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

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## Abstract

In spite of a century of production in California, the Monterey Formation still holds tremendous quantities of recoverable oil, and much of it may be in truly unconventional reservoirs. Maximizing recovery and developing accurate reserve estimates requires understanding all factors influencing reservoir quality. Little is known concerning the importance of wettability variations in the fluid distribution of Monterey Formation porcelanite reservoirs. Observed differences in charge and producibility of opal-CT- and quartz-phase rocks have previously been attributed to pore throat size and geometry that relate to the silica phase and clay content. Yet with significant variation in bound water content of common clay and silica phases, it is reasonable to expect differences in fluid-solid surface interactions exist and may influence oil movement through the rocks. This study will be the first comprehensive investigation of variation in wettability in siliceous sedimentary rocks because of silica phase, crystallographic ordering and clay content. Contact angle measurements directly demonstrate the affinity of a fluid to a substrate, thus eliminating variables inherent in other wettability measurement methods. Wettability measurements in this study will accordingly be determined by the contact angles of distilled water and mineral oil on a suite of Monterey Formation siliceous rocks collected from subsurface cores. Multiple samples from each silica phase — opal-A, opal-CT and quartz — will be measured over a range of clay content from 0 to 30% in both natural and hydrocarbon—cleaned states. The composition of each sample will be determined by XRD. For uniformity in measurement, samples are crushed and sieved to <500 micrometer, then cleaned of hydrocarbons through methylene chloride extraction process, and then compressed into discs in a hydraulic press. Water and oil are placed onto the sample discs and the drop process is photographed with a high-speed camera

tensiometer. Contact angles and surface free energy are then calculated. Multivariate statistical analysis will quantify the correlation between the variables of silica diagenesis (phase and ordering), clay content and wettability.

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

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Geology CSULB

## Abstract

In spite of a century of production in California, the Monterey Formation still holds tremendous quantities of recoverable oil, and much of it may be in truly unconventional reservoirs. Maximizing recovery and developing accurate reserve estimates requires understanding all factors influencing reservoir quality. The importance of wettability variations in the fluid distribution of Monterey Formation porcelanite reservoirs is little known. Observed differences in charge and producibility of opal-CT- and quartz-phase rocks have previously been attributed to pore throat size and geometry that relate to the silica phase and clay content. Yet with significant variation in bound water content of common clay and silica phases, it is reasonable to expect differences in fluid-solid surface interactions exist and may influence oil movement through the rocks. This study will be the first comprehensive investigation of variation in wettability in siliceous sedimentary rocks as a result of silica phase, crystallographic ordering and clay content.

Contact angle measurements directly demonstrate the affinity of a fluid to a substrate, thus eliminating variables inherent in other wettability measurement methods. Wettability measurements in this study will accordingly be determined by the contact angles of distilled water and mineral oil on a suite of Monterey Formation siliceous rocks collected from subsurface cores. Multiple samples from each silica phase – opal-A, opal-CT and quartz – will be measured over a range of clay content from 0 to 30% in both natural and hydrocarbon–cleaned states. The composition of each sample will be determined by XRD. For uniformity in measurement, samples are crushed and sieved to <500 micrometer, then cleaned of hydrocarbons through methylene chloride extraction process, and then compressed into discs in a hydraulic press. Water and oil are placed onto the sample discs and the drop process is photographed with a high speed camera tensiometer. Contact angles and surface free energy are then calculated. Multivariate statistical analysis will quantify the correlation between the variables of silica diagenesis (phase and ordering), clay content and wettability.

## Purpose & Significance

Understanding fluid migration and charge in low permeability fine-grained rocks is critical to improved development of Monterey Formation reservoirs, yet their controls are still poorly understood. To date, much work has been done on the wettability of quartz, clay, feldspar and calcite in conventional sandstone reservoirs, but little comprehensive study has been published for biogenic and diagenetic silica phases. Although several studies have completed limited wettability studies of siliceous rocks as a part of larger Monterey Formation reservoir characterizations, the alteration in wettability of biogenic and diagenetic siliceous rocks potentially caused by silica phase changes has not been characterized in detail. Pore throat size and geometry, as well as rock wettability to oil and water are widely accepted as primary controls of fluid distribution in most conventional reservoirs, yet hydrocarbon saturations in the Monterey Formation are primarily attributed to permeability (See Schwalbach et al., 2007 figure, right). However, the increased rock surface area per fluid volume in nano- and microporous siliceous rocks makes the influence of wettability on reservoir fluid distribution likely an even more important control.

## Hypothesis

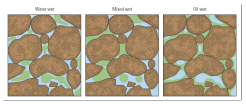
Each diagenetic phase transition from opal-A to opal-CT, and opal-CT to quartz, entails a release of structural H2O from the opal mineral lattice. We hypothesize that the loss of polar water molecules with progression of silica diagenesis will result in a decreased wettability to water and increase in wettability to oil with each silica phase transition in siliceous rocks. We also hypothesize that clay content is very important to the bulk wetting properties - that increased clay (even still minor amounts) can make the bulk rock wettable to water.

## Background

- Wettability is …
  - The relative affinity between a surface and a fluid.
  - The product of the hydrostatic intermolecular interactions between a tested solid and a fluid phase
- Wettability affects …
  - Fluid distribution
  - Nuclear Magnetic Resonance
  - Effect increased in tight, low permeability rocks

(Abdallah et al., 2007, right)

- Wettability is affected by…
  - Temperature
  - Fluid chemistry & rock mineralogy
  - Secondary constituents (e.g., clay, carbonates, clastics, organic material, etc.)




## References

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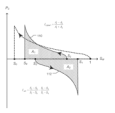
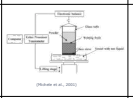
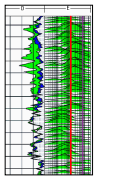
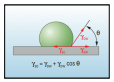
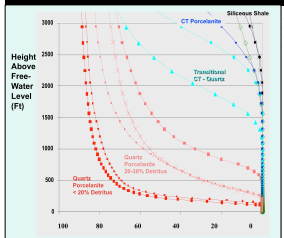
2) J. R. Schwalbach, S. A. Gordon, C. P. O'Brien, D. F. Lockman, W. C. Benmore, and C. A. Huggins, Reservoir Characterization of Monterey Formation Siliceous Shales: Tools and Applications, Pacific Section AAPG Miscellaneous Publication MP 48, 2007
3) R Freedman, N Heaton, M Flaum, G J Hirasaki, C Flaum, M Hürlimann, Wettability, Saturation, and Viscosity from NMR measurements, SPE Journal - SPE J 01/2003; 8(4)
4) J. C. Michel, L. M. Rivière, and M. N. Bollon-Fontaine, Measurement of the wettability of organic materials in relation to water content by the capillary rise method, European Journal of Soil Science, September 2001, 52, 459-467

## Wettability Measurements

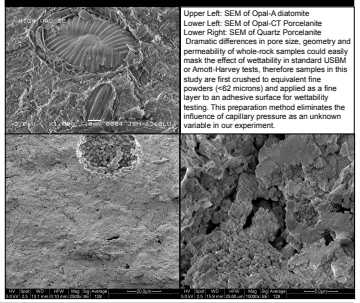
| Method | Analysis | Description | Advantages | Disadvantages |
|---|---|---|---|---|
| Amott-Harvey |  | Measures the rate of spontaneous imbibition of a fluid into a solid rock sample, usually a core plug | Pre-established and industry standard wettability index | Cost, variability of permeability, geometry and distribution of porosity, unsuitable for limited quantity powders, method designed for high permeability sandstones and vuggy limestones. |
| USBM | | Measures the rate of fluid imbibition into a core plug with known pore pressure, by use of a centrifuge | | |
| Capillary Rise |  | Measures rate of imbibition of a fluid into a packed powder | Suitability to powder samples, mathematic conversion potential to correlate with other measurement methods. | Difficult to control packing, accurately measure fluid intake, method designed for high permeability sandstones and vuggy limestones. |
| NMR |  | 2) Surface relaxation of the wetting phase in a rock results in shorter relaxation times than would otherwise be observed for the bulk fluid. The non-wetting phase fluid molecules do not come into contact with the pore surfaces, and therefore their relaxation rate in the rock is the same as in the bulk fluid. (Freedman et al., 2003) | Accessibility of data, proven consistency with Amott-Harvey wettability index | 1) The surface relaxation rate must be significant compared to the bulk relaxation rate in order for wettability to noticeably affect the NMR response. (Freedman et al., 2003), potentially unsuited to hydrous rock minerals, such as opal, method successful in sandstone experiments, but untested and potentially problematic in hydrous mineral bearing rocks, such as opal-A diatomites and opal-CT rocks. |
| Contact Angle |  | Angle Theta between fluid and a prepared surface are measured using the Young-Laplace equation. | Easily understood, definitive and accurate results with well developed technology, potential to eliminate porosity and permeability as variables by creating a smooth surface with crushed rock samples. | **Due to lack of significant disadvantages, this method was chosen for the current wettability study.** |

## Permeability as a Stand Alone Saturation Control




Hydrocarbon pressure from [Mercury Injection Capillary Pressure] MICP data as a function of height above water level. (Schwalbach et al., 2007)

## Character of Siliceous Rocks



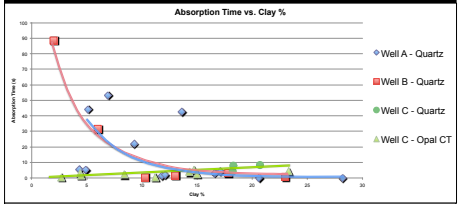
Upper Left: SEM of Opal-A diatomite
Lower Left: SEM of Opal-CT Porcelanite
Lower Right: SEM of Quartz Porcelanite
Dramatic differences in pore size, geometry and permeability of whole-rock samples could easily mask the effect of wettability in standard USBM or Amott-Harvey tests, therefore samples in this study are first crushed to equivalent fine powders (<62 microns) and applied as a fine layer to an adhesive surface for wettability testing. This preparation method eliminates the influence of capillary pressure as an unknown variable in our experiment.

## Water Imbibition Test Methods

Contact angle test data will provide the primary results for this study. Sample preparation for this method is currently in progress, and preliminary imbibition tests performed as a means of determining relative wettability to water until contact angle measurements can be successfully performed.

Samples were collected from Monterey Fm. columns in 5 different San Joaquin Valley wells and crushed in a ball mill, then stored in plastic-topped glass vials. Hydrocarbons were removed from each powdered sample by Soxhlet extraction with methylene chloride. Cleaned samples were pressed into 3.175cm diameter pellets with a hydraulic press at 10,000 lbs. of pressure. Using a CAM101 tensiometer, drops of distilled water were dispensed from a needle onto each sample pellet and the rate of absorption recorded with timed imaging.

## Water Imbibition Test Results

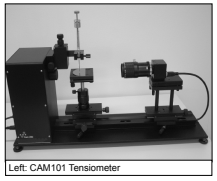



A key observation from water imbibition tests is a marked decrease in wettability to water with the phase transition from opal-CT to quartz, until clay content exceeds approximately 15%. Above clay concentrations of 15%, all samples demonstrate a strong and similar wettability to water, regardless of silica phase.

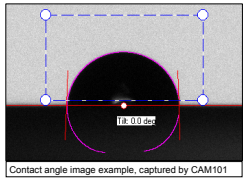
## Contact Angle Test Plans

Test Subjects: Monterey Fm. rocks from 5 wells in the San Joaquin Valley, including diatomite, opal-CT and quartz phase rocks will be tested for their interaction with distilled water and mineral oil

For contact angle measurements, glass slides will be prepared with double-sided scotch tape covered on one side with sample powdered to <62 microns, insuring the grain size and powder coverage is small enough to prevent interaction between fluid and tape surface. Using a CAM101 tensiometer, test fluids will be dispensed on each prepared sample surface and the contact angle measured using the Young-Laplace equation.



Left: CAM101 Tensiometer




Contact angle image example, captured by CAM101

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