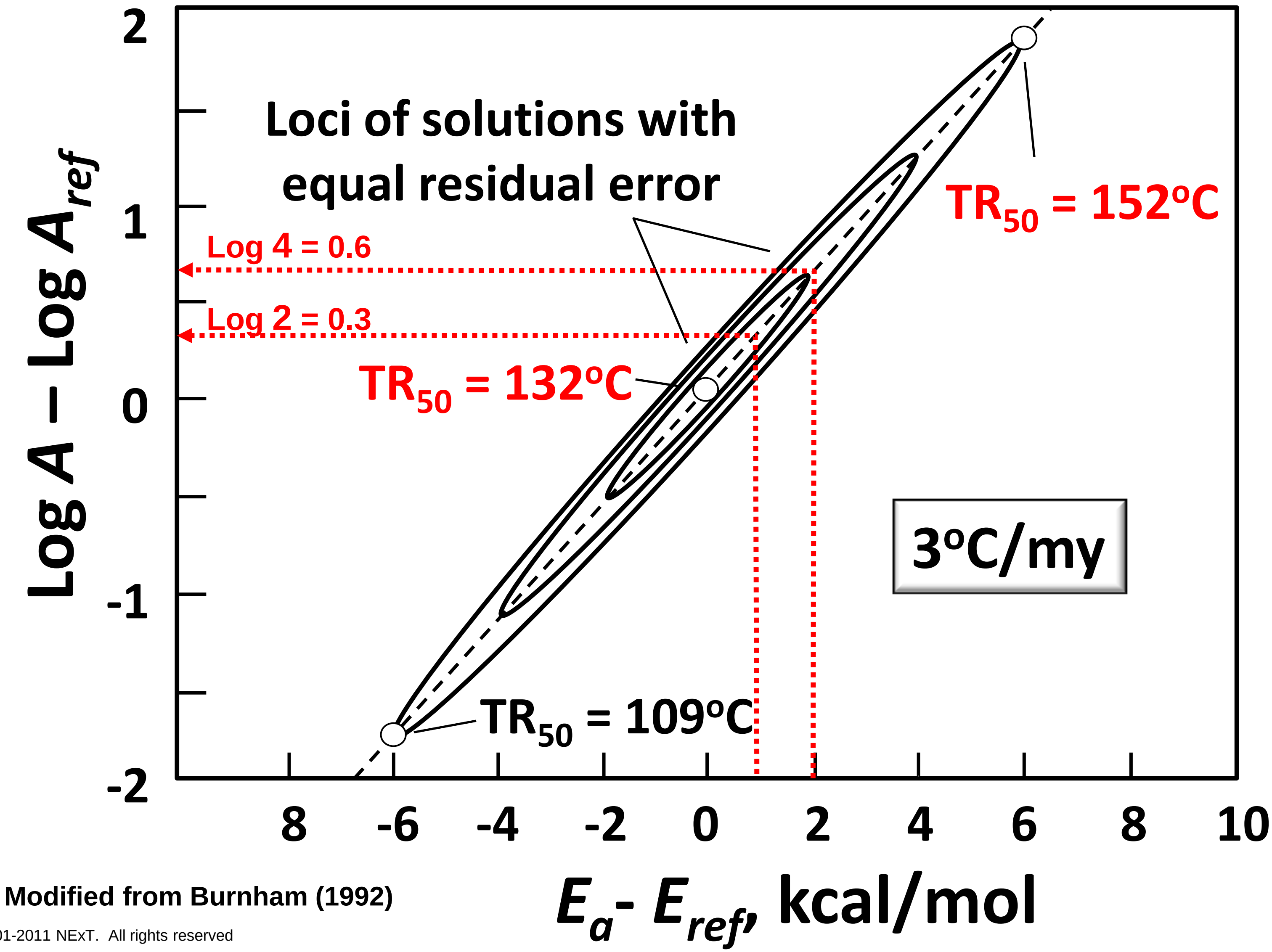
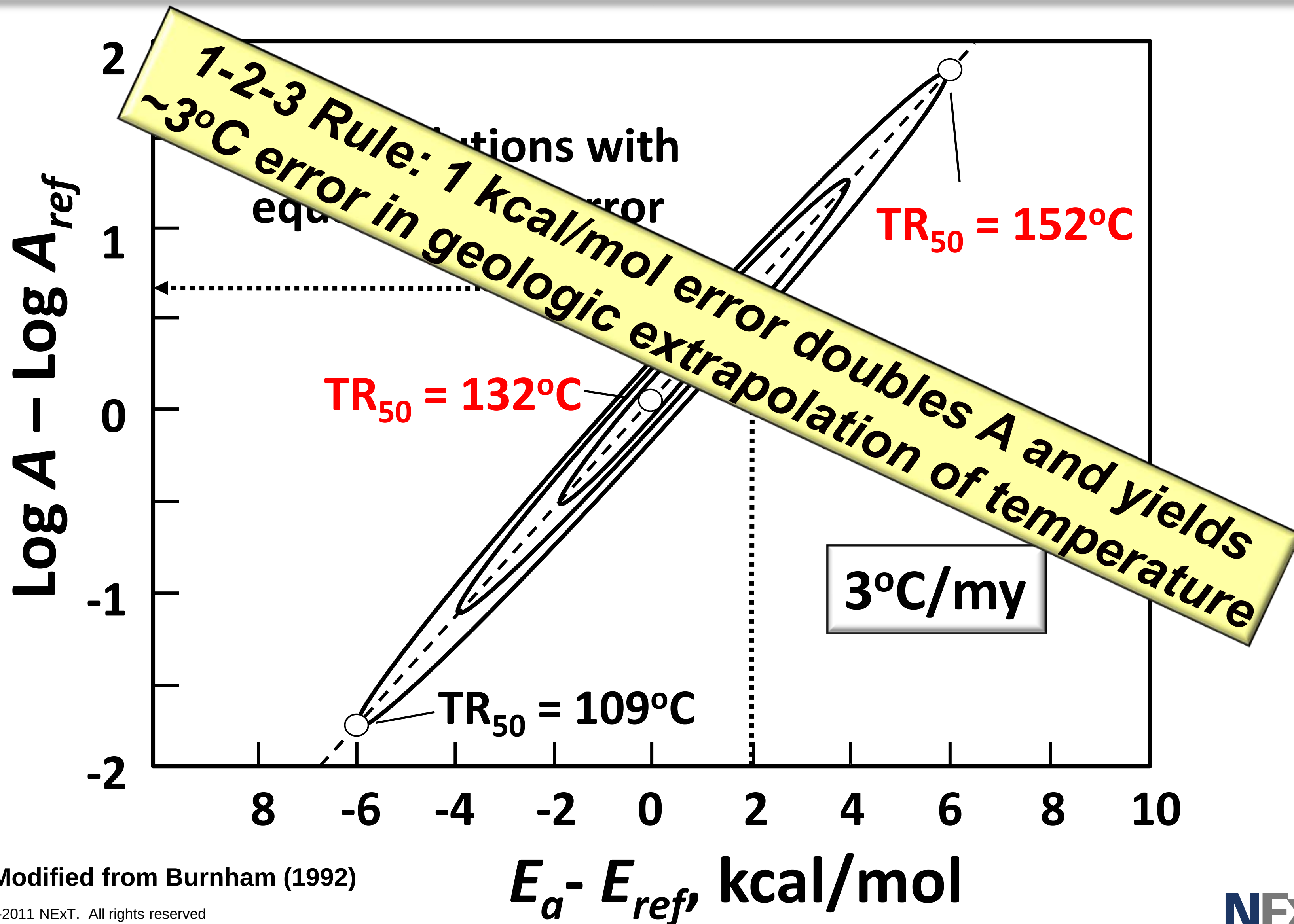
Errors in Predicted Geologic Temperature Can be Substantial



Modified from Burnham (1992)

NExT

1 Kcal/mol Error in E_a is *Compensated* by 2-Fold Change in A



Modified from Burnham (1992)

NExT

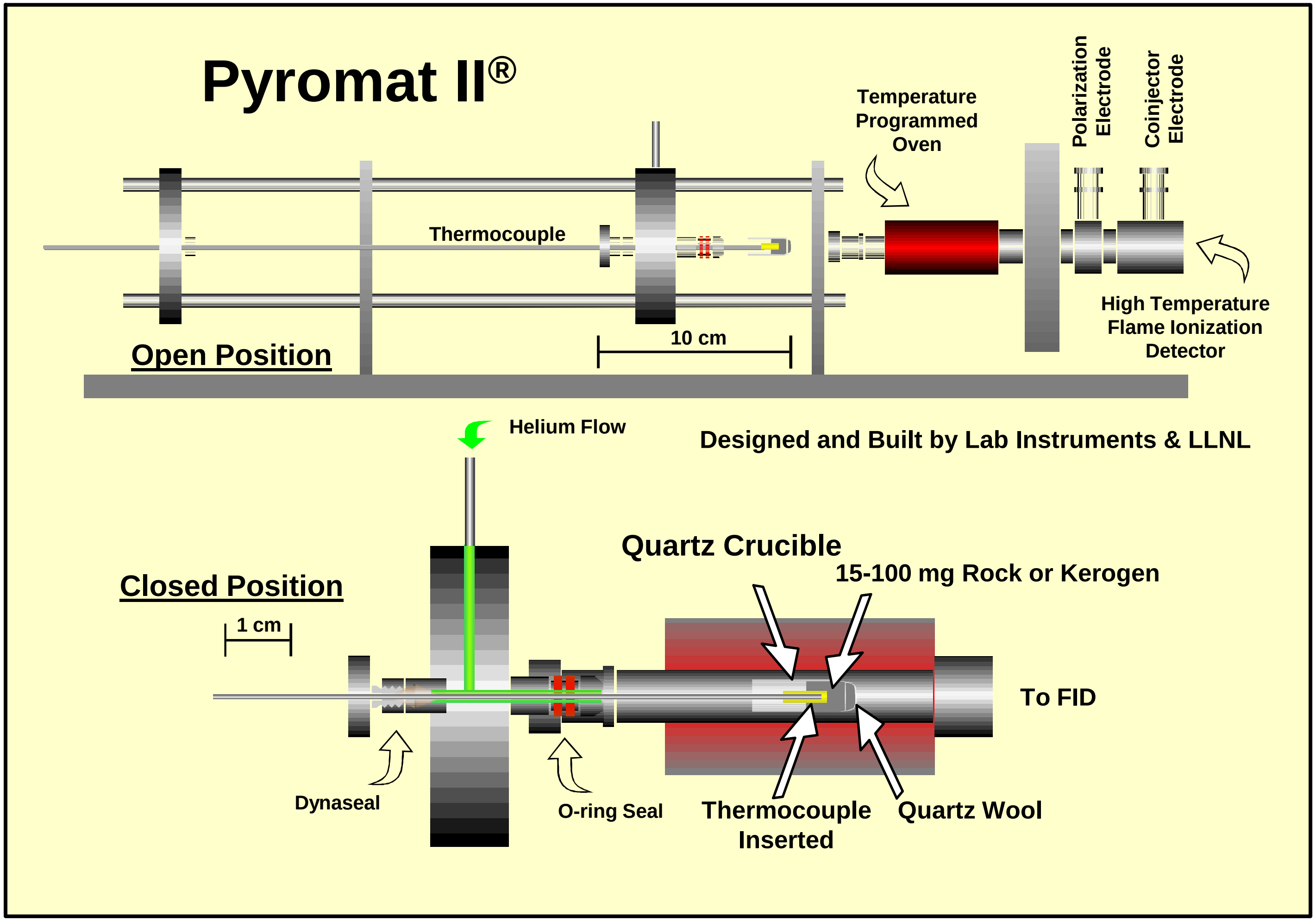
Fixed *A* Introduces Error in Geologic T Extrapolation (~20^{o}C)

1-2-3 Rule: 1 kcal/mol error doubles A and yields ~3^{o}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^{o}C/my ~ 20^{o}C error ←

52 Samples Were Analyzed by Pyromat II® Micropyrolysis



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

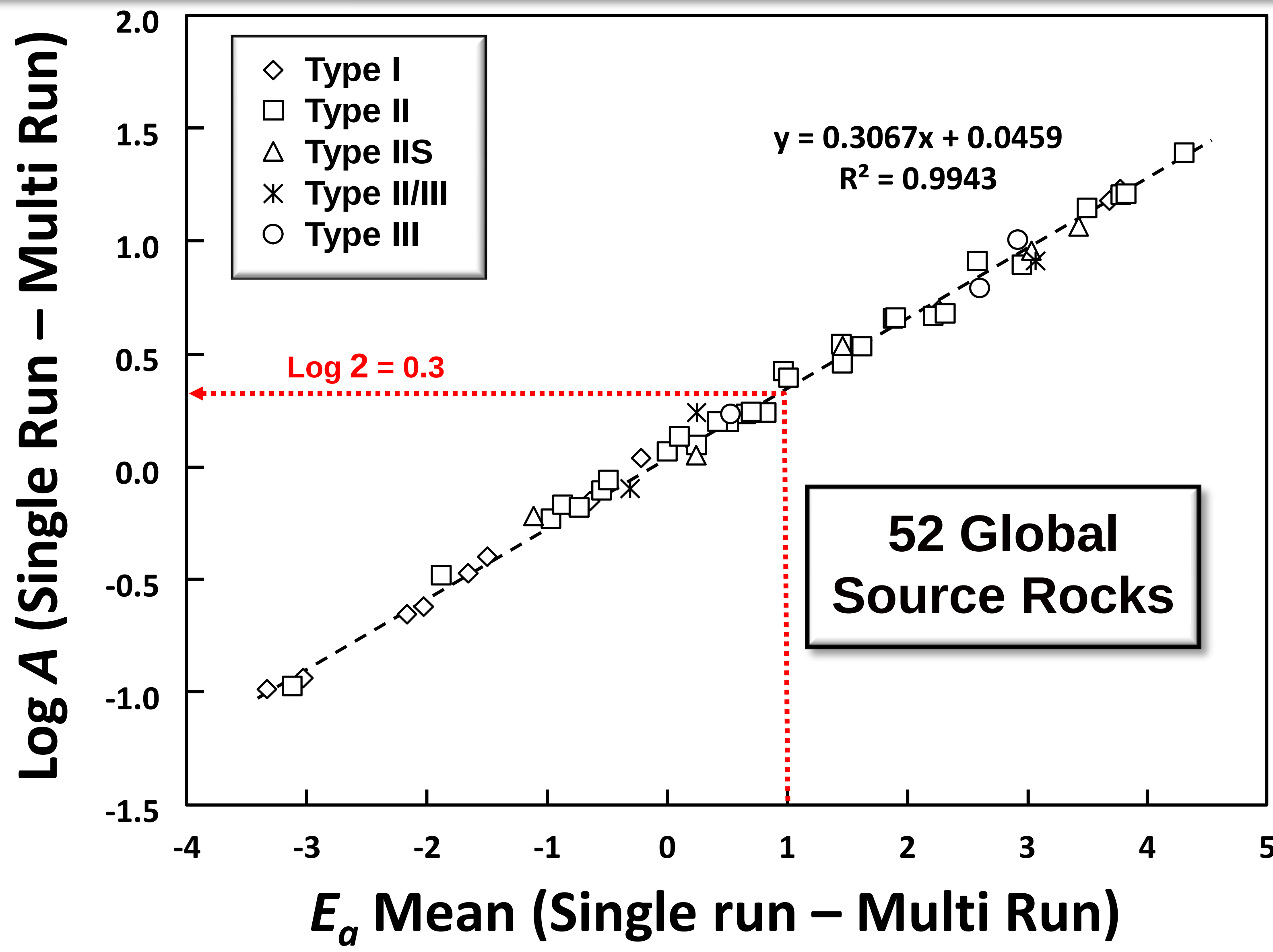
Bellagio Road outcrop (type II)
A_{fixed} = 1 x 10^{14} sec^{-1}

Geologic Extrapolation Assuming 3°C/my

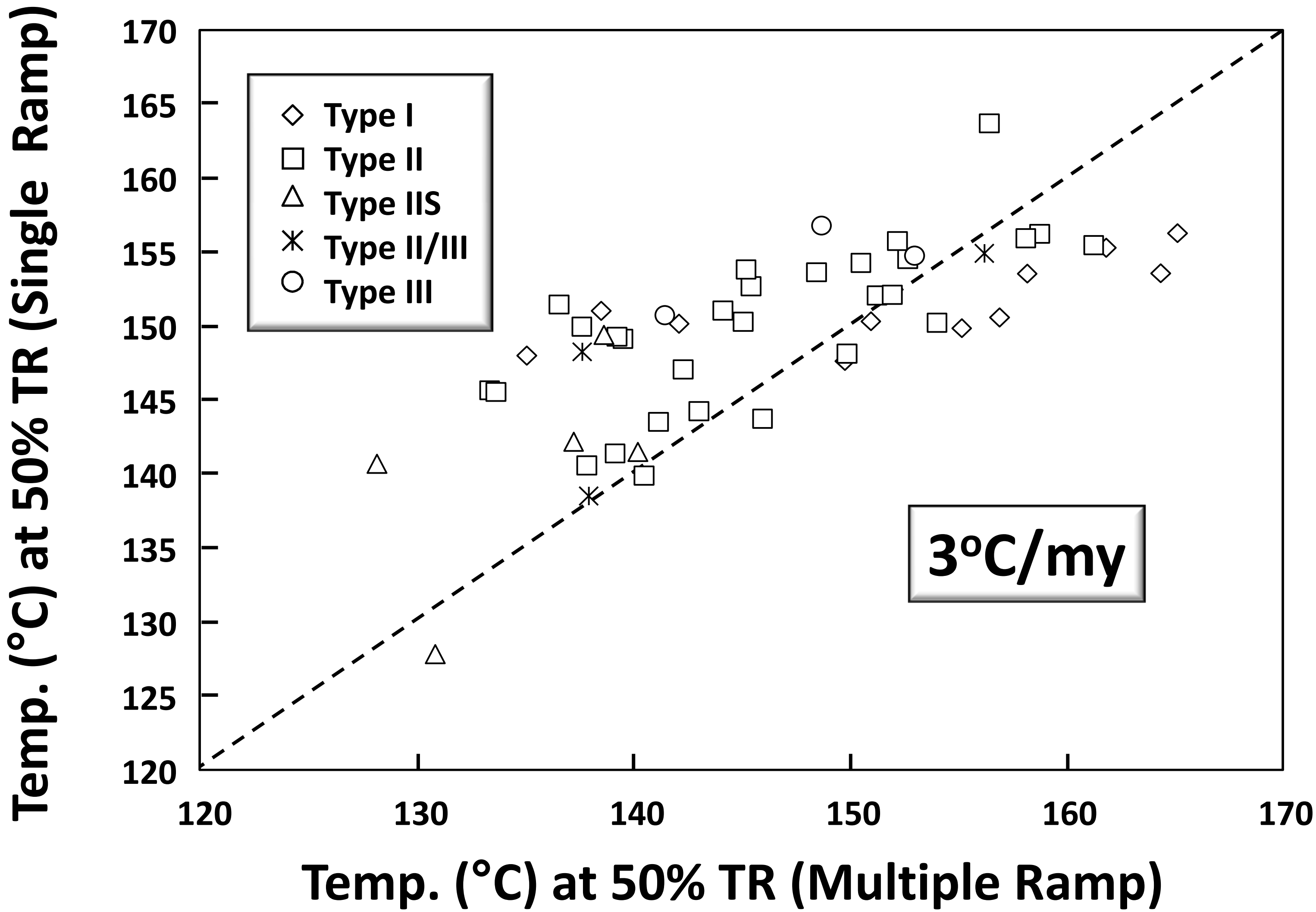
	T_{max}, °C	Mean E_a, kcal/mole	Temp °C at 10% TR	Temp °C at 50% TR	Temp °C at 90% TR
Average	449.3	53.54	112.0	137.3	163.7
Minimum	447.8	52.97	105.2	135.8	160.4
Maximum	452.1	53.87	115.0	138.4	168.2
Std. Dev.	1.3	0.28	2.3	0.8	2.2

TR = transformation ratio (extent of conversion of kerogen to petroleum)

Fixed vs. Optimized A: Offset of E_a by Compensation Law



Single- and Multi-Ramp Models Yield Different Temperatures



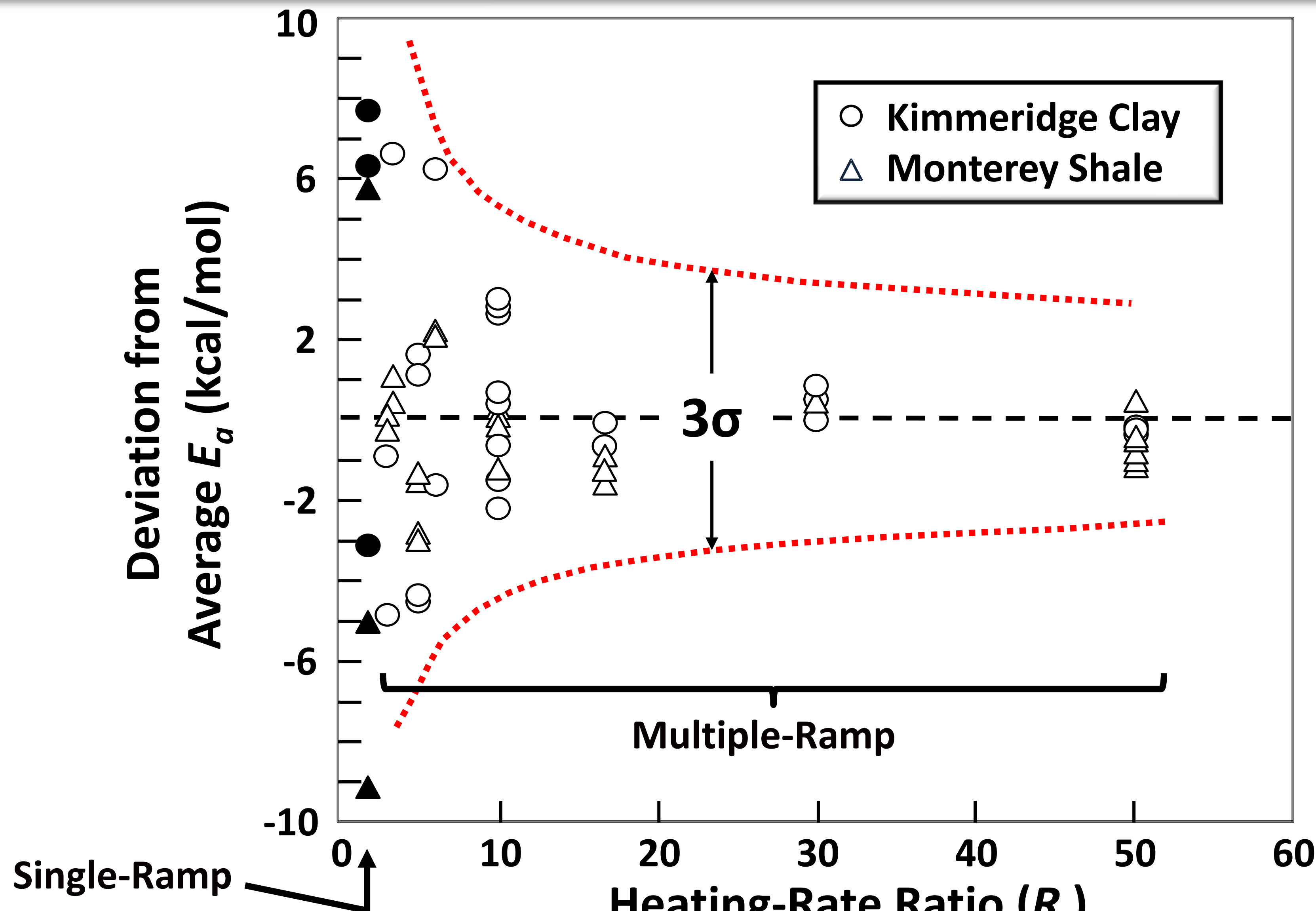
Heating-Rate Ratio (R_r) = Maximum / Minimum Ramp

- **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*):**

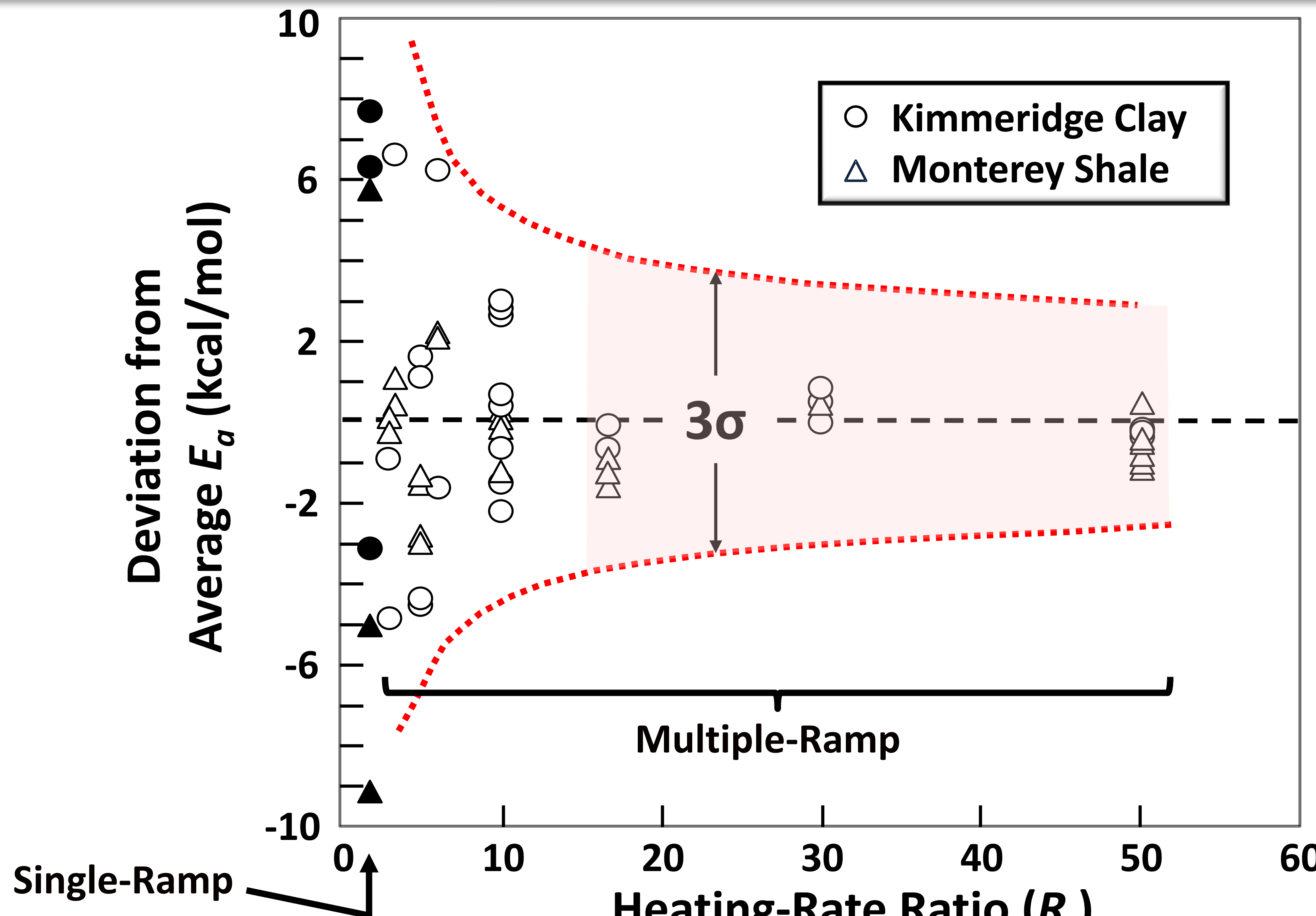
1,50
1,3,50
1,5,50
1,10,50
1,3,5,50
1,5,10,50
1,10,30,50
1,3,5,10,30,50

°C/min

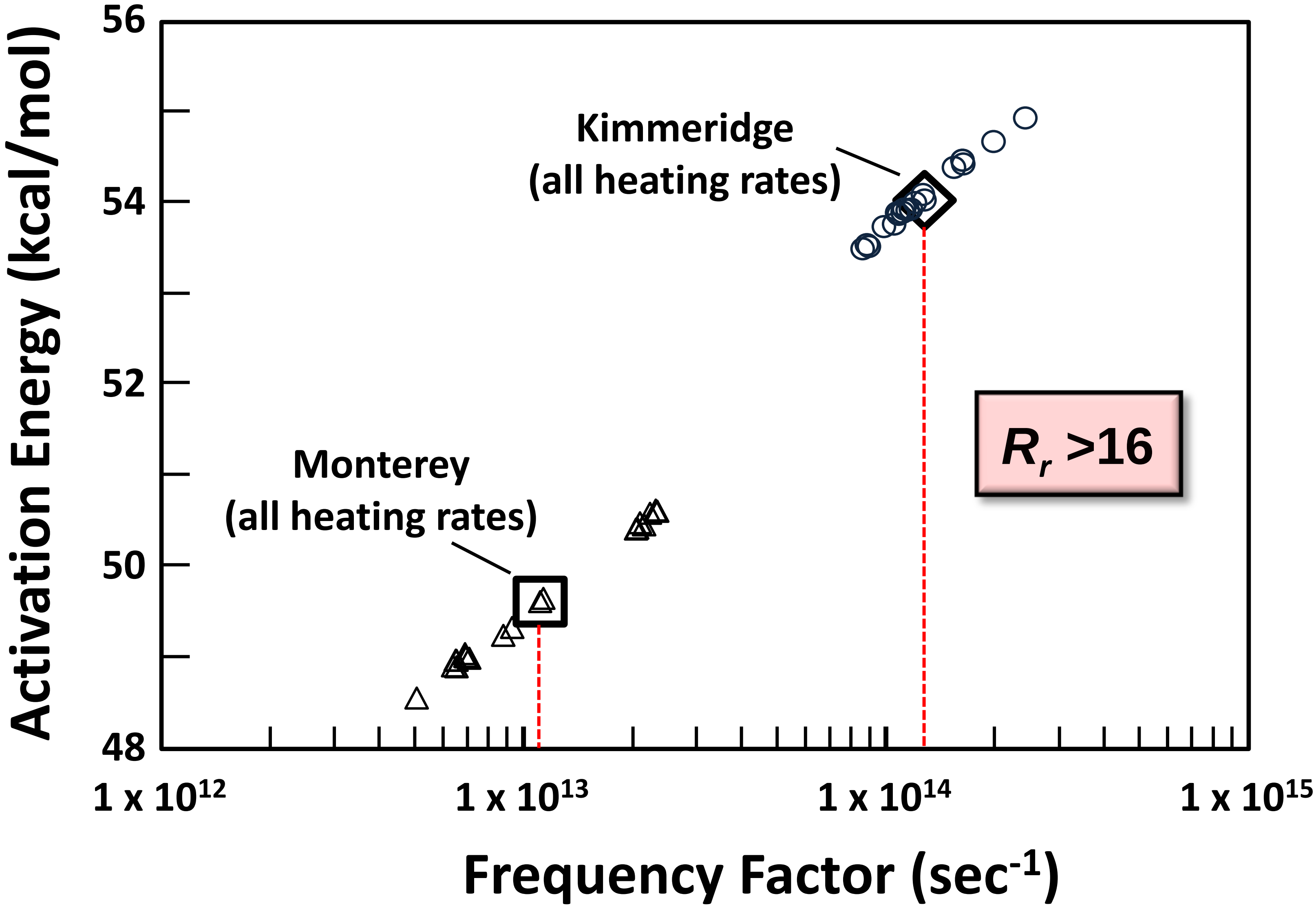
Single- vs. Multi-Ramp: Wide vs. Narrow Deviation in E_a



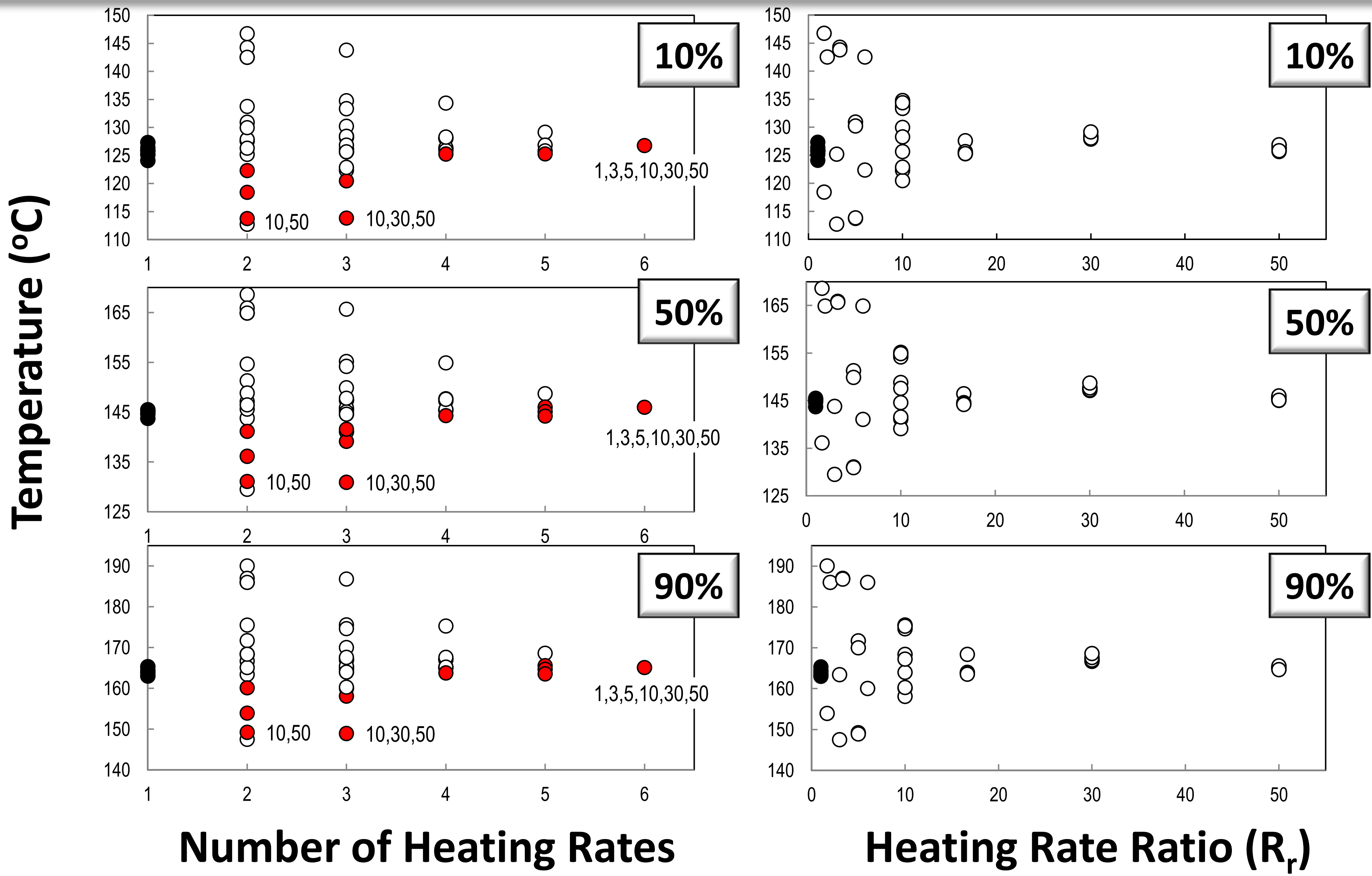
Variation in E_a Becomes Small for Heating-Rate Ratios >16



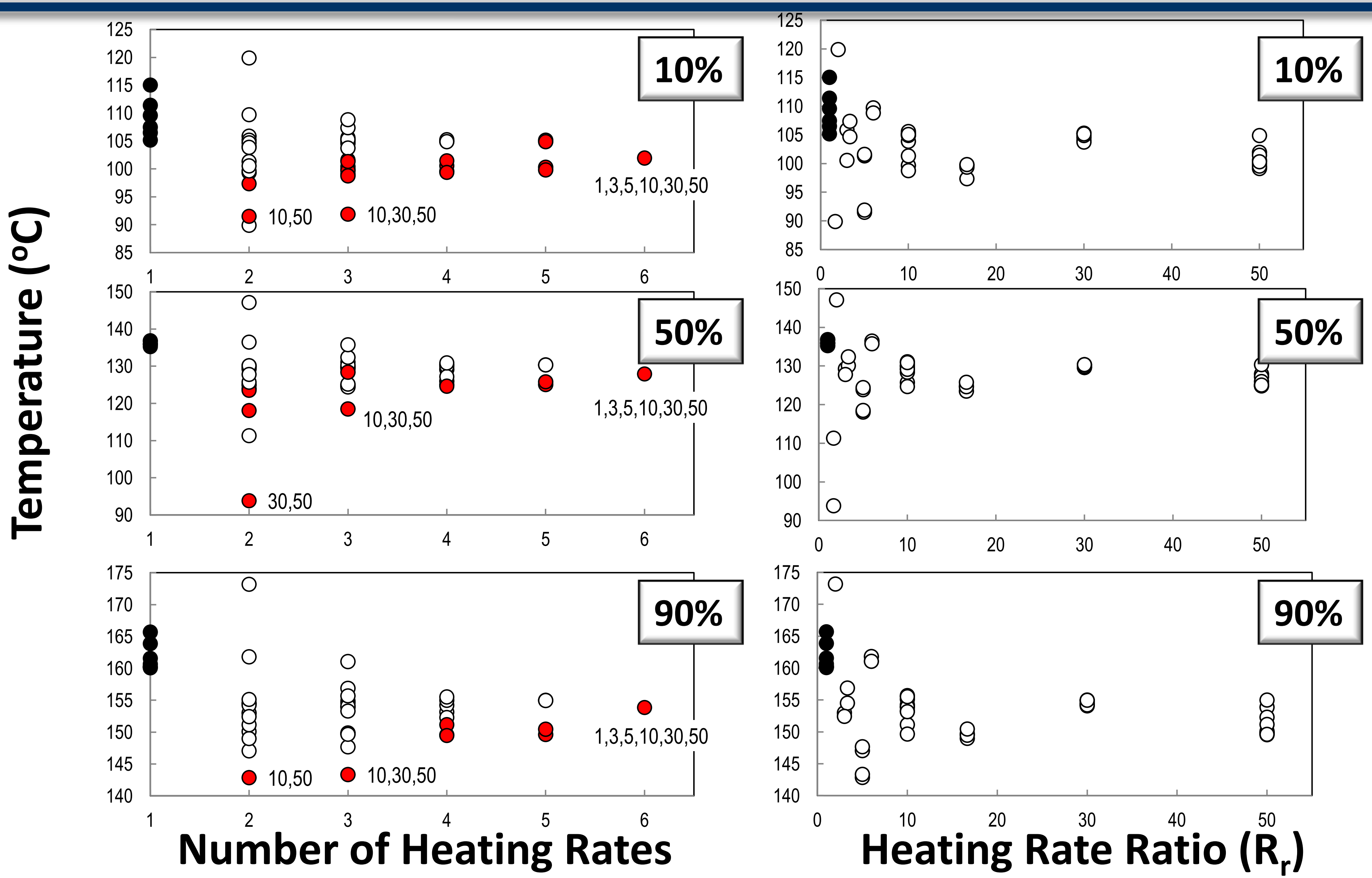
Differing *A* and E_a are Real and Not Measurement Artifacts



Kimmeridge Clay: Predicted T at Transformation Ratio (TR)



Monterey Shale: Predicted T and Transformation Ratio (TR)



Conclusions (I)

- **Single-ramp pyrolysis *can* yield kinetic results that are inconsistent with those from multiple-ramp experiments.**
- **Frequency factors for 52 global source rocks are statistically distinct within measurement uncertainty and vary over four orders of magnitude (10^{12} to 10^{16} sec^{-1}).**
- **Assuming a universal value for *A* erroneously presumes that temperature measurements do not have sufficient accuracy for reliable kinetics.**
- **Adoption of fixed *A* of 1 x 10^{14} sec^{-1} can result in error in geologic temperature extrapolation of up to ~20^{o}C.**

Conclusions (II)

- **Pyrolysis ramps of 30-50^{o}C/min can be too fast for good kinetic fit because of thermal lag; minimize sample and thermocouple size, optimize thermocouple orientation.**
- **Heating rate x sample size should be <100mg^{o}C/min.**
- **20- to 30-fold variation in heating rate using at least three ramps is recommended (e.g., 1, 5, 25^{o}C/min or 1, 3,10, 25^{o}C/min) with replicates at highest and lowest rates.**
- **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.**

References

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- **Waples, D.W., and V.S. Nowaczewski, 2014. Source-rock kinetics, *in* Encyclopedia of Petroleum Geoscience, New York, Springer.**
- **Waples, D.W., A. Vera, and J. Pacheco, 2002. A new method for kinetic analysis of source rocks: development and application as a thermal and organic facies indicator in the Tithonian of the Gulf of Campeche, Mexico: Abstracts, 8th Latin American Congress on Organic Geochemistry, Cartagena, p. 296-298.**
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