

Kinetics of the Opal-CT to Quartz Phase Transition Control Diagenetic Traps in Siliceous Shale Source Rock from the San Joaquin Basin and Hokkaido*

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Search and Discovery Article #40771 (2011)

Posted July 18, 2011

*Adapted from oral presentation at AAPG Annual Convention and Exhibition, Houston, Texas, USA, April 10-13, 2011

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Abstract

Porcelanite and chert originate from marine diatoms as diatomite, which undergoes diagenetic conversion of amorphous opal (opal-A) to cristobalite and tridymite (opal-CT) and finally quartz. Porosity decreases during this process, but permeability increases during transformation of opal-CT to quartz and results in stratigraphic traps for petroleum like those in recent discoveries in the San Joaquin Basin (Grau et al., 2003). The ability to accurately predict locations of these diagenetic traps would be a valuable exploration tool.

Ernst and Calvert (1969) determined zero-order kinetics for the opal-CT to quartz phase transition based on hydrothermal experiments using distilled water. However, the transition is a dissolution and re-precipitation process, where both the silica dissolution rate and solubility contribute to the rate of the reaction. We determined first-order kinetic parameters for the opal-CT to quartz transition based on hydrous pyrolysis of weathered Monterey Formation porcelanite from Lompoc, California, which also contained dolomite; and a Wakkanai Formation porcelanite from Hokkaido, Japan, which also contained quartz, albite, and some organic material. Temperatures were kept below the critical temperature of water and the aqueous solution was buffered so that final fluid pH values measured between 7.0 and 8.2. Under these conditions, the samples showed large variations in opal-CT to quartz conversion rates, where the rates of the Monterey and Wakkani conversions were approximately five times faster and three times slower, respectively, than that predicted by Ernst and Calvert.

We built a module in our petroleum system modeling software and used the hydrous pyrolysis kinetics to determine the depth of the opal-CT to quartz phase transition along a cross-section in the east-central portion of the San Joaquin Basin. The kinetics and software module may be useful to identify silica-phase-transition stratigraphic traps throughout the Pacific Rim where siliceous source rocks are common.

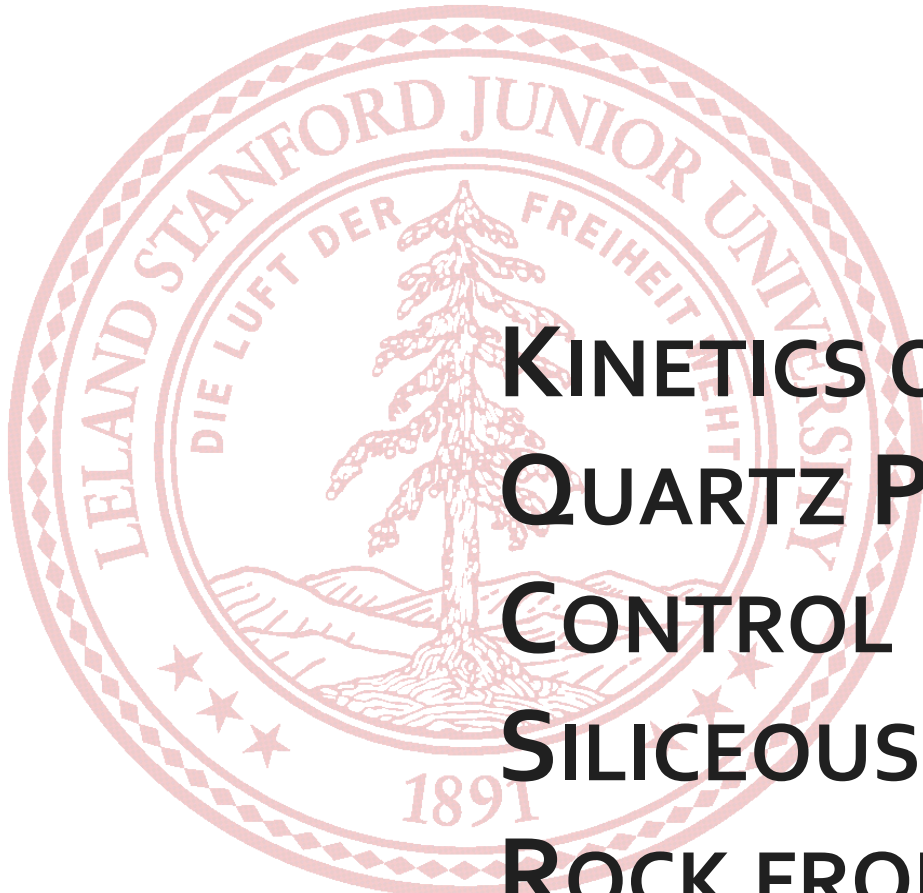
References

Bloch, R.B., 1991, Studies of the stratigraphy and structure of the San Joaquin Basin, California: Ph. D. thesis, Stanford University, California, 2 v., 319 p.

Ernest, W.G., and S.E. Calvert, 1969, An experimental study of the recrystallization of porcelanite and its bearing on the origin of some bedded cherts: *American Journal of Science*, v. 267-A, p. 114-133.

Grau, A., R. Kidney, and R. Sterling, 2003, Success! Using seismic attributes and horizontal drilling to delineate and exploit a diagenetic trap, Monterey Shale, San Joaquin Valley, California *in* T.C. Chidsey Jr., (chair) 2003 AAPG Annual Convention with SEPM: AAPG Annual Meeting Expanded Abstracts, v. 12, p. 66-67.

Peters, K.E., F.D. Hostettler, T.D. Lorenson, and R.J. Rosenbauer, 2008, Families of Miocene Monterey crude oil, seep, and tarball samples, coastal California: *AAPG Bulletin*, v. 92/9, p. 1131-1152.

The background of the slide features a large, faint, circular watermark of the Stanford University seal. The seal contains a redwood tree in the center, with the text "LELAND STANFORD JUNIOR UNIVERSITY" around the top edge, "DIE LUFT DER FREIHEIT" (The Air of Liberty) around the inner circle, and "1891" at the bottom. There are also five stars along the bottom edge of the seal.

KINETICS OF THE OPAL-CT TO QUARTZ PHASE TRANSITION CONTROL DIAGENETIC TRAPS IN SILICEOUS SHALE SOURCE ROCK FROM THE SAN JOAQUIN BASIN AND HOKKAIDO

AAPG ACE
April 11, 2011
Houston, TX

**Danica Dralus, Michael Lewan,
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Kunihiro Tsuchida, Kenneth Peters**

Key points

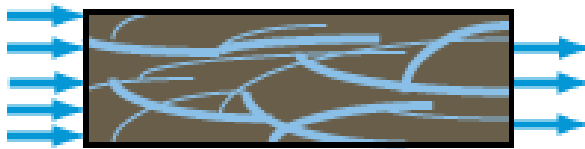


- Phase transitions in minerals affect petroleum **trapping** and **migration** (storage and transport).
- Our experiments show the opal-CT to quartz transition occurs at a very different rate than a previous study.
- Controlling mechanisms for this transition are poorly understood.

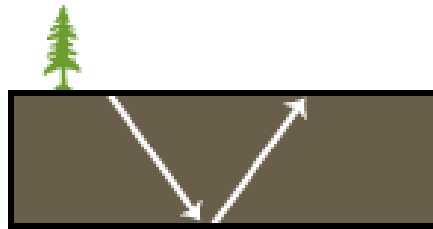
Rock physics meets geochemistry



porosity



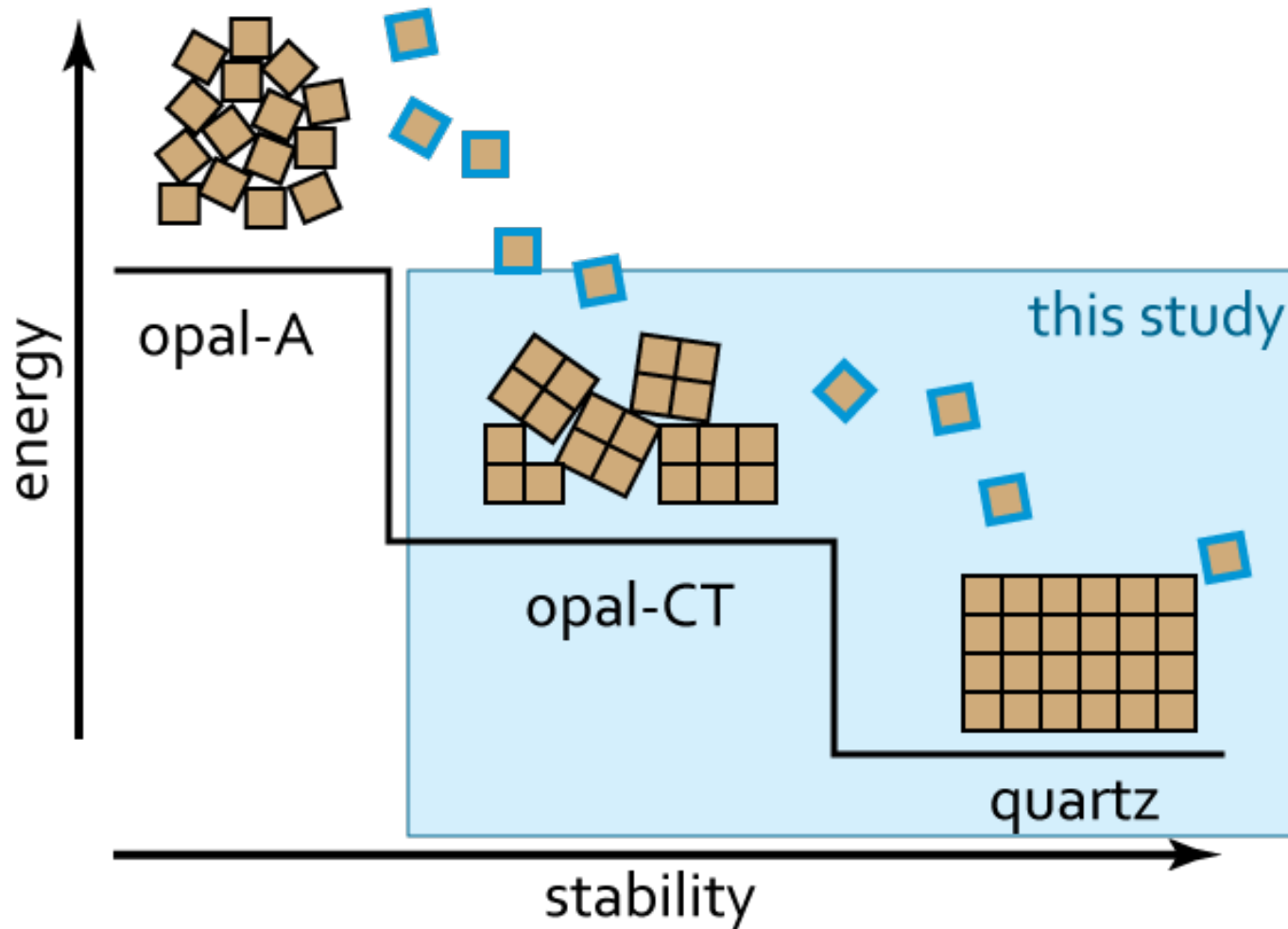
permeability



acoustic velocities

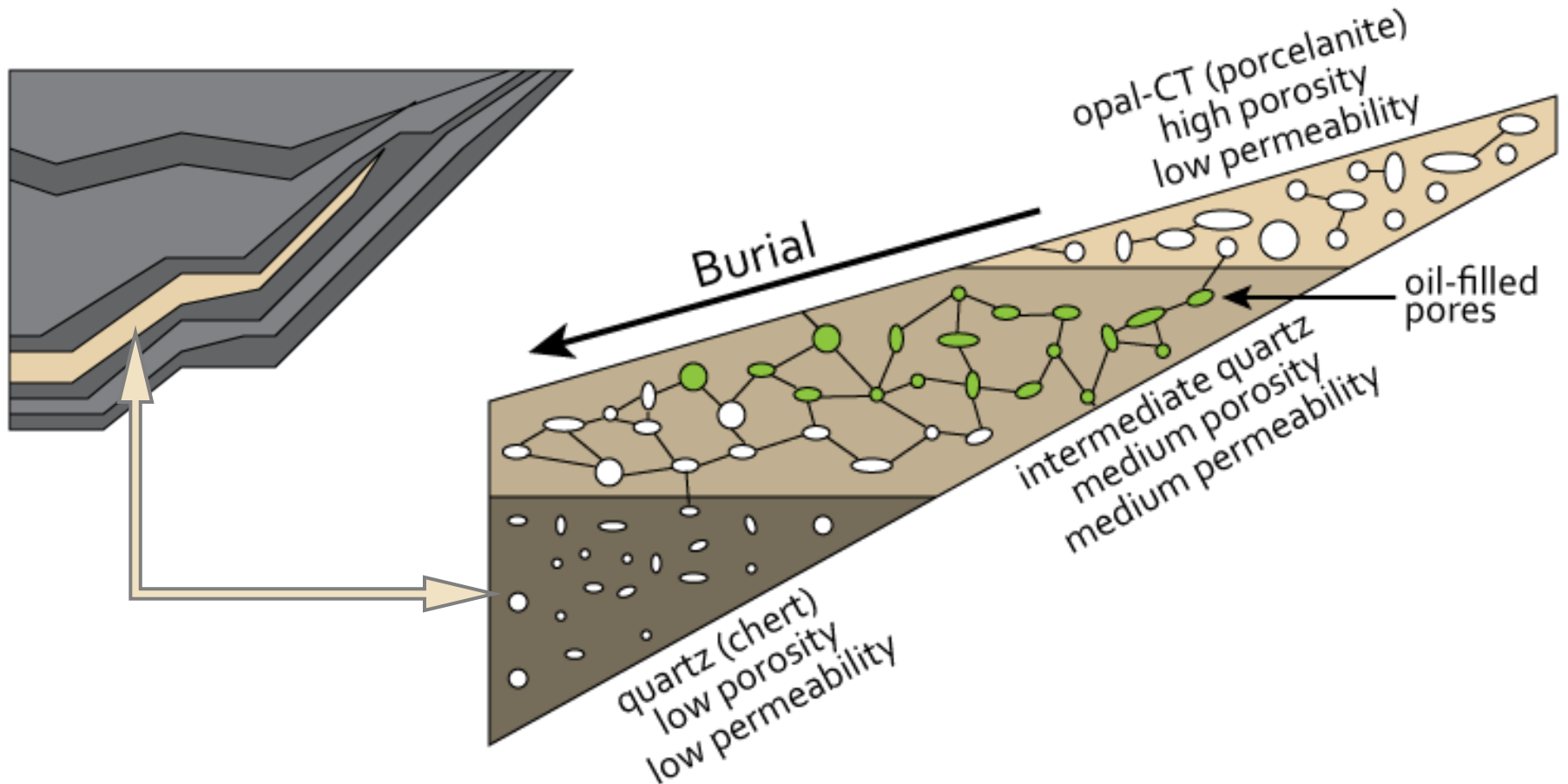
- effects of **mechanical** alterations are (relatively) well known
- effects of **chemical** alterations are largely mysterious

Silica polymorphs dissolve in water



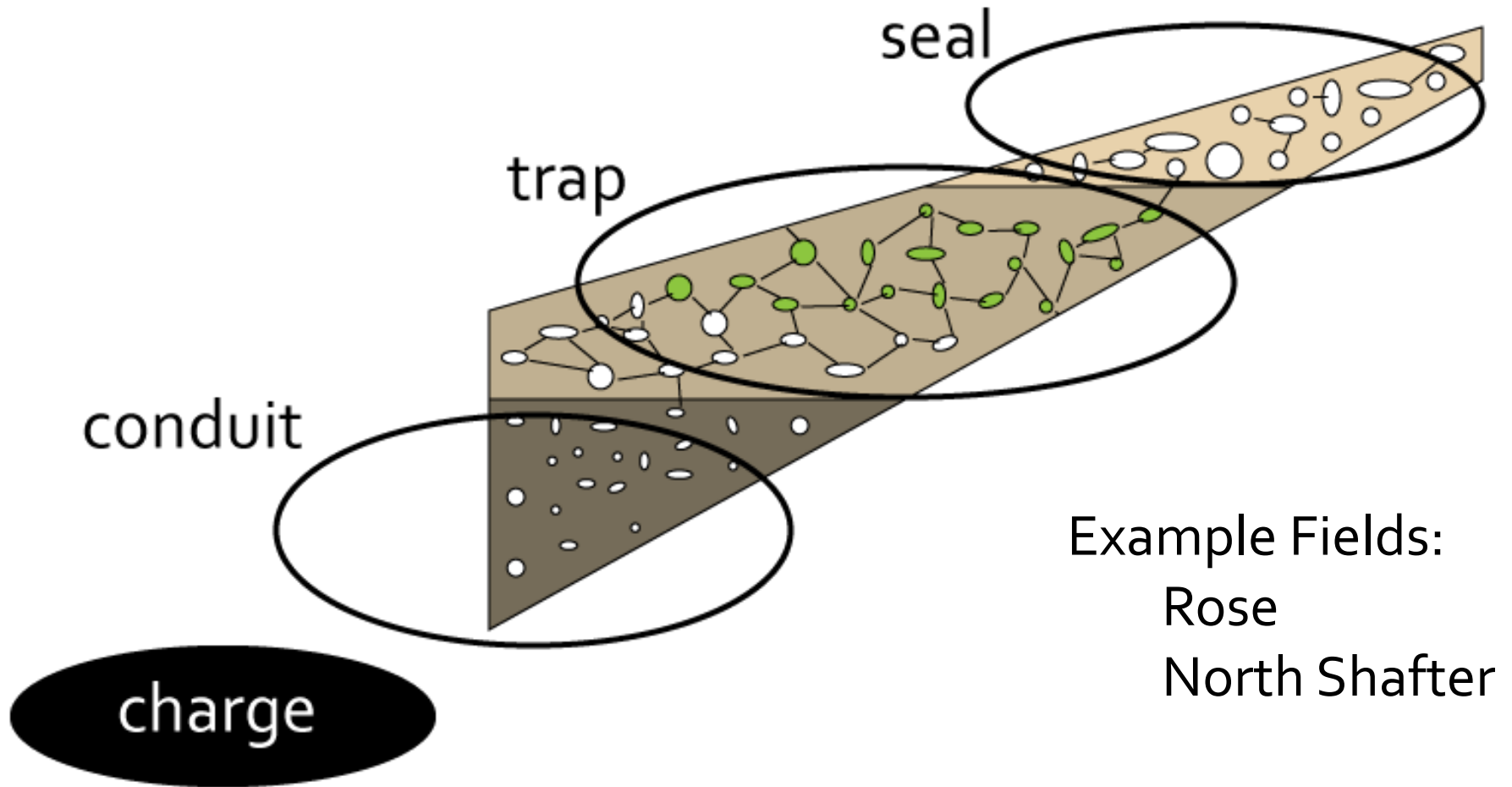
Phase changes affect HC trapping

Diagenetic traps can form within a depositional layer



Phase changes affect HC trapping

Diagenetic traps can form within a depositional layer



Variable silica phase transitions



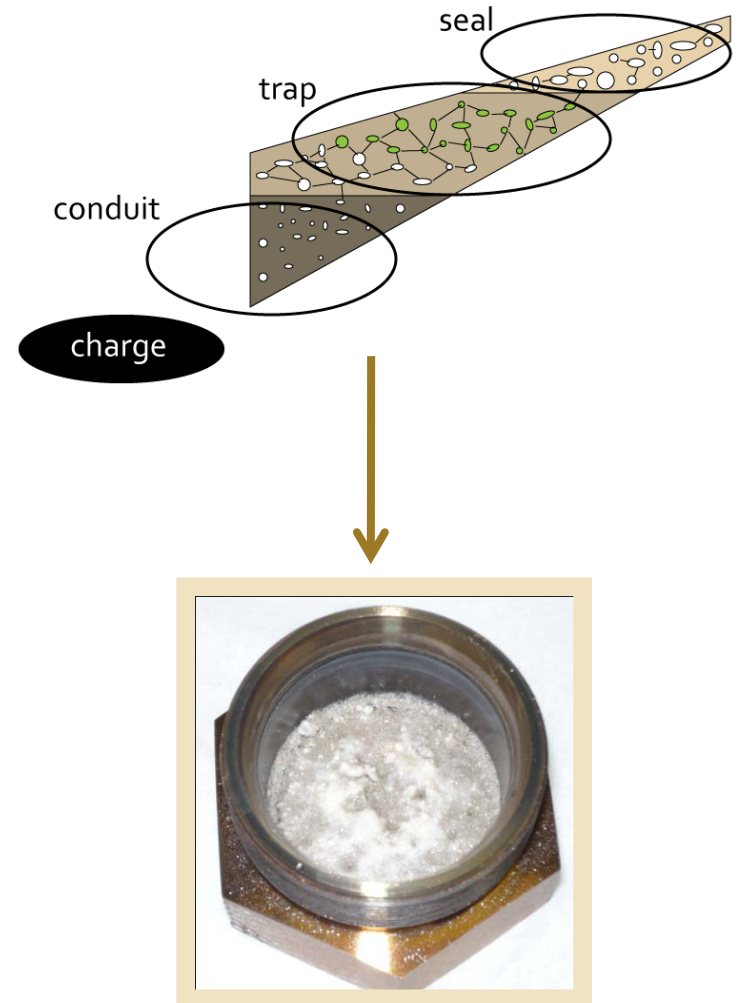
Chico Martinez Creek; Courtesy of R. Behl, CSULB



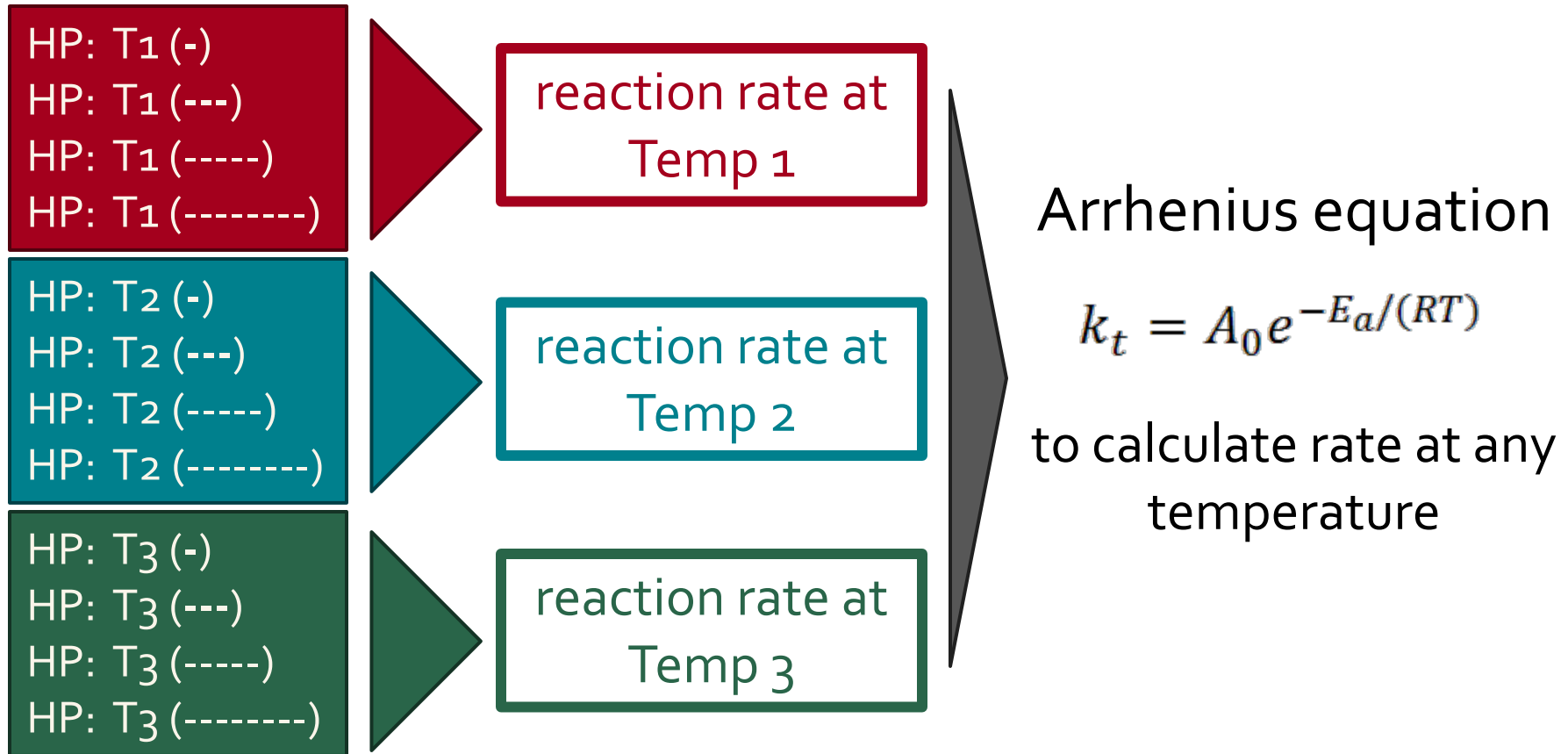
Monterey Fm. chert, cored

Field to laboratory

- If you want to predict this type of diagenetic trapping in your basin modeling, you need kinetics for the reaction.
- To the laboratory!
- We use hydrous pyrolysis to determine these kinetics.

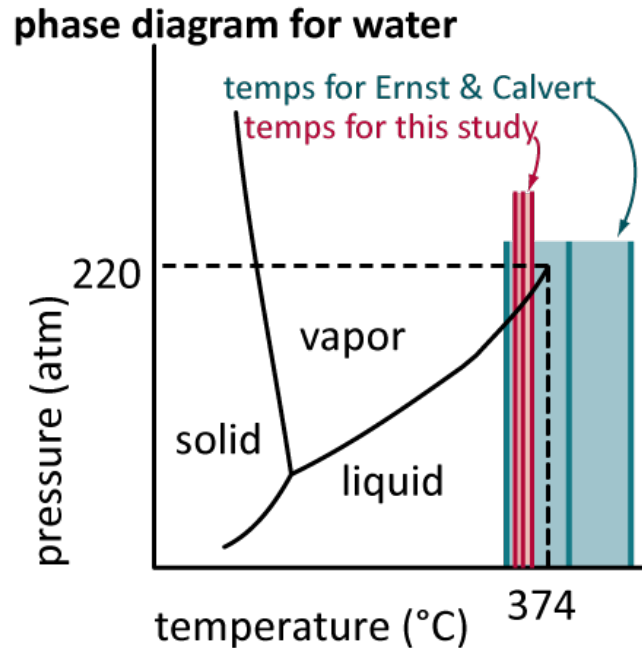


Kinetics from hydrous pyrolysis (HP)



Comparing experimental conditions

This study



- 310, 333, 360 °C
- buffered aqueous solution
- grain size 177-250 μm
- Lompoc, CA

Ernst & Calvert (1969)



- 300, 400, 500 °C
- distilled water
- grain size “fine”
- San Luis Obispo, CA

Porcelanite from Monterey Fm.



Experiments

assemble



cook

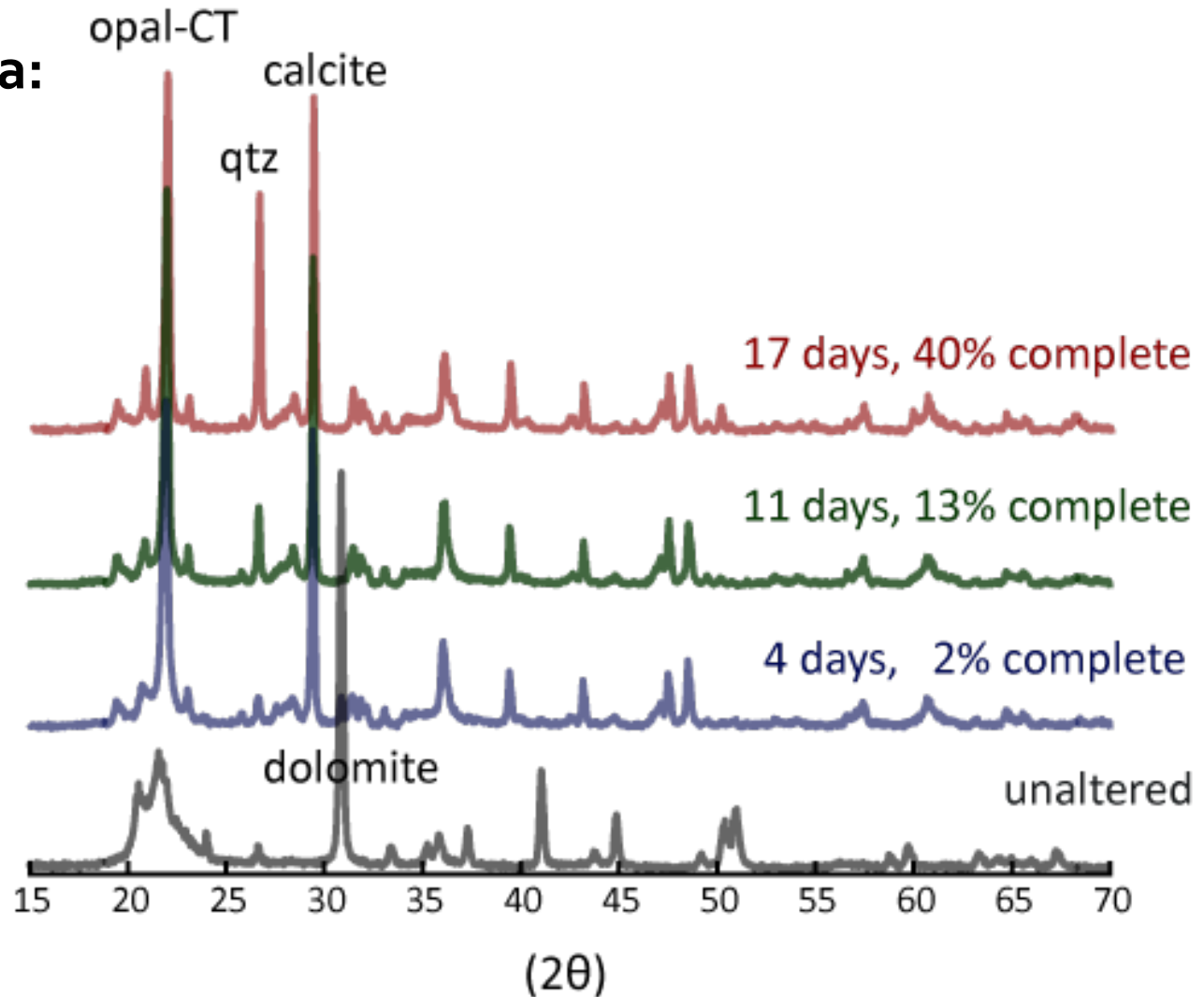


recover

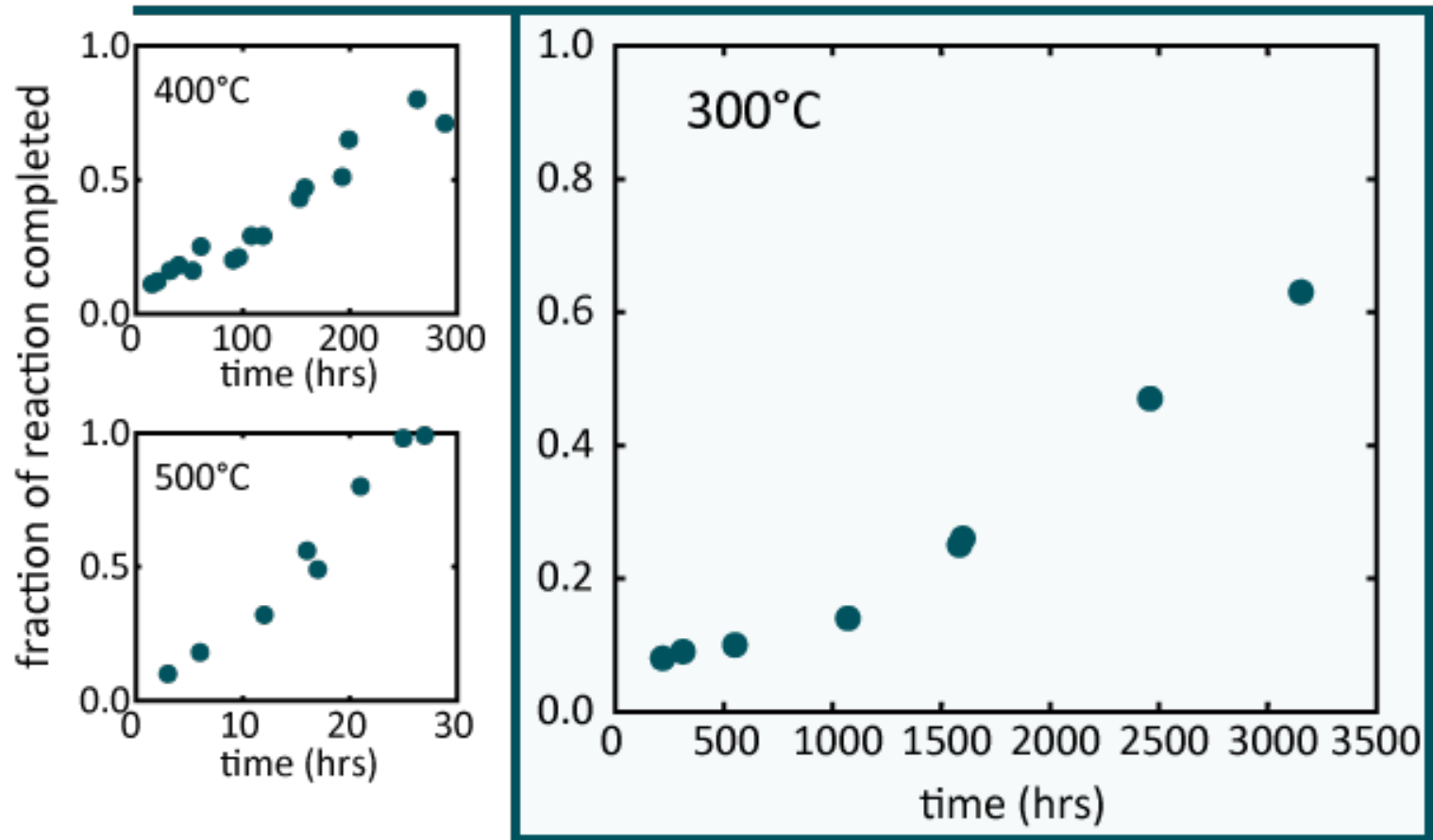


XRD gives converted fraction

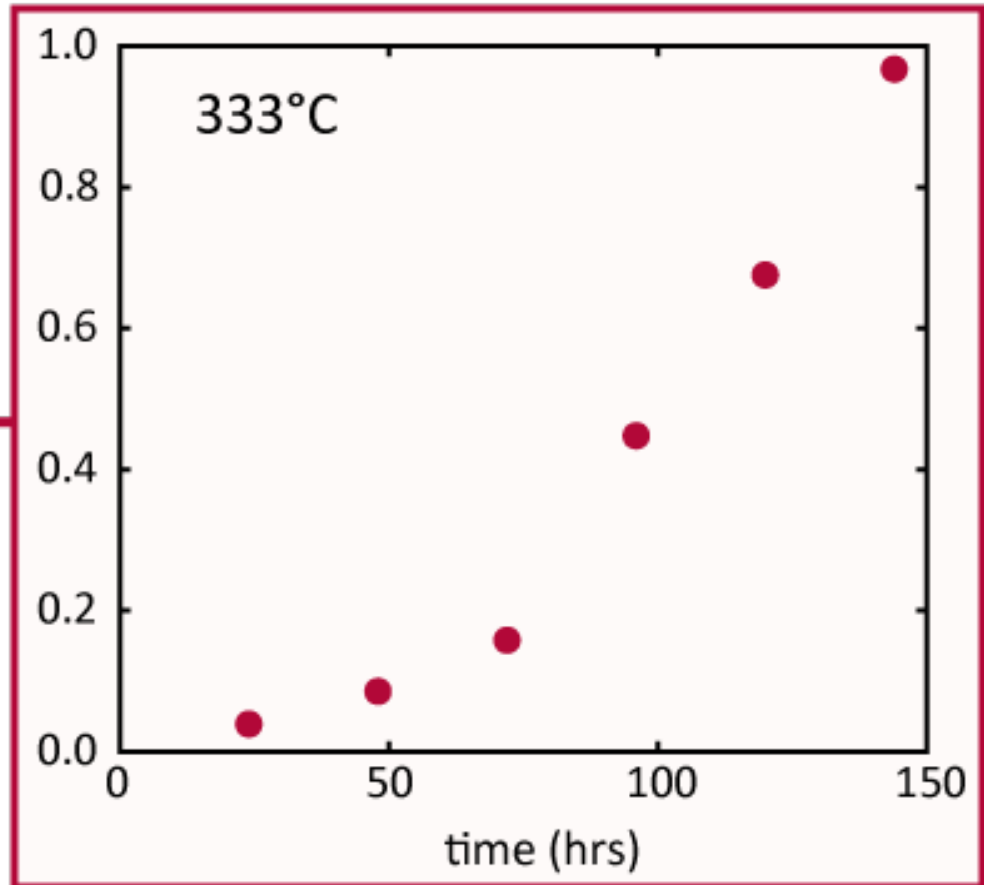
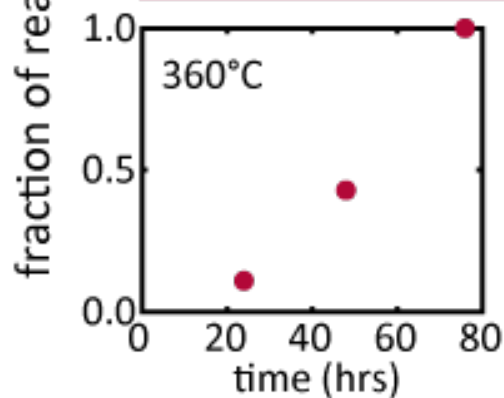
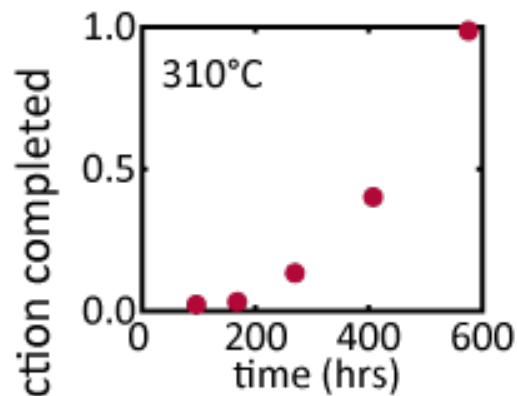
Sample spectra:
310°C



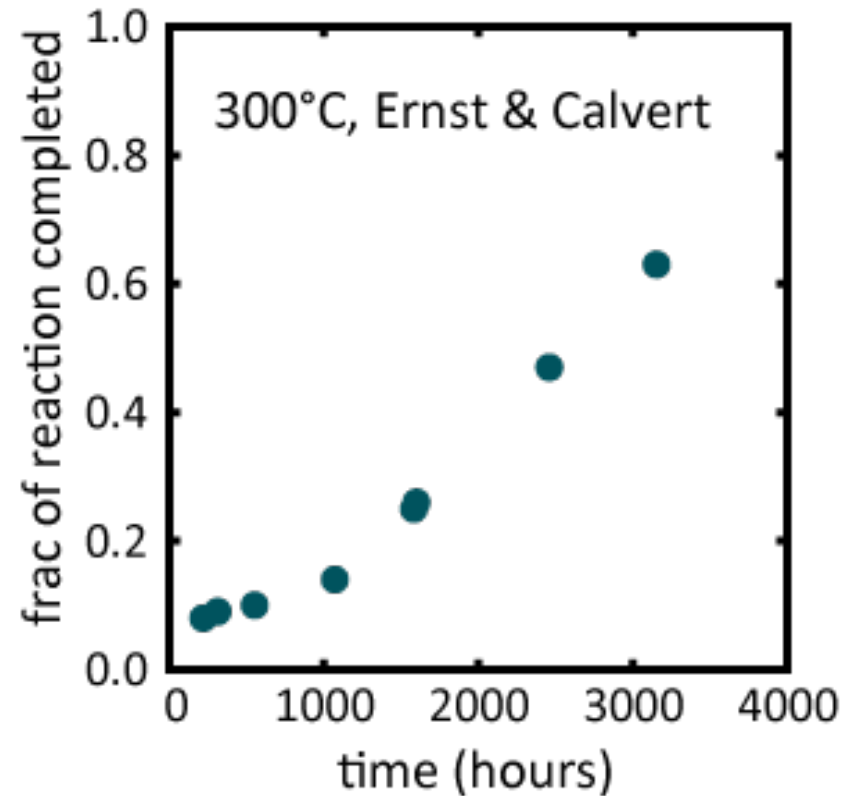
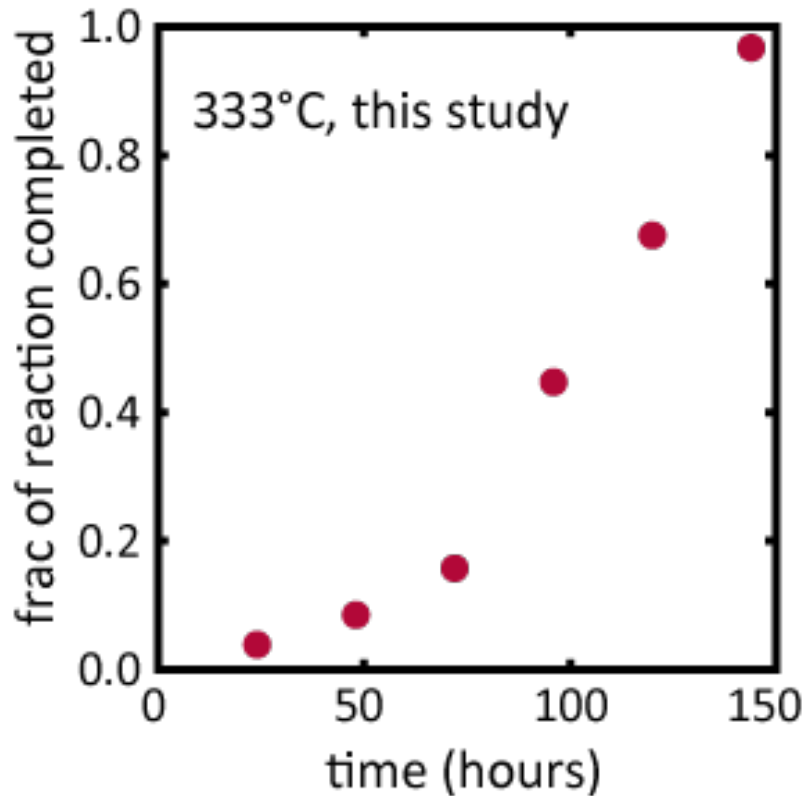
Ernst & Calvert data



This study's data

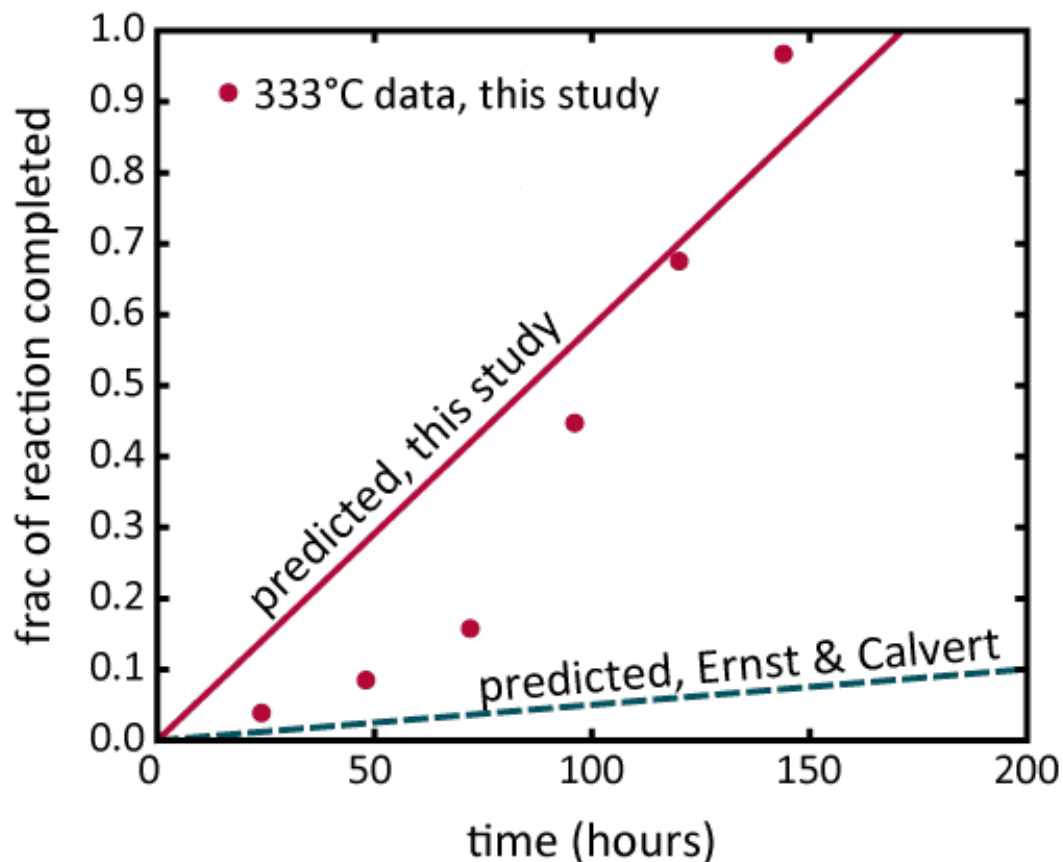


Data show changed conversion rate



- Does the reaction speed up?
- If so, why?

Comparing kinetic parameters



kinetic parameters

this study:

$$A_0 = 4.84 \times 10^7 \text{ hr}^{-1}$$

$$E_a = 27.49 \text{ kcal/mol}$$

Ernst & Calvert:

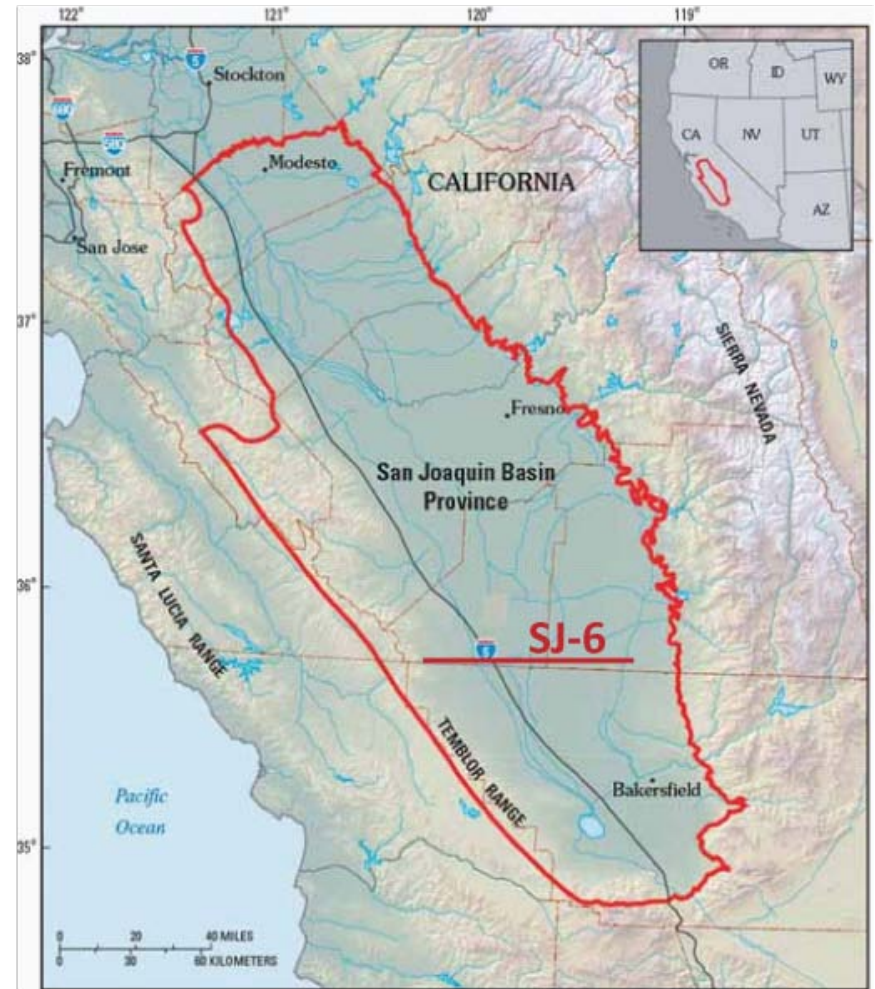
$$A_0 = 0.0134 \times 10^7 \text{ hr}^{-1}$$

$$E_a = 23.36 \text{ kcal/mol}$$

That's well and good, but...

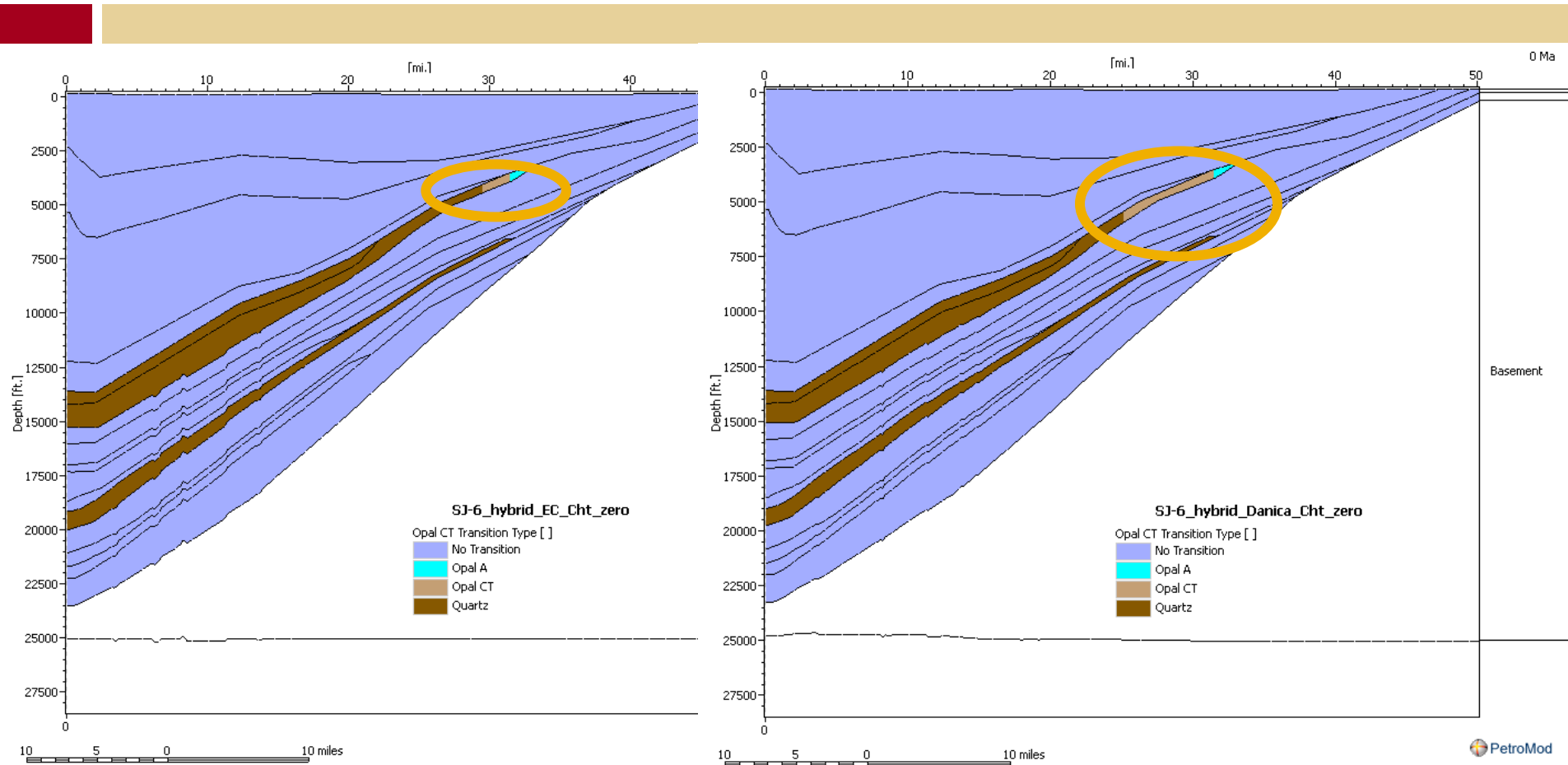
does this really affect
a petroleum system
model?

Example:
SJ-6 line in the
San Joaquin Basin, CA



Peters et al. (2008); Bloch (1991)

Opal-CT layer persists



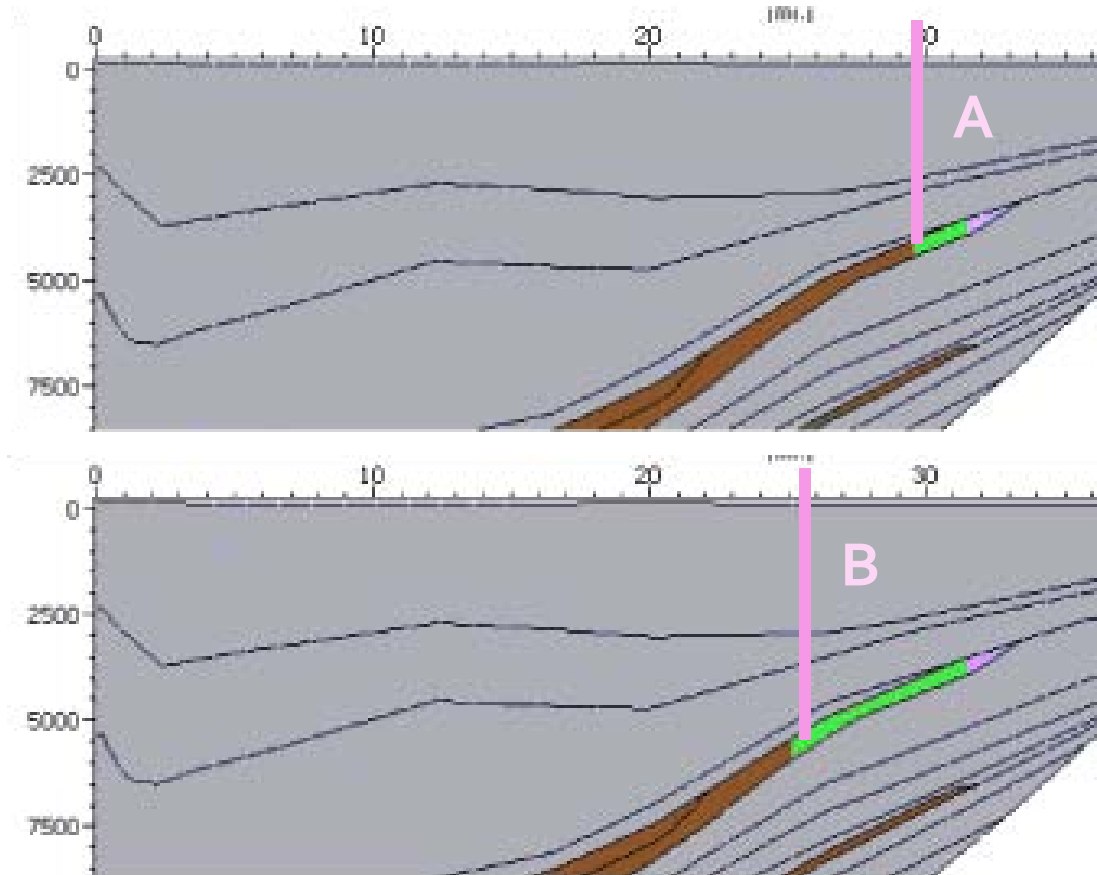
Ernst & Calvert

this study

San Joaquin Basin

Well locations change

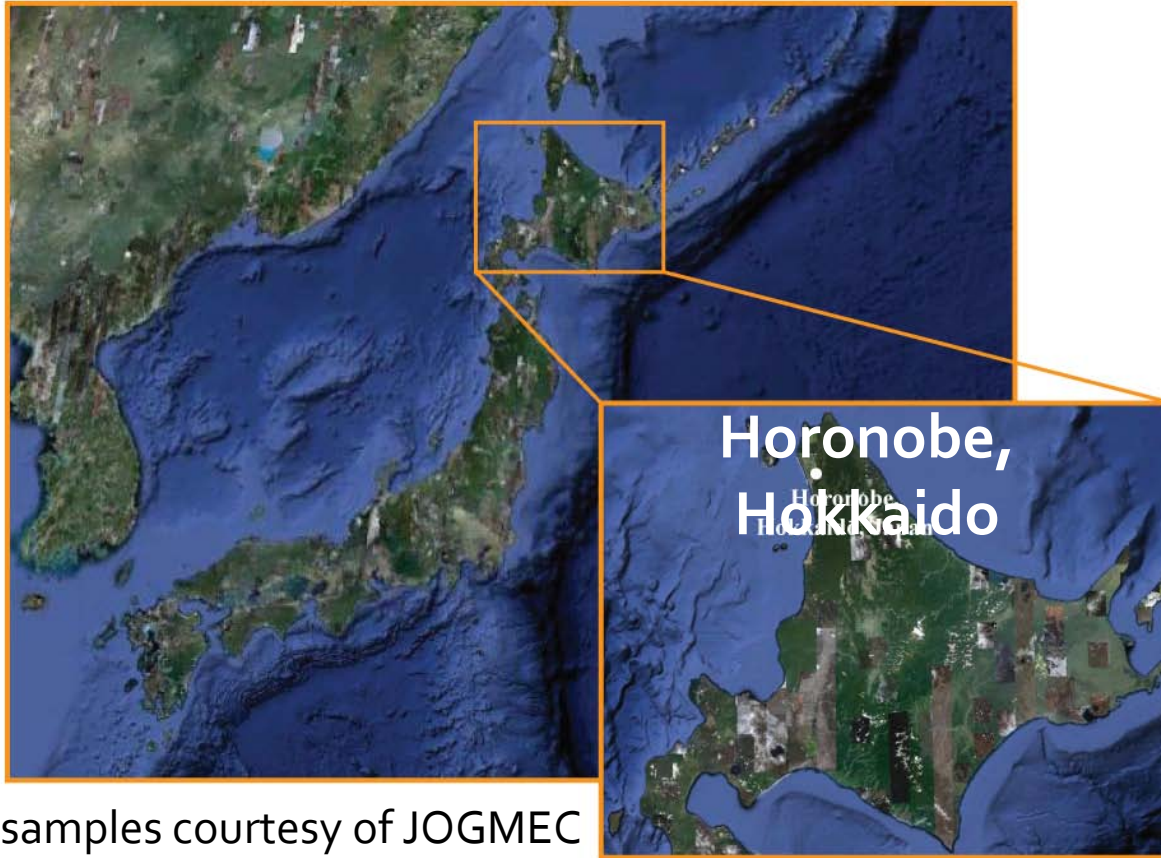
this study Ernst & Calvert



Well A
30 miles
4000 feet depth

Well B
35 miles
5500 feet depth

And other basins?



samples courtesy of JOGMEC



No detected transformation in Wakkanai Fm
samples from Horonobe, Hokkaido, Japan

Conclusions



- Phase transitions in minerals affect petroleum **trapping** and **migration** (storage and transport).
- Basin models are sensitive to kinetic parameters.
- Kinetics customized to a basin may be required until all controlling mechanisms for the reaction are understood.

Acknowledgements



- Stanford Basin and Petroleum System Modeling industrial affiliates
- Stanford Rock Physics and Borehole Geophysics industrial affiliates
- Bill Benzel (USGS, Denver)