Fundamental Understanding of Methane-Carbon Dioxide-Water (CH_4-CO_2-H_2O) Interactions in Shale Nanopores under Reservoir Conditions

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Project Goals

Fundamental understanding of CH_4-CO_2-H_2O behavior and their interactions in shale nanopores is of great importance for gas production and the related CO_2 sequestration. We propose to systematically study CH_4-CO_2-H_2O interactions in shale nanopores under high-pressure and high temperature reservoir conditions.

Key R&D Goals/Milestones

- Report on material preparation, characterization & preliminary testing; one conference paper on testing methodology.
- Report on sorption-desorption measurements and preliminary modeling work; one journal paper on sorption measurements.
- Final report; two journal articles on MD and CDFT modeling.

R&D Approach

- Collect representative core samples from a diverse set of shale formations, in terms of mineral composition, kerogen thermal maturity, etc.
- Conduct a series of full cycle methane sorption-desorption experiments on both model materials and shale samples under simulated reservoir conditions (up to 120 ^oC and 70 MPa).
- Perform molecular dynamic modeling and develop a classical density functional theory to assist experimental data interpretation.
- Develop a high-precision Equation of State (EOS) for CH_4-CO_2-H_2O nanofluidic system.

Significance of Results

- Significantly advance fundamental understanding of hydrocarbon storage, release, and flow in shale,
- Provide more accurate predictions of gas-in-place and gas mobility in reservoirs.
- Help to develop *new stimulation strategies to enable efficient resource recovery from fewer and less environmentally impactful wells*.
- Provide the basic data set to test the concept of using supercritical CO2 as an alternative fracturing fluid for simultaneous methane extraction and CO2 sequestration.

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Research Team

Yifeng Wang	Geochemistry and materials science Responsible for material characterization & classical density functional theory modeling
Yongliang Xiong	Geochemistry Responsible for high pressure/high temperature sorption-desorption measurements
Louise Criscenti	Geochemistry; Responsible for molecular dynamics modeling

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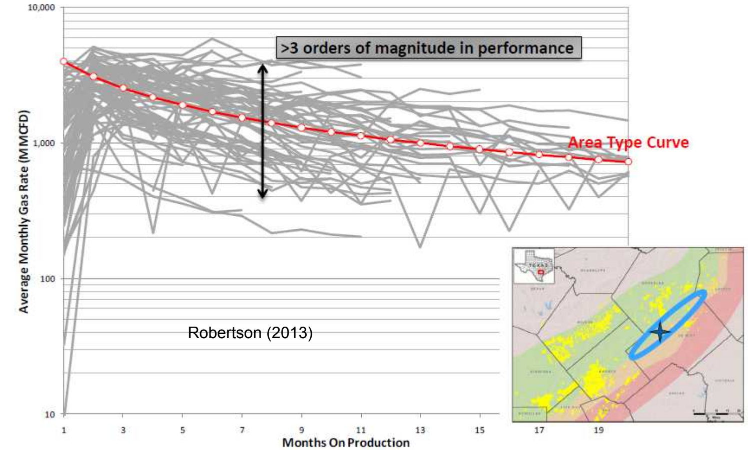
Problem Statement

- Sustainability of shale gas production:
  - Large variability and unexpected rapid decline in well production (up to 95% reduction over first 3 years)
  - Low recovery rates (<10%)
  - New well required to maintain the supply
  - $9 M/well; $42 B/year in US; increasing cost/well
  - Little known about secondary gas recovery in “brown fields” (>90% of total gas reserve!!!)
- Maximizing individual well production while minimizing environmental impacts is the key to realizing energy security benefits of shale gas
- Understanding methane disposition and release in shale gas reservoirs is key step toward maximizing wellbore production.
- Supercritical CO_2 is proposed as an alternative fracturing agent for simultaneous CH_4 extraction and CO_2 sequestration.



COMMENT

Gas being burnt off at the Bakken shale oil field in North Dakota as a by-product of oil extraction.

A reality check on the shale revolution

The production of shale gas and oil in the United States is overhyped and the costs are underestimated, says **J. David Hughes**.

The 'shale revolution' — the extraction of gas and oil from previously inaccessible reservoirs — has been declared an energy game changer. It is offsetting declines in conventional oil and gas production, with shale gas being heralded as a transition fuel to a low-carbon future, and shale oil as being capable of reinstating the United States as the largest oil producer in the world, eliminating the need for foreign imports.

These heady claims have been largely accepted by government forecasters, including the International Energy Agency[1] and the US Energy Information Administration (EIA). The oil firm BP predicts that production of shale gas will treble and shale oil — also known as 'tight oil' — will grow sixfold from 2011 levels by 2030 (ref. 2).

The claims do not stand up to scrutiny. In a report published this week by the Post Carbon Institute[3] in Santa Rosa, California, I analyse 30 shale-gas and 21 tight-oil fields (or 'plays') in the United States, and reveal that the shale revolution will be hard to sustain. The study is based on data for 65,000 shale wells from a production database that is widely used in industry and government. It shows that well and field productivities exhibit steep declines. Production costs in many shale-gas plays exceed current gas prices, and maintaining production requires ever-increasing drilling and the capital input to support it.

Although the extraction of shale gas and tight oil will continue for a long time at some level, production is likely to be below the exuberant forecasts from industry and government. I see supplies of shale gas declining substantially in the next decade unless prices rise considerably. A more realistic debate around shale gas and tight oil is urgently needed — one that accounts for the fundamentals of production in terms of sustainability, cost and environmental impact.

SHALE GAS

Two technologies — horizontal drilling coupled with large-scale, multi-stage hydraulic fracturing (fracking) — have made it possible to extract hydrocarbons trapped in impermeable rocks (see *Nature* 477, 271–275; 2011). In 2004, less than 10% of US wells were horizontal; today, the figure is 61%.

Most shale-gas production worldwide is in North America, although pilot projects are being conducted in many countries. Production has been on a plateau since early 2012 after a period of sharp growth. Shale gas has risen from about 2% of US gas production in 2000 to nearly 40% in 2012 (ref. 3); overall US gas production grew by 25% over the same period. The resulting supply glut drove US gas prices down severely. Prices have since recovered slightly but remain too low for many shale-gas plays without liquids production to be economically viable.

Large-scale shale-gas production was

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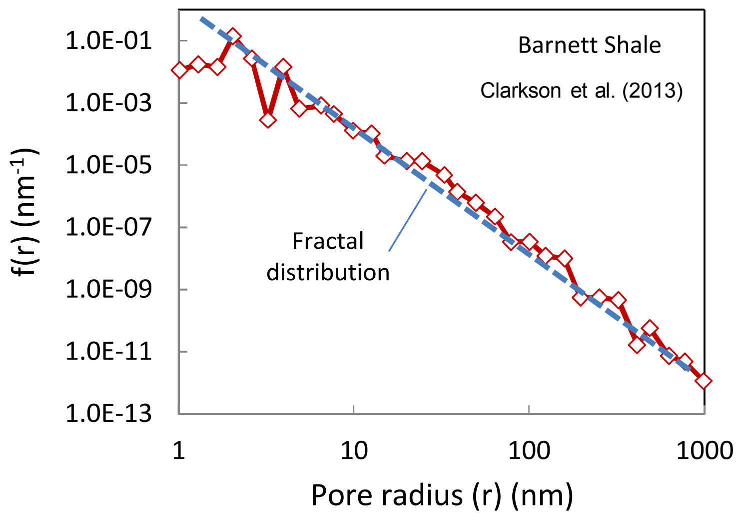
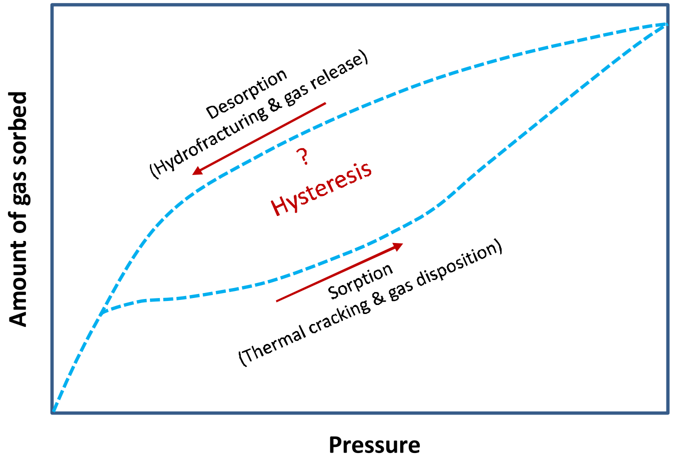
Problem Statement (cont.)

- **Knowledge gaps to be addressed**
  - Little is known about multicomponent interactions of CH_4-CO_2-H_2O in nanopores.
  - No measurements have been made on the whole cycle of gas sorption and desorption in shale samples.
  - Equation of state (EOS) for predicting thermodynamic behaviors of CH_4-CO_2-H_2O in shale is yet to be developed.





Nanopore confinement can substantially modify the physical and chemical properties of a chemical species.

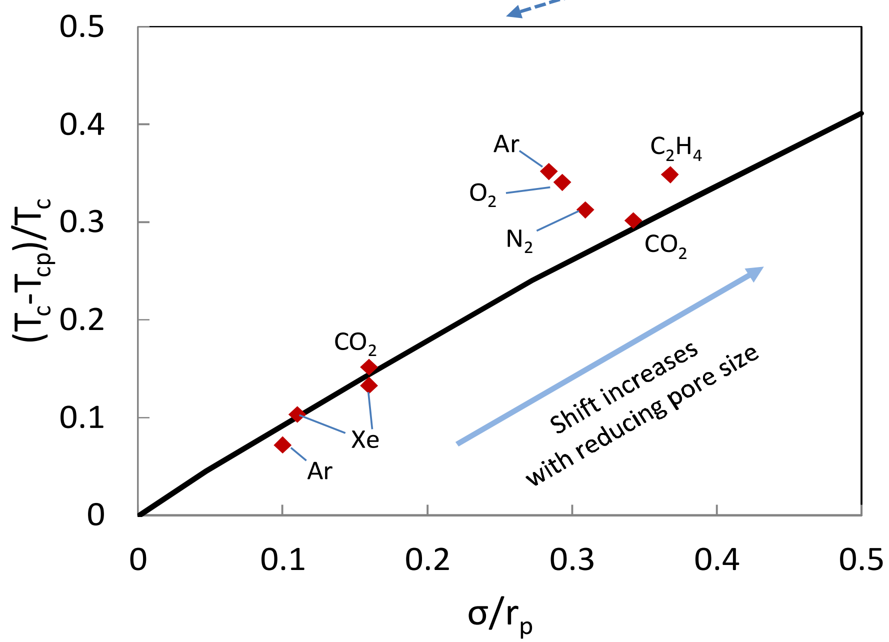
Bulk phase fluids
(Unconfined or pore size > ~100 nm)

EOS = f(P, T, composition)

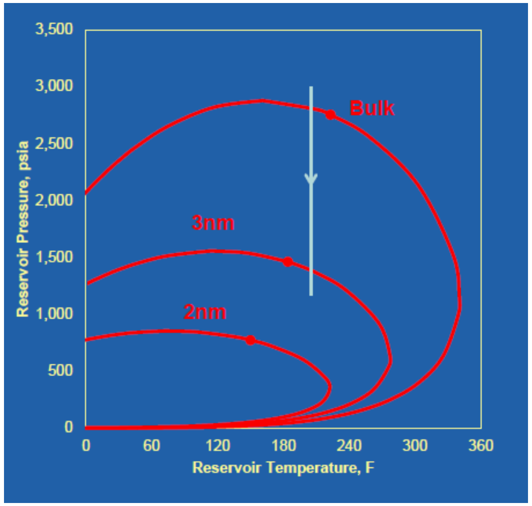
Nanoconfinement →

Nanofluids
(Confined in nanopores, pore size < ~100 nm)

EOS = f(P, T, composition, pore size, surface chemistry)



Wang (2014); Zarragoicoechea and Kuz (2004)



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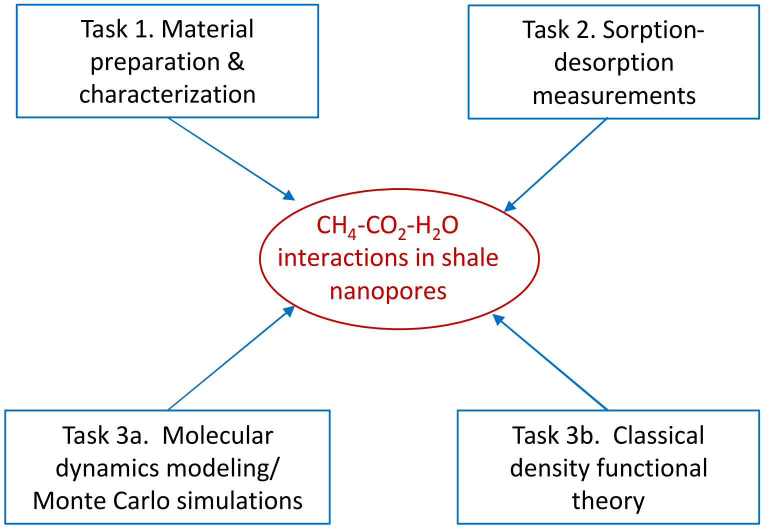
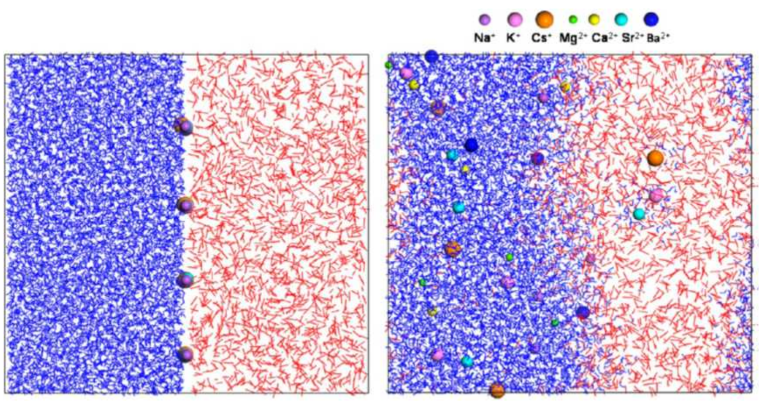
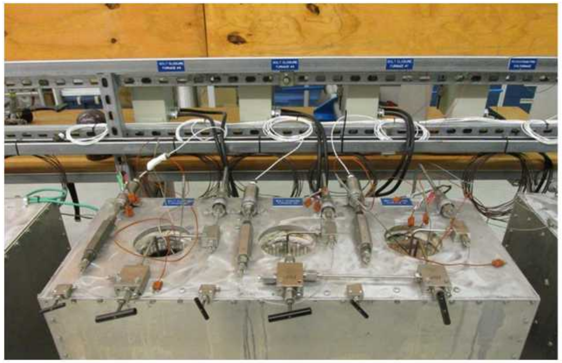
Proposed Work

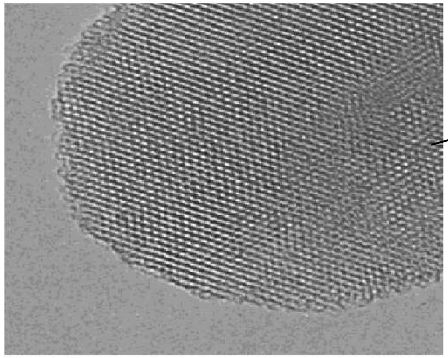
- **Task 1.** Collect representative core samples from a diverse set of shale formations, in terms of mineral composition, kerogen thermal maturity, etc. The samples will be characterized with various microanalysis techniques.
- **Task 2.** Conduct a series of full cycle methane sorption-desorption experiments on both model materials and shale samples under simulated reservoir conditions (up to 120 °C and 70 MPa). The measurements will be conducted with a mixture of CH_4-CO_2-H_2O to test if and to what extent the presence of CO_2 or H_2O influence on methane disposition and release.
- **Task 3.** Perform molecular dynamic modeling and develop a classical density functional theory to assist experimental data interpretation. The outcome of this research will include the key data set and a predictive model for CH_4-CO_2-H_2O interactions in shale nanopores under reservoir conditions.





High Pressure & High Temperature Measurements of Gas Sorption Desorption

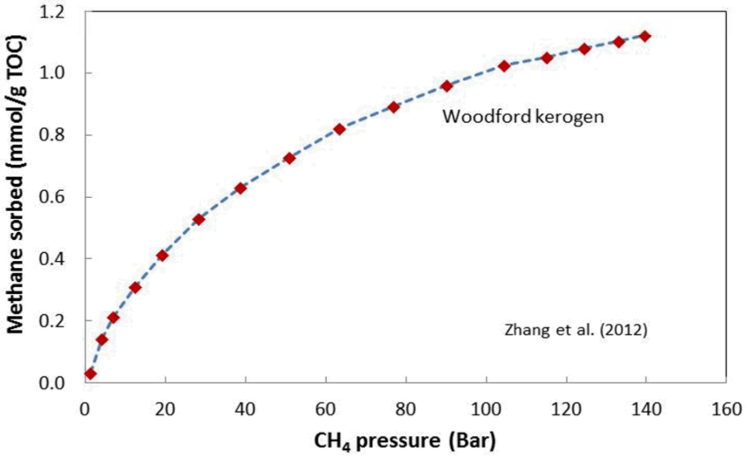




Model material – nanoporous silica

A

B



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Key Milestones & Deliverables

Milestone	Deliverable
Title: Complete material preparation & characterization **Planned Date: End of month 5** **Verification Method: Submittal of progress report**	Report on material preparation, characterization & preliminary testing; one conference paper on testing methodology
Title: Complete majority of sorption-desorption measurements **Planned Date: End of month 15** **Verification Method: Submittal of progress report**	Report on sorption-desorption measurements and preliminary modeling work; one journal paper on sorption measurements
Title: Complete modeling and data synthesis **Planned Date: End of month 18** **Verification Method: Submittal of final report**	Final report; two journal articles on MD and CDFT modeling

The project is divided into two phases. After Phase I, we will decide if we want to expand the chemical system to include other components.