Thermal Maturity Modeling of Organic-Rich Mudrocks in the Delaware Basin Using Raman Spectroscopy of Carbonaceous Material*

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Abstract

Raman spectroscopy of carbonaceous material (RSCM) is an emerging tool to investigate the peak temperature organic-rich sediments reach during burial and exhumation. Previously, peak temperature has been commonly determined using vitrinite reflectance (%Ro), which is subject to user bias, organic material composition, hydrogen-index, and pressure suppression. Because thermal maturity of organic material is an important factor in determining source rock viability, RSCM presents an opportunity to develop a quick, objective, and cost-effective alternative to %Ro immune to the bias of suppression. This study proposes to test the viability of RSCM thermometry on well cuttings retrieved from Permian through Ordovician intervals of the Delaware Basin in West Texas to further investigate peak temperatures and paleogeothermal gradients.

The Delaware Basin displays counterintuitive gas-oil ratios, with higher ratios in the shallower western portions than in the deeper eastern portions. This suggests that western portions were previously buried deeper and later exhumed to modern depths, or subject to a variable geothermal gradient as a result of increased heat flow from igneous intrusions. This study will construct a paleogeothermal profile of the basin by incorporating 12 wells along five E/W and N/S trending cross sections, including wells which have intersected igneous intrusions. RSCM measurements will be compared against existing %Ro and pyrolysis data to constrain regional thermal maturity patterns. Igneous bodies will be dated using Zircon U-Th/He LA-ICP-MS to determine timing of elevated maturity. Combined with 1D and 2D backstripping methods, this study will provide insights to the lateral distribution of subsidence, exhumation, and elevated heat flow.

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THERMAL MATURITY MODELING OF ORGANIC-RICH MUDROCKS IN THE DELAWARE BASIN USING RAMAN SPECTROSCOPY OF CARBONACEOUS MATERIAL (RSCM)

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Bottom Line up Front:

(1) Raman Spectroscopy of Carbonaceous Material (RSCM) determines the peak temperature organic materials reach in the subsurface.

(2) RSCM is time-independent, and differences between vitrinite reflectance, or (%Ro) and RSCM can be used as an index for heating duration.

(3) When applied to the Delaware Basin, we observe the western regions of the basin had higher geothermal gradients and shorter heating durations than the east.

(4) Heating duration has implications for discriminating different sources of heat.

→ Western Delaware Basin is HOT!

What is Raman Spectroscopy of Carbonaceous Material (RSCM)?

↓

Application to Sediments in the Delaware Basin

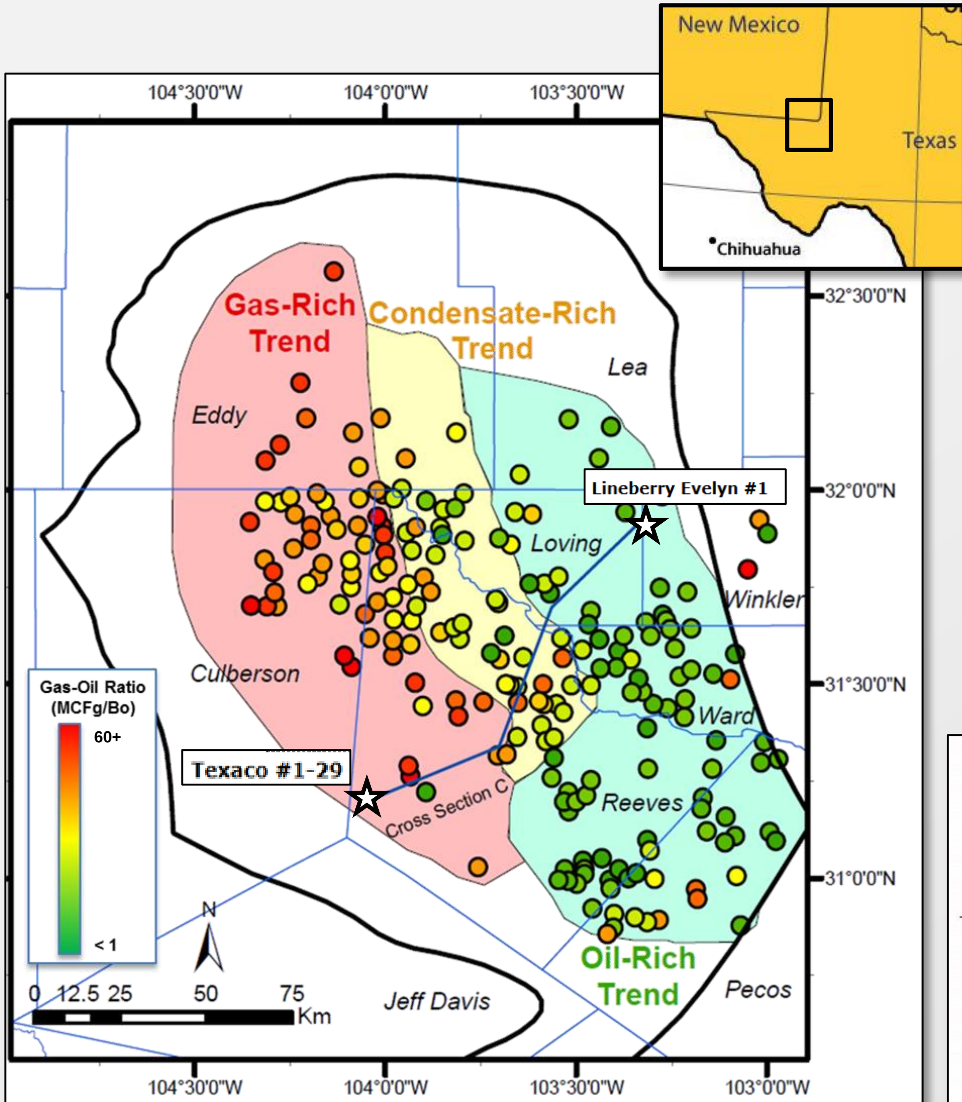
↓

Comparison with Vitrinite Reflectance

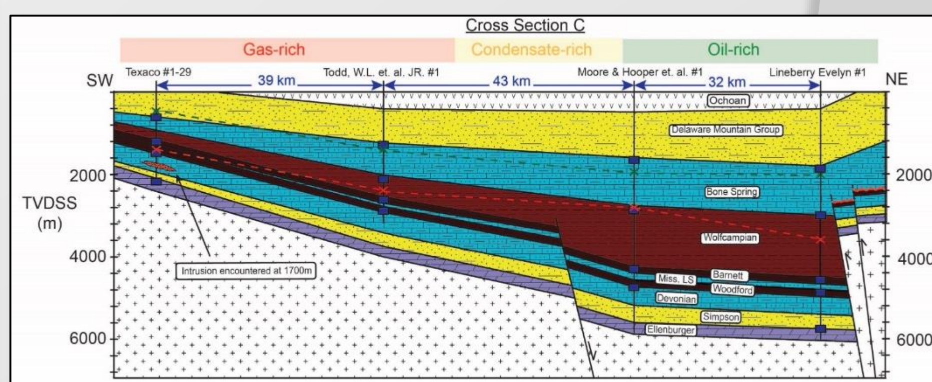
↓

Input into a Basin Model for Regional Implications

Application to Gas-Oil Ratios

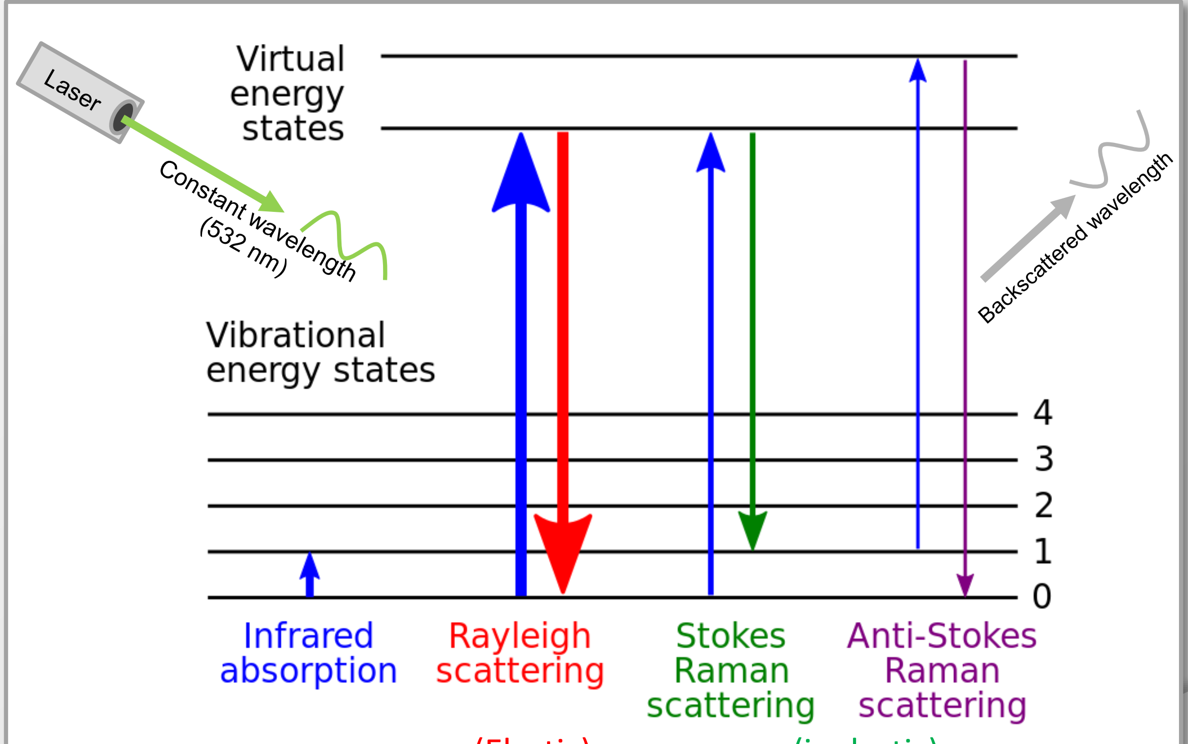


- Gas-Oil ratios increase east to west, counterintuitive to modern depth.
- Potentially a function of:
  - Thermal maturity ← Tested here
  - Kerogen type
  - Hydrocarbon mobilization in low-permeability environments



What is Raman Spectroscopy?

- Backscattering of photons when monochromatic light interacts with vibrational modes in a material.
- Molecules excited to a “virtual” energy state, then return to equilibrium, emitting a photon to conserve energy.
- If final energy state is not equal to the initial state, the energy difference is transferred to the emitted photon.
- Change in photon energy causes “waveshift"

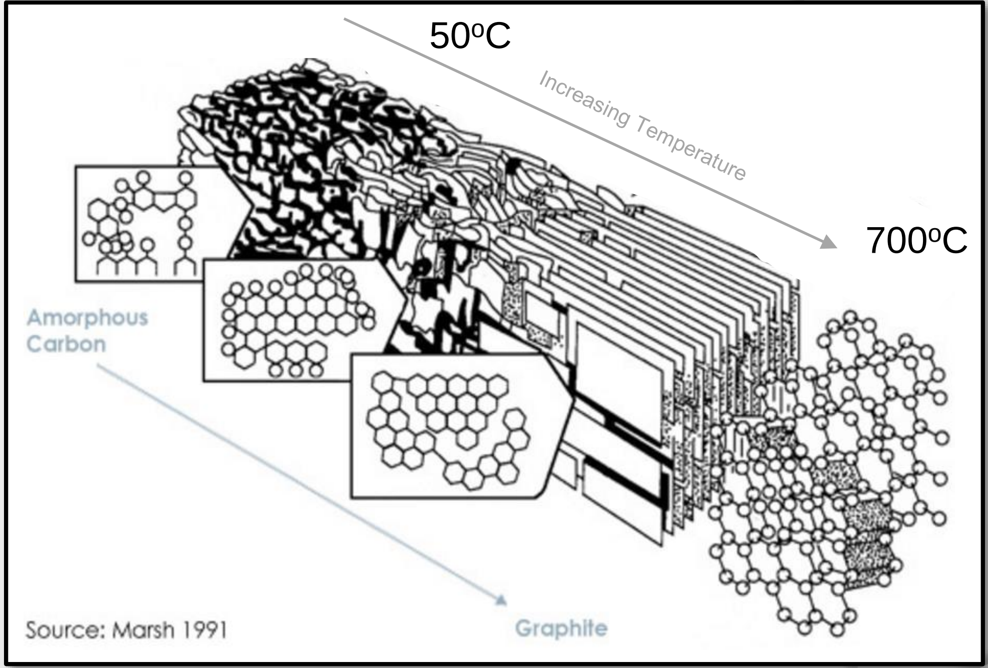


Ember et al. (2017)

How can we apply Raman Spectroscopy to Carbon?

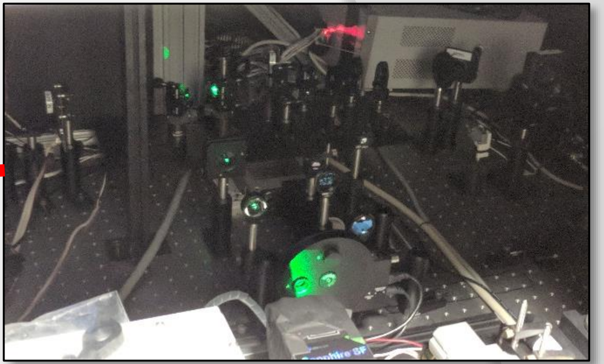
Quantify the degree of graphitization

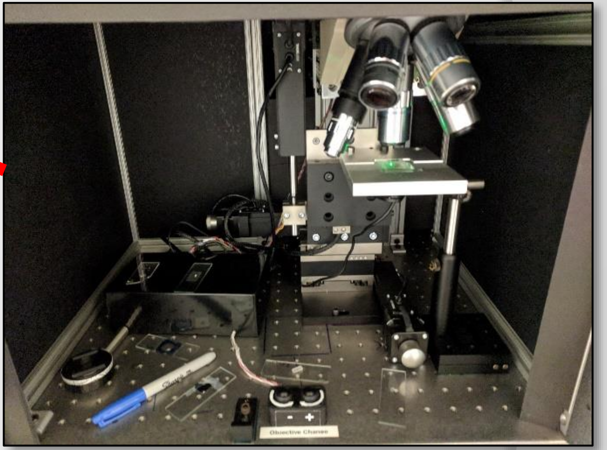
- With increasing temperature, amorphous carbon orders itself into stacked graphite sheets
- RSCM is sensitive to carbon bond structure, not grain texture, so it can be applied to a variety of organic grain macerals.
  → not just vitrinite
- Carbon structure does not experience retrograde ordering.



This makes RSCM an effective measure of Peak Temperature, similar to %Ro

Raman Laser Setup





Laser Parameters:

30µm thick open-face thin section

532nm laser

1µm focal diameter

1.3mW power

} Balance quality and power

1200nm grating

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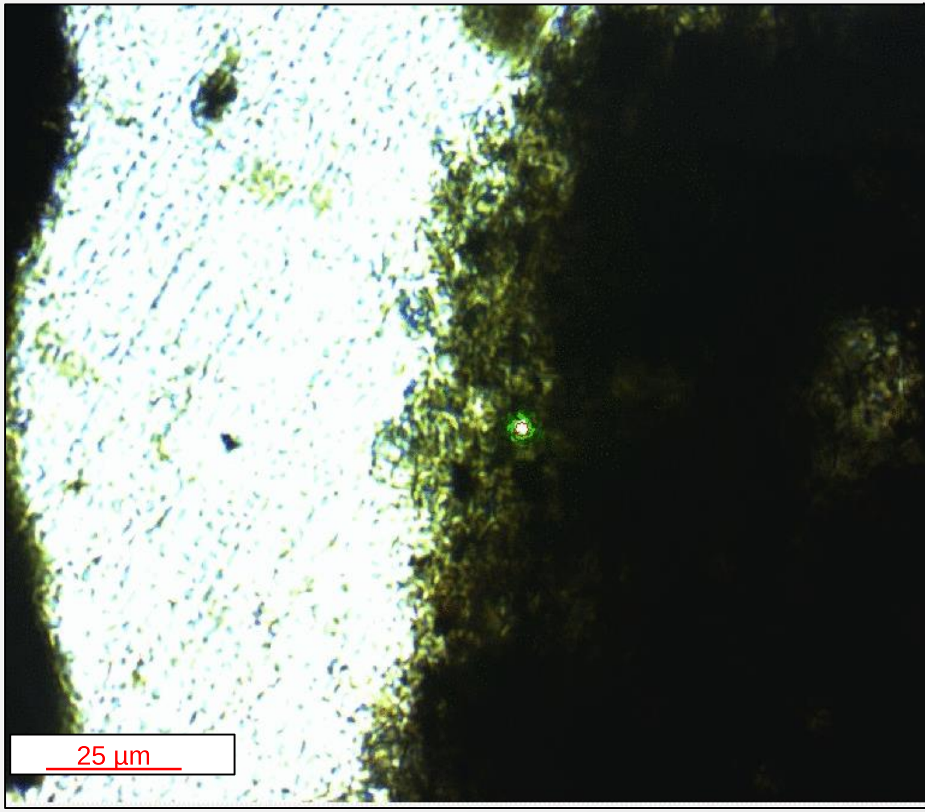
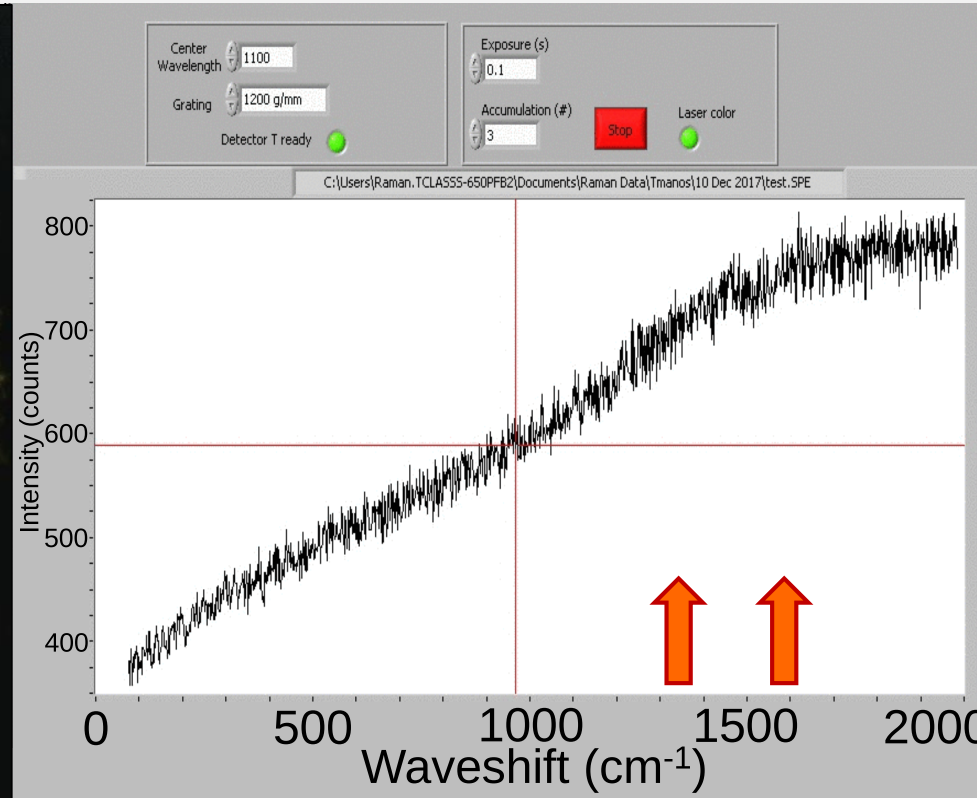
Raman setup provides instantaneous feedback of data



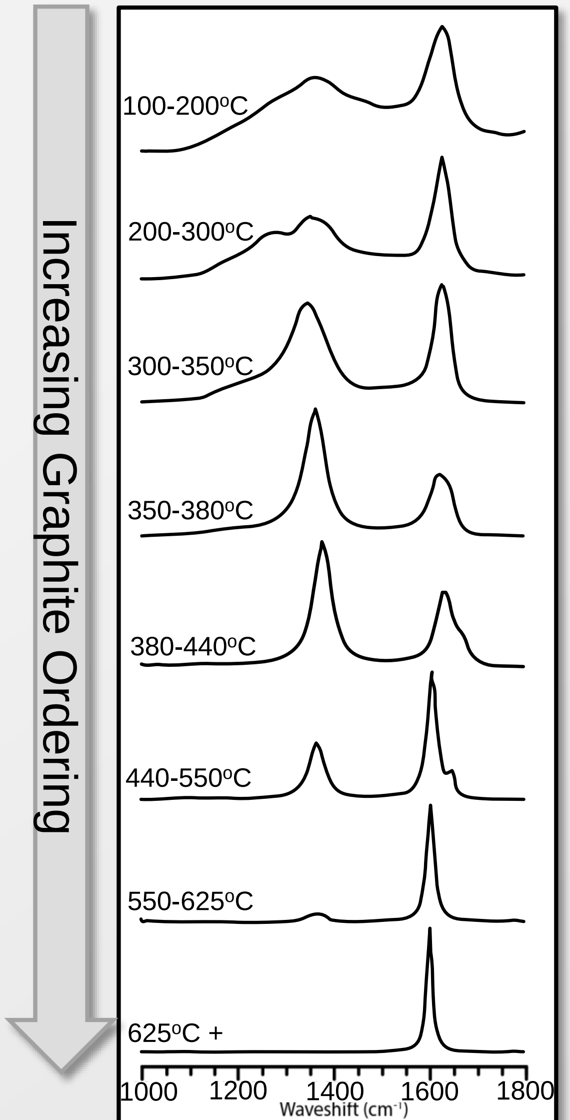


- Digital, objective measurement (unlike %Ro)
- Can be used on most macerals (no ID needed)
- Can take multiple measurements at the same point

Low-T(C°) carbon exhibits two dominant peaks at:
1350 cm^{-1} (disordered)
1600cm^{-1} (ordered graphene)

RSCM Spectra

- Raman spectra evolve systematically with increasing temperature
- 1350cm^{-1} **(Disordered)** peak narrows and amplitude decreases with increasing temp.
- 1600cm^{-1} **(Ordered)** narrows with increasing temp.



Modified after Kouketsu et al. (2014)

Amorphous carbon
high disorder and variability

Transitional material
Increasing ordering, becoming less variable

Crystalized graphite
High degree of ordering

Well-crystalized graphite
Nearly uniform lattice

Low-T(C°) RSCM

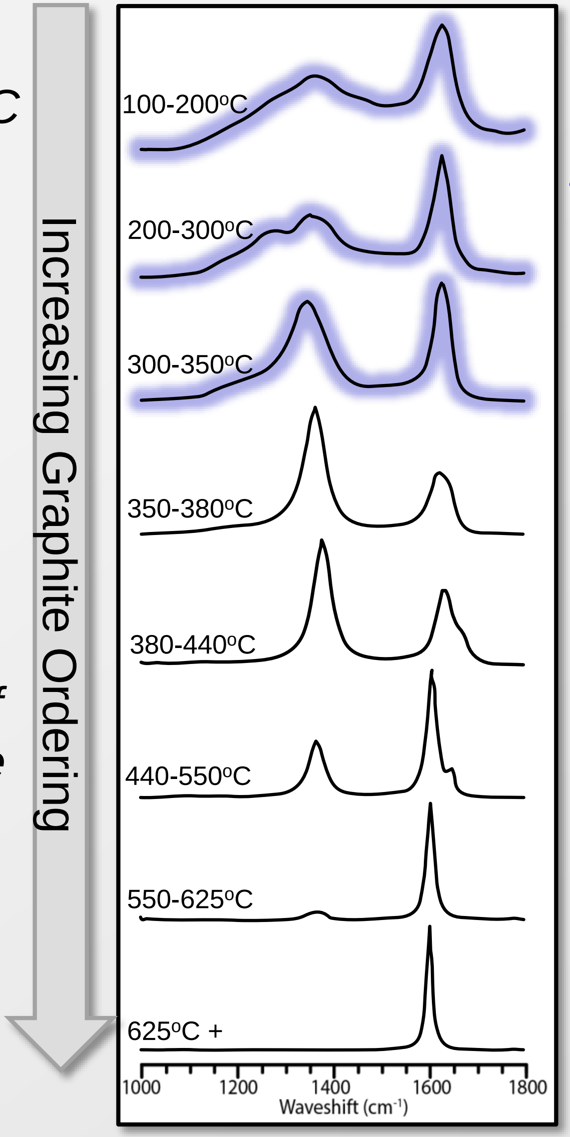
Peak temperatures <300°C

- Two dominant bands comprised of 4 disorder bands:

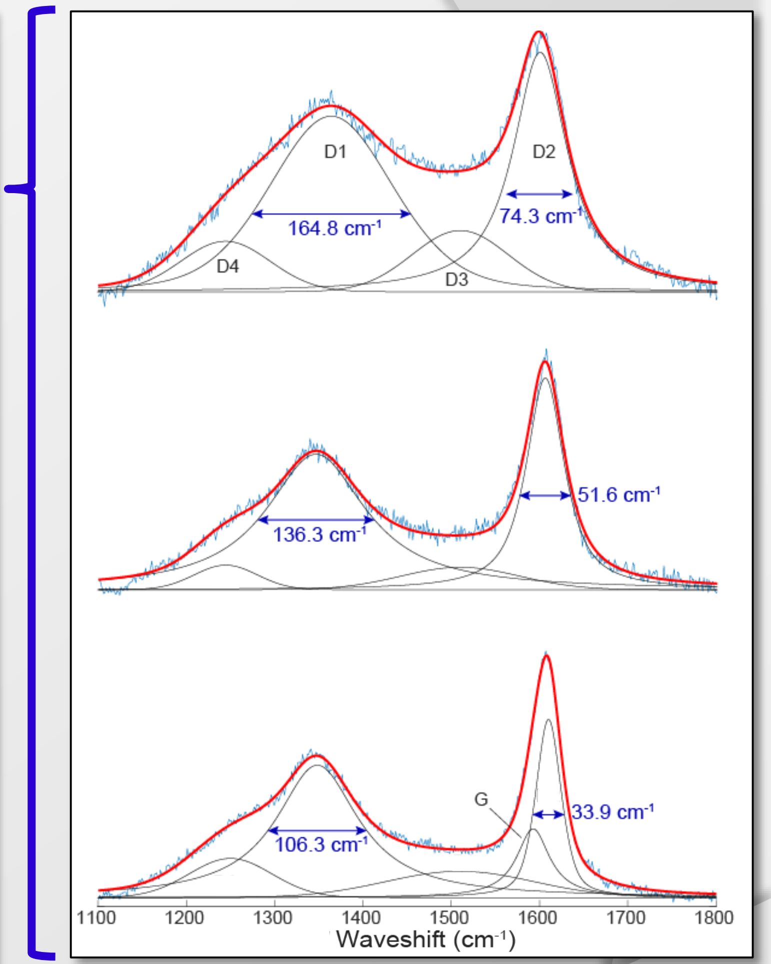
  D1 and D2:
  disordered vibration within aromatic rings

  D3 and D4:
  out-of-plane defects of non-aromatic structure

- Additional G peak appears at ~250°C, representing graphene-like cluster



Modified after Kouketsu et al. (2014)



D1 and D2 peaks get narrower with increasing peak temperature

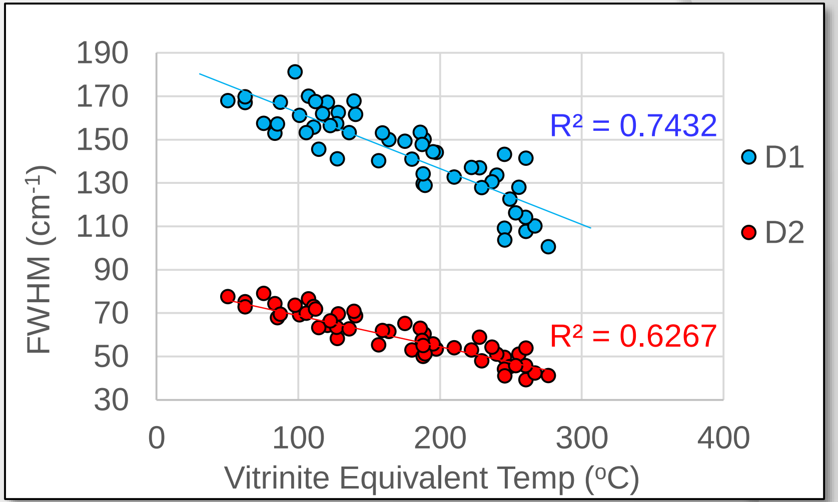
Peak-fitting

$$T(^{o}C) = -2.15\,(FWHM\ D1) + 478$$

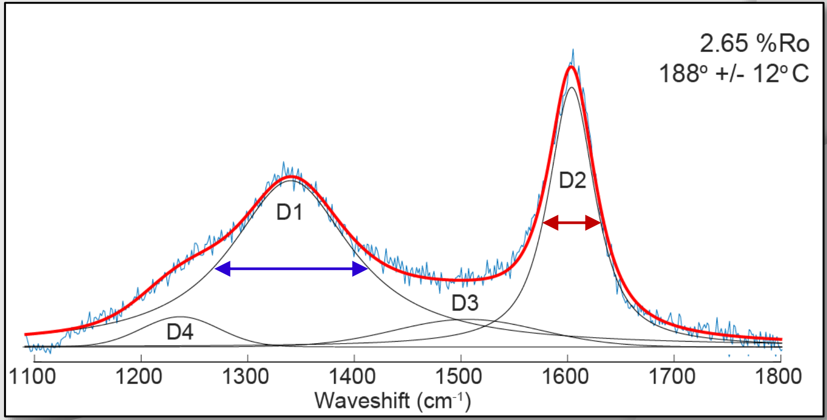
$$T(^{o}C) = -6.78\,(FWHM\ D2) + 535$$

Kouketsu et al. (2014)

FWHM
(full width at half maximum)
of the D1 and D2 peak decrease with higher maximum temperature.

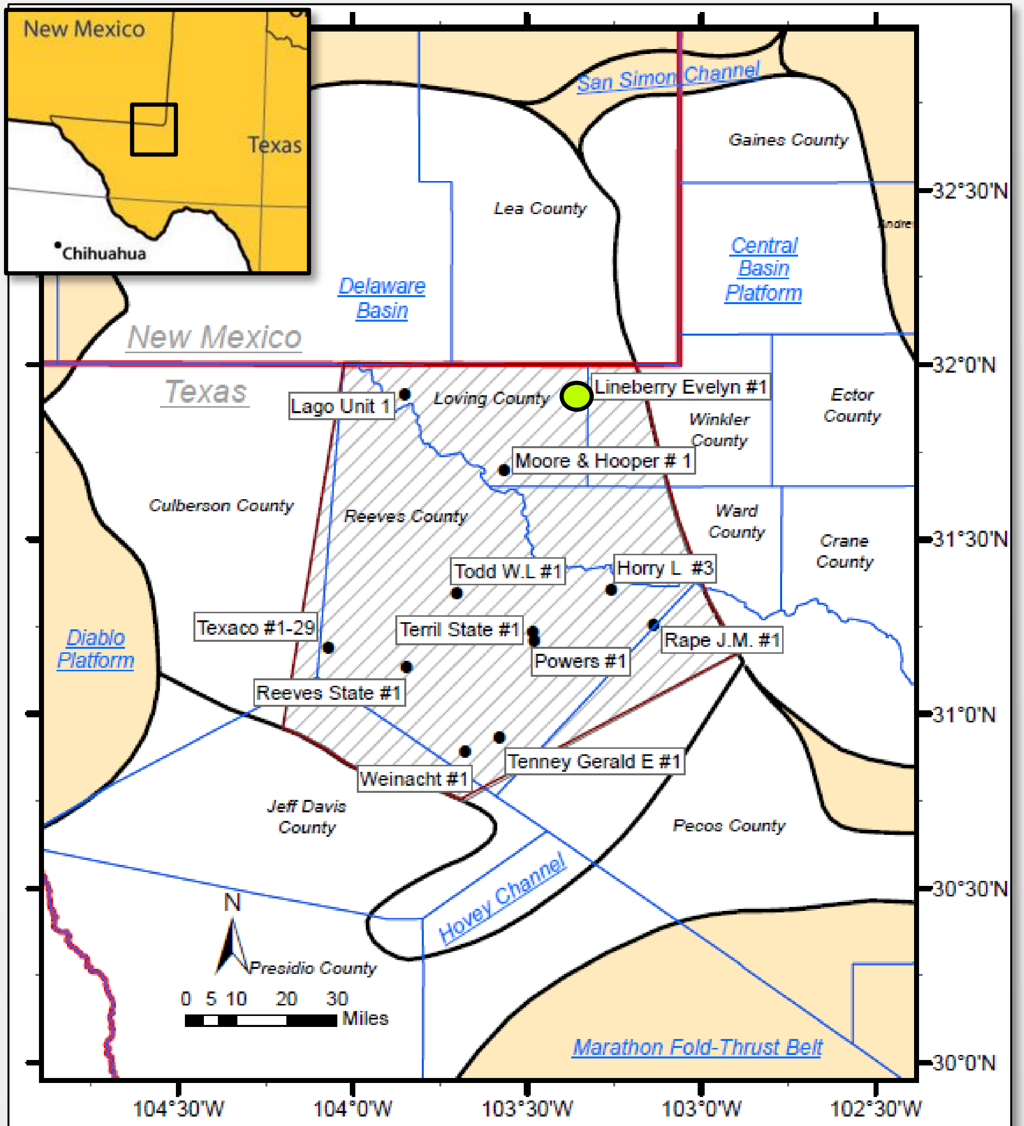


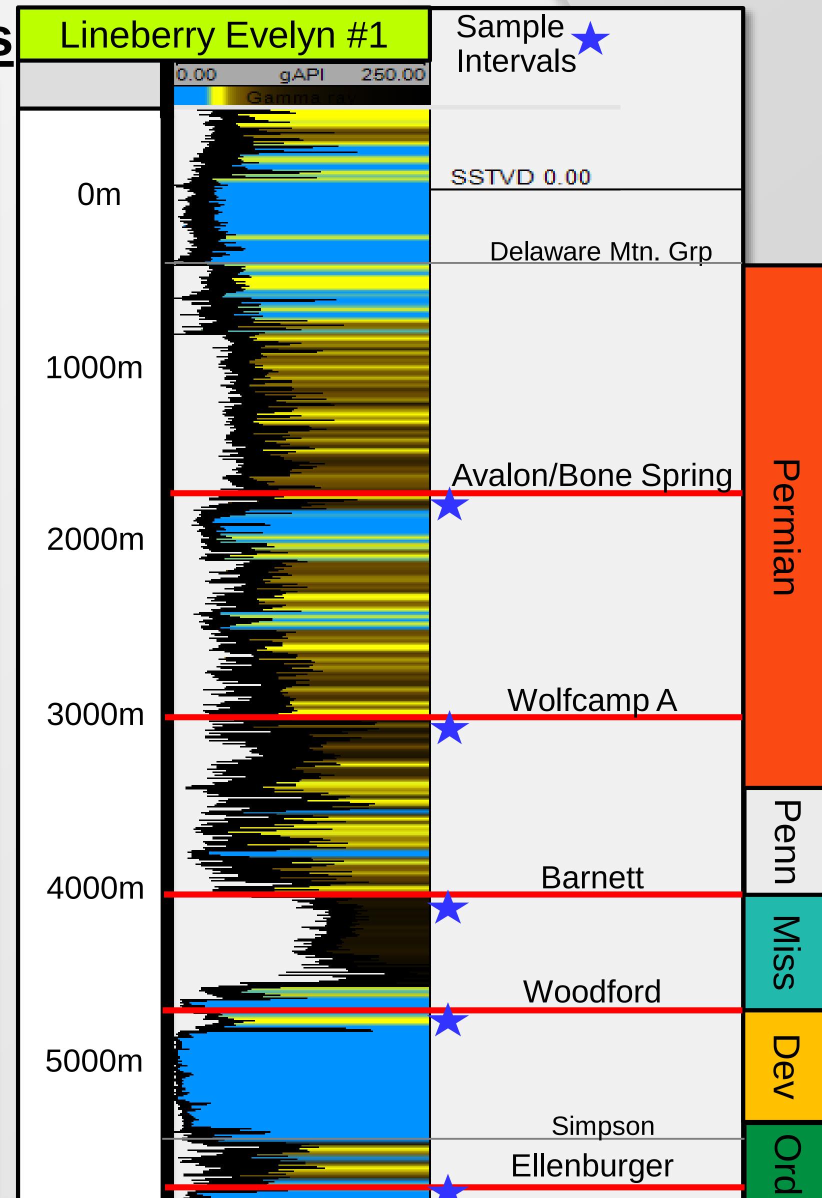
D1 and D2 peaks correlate with peak temperature from ~60-275ºC



Arithmetic average between D1 and D2 outputs ensures most consistent results

Application to Delaware Basin Mudrocks

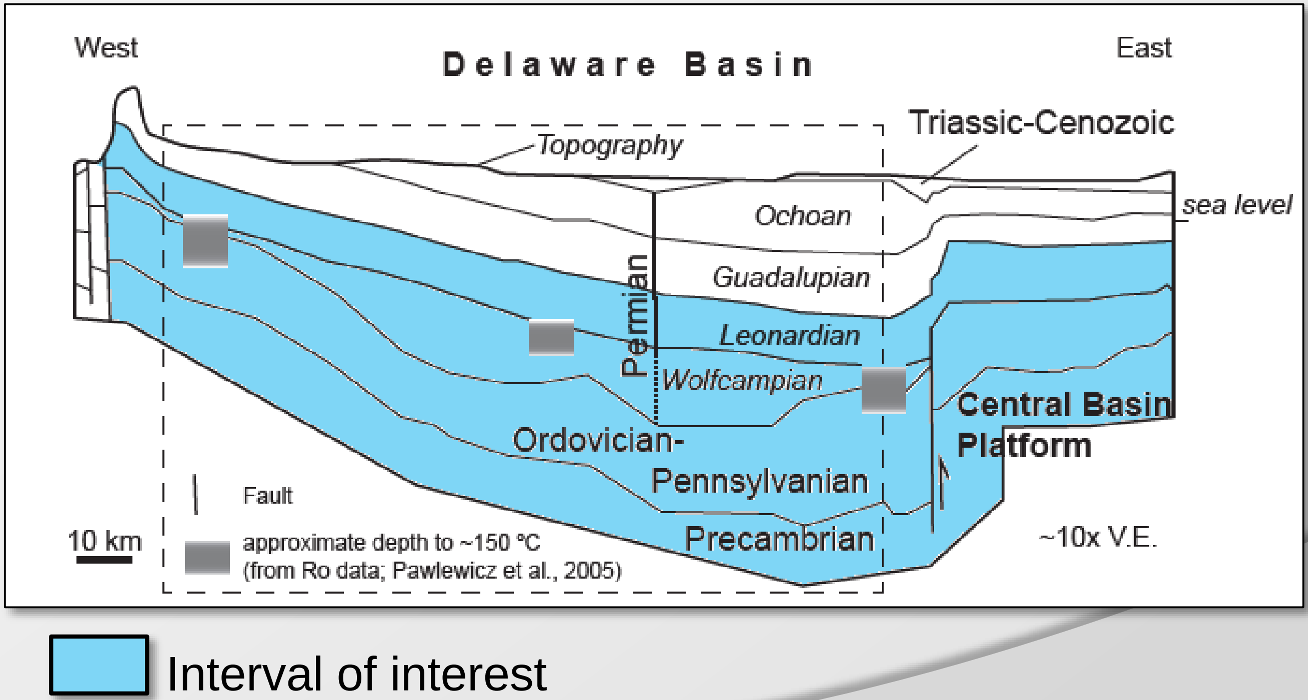




Testing the Spatial distribution of Peak Temperatures and Geothermal Gradients

- Stratigraphy shallows and is eroded to the west, making predictions of beak burial and heat flow difficult → paleo depth not preserved

- Peak geothermal gradient can highlight areas with increased basal heat flow or increased paleoburial.



Testing for Three Potential Scenarios

1. Peak temperatures and peak geothermal gradients higher in the west than in the east.

   $T_W > T_C > T_E$ $G_W > G_C > G_E$

   → Increased basal heat flow

2. Peak temperatures and peak geothermal gradients are equal in the west and east.

   $T_W = T_C = T_E$ $G_W = G_C = G_E$

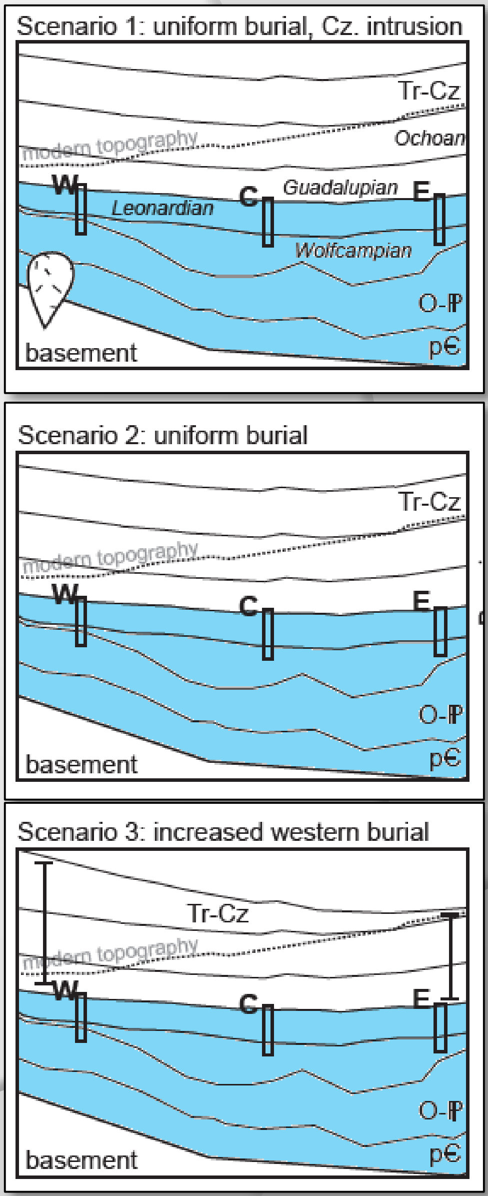
   → Uniform burial throughout the basin

3. Peak temperatures are higher in the west than in the east, but peak geothermal gradients are equal.

   $T_W > T_C > T_E$ $G_W = G_C = G_E$

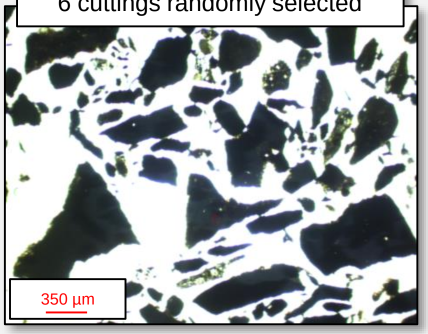
   → Increased paleoburial in the west than in the east

Interval of interest

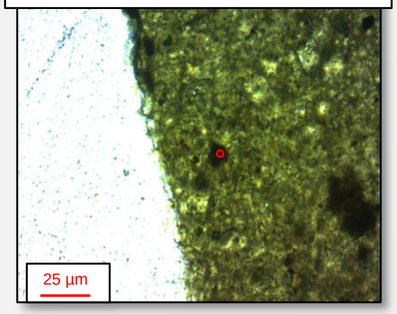


RSCM Workflow

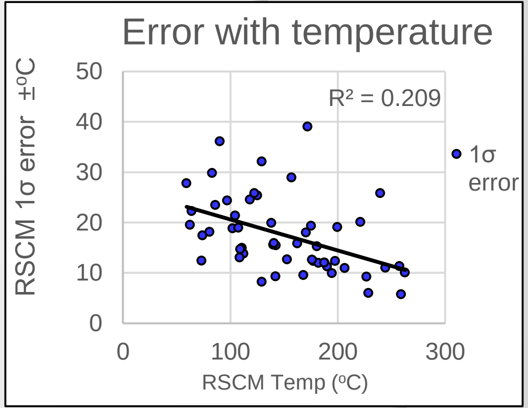
6 cuttings randomly selected

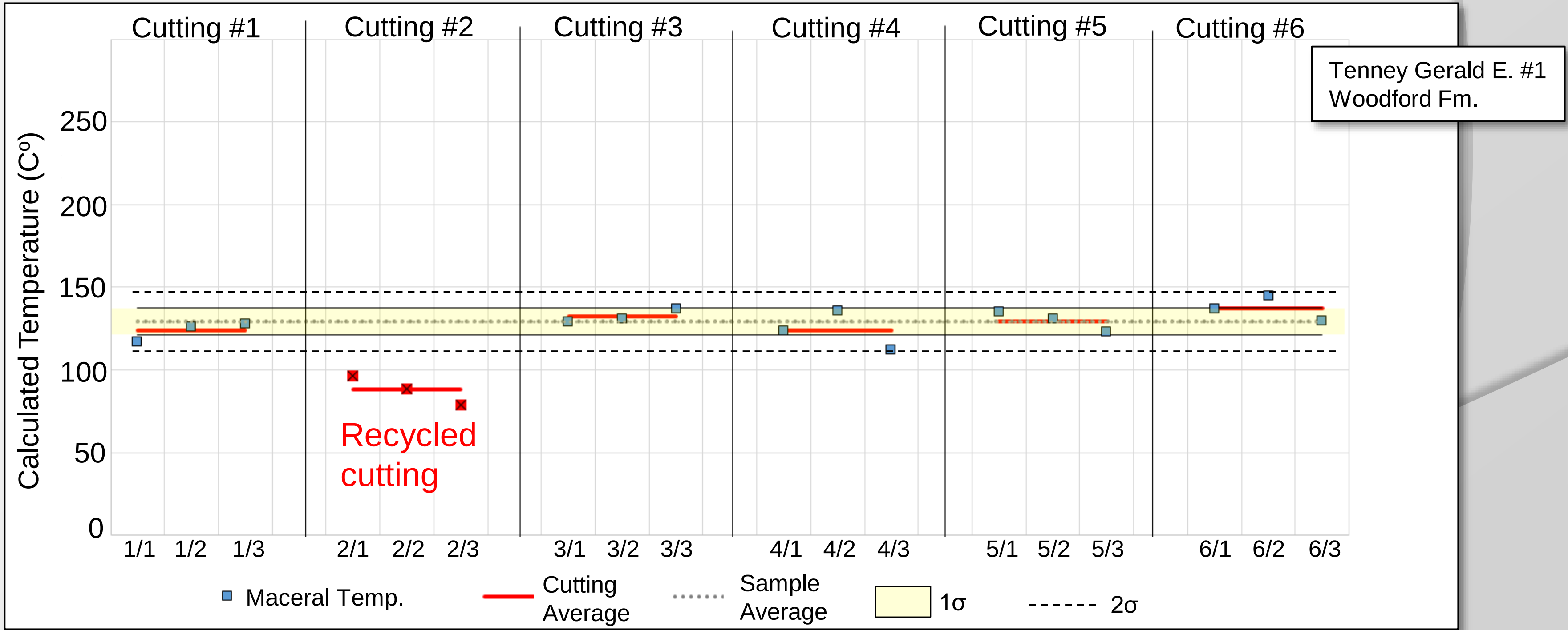


3 Macerals per cutting analyzed



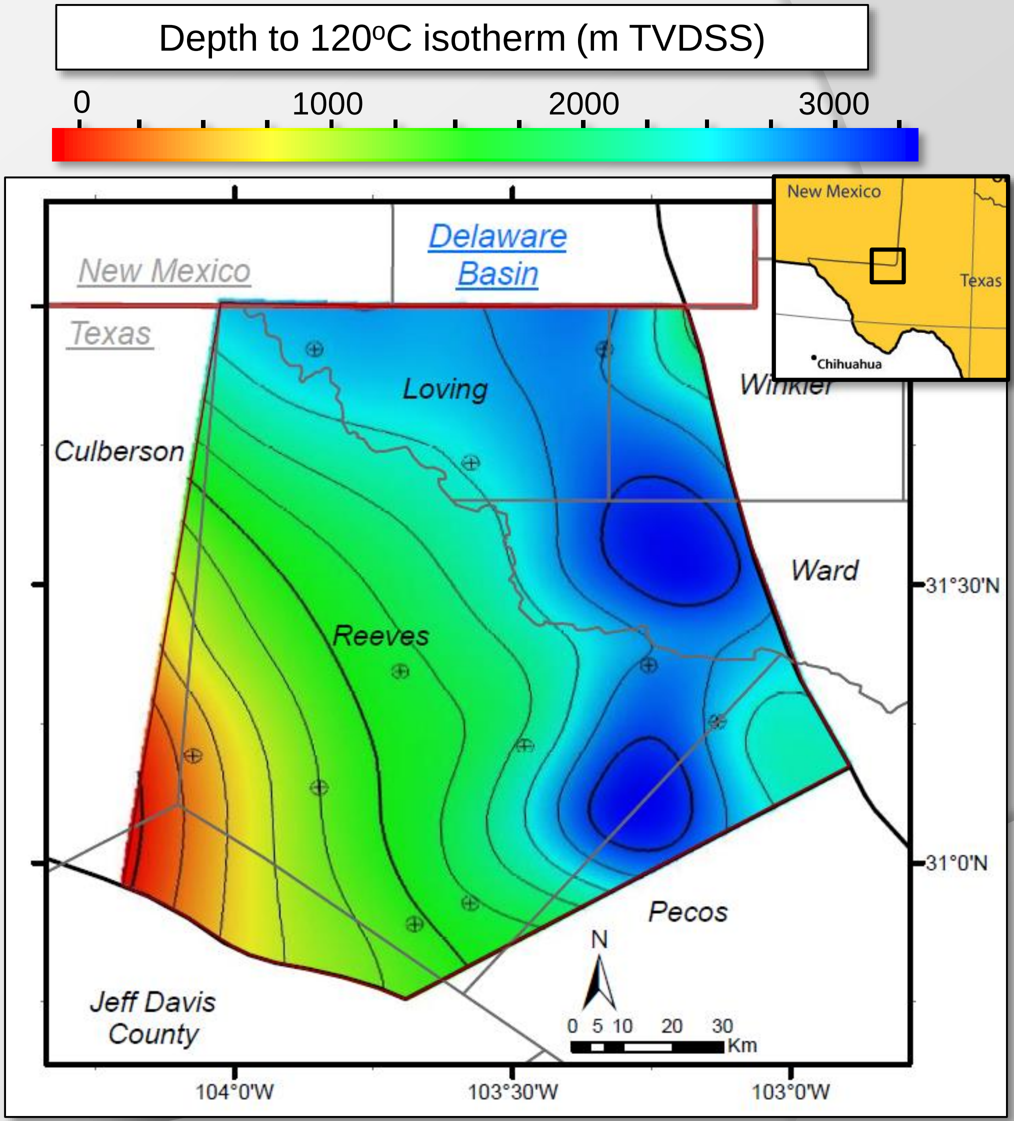
Each maceral shot <u>three times at 10 seconds each</u> and averaged together to reduce noise



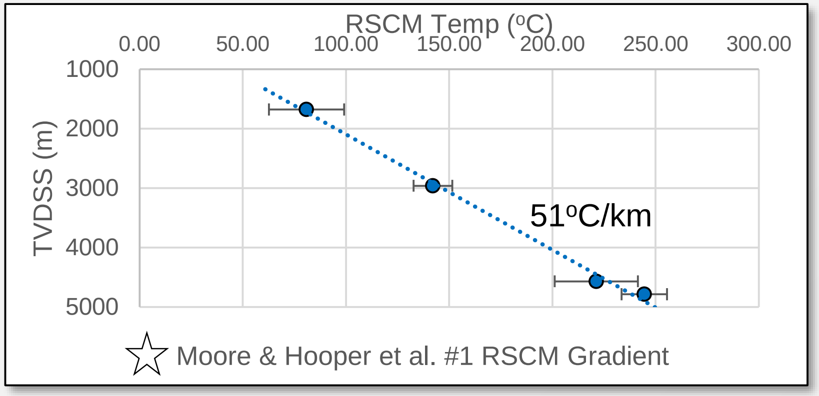


Map Temperature/Depth Pairs

- Isotherms are shallower in the west than in the east.
- Trends similar to modern-day structure
- Sediments in the west experienced higher peak temperatures in the past



RSCM Peak Temperature Paleogeothermal Gradient

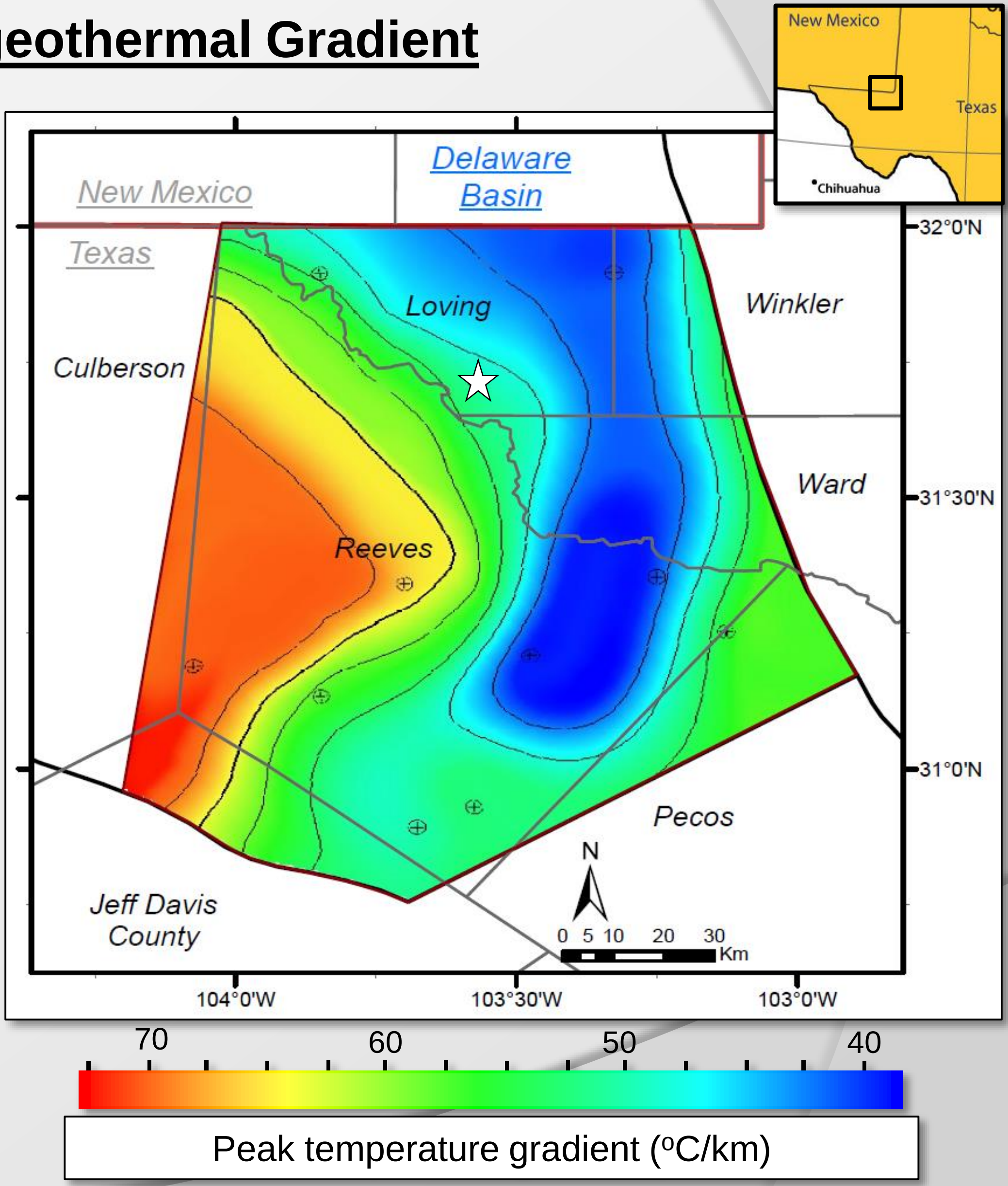


Rocks in the west have generally higher peak geothermal gradients

Peak temperature gradients according to RSCM are 40-72°C/km.

Modern surface-TD measurements suggest 18-25°C/km gradient covering same area (Ruppel, 2005)

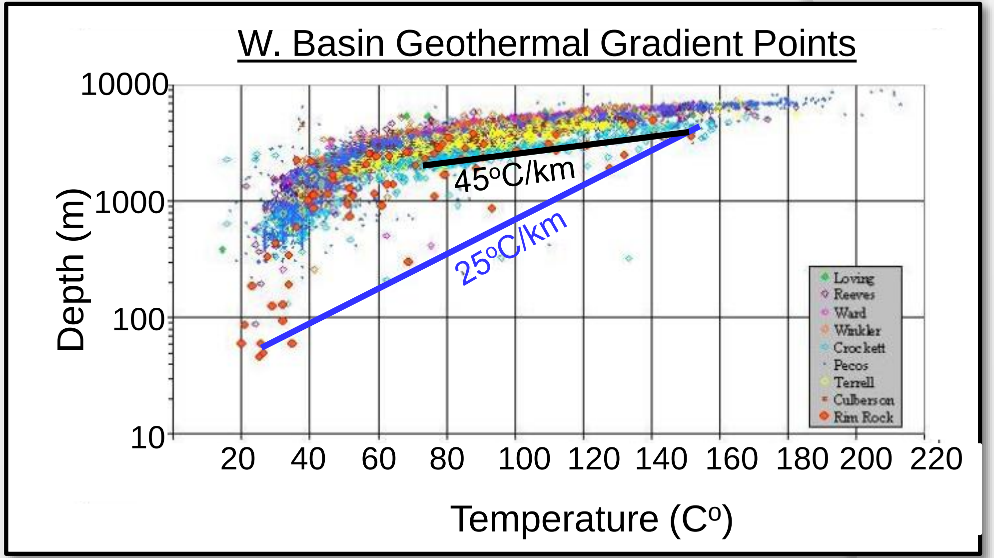
Is that reasonable?



RSCM Peak Temperature Paleogeothermal Gradient

Modern geothermal gradients are not static!

- Geothermal gradient in West Texas is better fit by a log-normal distribution
- Geothermal gradient increases with depth
- Geothermal gradient increases to the west
- Geothermal gradients are 21.5°C/km at the surface, up to 44.5°C/km at 10,000' depth.
- RSCM doesn't experience retrograde, only records peak gradient.

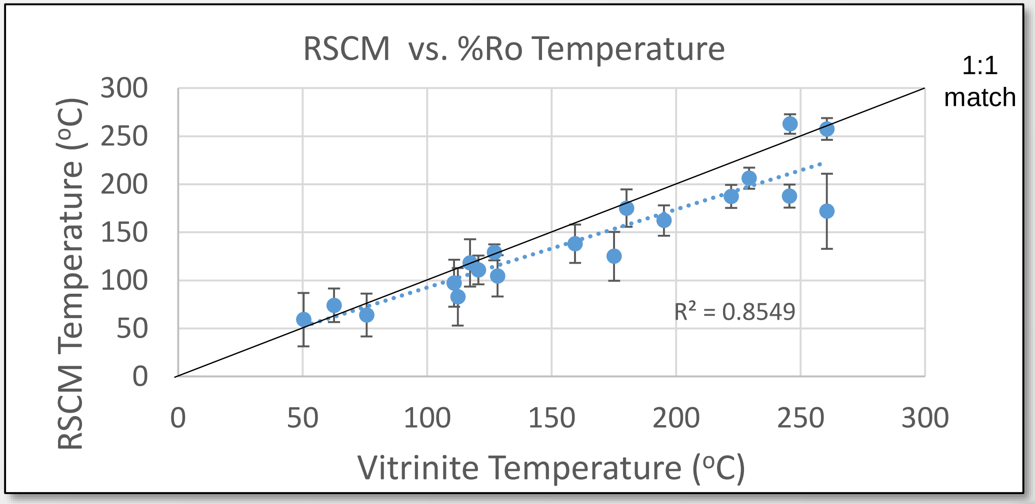


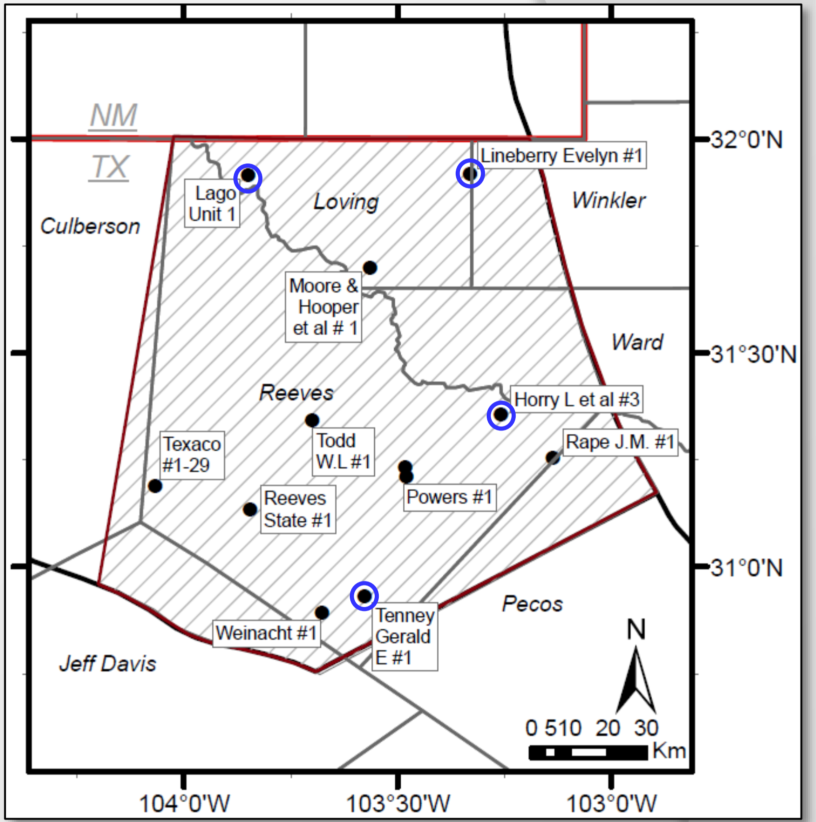
(Erlac and Swift, 2004; 2007)

Higher gradients suggest temperatures were higher in the past than they are today.

RSCM Comparison with %Ro

- 4 wells with %Ro were selected to calibrate initial peak-fitting methods
- %Ro equated to temperature using time-independent conversion
  (Barker and Pawlewicz, 1986)
- Strong correlation between RSCM and %Ro



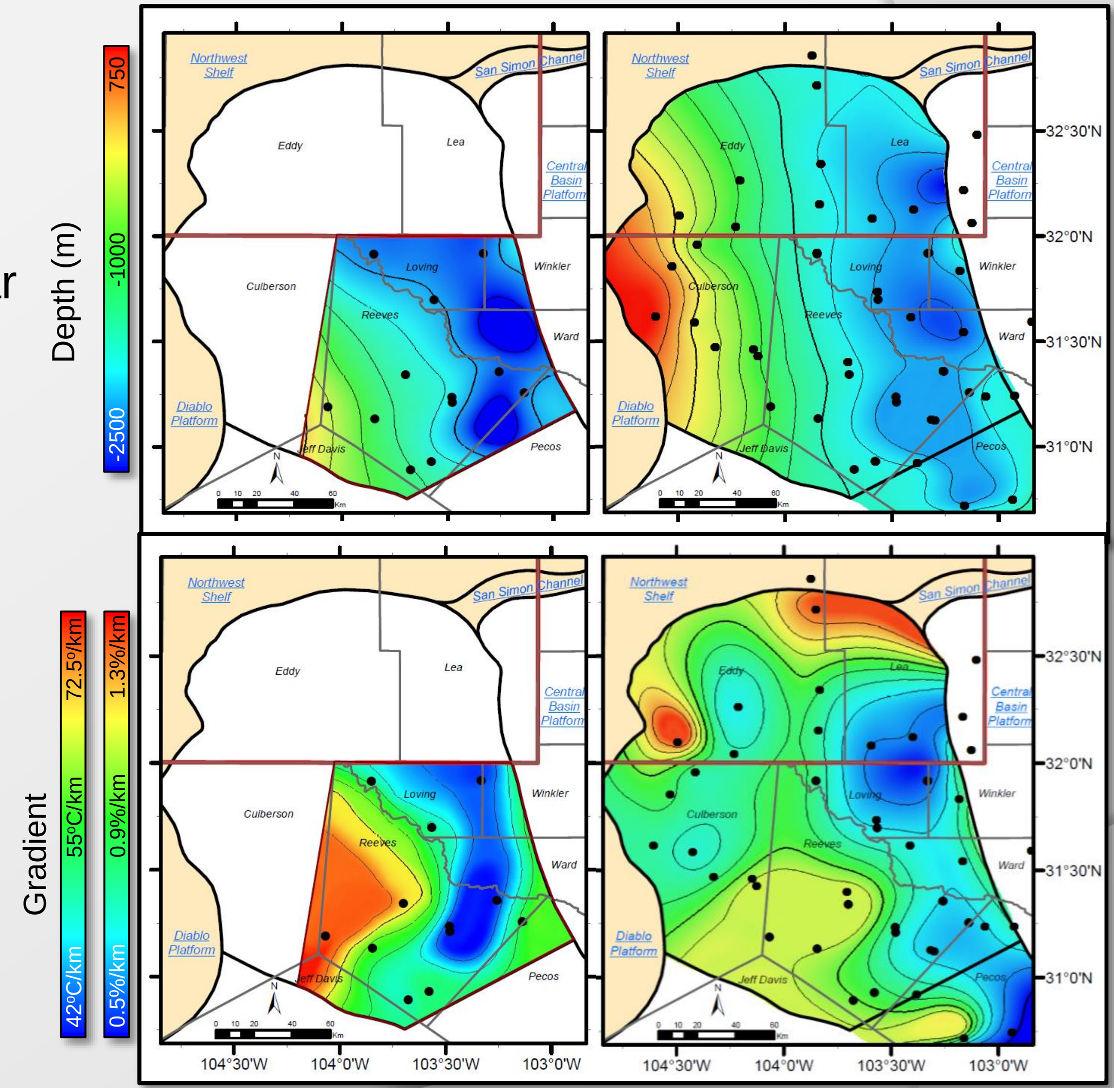


○ = direct RSCM and %Ro comparison

RSCM vs. %Ro

- Isoreflectance surfaces generated from 41 wells with %Ro data
- RSCM and %Ro suggest similar trends in peak temperature
- RSCM and %Ro also show increased gradients in similar locations
- %Ro shows trends continue outside the study area, with localized hotspots in the north and northwest.

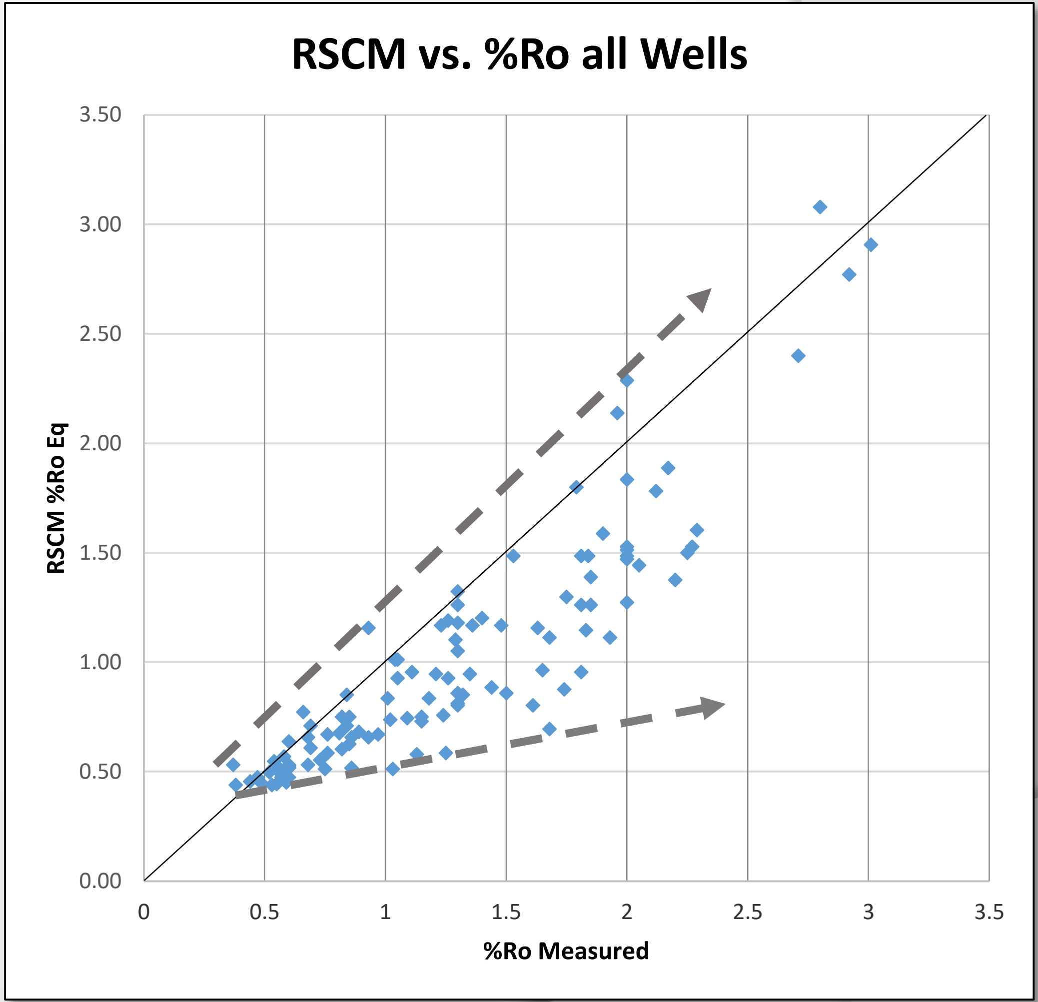
RSCM (120ºC) Vitrinite Reflectance (0.8%)



*Vitrinite and temperature gradients do not scale linearly

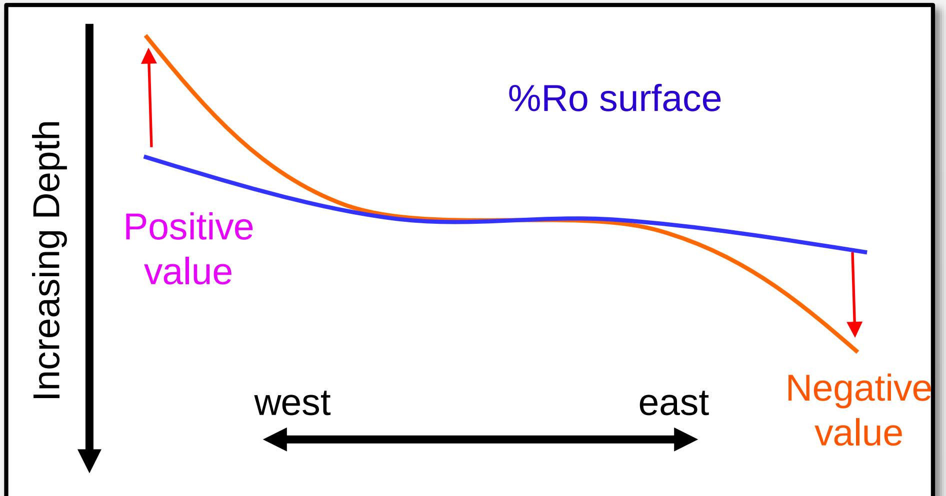
RSCM vs. %Ro: Basin Total

When correlated for all sample wells in the study area, samples diverge with increasing temperature



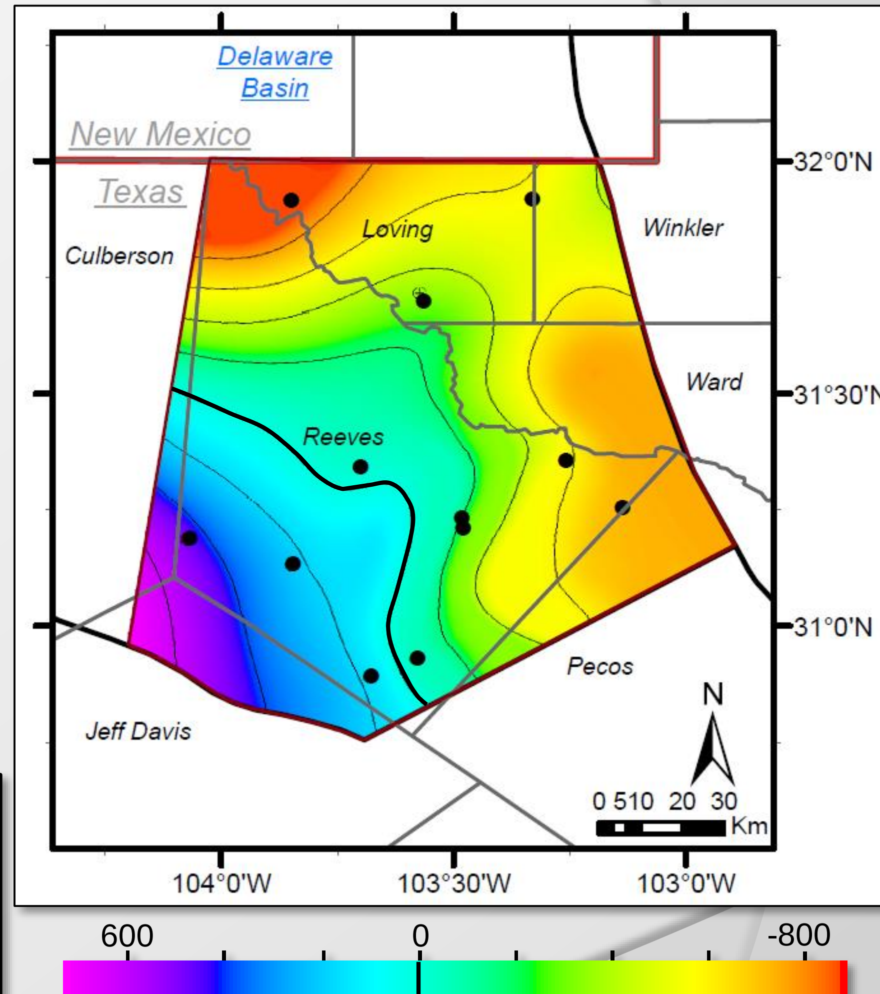
- RSCM underestimates %Ro in eastern deepest samples.
- Increased duration of heating could be differential mechanism.
- **Assumption:** RSCM measurements are not time-cumulative like vitrinite.
- RSCM may not follow Time-Temperature Index (TTI) models like %Ro does.

RSCM vs. %Ro difference as an index for heating duration



If %Ro is time/temperature dependent, and RSCM is only temperature dependent, then the offset between them may be a useful index for heating duration.

Positive values mean RSCM predicts temperatures shallower than %Ro, and has shorter heating duration.
Negative values mean RSCM predicts temperatures deeper than %Ro, and has longer heating duration.



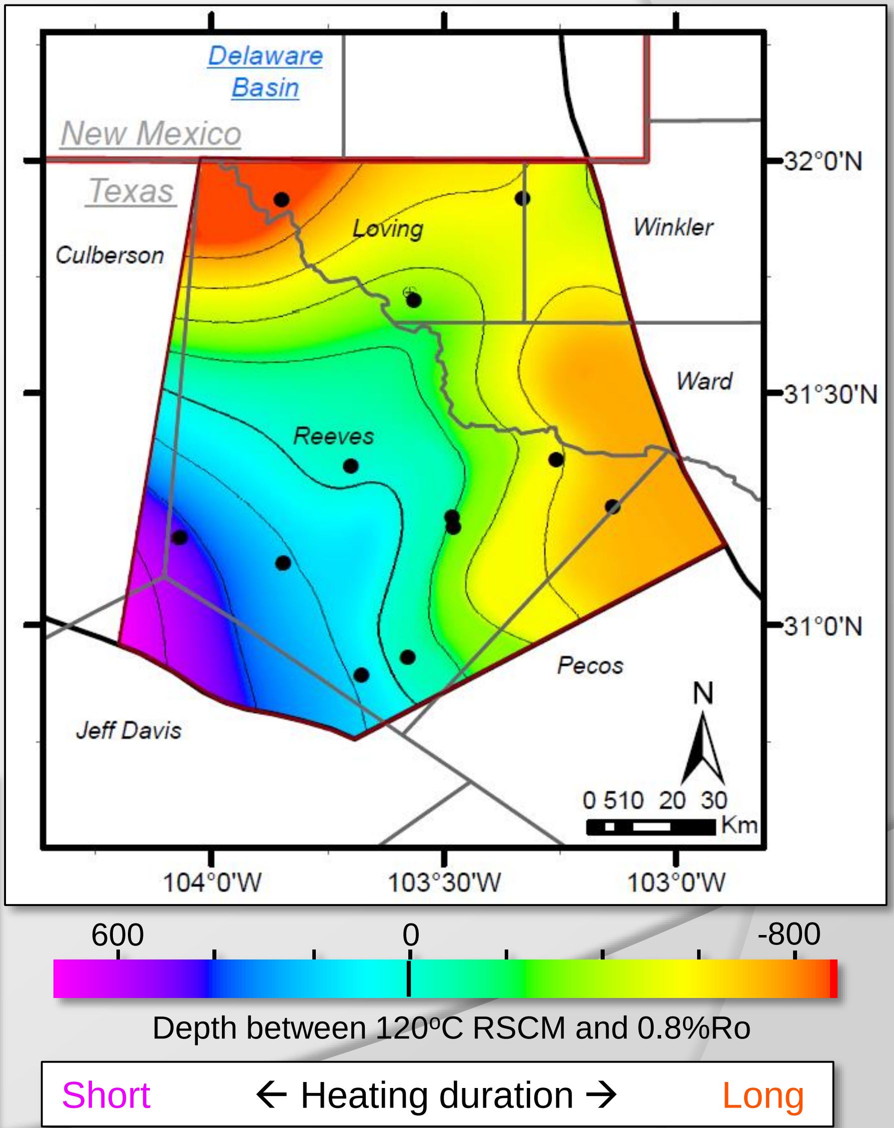
Depth between 120°C RSCM and 0.8%Ro

Short ← Heating duration → Long

RSCM vs. %Ro difference as an index for heating duration

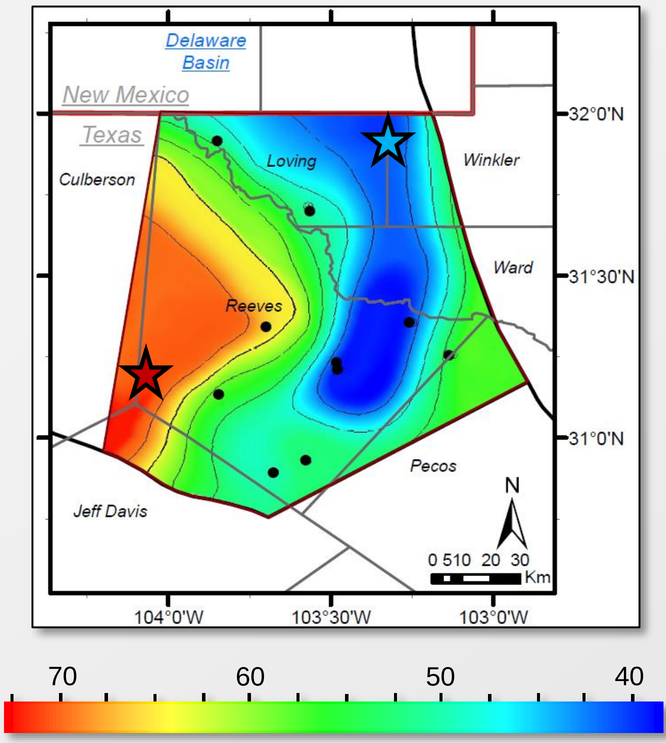
- Western regions have higher peak T(Cº) by RSCM, and eastern regions have lower peak T(Cº) by RSCM
- Difference between %Ro and RSCM trends align closely with geothermal gradient trends.
  High gradient → larger difference

Positive values mean RSCM predicts temperatures shallower than %Ro, and has shorter heating duration.
Negative values mean RSCM predicts temperatures deeper than %Ro, and has longer heating duration.



Input of RSCM into 1D basin models

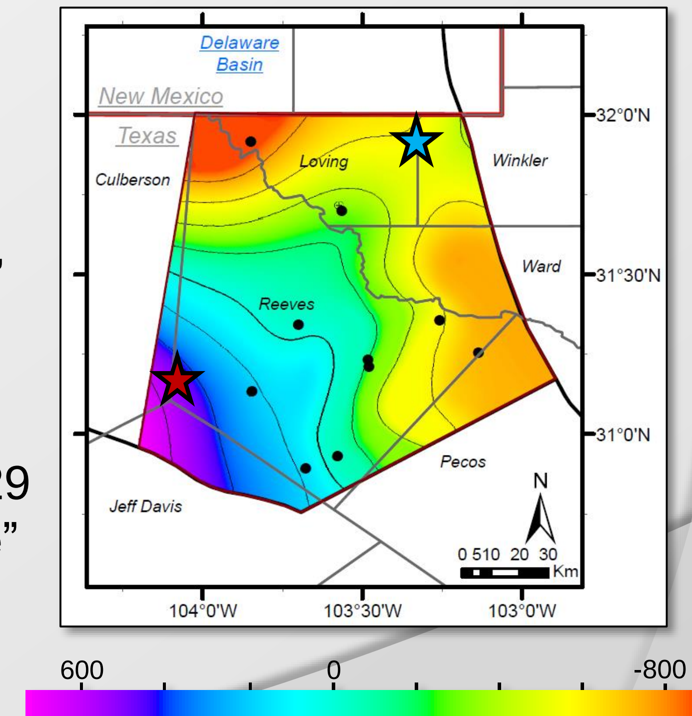
- We can test if RSCM is time-independent by modeling burial and temperature over time
- Utilize a Time Temperature Index (TTI)-based model such as Easy%Ro



Peak paleogeothermal gradient (°C/km)

Lineberry Evelyn #1 “cool case”

Texaco #1-29 “warm case”

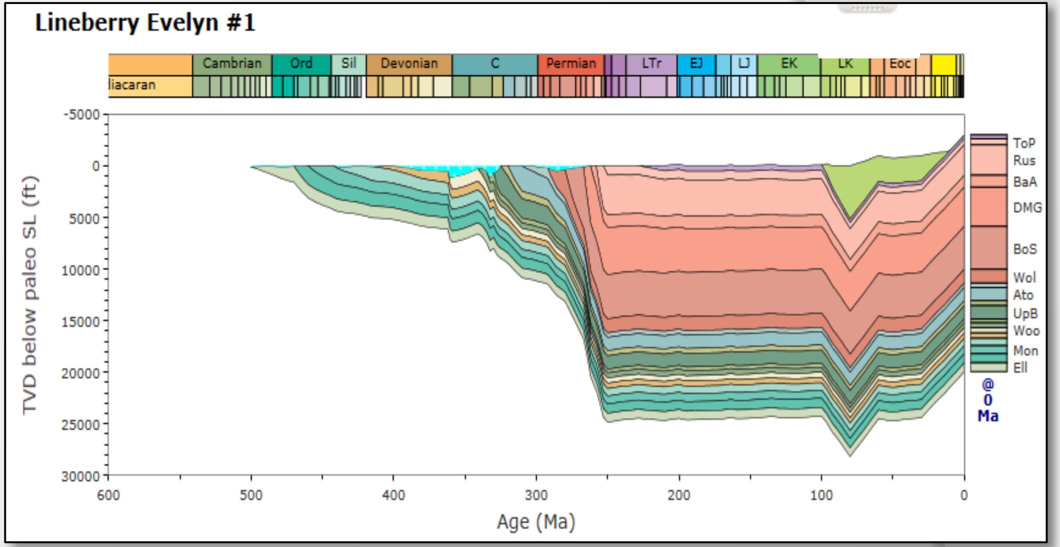


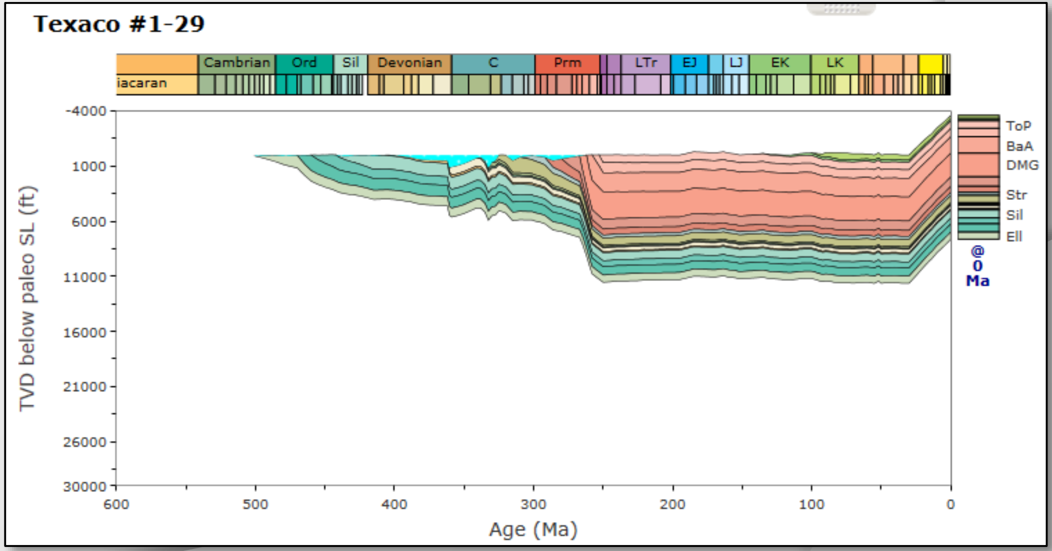
Depth between 120°C RSCM and 0.8%Ro

Backstripping Models East vs. West from Well Logs

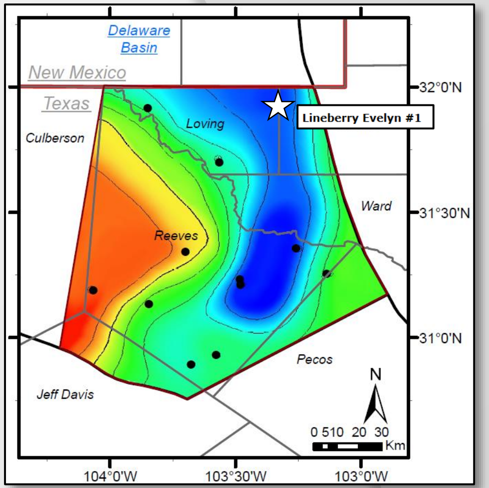
- **East**
  - Deeper subsidence in all Paleozoic formations
  - Maximum burial in late Cretaceous
  - 1500m Cretaceous overburden removed from modern uplift
- **West**
  - Less subsidence in Paleozoic formations
  - Less maximum burial in late Cretaceous
  - 200m Cretaceous overburden removed from modern uplift.

Iteratively Adjust:
Basal heat flow
Cretaceous overburden removed
Heating duration





Matching Modelled with Observed: Easy%Ro

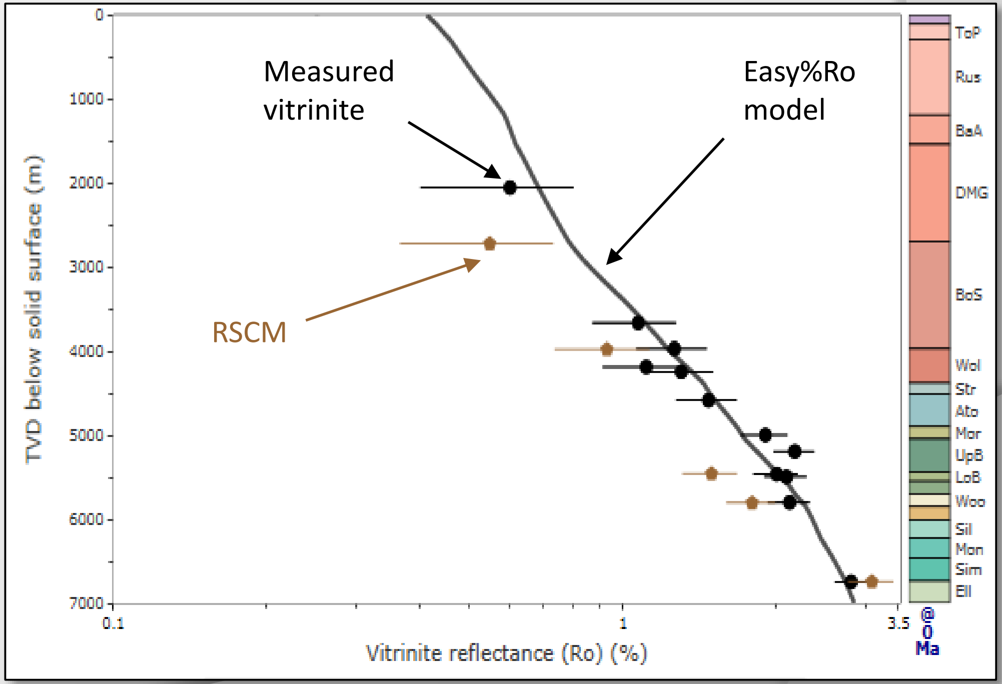


East:

Lineberry Evelyn #1:

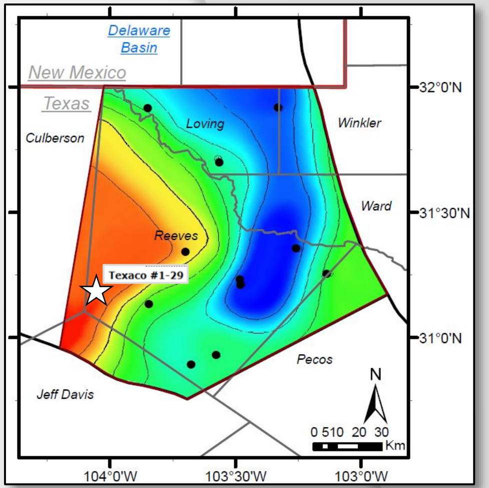
45mW/m² basal heat flow
1500m Cretaceous overburden
Heating duration 250 Ma

- Easy%Ro model matches observed %Ro data when using regional background values.
- 1500m of missing Cretaceous overburden removed during post-Laramide uplift
- This suggests the eastern basin history has simple and consistent geothermal controls, most likely due to burial depth alone.



RSCM equated to %Ro using Barker and Pawlewicz (1986) time-independent conversion ►

Matching Modelled with Observed: Easy%Ro



West:

- Easy%Ro model does not match observed %Ro data if parameters are held constant from east to west

Texaco #1-29

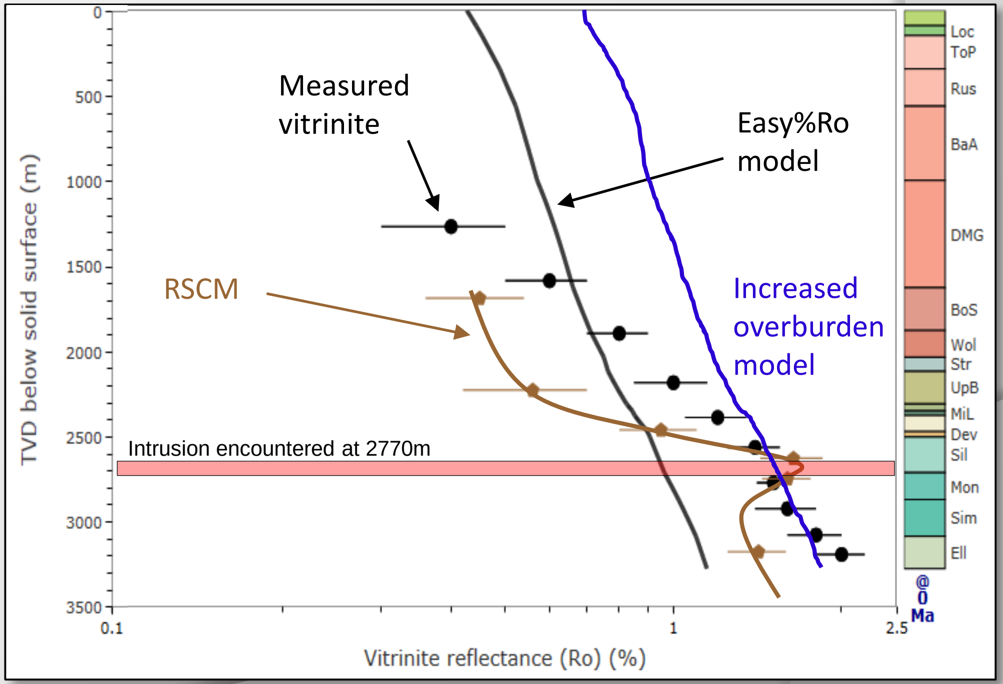
Basin characteristics in the east are not consistent in the west!

- Deeper %Ro measurements are higher than Easy%Ro model

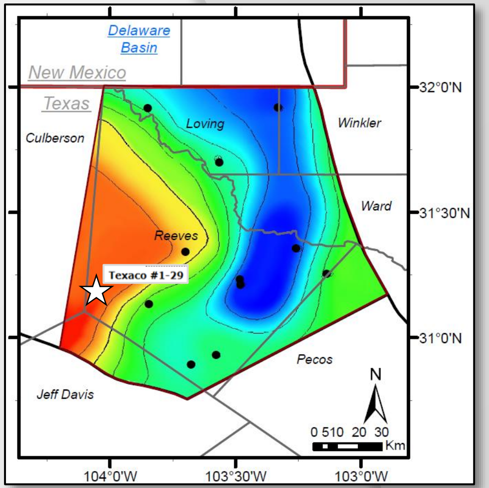
→ increase overburden?

- Shallower measurements are lower than Easy%Ro model, and the %Ro gradient is higher.

→ increase basal heat flow?



Matching Modelled with Observed: Easy%Ro



West:

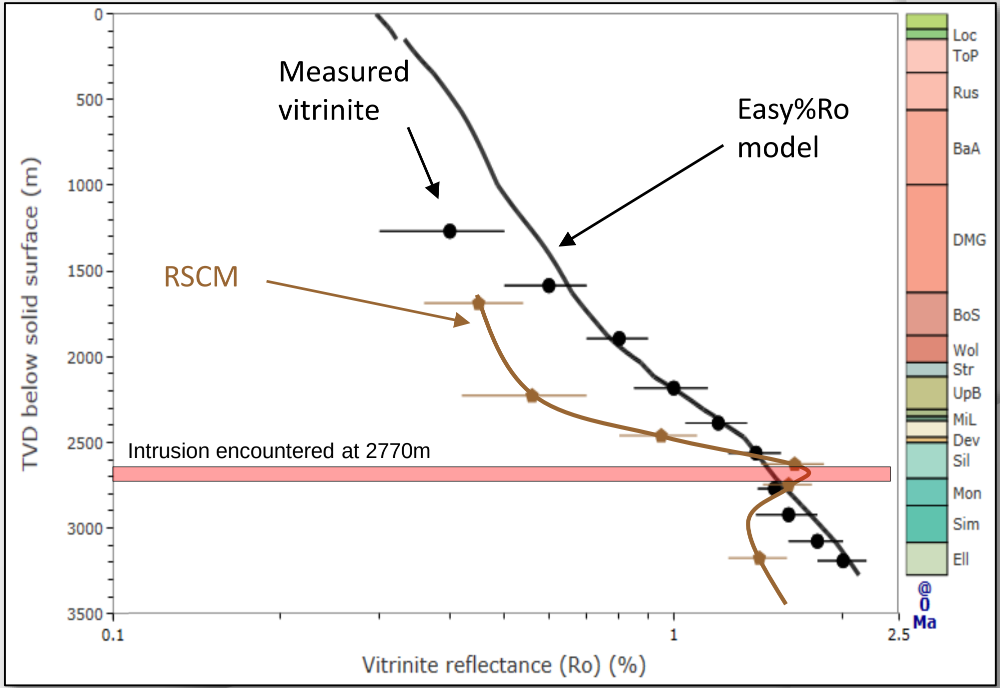
(1) reduce missing Cretaceous overburden to 200m

(2) Increase basal heat flow to 90mW/m²

→ double the regional background of 45mW/m²

Texaco #1-29
90mW/m² total required to match gradient

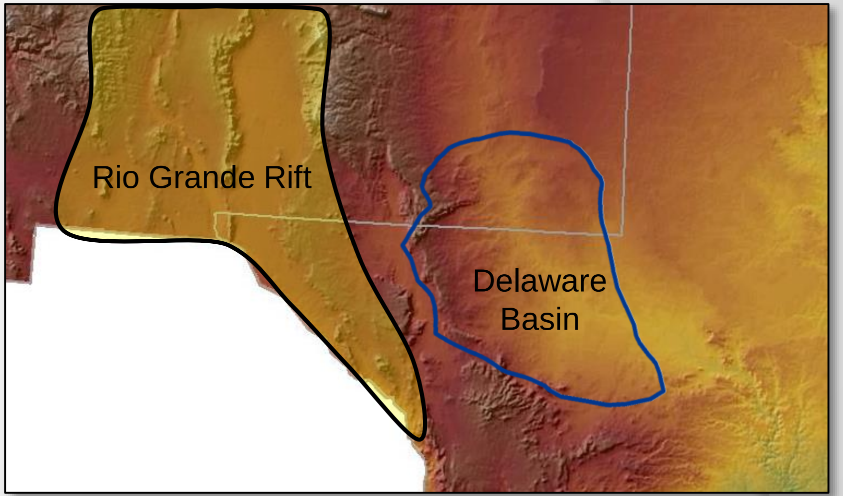
200m missing Cretaceous overburden



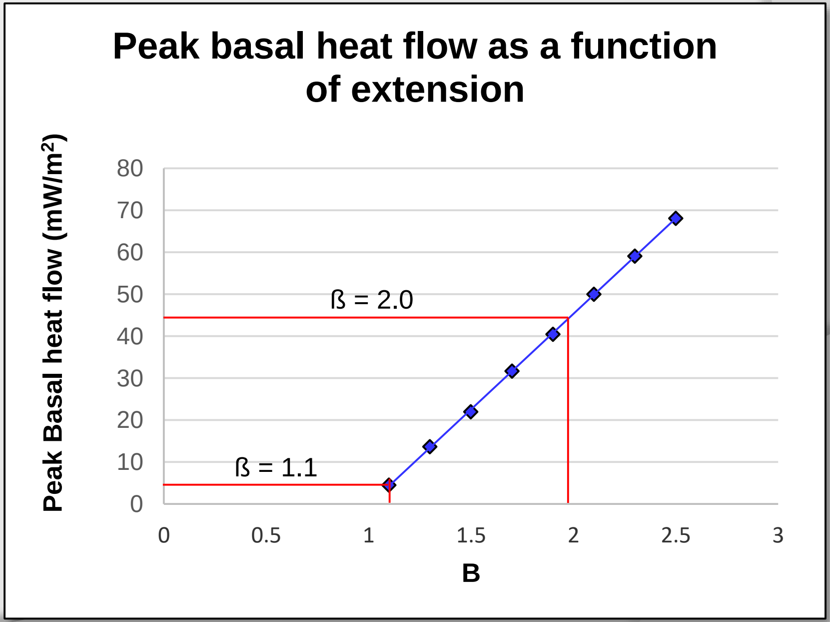
- We have to identify sources of heat that could contribute to the overall heat budget:

  1. rifting
  2. igneous intrusion
  3. crustal thinning

Rio Grande Rift (RGR)



- RGR initiates Oligocene west of the basin
- Crustal thinning of RGR best modeled by McKenzie-style heat flow
- 90-110% extension (ß = 1.9-2.1) required for additional 45mW/m^2
- Proximal to Delaware Basin, extension is only 10% (Henry, 1998) → 5.5mW/m^2



Rifting alone is not enough to account for the increased basal heat flow

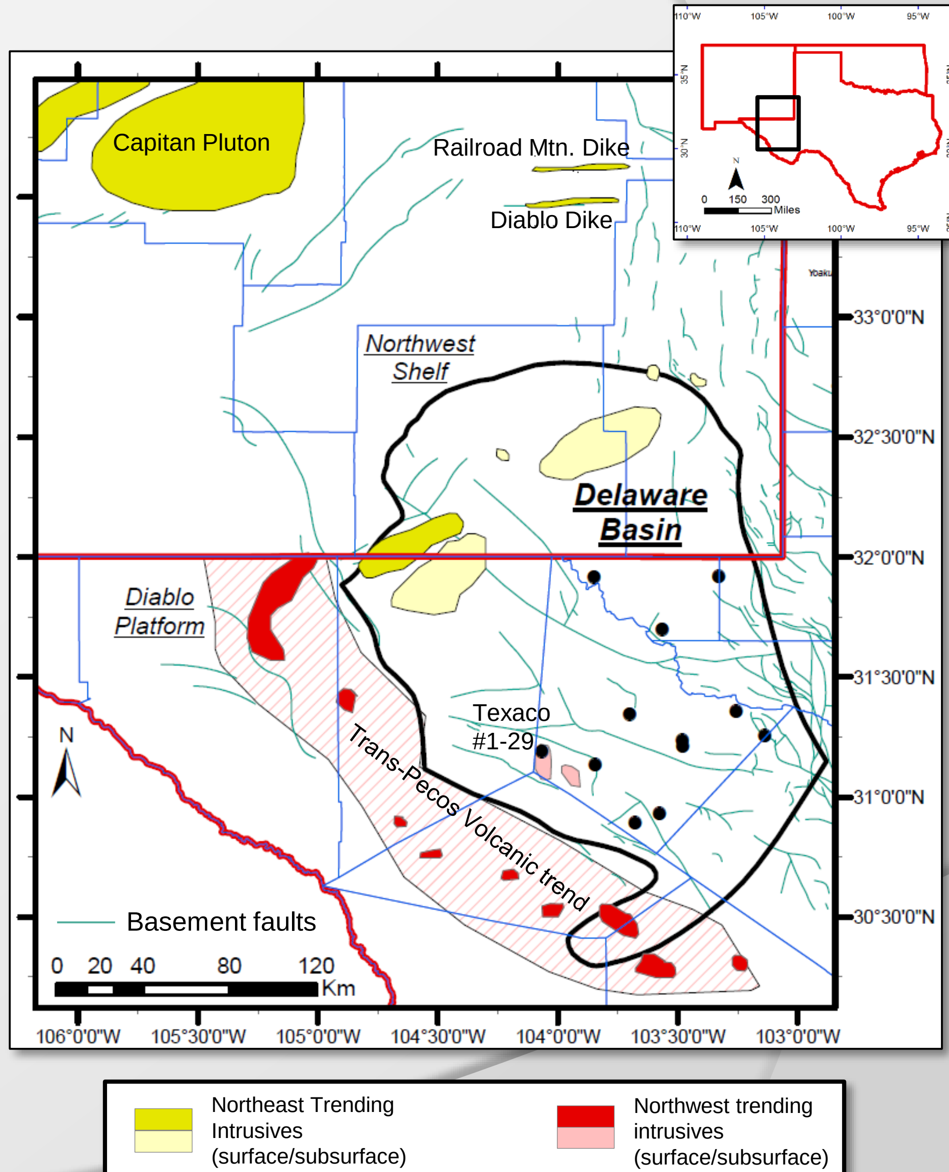
West Texas Igneous Intrusions

- Two main trends of igneous intrusions:

  (1) NE trending alkaline → 40-30Ma
  (2) NW trending mafics → 35-18Ma

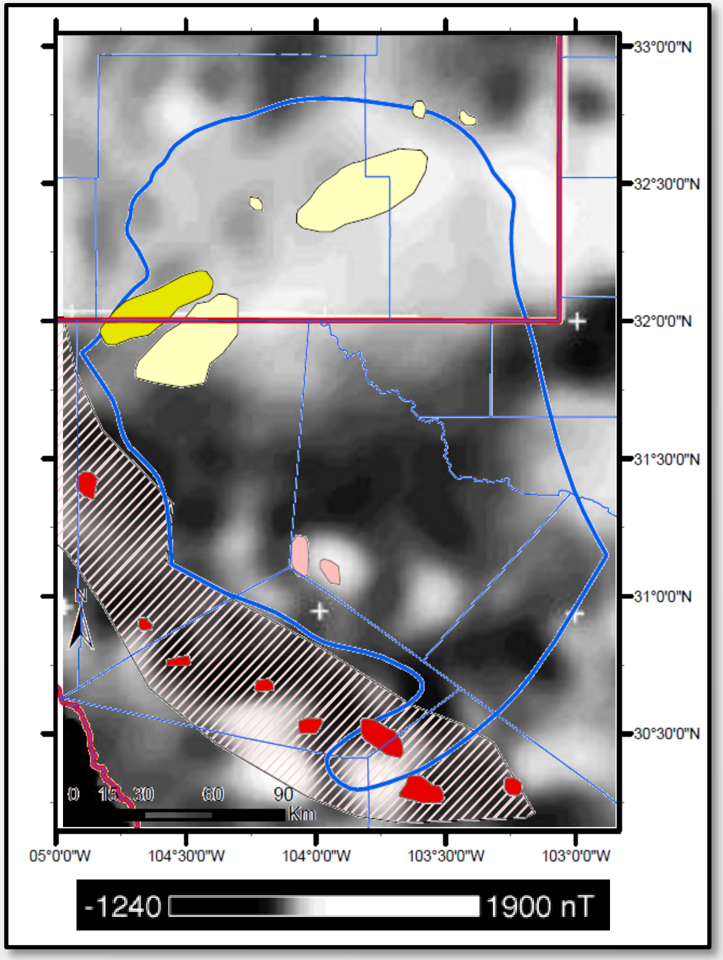
- Shift in magmatic composition and orientation complements shift in regional stresses post-Laramide.
  (McMillian et al 2000; James and Henry, 1991; Price & Henry, 1984)

- While heat flow effects are typically localized, migrating pore fluids and several dykes in close proximity can compound and extend the aureole.

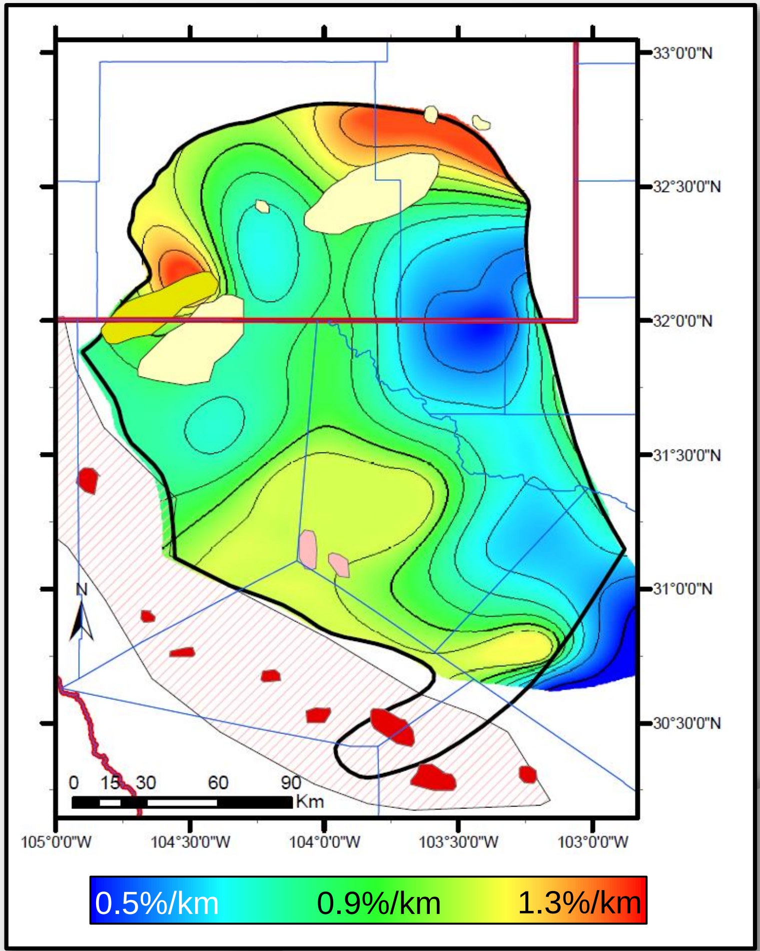


Overlap with Positive Magnetic Anomalies and Maturity Hotspots

Magnetic Anomaly Map
(Adams and Keller, 1996)



Maturity Gradient Map



Final Observations

- Thermal hotspot anomalies align with:
  1. Magnetic anomalies
  2. Mapped Cenozoic intrusions

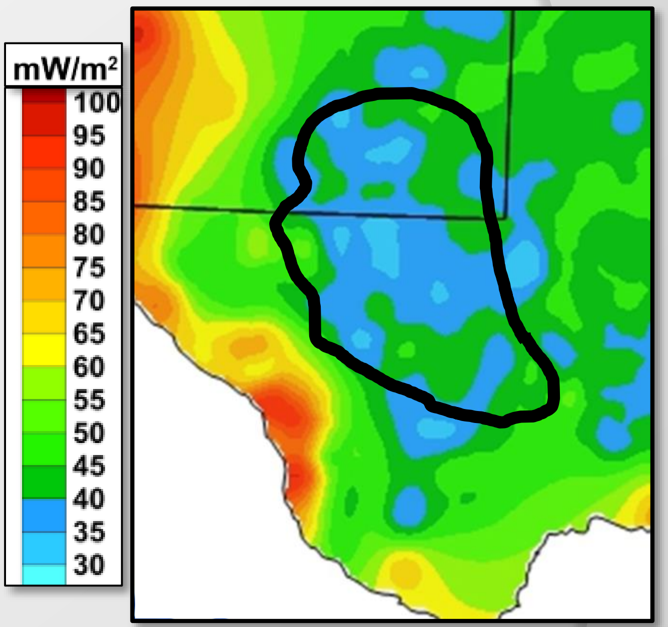
- Rifting alone is insufficient to provide enough additional heat in the west basin

- Texaco #1-29 encountered a 30m igneous intrusion similar to mafics exposed at the surface to the west of the basin.

West in the RGR center, basal heat flow is as high as 90mW/m^2.

Could this anomaly have previously extended further east into the basin?

Modern Basal Heat Flow



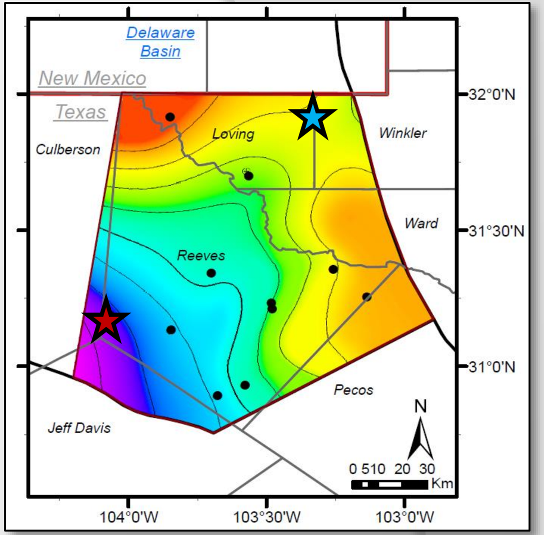
Blackwell and Richards (2004)

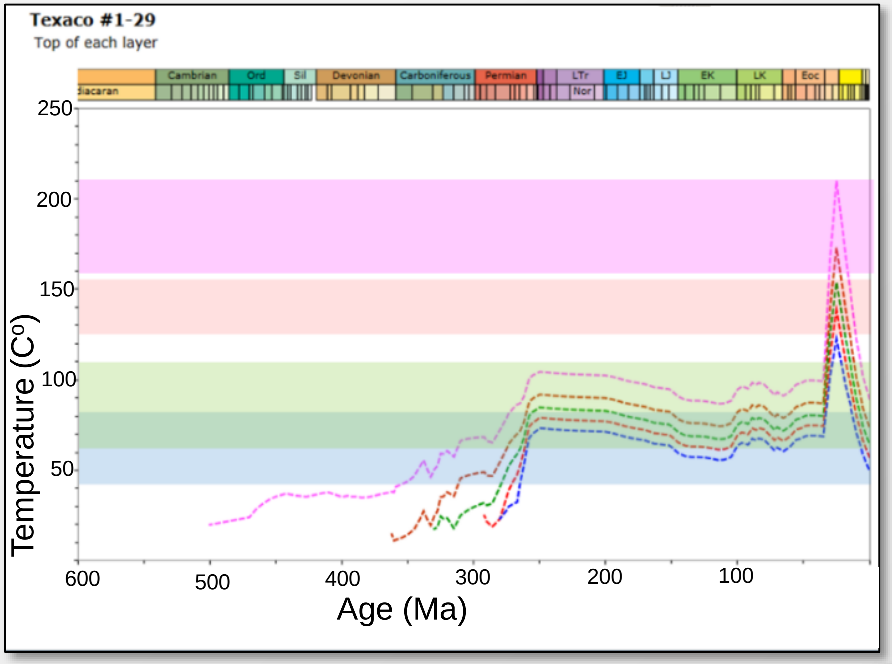
Peak Temperature Over Time

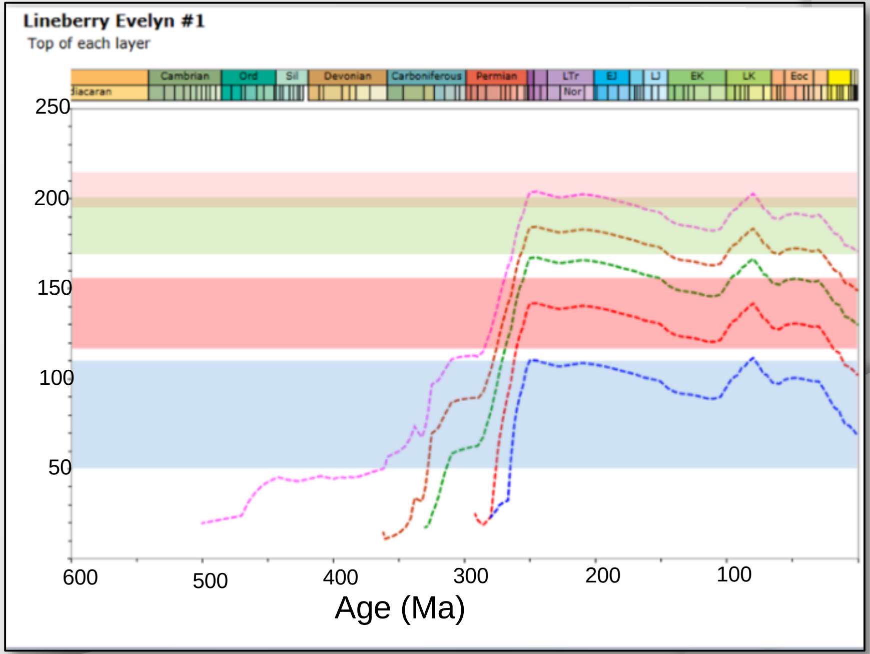
Extract peak temperature over time using the regional geologic context, basal heat flow, and burial depth.

Bone Spring	Woodford
Wolfcamp A	Ellenburger
Barnett	

West experienced less burial, but short-duration basal heat flow increase



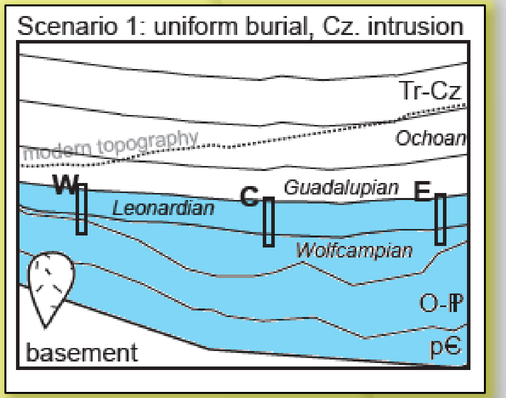




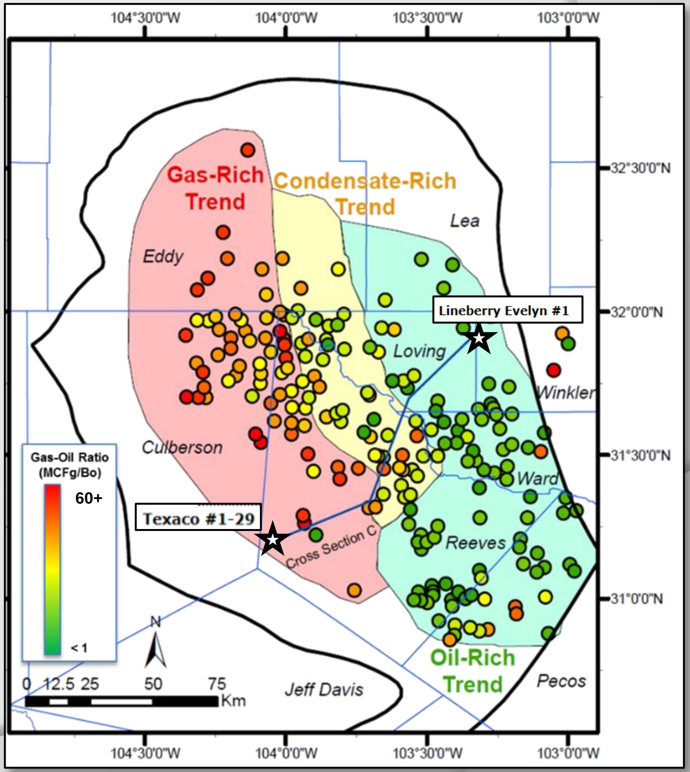
Conclusions:

Peak temperatures and peak geothermal gradients higher in the west than in the east.

$T_W > T_C > T_E$ $G_W > G_C > G_E$



Elevated peak temperatures, peak gradients, and fast heating rate support a thermal control on gas-oil ratios.



Conclusions:

→ Western Delaware Basin is HOT!

(1) RSCM determines the peak temperature organic materials reach in the subsurface.

- *Function of D1 and D2 FWHM*

(2) RSCM is time-independent, and differences between Vitrinite (%Ro) and RSCM can be used as an index for heating duration.

- *RSCM and %Ro diverge with increasing burial duration*

(3) When applied to the Delaware Basin, we observe the west had higher peak geothermal gradients and shorter heating durations than the east.

- *Burial controlled vs. intrusion controlled*

(4) Peak temperatures as compared to %Ro has implications for discriminating different sources of heat.

- *Regional background vs. localized hotspots*

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BERG-HUGHES CENTER

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