# Diagenetic and Compositional Controls of Wettability in Siliceous Sedimentary Rocks, Monterey Formation, California*

**Kristina M. Hill[1] and Richard J. Behl[2]**

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## Abstract

Modified imbibition tests were performed on 69 subsurface Monterey Formation reservoir samples from the San Joaquin Valley to measure wettability variation as a result of composition and silica phase change. Contact angle tests were also performed on 6 chert samples from outcrop and 3 nearly pure mineral samples. Understanding wettability is important because it is a key factor in reservoir fluid distribution and movement, and its significance rises as porosity and permeability decrease and fluid interactions with reservoir grain surface area increase. Low permeability siliceous reservoirs of the Monterey Formation are economically important and prolific, but a greater understanding of factors that alter their wettability will help better develop them. Subsurface reservoir samples from 3 oil fields were crushed to eliminate the effect of capillary pressure and cleansed of hydrocarbons to eliminate wettability alterations by asphaltene, then pressed into discs of controlled density. Powder discs were tested for wettability by dispensing a controlled volume of water and motor oil onto the surface and measuring the time required for each fluid to imbibe into the sample. The syringe and software of a CAM101 tensiometer were used to control the amount of fluid dispensed onto each sample, and imbibition completion times were determined by high-speed photography for water drops; oil drop imbibition was significantly slower and imbibition was timed and determined visually. Contact angle of water and oil drops on polished chert and mineral sample surfaces was determined by image analysis and the Young-Laplace equation. Oil imbibition was significantly slower with increased detrital composition and faster with increased silica content in opal-CT and quartz phase samples, implying decreased wettability to oil with increased detrital (clay) content. However, contact angle tests showed that opal-CT is more wetting to oil with increased detritus and results for oil on quartz-phase samples were inconsistent between different proxies for detritus over their very small compositional range. Water contact angle trends also showed inconsistent wetting trends compared to imbibition tests. We believe this is because the small range in detrital composition between the “pure” samples used in contact angle tests was close to analytical error. These experiments show that compositional variables significantly affect wettability, outweighing the effect of silica phase.

## References Cited

Abdullah, W., J.S. Buckley, A. Carnegie, J. Edwards, B. Herold, E. Fordham, A. Graue, T. Habashy, N. Seleznev, C. Signer, H. Hussain, B. Montaron, and M. Ziauddin, 2007, Fundamentals of Wettability: Schlumberger Oilfield Review, v. 19/2, p. 44-61.

Civan, F., 2004, Temperature Dependence of Wettability Related Rock Properties Correlated by the Arrhenius Equation: Petrophysics, v. 45/4, p. 350-362.

Hirasaki, G.J.S., 1991, Wettability: Fundamentals and Surface Forces: SPE Formation Evaluation, v. 6/3, p. 217-226.

Isaacs, C.M., 1980, Diagenesis in the Monterey Formation Examined Laterally along the Coast near Santa Barbara, California: USGS Open-File Report 80-606, 343 p.

Karabakal, U., and S. Bagci, 2004, Determination of Wettability and its Effect on Waterflood Performance in Limestone Medium: Energy & Fuels, v. 18/2, p. 438-449.

## Website Cited

http://www.uws.ac.uk/research/research-institutes/science/eirg/geosciences/

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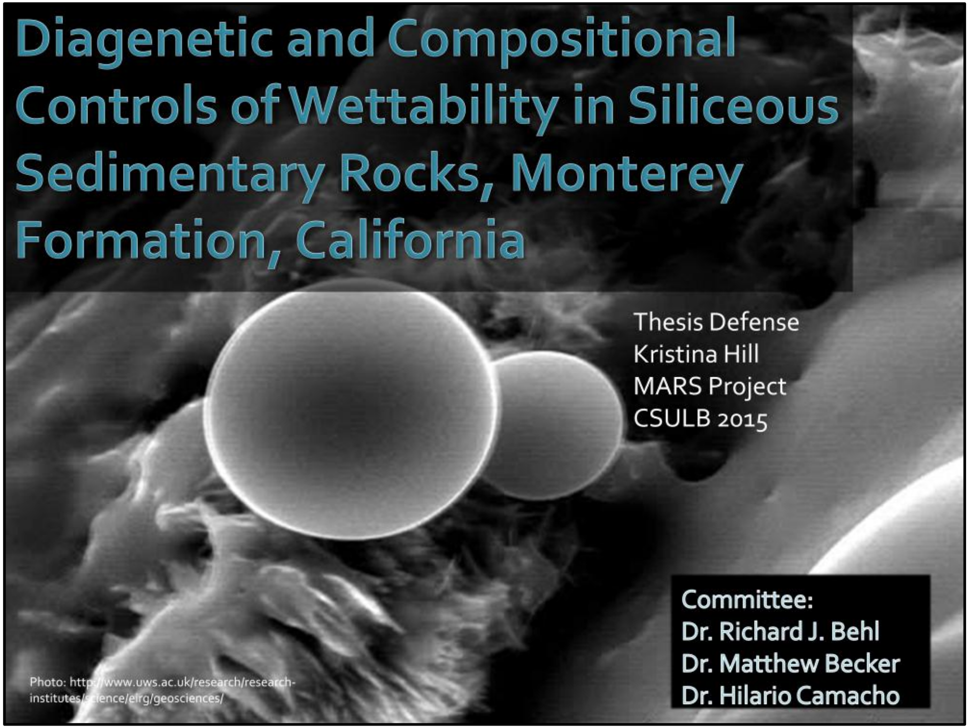


Thesis Defense
Kristina Hill
MARS Project
CSULB 2015

**Committee:**
**Dr. Richard J. Behl**
**Dr. Matthew Becker**
**Dr. Hilario Camacho**

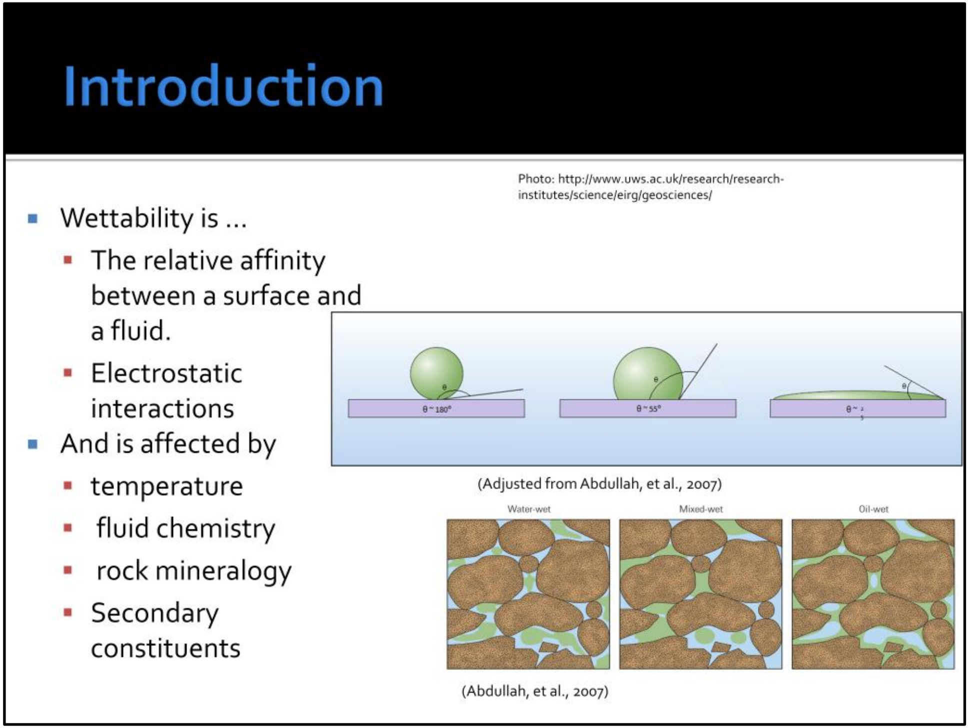
Photo: http://www.uws.ac.uk/research/research-institutes/science/eirg/geosciences/

# Overview

- Experiment Objective
- Introduction
  - Review of Wettability
  - Importance of Project
- Methods
- Results & Discussion
- Conclusions
- Future Work

# Objective

- Identify and quantify alteration in wettability of siliceous rocks due to silica diagenesis
- Characterize and quantify alteration in siliceous rock wettability due to abundance of detritus



# Introduction

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- Wettability is …
  - The relative affinity between a surface and a fluid.
  - Electrostatic interactions
- And is affected by
  - temperature
  - fluid chemistry
  - rock mineralogy
  - Secondary constituents

(Adjusted from Abdullah, et al., 2007)

(Abdullah, et al., 2007)

Presenter's notes: Wettability is demonstrated in a fluids propensity to spread or bead on a surface the product of the hydrostatic intermolecular interactions between the rocks and a fluid phase (Hirasaki, 1991, as cited in Civan, 2004).

Wettability affectslocation, flow, and fluid distribution in a reservoir (Karabakal and Bagci, 2004).

Environmental SEM image of water droplets on kaolinite (spherical droplets, left) and quartz (low dome droplets, right) in sandstone, showing contrasting wetting characteristics of different mineral surfaces (image created in collaboration with Heriot-Watt University Dept. of Petroleum Engineering ESEM facility).

# Introduction

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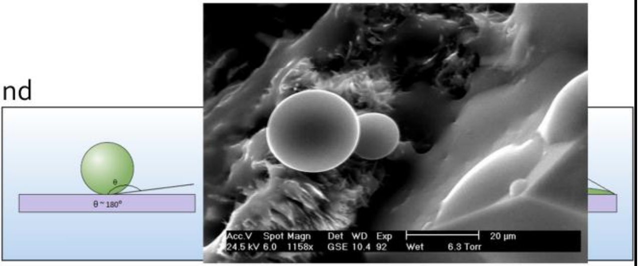

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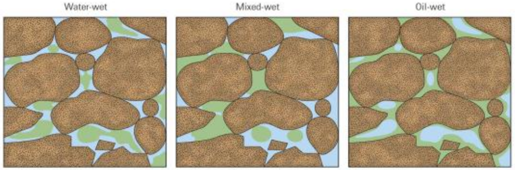

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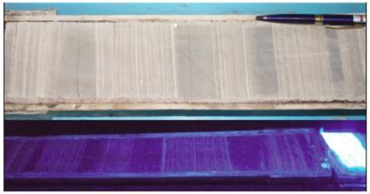
# Introduction

- Importance of project
  - Extensive reserves in Monterey
  - Still inefficiently exploited
  - Low permeability (quartz and opal-CT phase)
    - high surface area to volume ratio of reservoir fluids
    - More interaction between fluid and rock surface
  - Silica diagenesis expels water from crystal structure
    - may impact hydrocarbon distribution



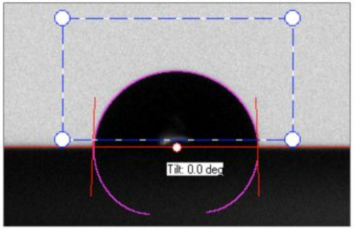
Presenter's notes:
- Silica diagenesis
- If the formation is losing polar molecules previously locked into the matrix crystal structure, the electrostatic interactions between the fluid and reservoir rock are likely to be affected.

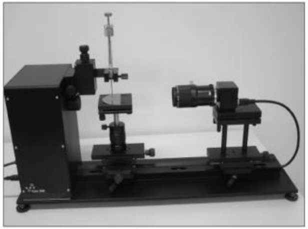
# Goals & Limitations

- Primary Goals:
  - Controlled wettability measurements on siliceous rocks of all 3 phases
- Limitations:
  - Low permeability opal-CT and quartz phase rocks rule out industry standard methods
  - Contact angle on pressed powder discs out – fluids imbibed
  - Lack of non-porous opal-A for contact angle
- Secondary Goals:
  - Eliminate differences in porosity and permeability between phases as variables
  - Eliminate *in situ* fluid chemistry as a variable

# Methods

- Imbibition Tests
  - Distilled $H_2O$
  - Castrol HD40 (after mineral oil)
  - 69 Core Samples
  - Controls:
    - Sample density (wt, size & compaction)
    - Fluid drop size

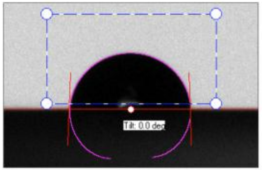




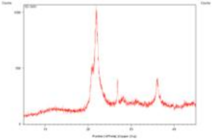
- Contact Angle Tests
  - Distilled $H_2O$
  - Castrol HD40
  - 6 chert samples (opal-CT & quartz)
  - 3 non-biogenic mineral samples
    - one from each phase

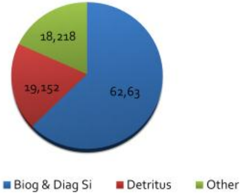
# Methods

- Wettability Measurements
  - Imbibition Rate
  - Contact Angle



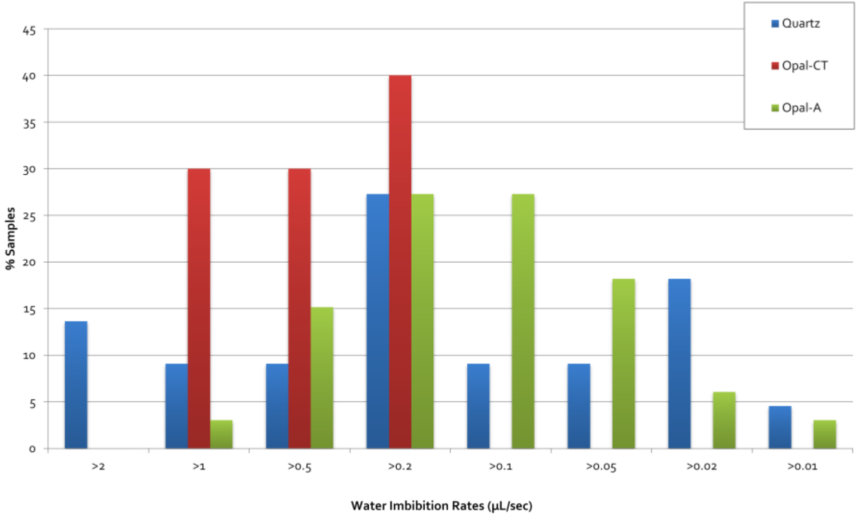
- Rock Composition
  - XRD – silica phase
  - ICP-MS & ICP-OES



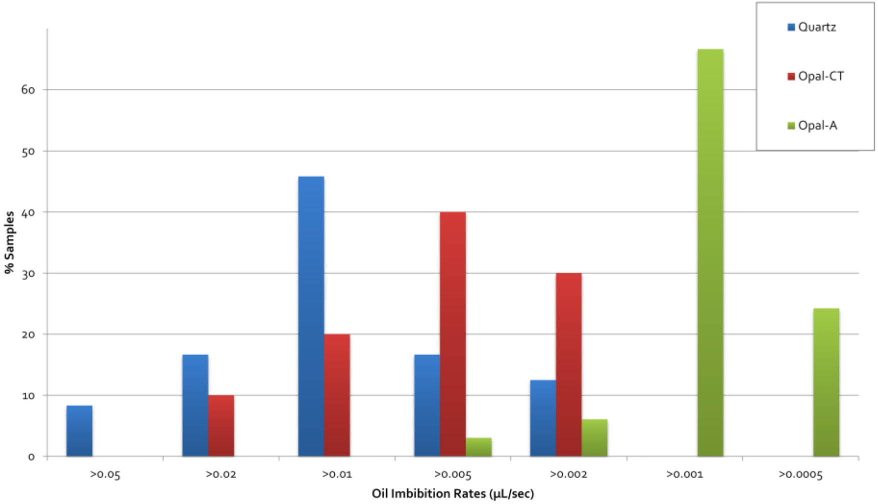


- Data Trends
  - Single Variable ($R^2$)
  - Multivariate Stats
    - PCA
    - Multiple Regression

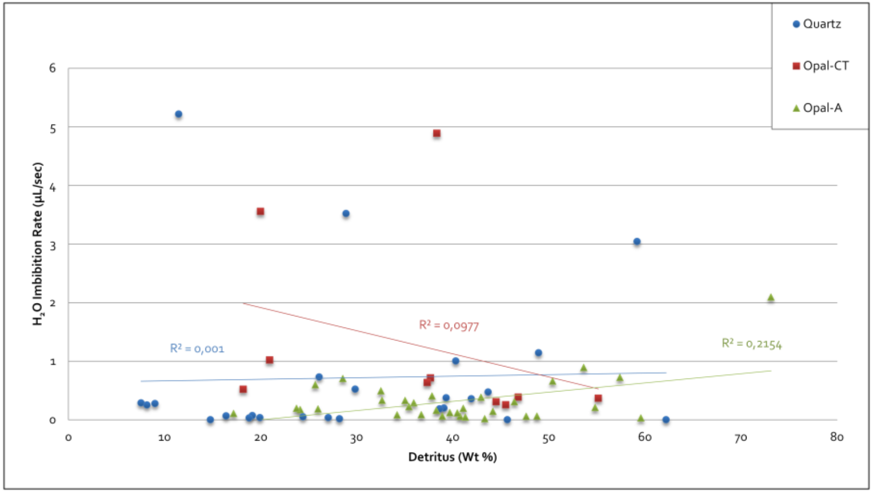
# Water Imbibition Rates



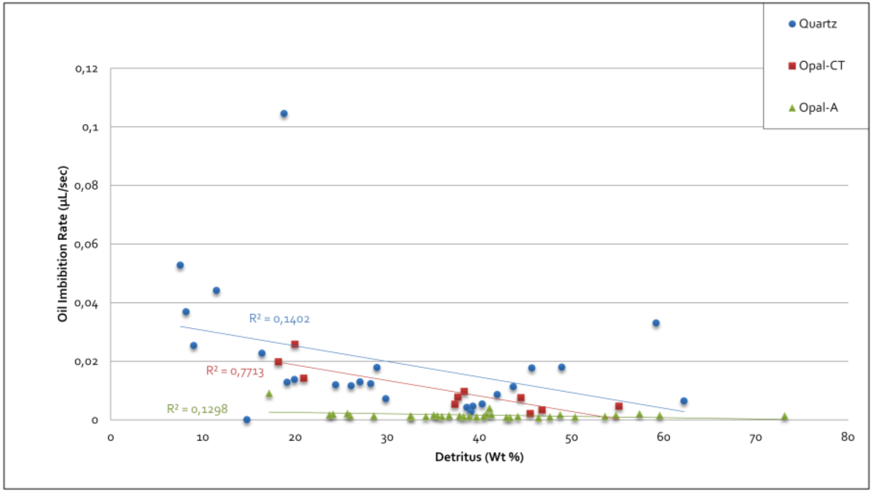
# Oil Imbibition Rates



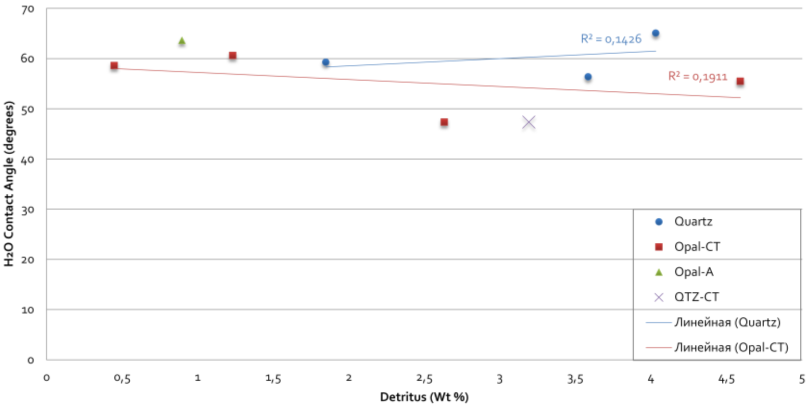
# Water Imbibition
# No Significant Trends with Detrital Content



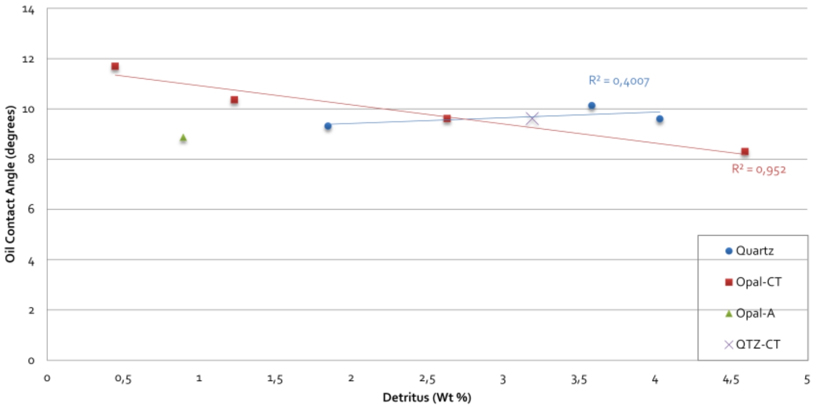
# Oil Imbibition
# Variation with Detrital Content



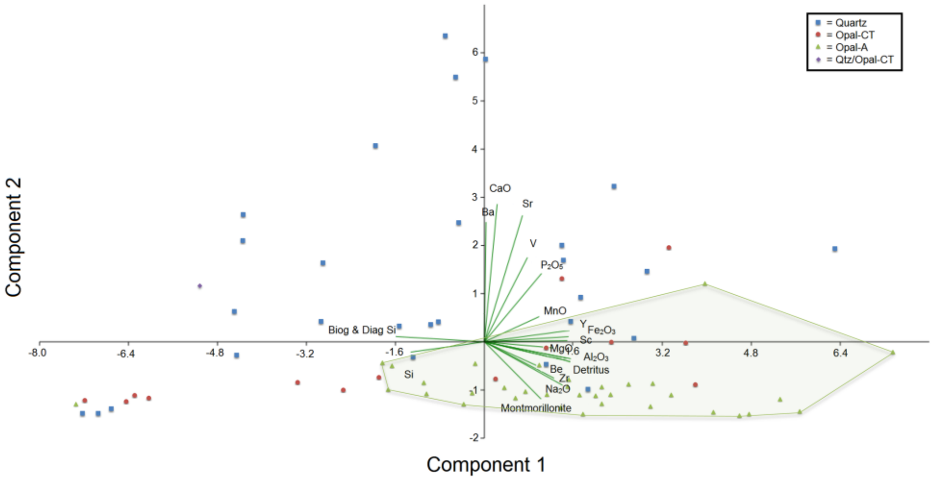
# Water Contact Angle
# No Significant Trends with Detrital Content



# Oil Contact Angle
# No Significant Trends with Detrital Content



# Principal Component Analysis



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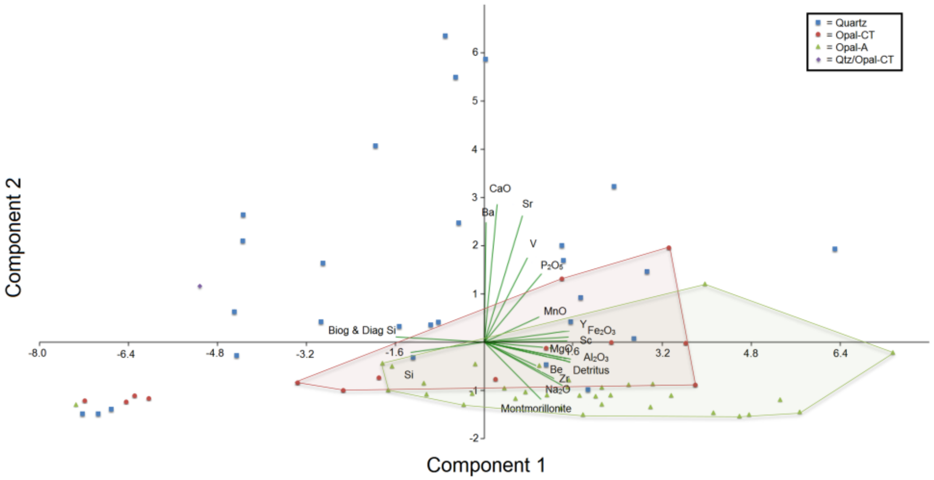

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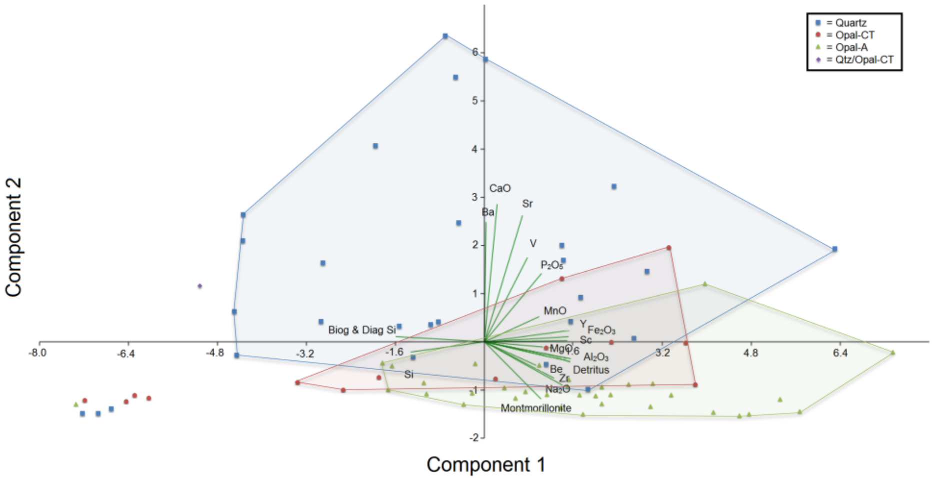
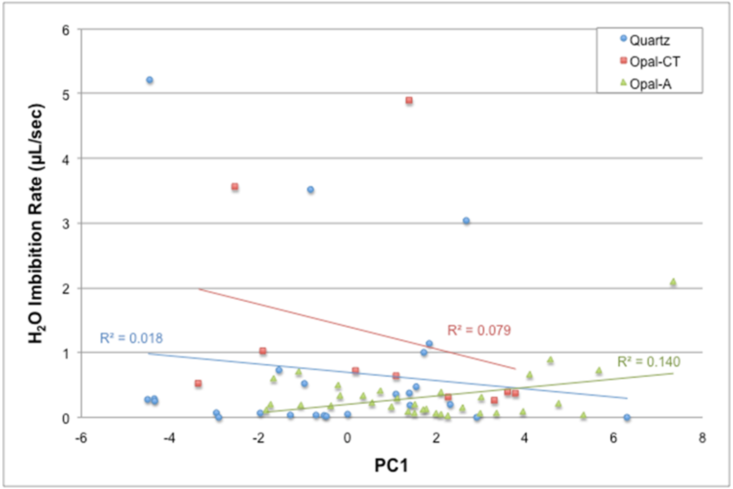
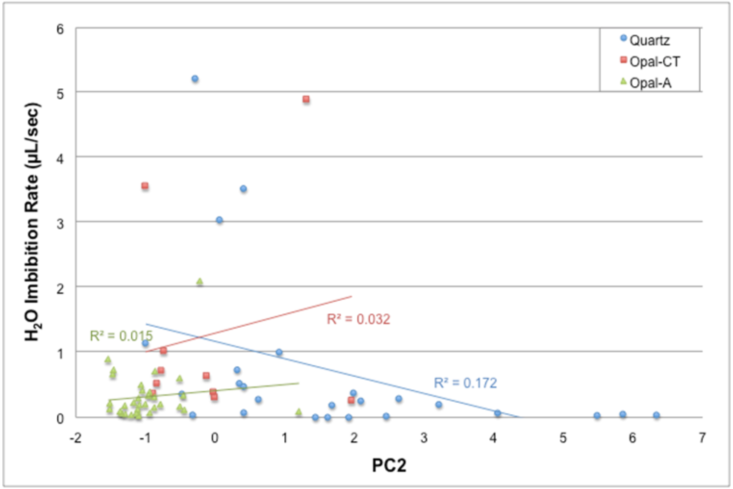


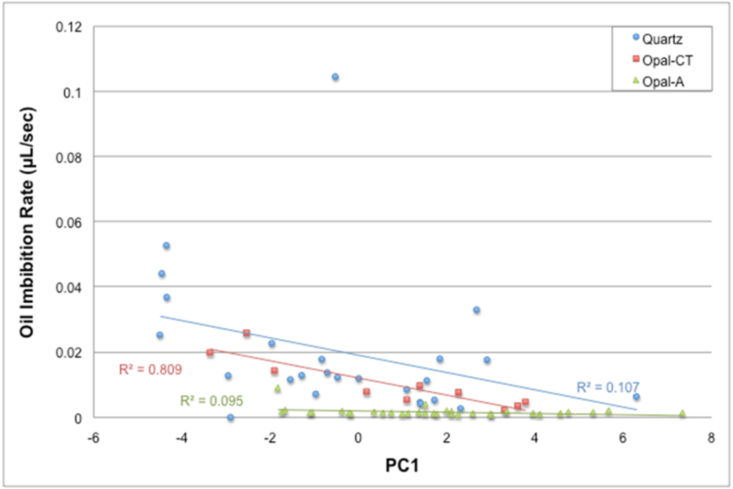
# PC1 vs. Water Imbibition
# No Significant Trends



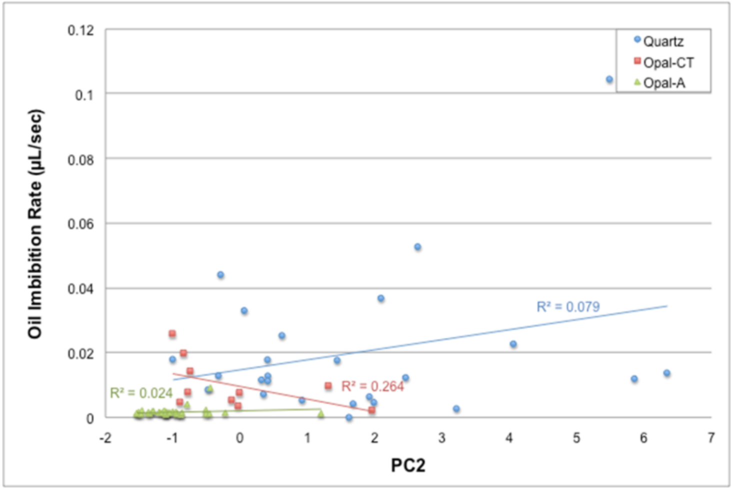
# PC2 vs. Water Imbibition
# No Significant Trends



# PC1 vs. Oil Imbibition Significant Trend for Opal-CT



# PC2 vs. Oil Imbibition
# No Significant Trends



# Multiple Regression

Predictors:
- PC1
- PC2
- PC1*PC2
- Silica Phase Group

Responses: (2 Models)
- Water Imbibition
- Oil Imbibition

**Water Imbibition**

Analysis of Variance

| Source | P-Value |
|---|---|
| **Regression** | 0.001 |
| **PC 1 Score** | 0.87 |
| **PC 2 Score** | **0** |
| **PC1*PC2** | 0.321 |
| **XRD Silica Phase** | **0.001** |
| **Error** | |
| **Total** | |

**Model Summary**

| R-sq(adj) | R-sq(pred) |
|---|---|
| 24.28% | 16.04% |

**Oil Imbibition**

Analysis of Variance

| Source | P-Value |
|---|---|
| **Regression** | 0 |
| **PC 1 Score** | **0** |
| **PC 2 Score** | 0.706 |
| **PC1*PC2** | **0.01** |
| **XRD Silica Phase** | **0** |
| **Error** | |
| **Total** | |

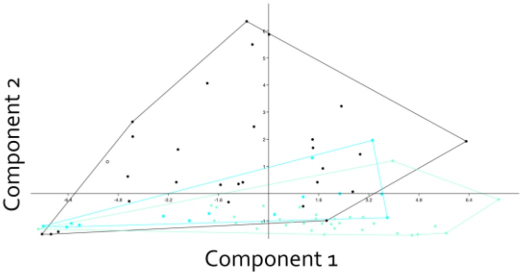
**Model Summary**

| R-sq(adj) | R-sq(pred) |
|---|---|
| 80.78% | 77.41% |

# Multiple Regression

Predictors:
- PC1
- PC2
- PC1*PC2
- Silica Phase Group

Responses: (2 Models)
- Water Imbibition
- Oil Imbibition



| | |
|---|---|
| 24.28% | 16.04% |

**Oil Imbibition**

Analysis of Variance

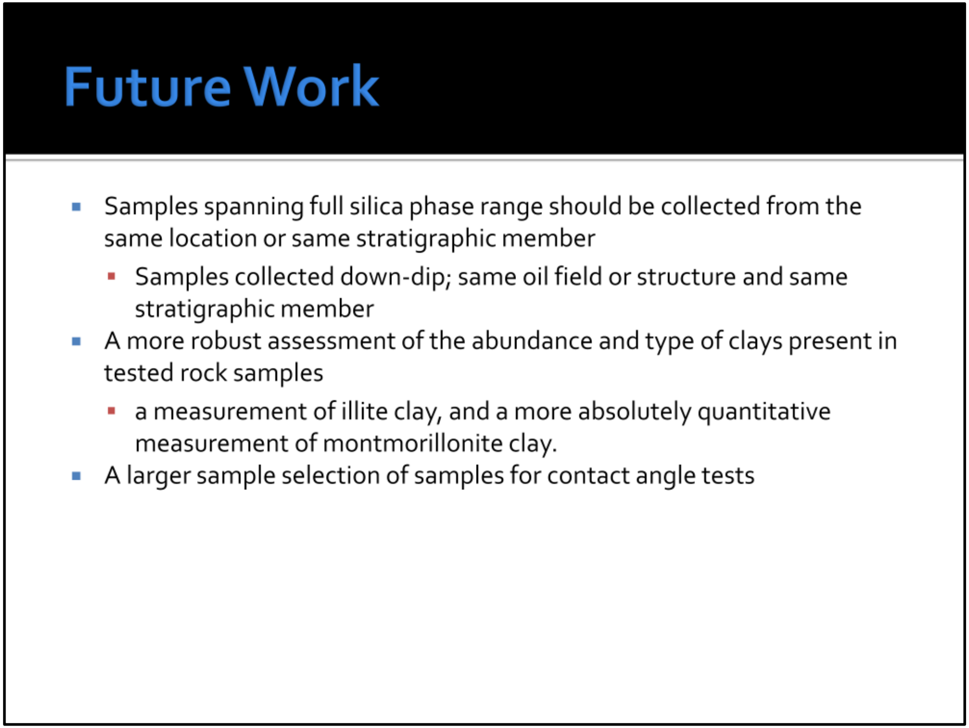
| Source | P-Value |
|---|---|
| **Regression** | 0 |
| **PC 1 Score** | **0** |
| **PC 2 Score** | 0.706 |
| **PC1*PC2** | **0.01** |
| **XRD Silica Phase** | **0** |
| **Error** | |
| **Total** | |

**Model Summary**

| R-sq(adj) | R-sq(pred) |
|---|---|
| 80.78% | 77.41% |

# Conclusions

- No provable change in water wettability due to silica phase or detritus
  - both imbibition and contact angle tests
- Wettability to oil impacted strongly by detrital content
- in opal-CT samples
  - both imbibition (-) and contact angle tests (+)
- Affect of silica phase on wettability overshadowed by detrital content, if it exists



# Future Work

- Samples spanning full silica phase range should be collected from the same location or same stratigraphic member
  - Samples collected down-dip; same oil field or structure and same stratigraphic member
- A more robust assessment of the abundance and type of clays present in tested rock samples
  - a measurement of illite clay, and a more absolutely quantitative measurement of montmorillonite clay.
- A larger sample selection of samples for contact angle tests

Presenter's notes: The discovery by this study that silica phase in Monterey Formation reservoir rocks is less important to reservoir wettability than non-matrix compositional differences is an important one.
- Furthermore, the relationships of wettability to specific secondary components is intriguing, but not entirely consistent between compositional proxies.
- Consequently, the findings of this study raise a number of questions that were not able to be answered with this sample set and experimental design.
- Samples for this study were collected from cores from subsurface reservoirs so that changes due to surficial weathering processes were eliminated from influencing test results. Unfortunately,
- this study was only able to obtain samples of rocks for different diagenetic stages (opal-A, opal-CT and quartz) that were from distinct members on the Monterey Formation that had different secondary compositions.
- This limitation restricted the ability to make direct comparison between different silica phase rocks that were of similar composition.

# Special Thanks to:

- Occidental Petroleum and Aera Energy for core sample donation
- Dr. Varenka Lorenzi and staff of the IIRMES Lab at CSULB for Soxhlet extraction materials, instruction & supervision
- Dr. Young Shon, CSULB Chemistry Dept., for CAM-101 Tensiometer use

# References

- F. Civan, Temperature dependence of wettability related rock properties correlated by the Arrhenius equation, Petrophysics (Houston, Tex.), August 2004, 45(4):350-362
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