

Kinetics of the Opal-A to Opal-CT Phase Transition in Low- and High-TOC Siliceous Shale Source Rocks*

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Search and Discovery Article #41708 (2015)**

Posted October 26, 2015

*Adapted from oral presentation given at AAPG Annual Convention & Exhibition, Denver, Colorado, May 31-June 3, 2015. Please see closely related article, "[Kinetics of the Opal-CT to Quartz Phase Transition Control Diagenetic Traps in Siliceous Shale Source Rock from the San Joaquin Basin and Hokkaido](#)", Search and Discovery article #40771.

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Abstract

Marine diatoms deposit biogenic silica as amorphous opal-A. These deposits interact with saturating aqueous solutions, transforming to microcrystalline opal-CT and eventually quartz through a series of dissolution and precipitation reactions. The mineralogical changes cause corresponding changes in rock properties such as porosity, permeability, and acoustic response. The enhanced permeability and preserved porosity during these transitions may result in formation of diagenetic hydrocarbon traps. Successful exploitation of diagenetic traps in oil and gas exploration requires an understanding of how quickly these phase transitions occur and how natural variations in rock composition affect the transition rates.

In this study, the kinetics of the opal-A to opal-CT phase transition were determined through a series of hydrous pyrolysis experiments. Two diatomite samples from the Miocene Monterey Formation, California were used, both from the same pedogenic weathering profile. The samples each comprise approximately 80 wt% opal-A, 10 wt% phyllosilicates, and 6 wt% quartz. However, they have different amounts of TOC (0.36 wt% and 4.65 wt%) and contain a thermally mature Type II kerogen. The samples were mixed with a buffered aqueous solution that ensured the fluid maintained pH 7 or greater, and the mixtures were pyrolyzed at multiple temperatures between 280°C and 330°C. The pyrolysis experiments sampled the transition

from opal-A to opal-CT and showed that the conversion in the high-TOC sample was significantly delayed compared to the low-TOC sample at the same temperature. Data at multiple temperatures were combined to determine the activation energy and pre-exponential factor for the conversion of each of the two samples. These kinetics data, combined with knowledge of the local thermal history, allow prediction of the opal-A to opal-CT transition depth in a basin. The estimated transition depth can then be used to predict diagenetic trap locations or identify mineralogical sources of cross-cutting reflectors in seismic data. Low-TOC kinetics provide a baseline for these estimates, whereas high-TOC kinetics demonstrate the extent to which organic material affects the reaction rate in source rocks.

Kinetics of the opal-A to opal-CT phase transition in low- and high-TOC siliceous shale source rocks

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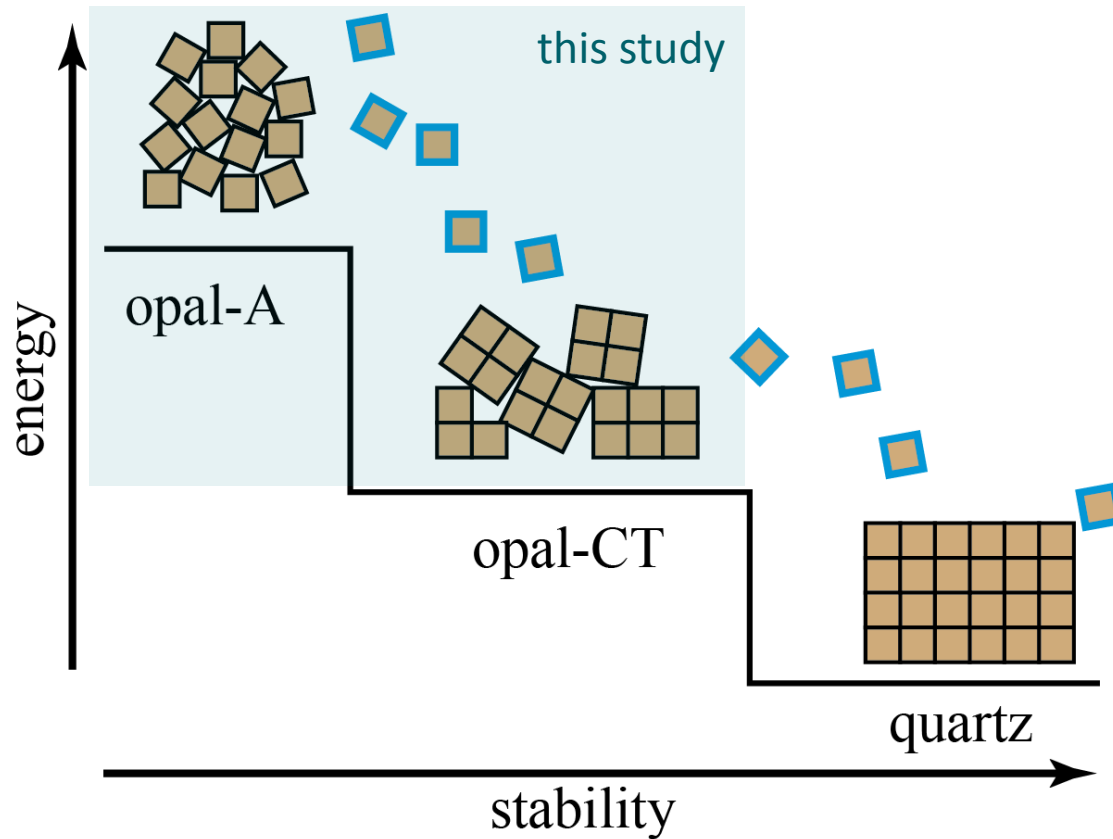
June 2, 2015

Denver, CO

Outline

- Silica phase transitions in the oil patch
- Hydrous pyrolysis experiments
- Opal-A to opal-CT phase transition kinetics data
- Extrapolation to geologic time
- Conclusions

Siliceous deposits undergo phase transitions.



Opal-A is **amorphous** and easy to dissolve.

Opal-CT is **microcrystalline**.

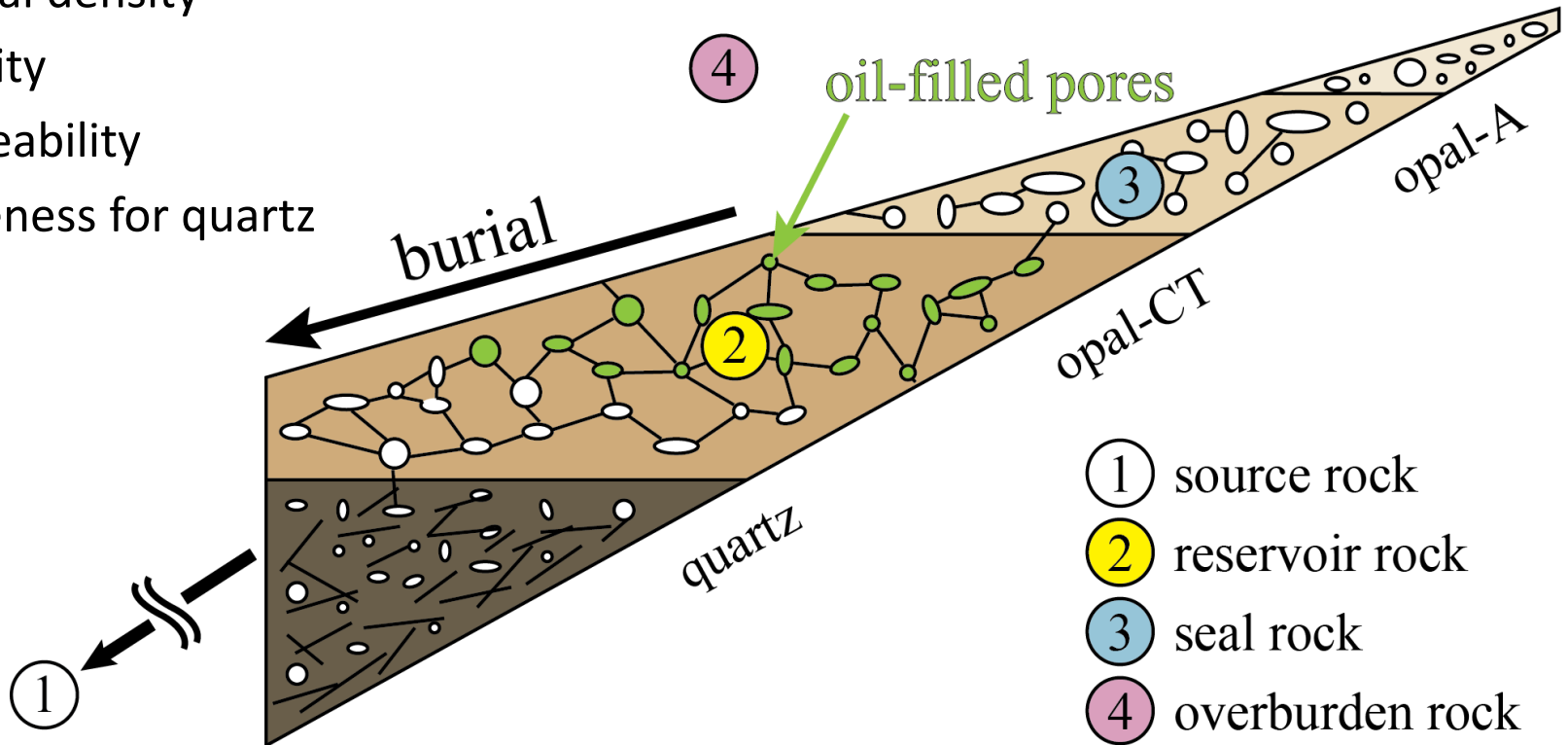
Quartz is fully **crystalline** and hard to dissolve.

They are all polymorphs of SiO_2 .

Phase transitions can result in diagenetic traps for petroleum.

Phase transitions can increase:

- mineral density
- porosity
- permeability
- brittleness for quartz



This is a known trapping feature in the San Joaquin Basin.

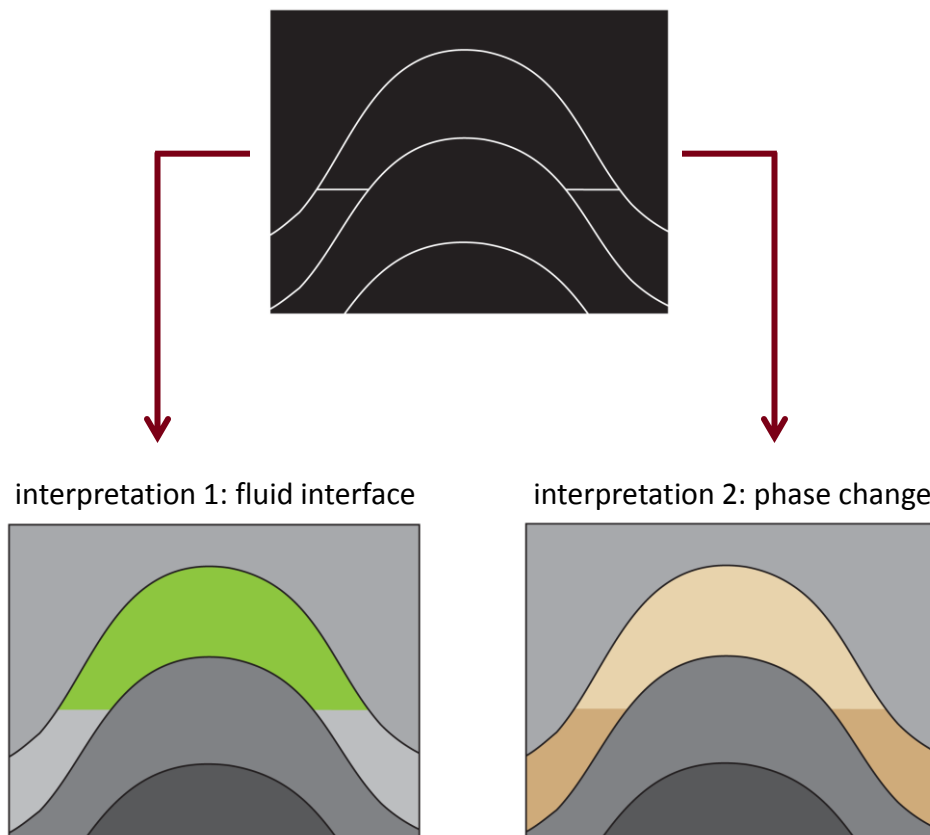
Finding diagenetic traps with seismic data is tricky.

Resolution



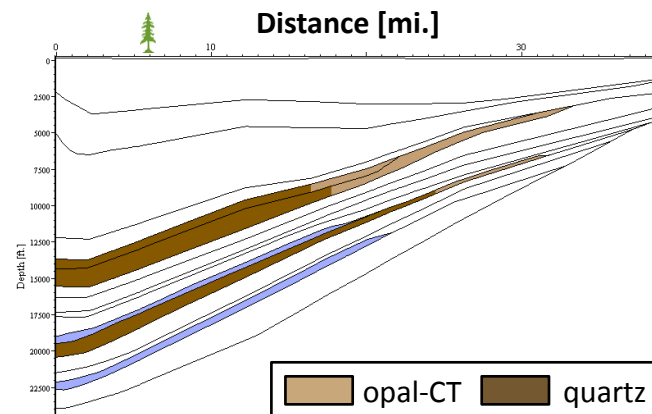
Chico Martinez Creek; Courtesy of R. Behl, CSULB

Interpretation



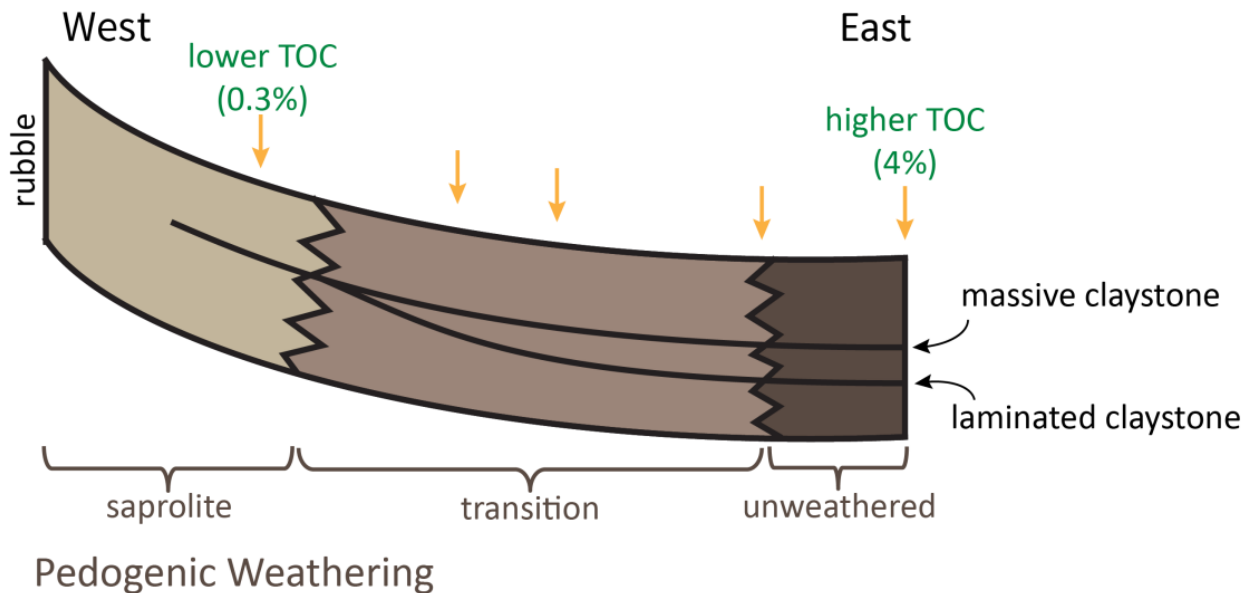
Our objective: estimate silica phase transition depths

- **Goal:** predict transition depths and their timing relative to petroleum generation
- **Tool:** predictive geochemistry
 - hydrous pyrolysis experiments (kinetics)
 - kinetics for opal-CT to quartz transition (previous work)
 - kinetics for low-TOC opal-A to opal-CT transition
 - kinetics for high-TOC opal-A to opal-CT transition



Experiments focused on the opal-A to opal-CT transition.

- Monterey Fm. samples from quarry at Lompoc, CA
- Samples were from a single 3 cm thick massive claystone bed with varying TOC resulting from pedogenic (i.e., soil forming) weathering.



Organic richness decreased systematically with increasing pedogenic weathering.

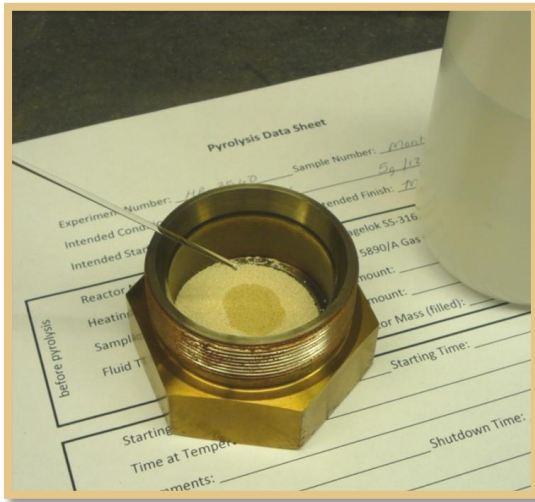


| | | | | | | | | |
|-------------------------------------|------|------|------|------|------|------|------|------|
| TOC (wt% HC) | 0.36 | 1.38 | 2.62 | 2.20 | 3.83 | 4.65 | 4.73 | 4.83 |
| HI (S ₂ x100/TOC) | 213 | 246 | 317 | 271 | 318 | 351 | 401 | 414 |
| Tmax (°C) | 390 | 406 | 402 | 400 | 392 | 386 | 385 | 388 |

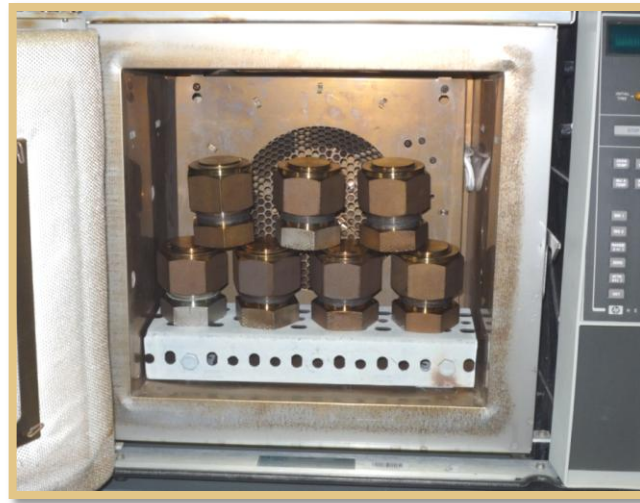
~10% phyllosilicates

Kinetics should reflect phase transitions in the subsurface.

- natural samples (w/ natural contaminants)
- plenty of fluid to circulate
- buffered aqueous solution to maintain high fluid pH (pH 7.0 – 7.5 after pyrolysis)



assemble

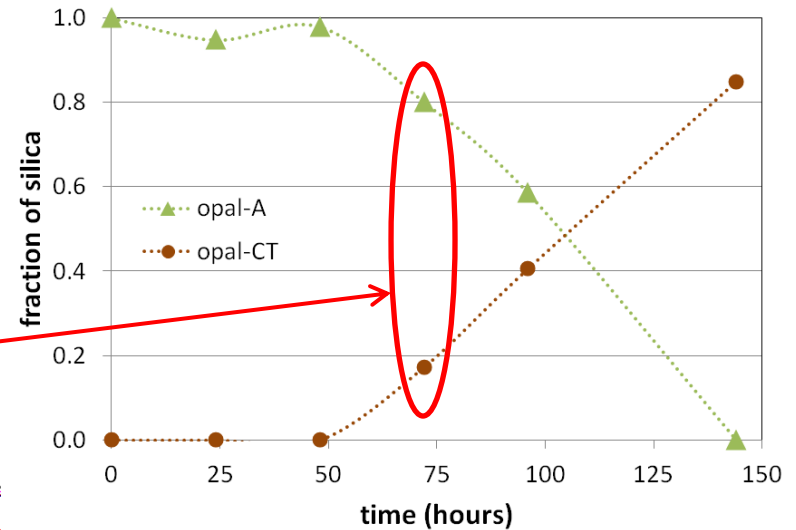
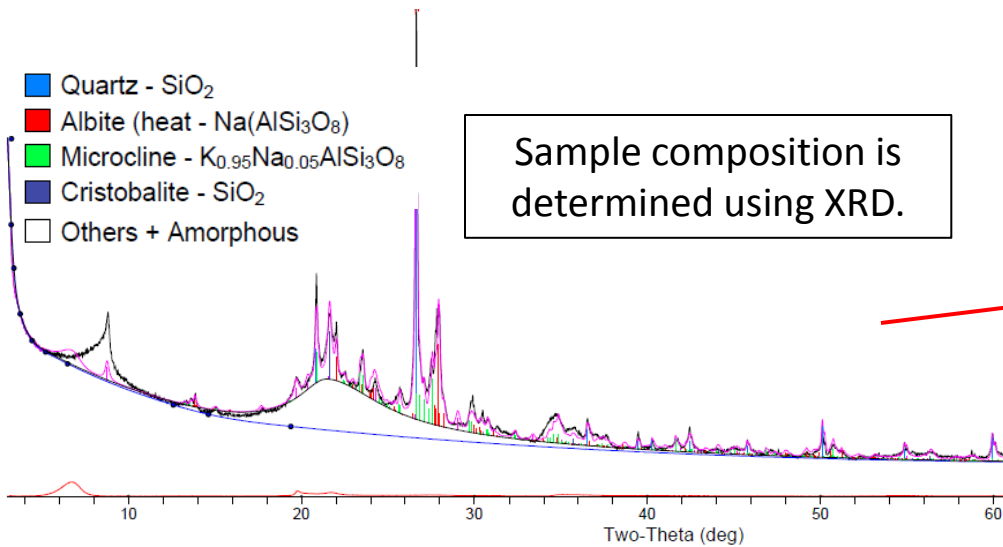


cook

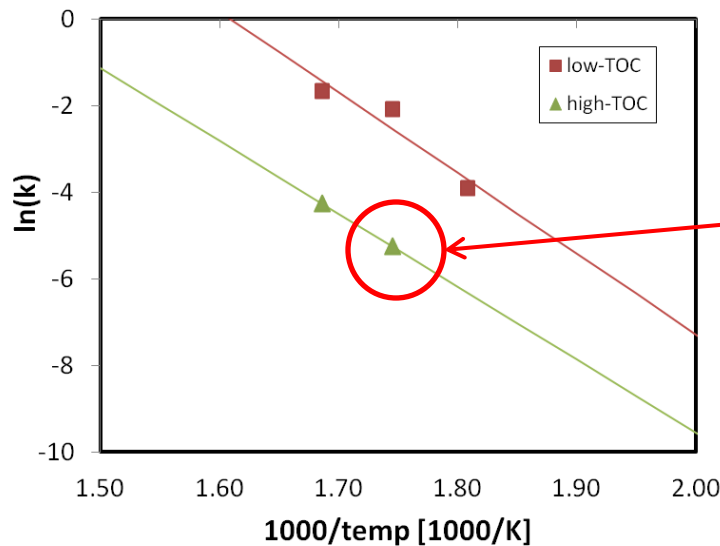


recover

Reaction rate is determined using XRD spectra and isothermal-kinetics models.



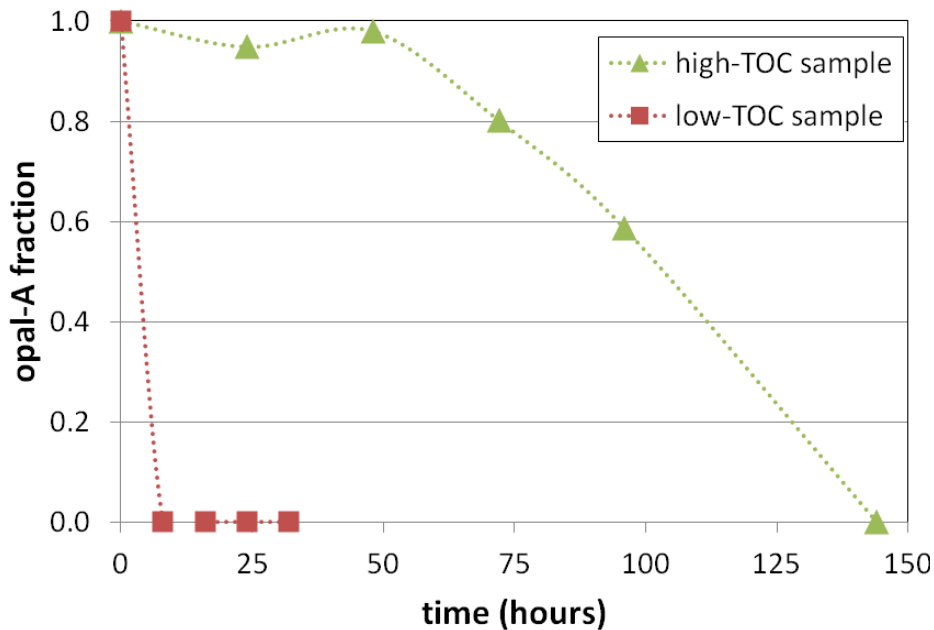
Arrhenius plot of reaction rate vs temperature gives E_a (slope) and A_0 (intercept).



Reaction is modeled as a function of time to determine the reaction rate.

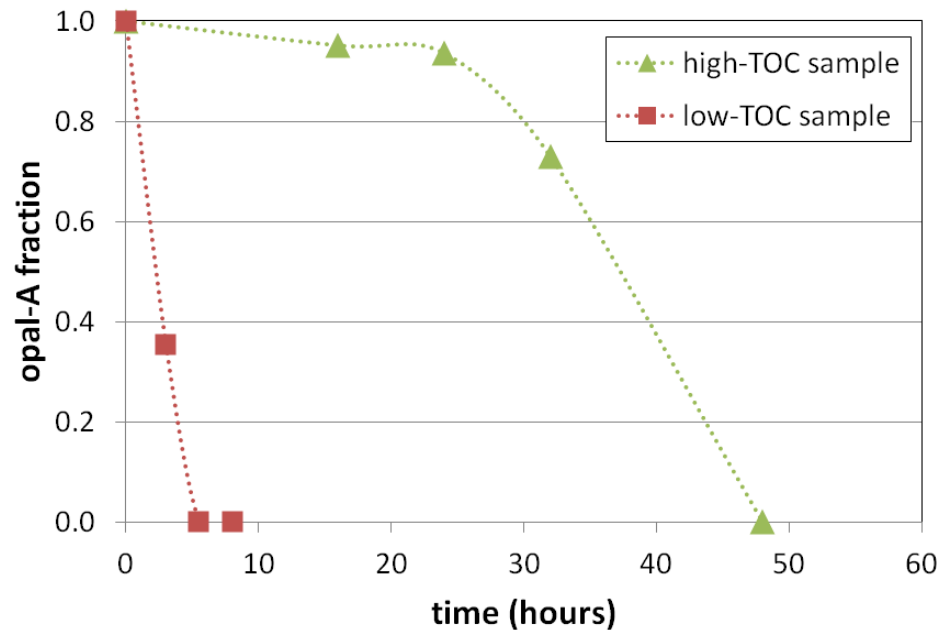
Low-TOC samples react faster than high-TOC samples.

pyrolysis at 300 °C



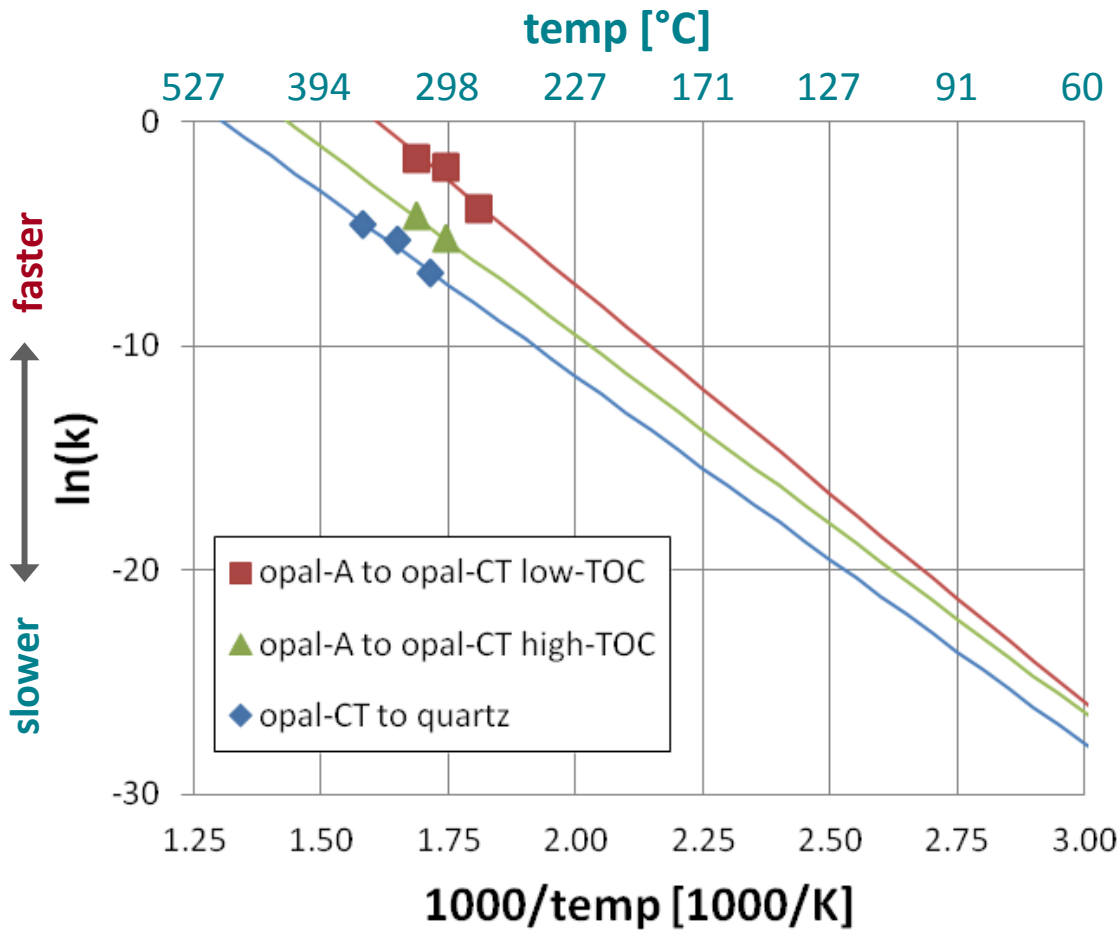
opal-A is gone within 8 hours vs. 144 hours

pyrolysis at 320 °C



opal-A is gone within 8 hours vs. 48 hours

Arrhenius equation predicts the reaction rate at any temperature.



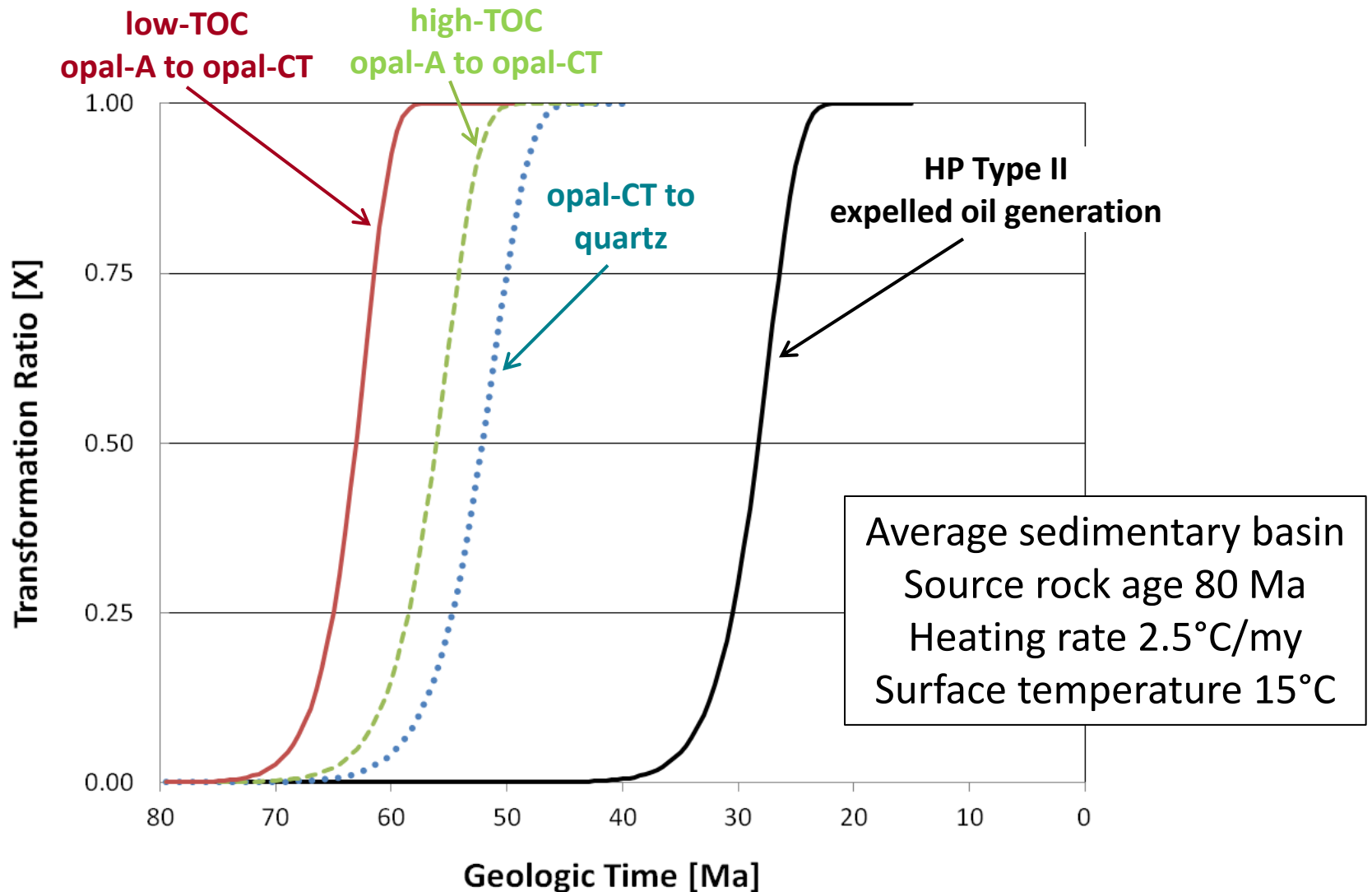
Rate constant at any temperature is:

A_0 pre-exponential factor
 E_a activation energy

$$k_T = A_0 \exp \left\{ -\frac{E_a}{RT} \right\}$$

| | E_a [kcal/mol] | A_0 [1/hr] |
|----------------------------|---------------------|-----------------------|
| opal-A to opal-CT low-TOC | 36.99 | 1.04×10^{14} |
| opal-A to opal-CT high-TOC | 33.44 | 3.01×10^{10} |
| opal-CT to quartz | 32.52 | 1.96×10^9 |

Silica diagenesis occurs before oil generation.



Summary

- Organic matter slows the conversion of opal-A to opal-CT and opal-CT to quartz (previous work), and as a result, slows the potential for increasing porosity, permeability, and brittleness.
- Different kinetics are required for silica diagenesis of high- and low-TOC rocks for determining timing and depth of optimum reservoir properties.
- The potential for silica diagenesis to generate higher porosity, permeability, and brittleness occurs long before oil generation is initiated.
- Additional experimental work is needed to better define the kinetics of silica diagenesis to more accurately predict diagenetic trap attributes in basin modeling.

Acknowledgements

- Stanford Basin and Petroleum System Modeling (BPSM) Industrial Affiliate Program for funding and support
- James Talbot (K-T GeoServices, Inc.) for detailed XRD analysis
- Bill Betterton and Bill Benzel (USGS) for preliminary XRD analysis
- Caroline Isaacs and John Ralston for sample collection