# Hydraulic Fracturing Fluid Reaction with Shale in Experiments at Unconventional Gas Reservoir Conditions

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Abstract MR41A-2620

## Motivation

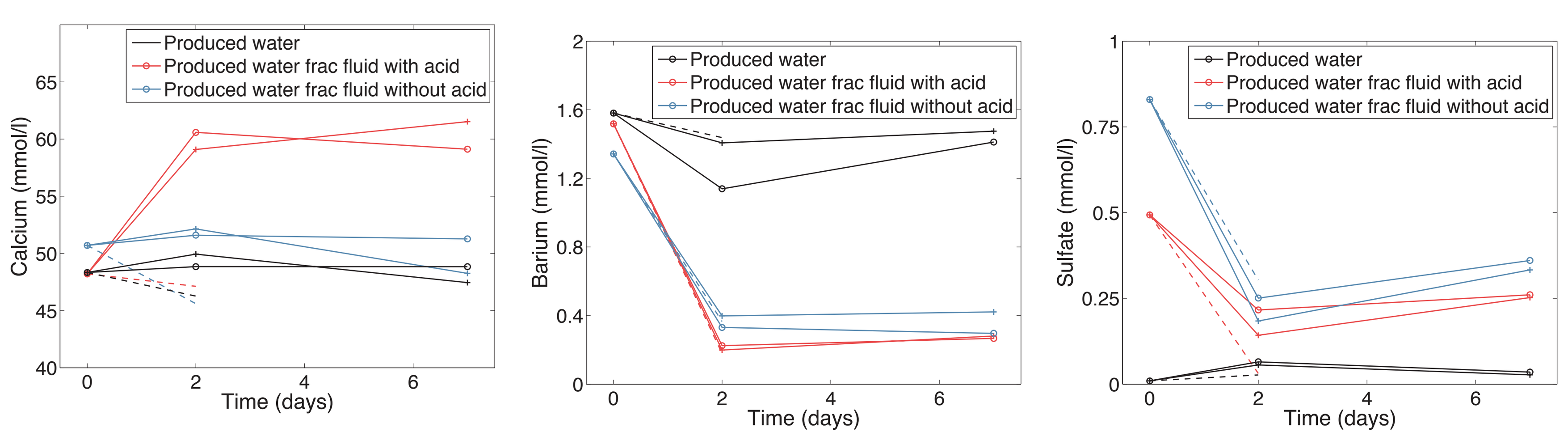
Despite the marked increase in hydraulic fracturing for unconventional natural gas production over the past decade, reactions between hydraulic fracturing fluids (frac fluids) and shale reservoirs remain poorly reported in the scientific literature. Shale-frac fluid interaction could cause mineral dissolution, releasing matter from the shale, or mineral precipitation that degrades reservoir permeability. Furthermore, data are limited on whether scale inhibitors are effective at preventing mineral precipitation and whether these inhibitors adversely affect reservoir fluid chemistry and permeability. We aimed to pin down some of the reactions that occur within shale reservoirs and the factors controlling fluid-rock reactions through controlled laboratory experiments.

## Experimental Set Up

To investigate frac fluid-rock interaction within shale reservoirs, we conducted flow-through experiments exposing outcrop samples of Marcellus Shale to synthetic frac fluid at reservoir conditions (66oC, 20MPa). Outcrop shale samples were cored, artificially fractured, and propped open with quartz sand. Each experiment used shale core with dimensions of 1.5" diameter and 6" length. Fluids were then pumped through the core for 1 week at a flow rate of 0.04 ml/min and collected in ISCO syringe pumps. Samples were taken from the syringe pumps after 2 days and again after 7 days of reaction. Cores were depressurized and cooled for analysis by x-ray CT scanning, then disassembled and the fracture face was analyzed by SEM with EDS. Baseline analyzes were conducted by the same methods prior to experiments.

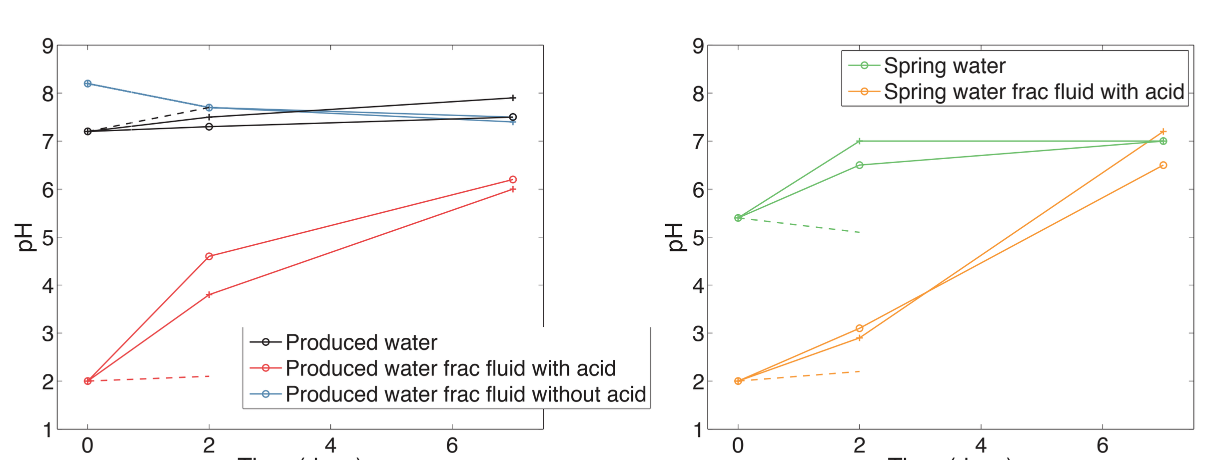
Synthetic frac fluids were mixed with chemical additives similar to those used for Marcellus Shale gas wells in Ohio and Southwestern Pennsylvania (Liu, 2013; FracFocus.org). We tested frac fluids made from natural freshwater from local springs, and frac fluids made from synthetic produced water (designed to simulate produced water that is diluted and re-used for subsequent hydraulic fracturing, as is often done in Pennsylvania). We also tested frac fluid with hydrochloric acid (HCl) to represent the initial acid stage, and frac fluids excluding HCl to simulate the fluids after neutralizing due to reaction with wellbore cement and the shale formation. Reactions were determined through changes in fluid chemistry, measured by IC, ICP-OES, and ICP-MS, SEM with EDS and x-ray CT imaging.

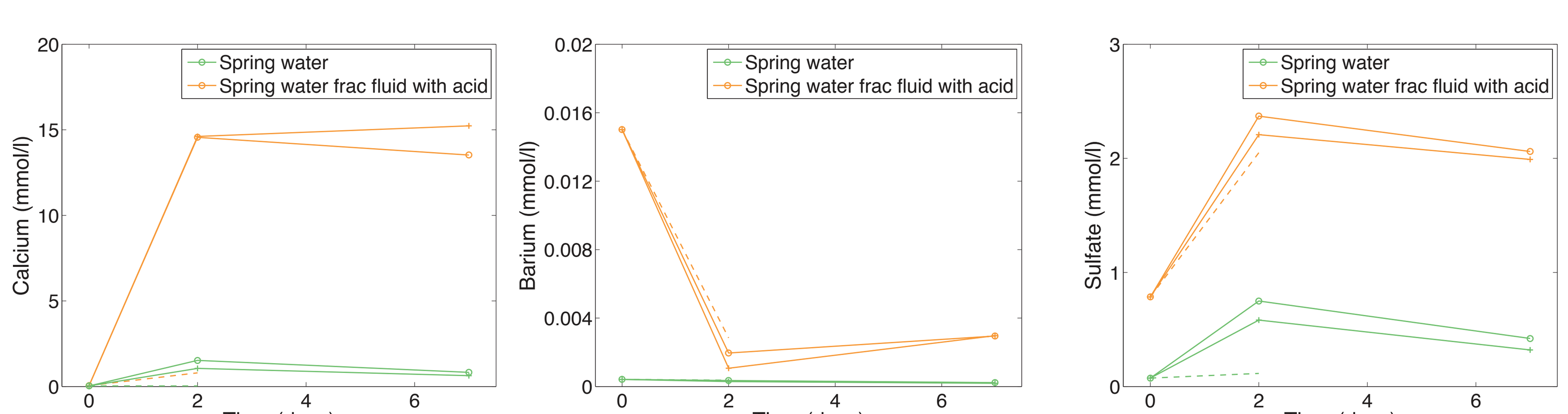
## Fluid Chemistry




Calcite dissolution

Barite precipitation




Sulfate increase in frac fluid

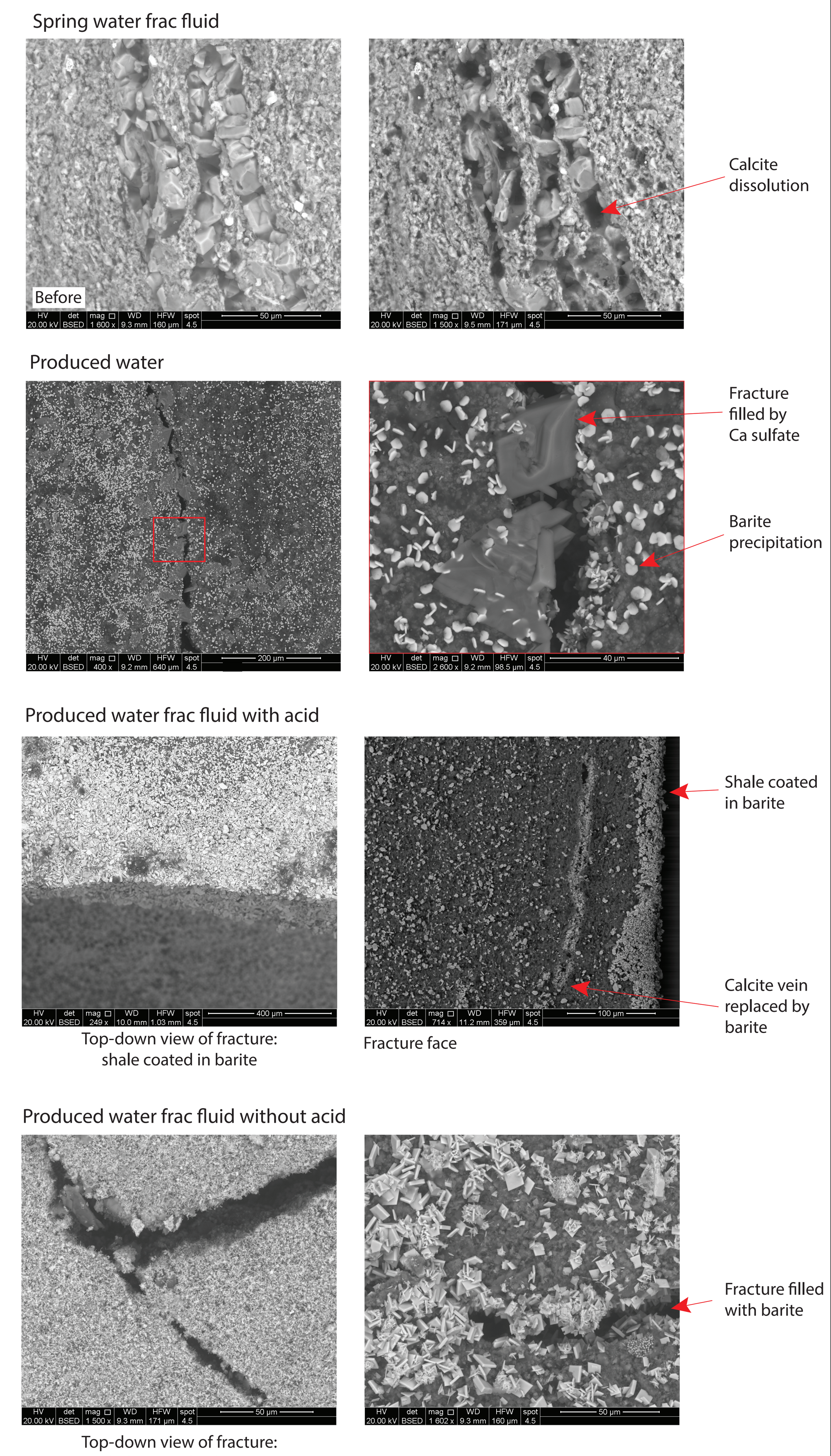
Calcite dissolution

Barite precipitation

Pyrite Oxidation

Solid lines indicate results from experiments with shale cores. Dashed lines indicate control runs where fluid was pumped at temperature and pressure through the core sleeve, but with with no shale core inside.

## SEM imaging




Top-down view of fracture: shale coated in barite

Fracture face

Top-down view of fracture: shale coated in barite

All images taken after 1 week of reaction unless otherwise specified.

## Chemicals added to frac fluids

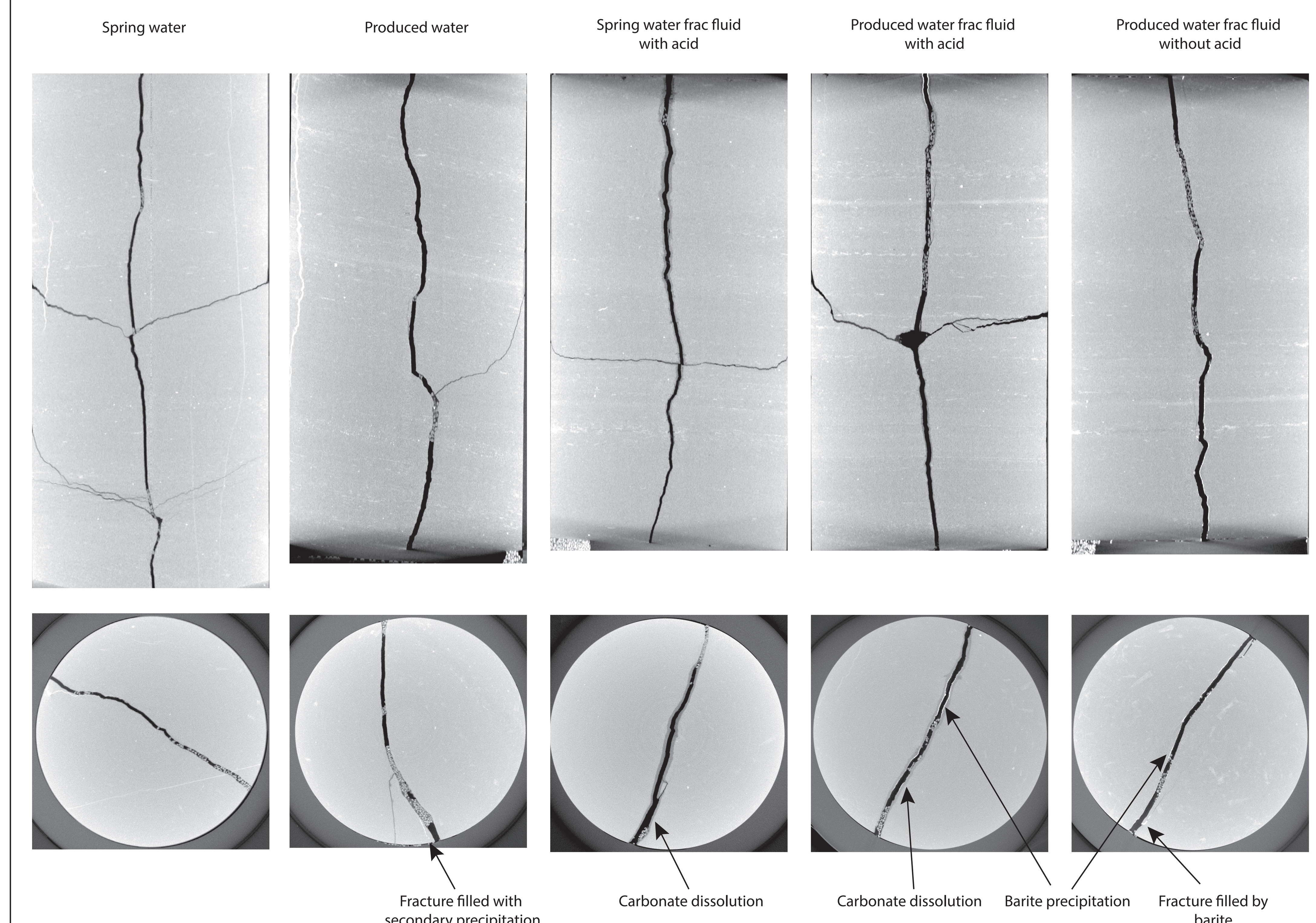
| Ingredient | Purpose |
|---|---|
| Moshannon State Forest Rock Springs water | |
| WFR-61LA | Friction reducer |
| WAI-251LC | Corrosion inhibitor |
| Revert Flow | Surfactant |
| WCS-631LC | Clay stabilizer |
| WGA-15L | Gelling agent |
| EC6110a | Biocide |

| | |
|---|---|
| Citric acid | Iron control |
| Ammonium persulfate | Breaker |
| Boric acid | Cross linker |
| Ethylene glycol | Cross linker |
| Ethanolamine | Cross linker |
| Potassium hydroxide (45%) | pH adjuster |
| Potassium carbonate | pH adjuster |
| Hydrochloric acid (37%)* | Cleaner/stimulator |

*only in frac fluid with acid Recipe modified from Liu (2013)

## X-ray CT imaging

Imaging of shale cores post reaction (depressurized and cooled). Each image represents 1.5 inches of core.




## Results and Conclusions

- Experiments utilizing produced water frac fluid (both with and without acid) had 70 - 90% removal of dissolved barium from solution by precipitation of barite, despite the presence of anti-scaling compounds in the frac fluids
- Barite precipitation in experiments with produced water frac fluid appears to be concentrated near the inlet, while in similar experiments without acid precipitation is distributed along the length of the shale core
- Dissolved calcium increased in all experiments, likely due to dissolution of calcite. Not surprisingly, dissolution was significantly enhanced in experiments with frac fluids that included hydrochloric acid
- X-ray CT images show dissolution primarily occurred along the main fracture, where frac fluid flow was highest
- SEM and x-ray CT images show secondary minerals precipitated along the main fracture, or filled secondary fractures and spaces left behind by dissolved minerals, such as calcite
- Fluid chemistry and SEM-EDS data match well, with visible dissolution and precipitation of minerals corresponding to increases and decreases in dissolved solutes, respectively
- Overall, these results suggest that chemical reactions from frac fluid injection have the potential to alter the structure of fractures in shale reservoirs by dissolution of primary carbonate minerals and precipitation of secondary sulfate minerals
- Further study should be done in order to determine the impact of hydraulic frac fluid reactions on reservoir permeability and natural gasextraction efficiency

**References:**

Liu, S (2013). Laboratory Investigations on the Geochemical Response of Groundwater-sediment Environment to Hydraulic Fracturing Fluids. Masters Thesis. Ohio State University.

www.FracFocus.org Frac Focus Chemical Disclosure Registry.

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