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

Danica Dralus¹, Kenneth E. Peters², Mike D. Lewan³, Oliver Schenk⁴, Michael Herron⁵, and Kunihiro Tsuchida⁶

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¹Stanford University, Stanford, CA (dralus@stanford.edu)
²Schlumberger, Mill Valley, CA
³U.S. Geological Survey, Denver, CO
⁴Schlumberger, Aachen, Germany
⁵Schlumberger, Cambridge, MA
⁶Japan Oil, Gas and Metals Corporation, Chiba, Japan

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


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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

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

porosity
permeability
acoustic velocities
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

Example Fields:
Rose
North Shafter
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)

Arrhenius equation

\[ k_t = A_0 e^{-\frac{E_a}{RT}} \]

to calculate rate at any temperature
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

**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
San Joaquin Basin

this study
Well locations change

Well A
- 30 miles
- 4000 feet depth

Well B
- 35 miles
- 5500 feet depth
And other basins?

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

samples courtesy of JOGMEC
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.
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