Improving Unconventional Hydrocarbon Recovery by Reducing Formation Damage*

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Abstract

The low commodity price for hydrocarbons has made increasing EURs while decreasing CAPEX for unconventional wells a critical factor to operator survival. While the DOE has been instrumental in advancing the science that formed the North American shale play, it will be necessary to have another technology renaissance to improve the hydrocarbon recovery factor from the 7 to 10% range that is currently being realized, to a step change to 15% or more. Although unconventional wells are typically fracked in even stages, production is not uniform. Why is that? Uneven production is likely due to differences in fracture-achieved surface area, pore connectivity, and permeability variability. Coupled geochemical-transport processes occurring at fluid-shale interfaces can profoundly alter these parameters and thus EUR. Our goal is to understand primary and secondary nanoscale reactions that are occurring in, and likely damaging, shale through the fracking process. Relatively little has been published on this subject.

The work, being conducted by SLAC and managed by NETL, is using world-class, synchrotron transmission x-ray microscopy (TXM), and reactor and modeling studies to advance the understanding of nanopore-scale reactions caused by fracking fluid-shale interactions. The TXM uses high-flux focused x-rays to image shales at a spatial resolution of 30 nanometers such that pore networks and reaction products can be directly observed. This research is yielding knowledge that supports a step change in hydrocarbon recovery by customizing stimulation fluids and techniques to the formation-specific chemistry. The work is also explaining the release of contaminants from kerogen and the rock matrix.

IMPROVING UNCONVENTIONAL HYDROCARBON RECOVERY BY REDUCING FORMATION DAMAGE

AN EFFORT BY US DOE NATIONAL LABS

David P. Cercone, Bargar, J., Brown, G., Harrison, A., Jew, A., Dustin, M., Maher, K., Joe-Wong, C., Zoback, M., Liu, Y.

U.S. Department of Energy

National Energy Technology Laboratory

SLAC National Accelerator Laboratory and Stanford University

Eastern Section Meeting, American Association of Petroleum Geologists

September 26, 2016

UNCONVENTIONAL RECOVERY FACTORS

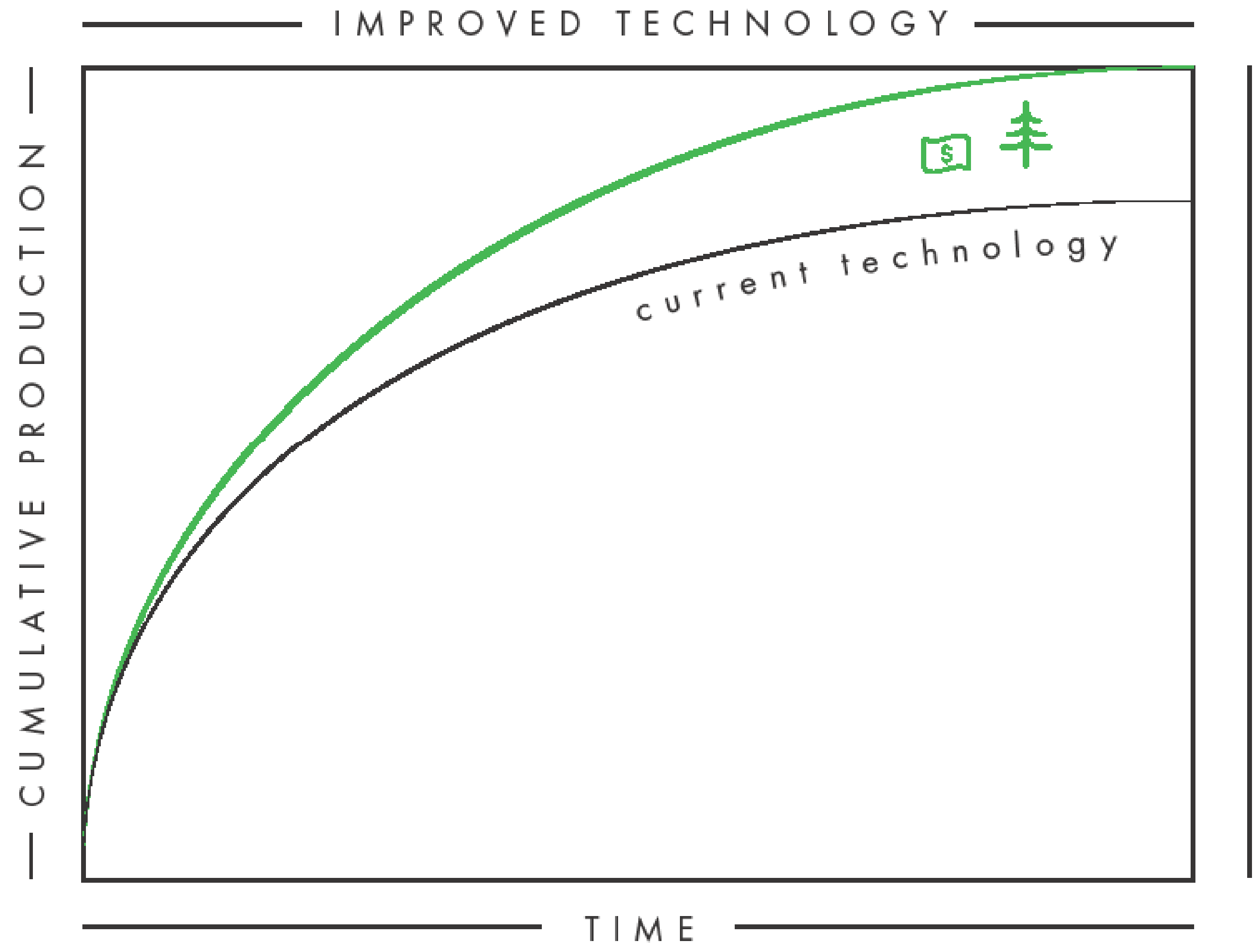
SHALE GAS: 2 TO 19%; AVERAGE 13%

SHALE OIL: LESS THAN 2 %

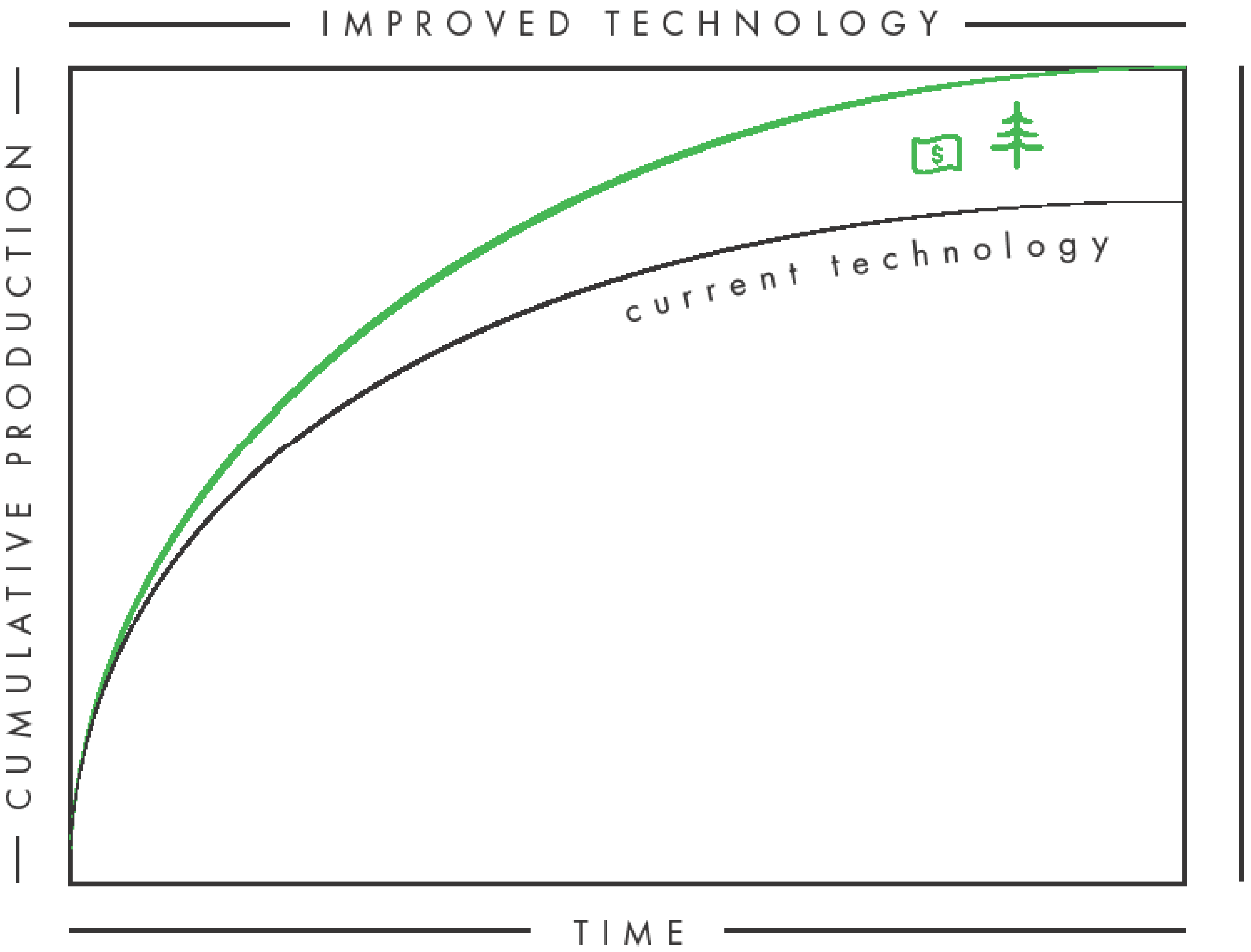
NOT GOOD ENOUGH !!!

WE NEED TO STUDY

Improved Technology



Improved Technology



ENVIRONMENTAL FACTORS

BIG QUESTION ?

CAN WE INCREASE RECOVERY FACTORS WHILE AT THE SAME TIME SEQUESTERING HEAVY METALS AND RADIOACTIVE COMPOUNDS ?

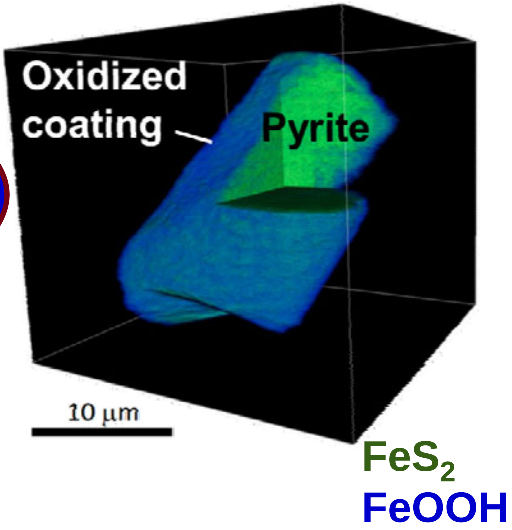
FUNDAMENTAL SCIENCE

- This research provides the knowledge base critical to understanding chemical and physical evolution of reservoir shale, assessing risk to reservoirs. Process knowledge obtained provides a framework and criteria to evaluate **improved fracture fluid compositions and stimulation best practices.**

Synchrotron:

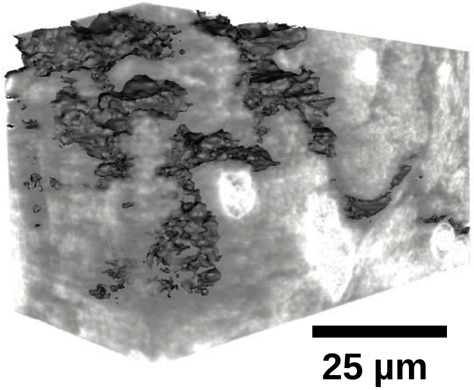
unique, time-resolved imaging

Spectroscopy



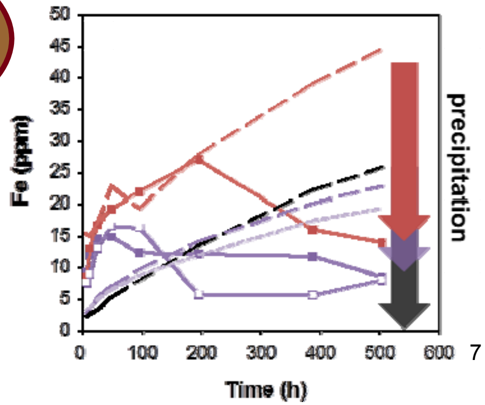
Imaging

Experiments



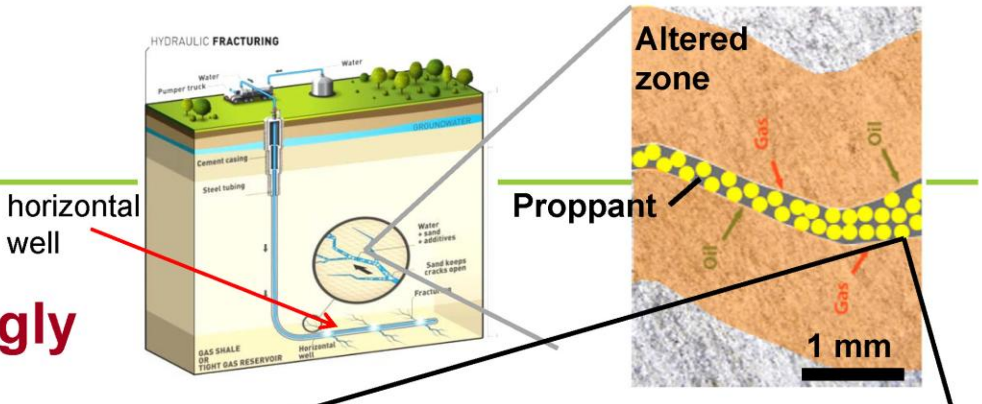
Barnett shale

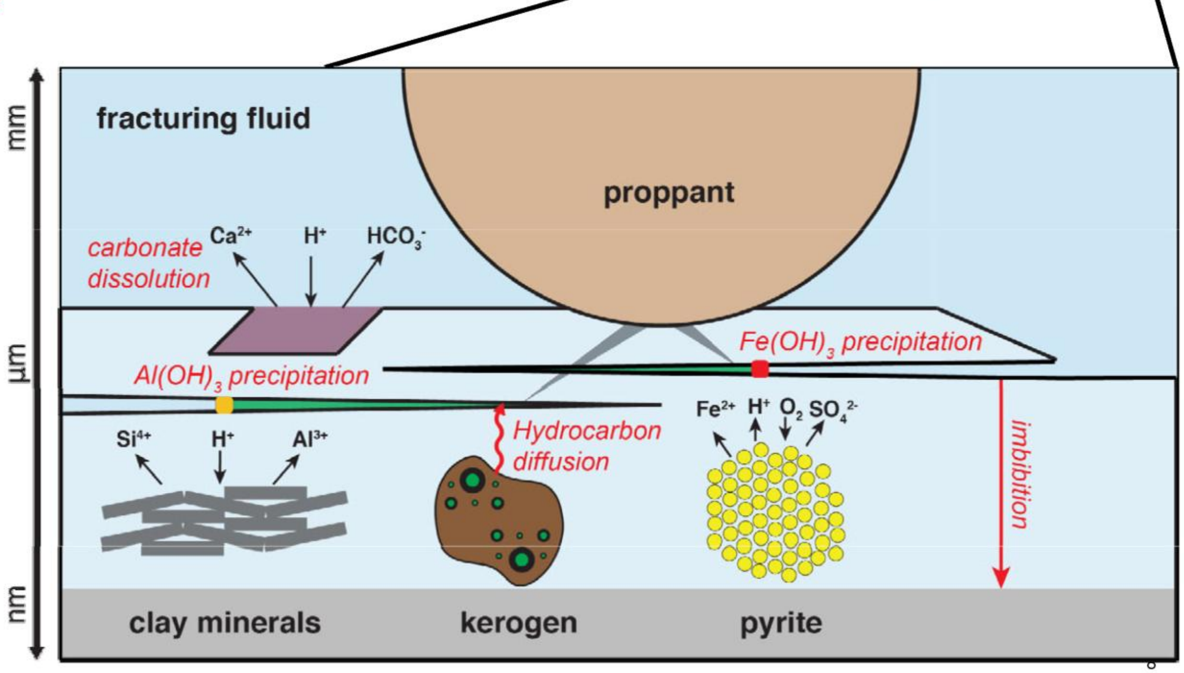
Modeling



Project overview

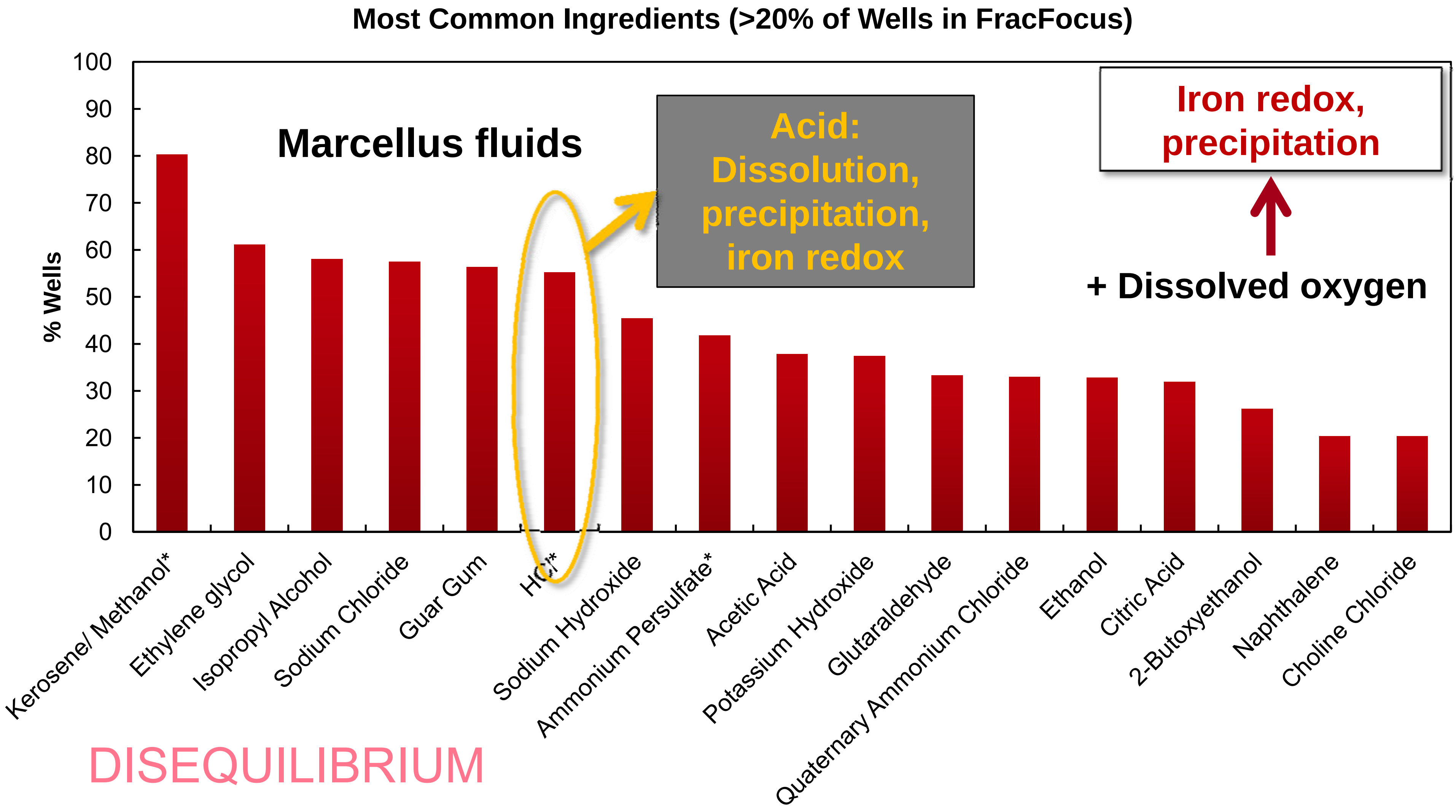
Fluids react strongly with shale





Presenter’s notes: SLAC has been part of this effort from the beginning and we intend to participate in the funding.

Fracture fluid compositions



Most Common Ingredients (>20% of Wells in FracFocus)

Marcellus fluids

Acid: Dissolution, precipitation, iron redox

Iron redox, precipitation

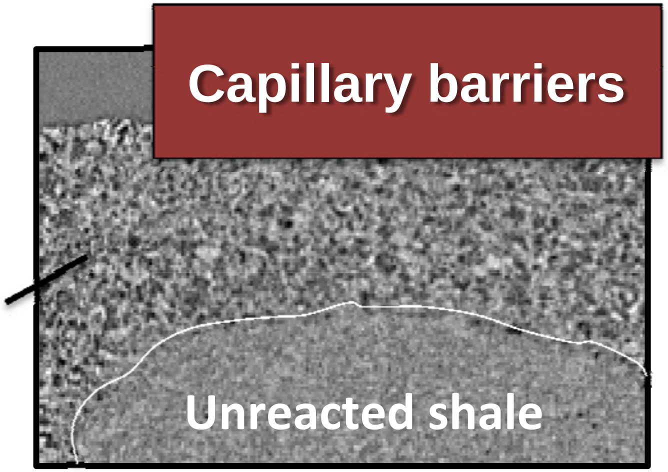
+ Dissolved oxygen

DISEQUILIBRIUM

Processes:

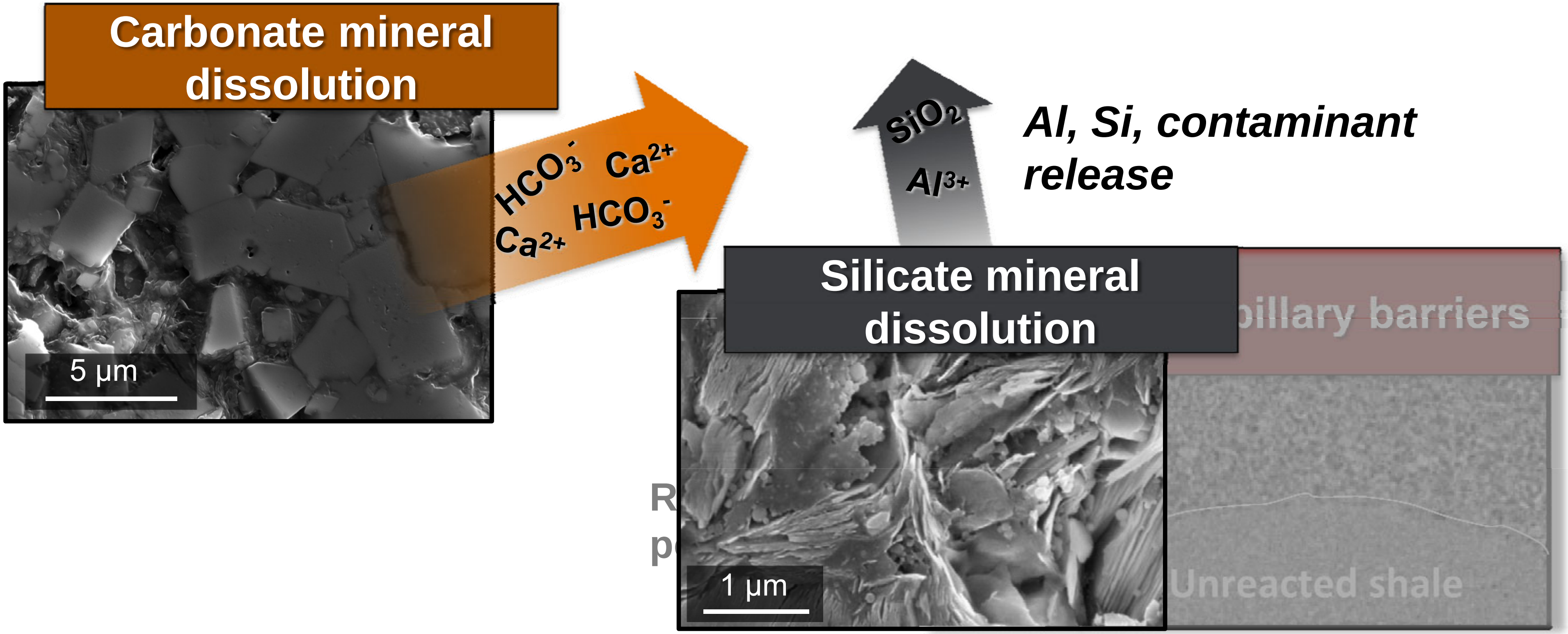
initial acid injection

Cation and trace metal release (Ca, U) and alkalinity generation



Reacted secondary porosity zone

Processes:
initial acid injection

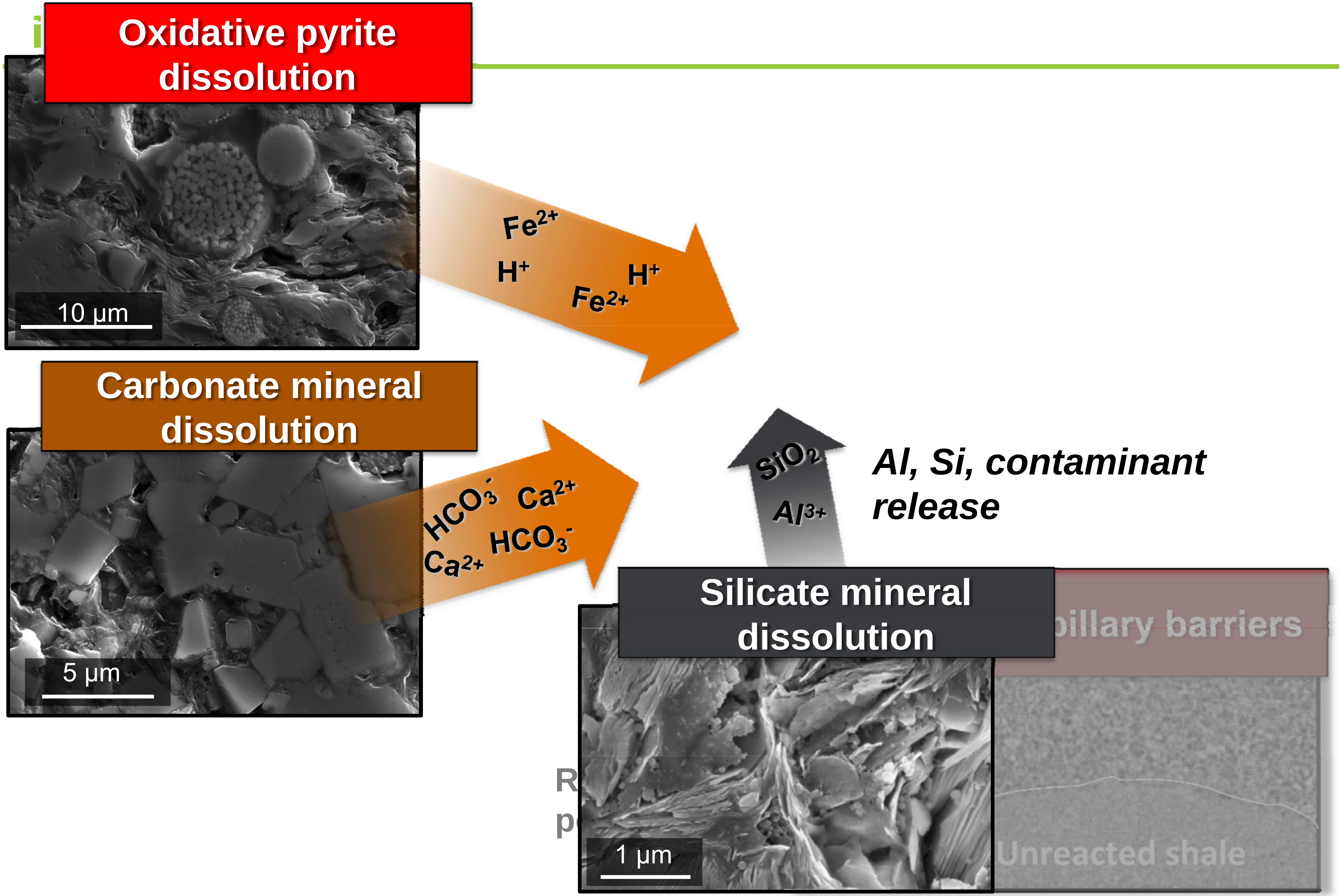


Carbonate mineral dissolution

Silicate mineral dissolution

Al, Si, contaminant release

Processes:



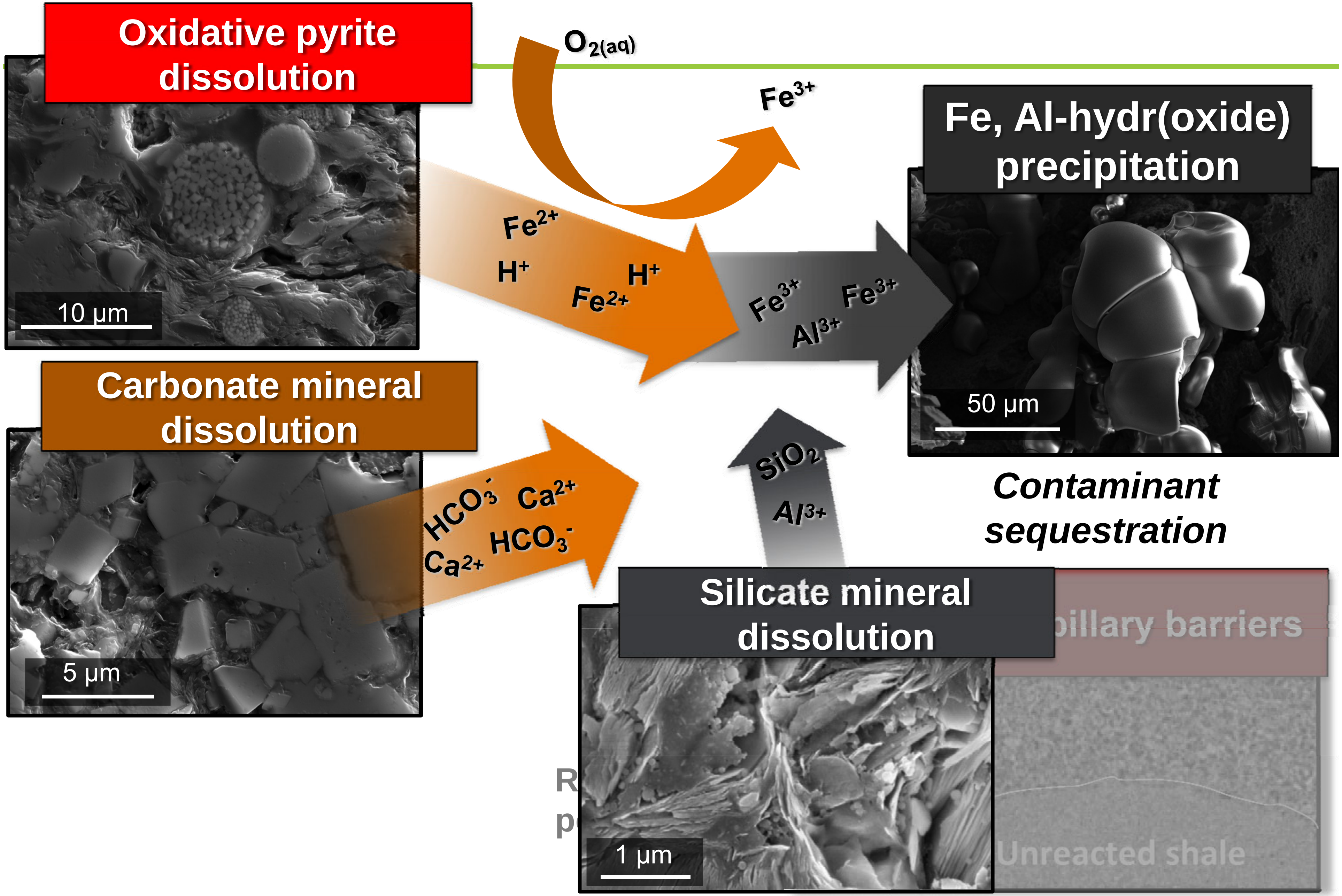
Oxidative pyrite dissolution

Carbonate mineral dissolution

Silicate mineral dissolution

Al, Si, contaminant release

Prediction: acid neutralization



Oxidative pyrite dissolution

Carbonate mineral dissolution

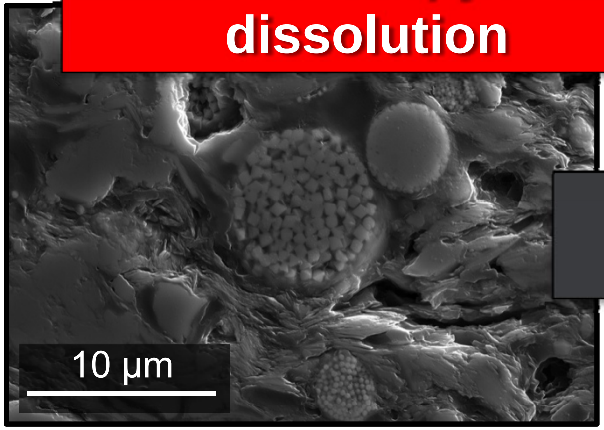
Silicate mineral dissolution

Fe, Al-hydr(oxide) precipitation

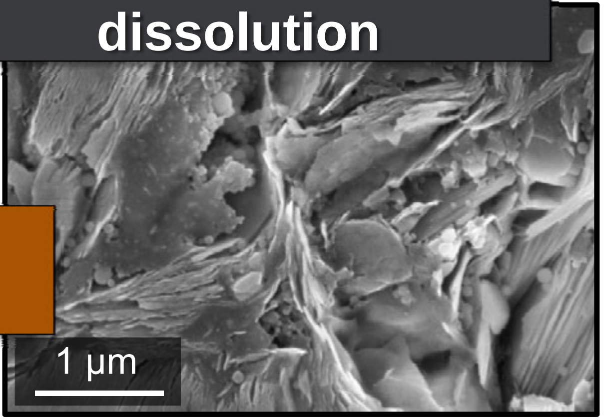
Contaminant sequestration

Positive and negative impacts on transport

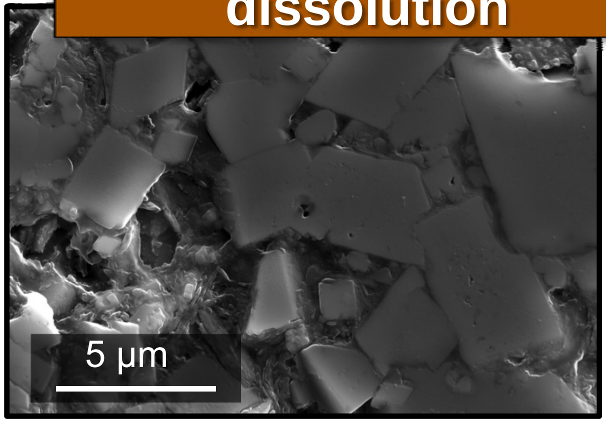
Porosity generation



Oxidative pyrite dissolution

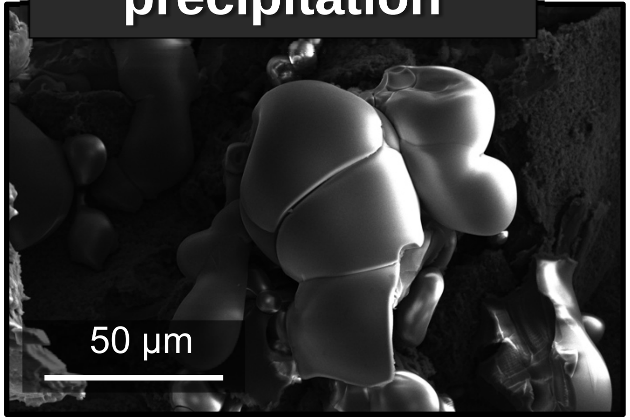


Silicate mineral dissolution

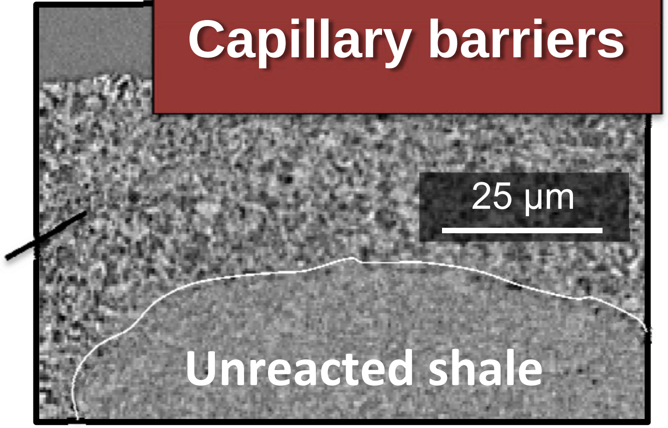


Carbonate mineral dissolution

Flow occlusion



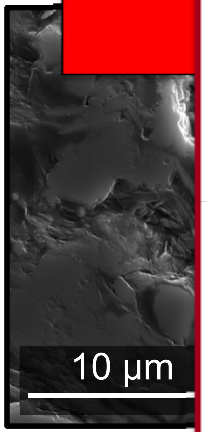
Fe, Al-hydr(oxide) precipitation

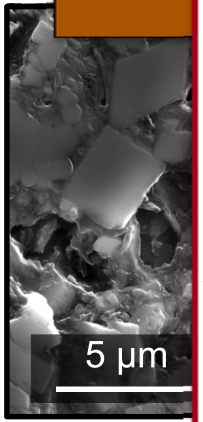


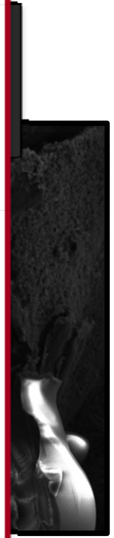
Capillary barriers

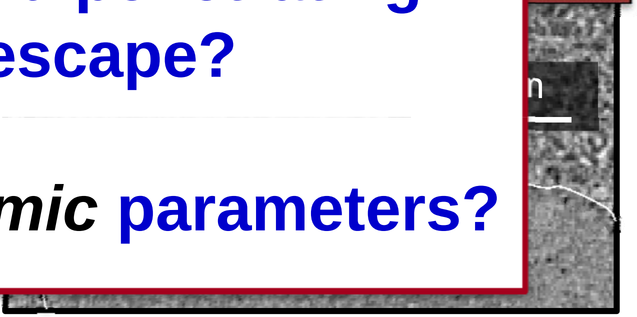
Reacted secondary porosity zone

Positive and negative impacts on transport









Can we predict (and mitigate) mineral precipitation and formation damage?

What are *rates* of reactions?; What reactions occur on relevant timescale?

Where does precipitation occur? (fracture apertures?, surfaces?, matrix?)

***Transport*: how quickly does fluid penetrating matrix / dissolved solids escape?**

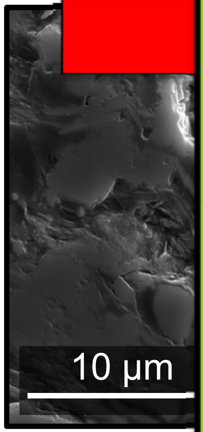
What are the relevant *thermodynamic* parameters?

Positive and negative impacts on transport

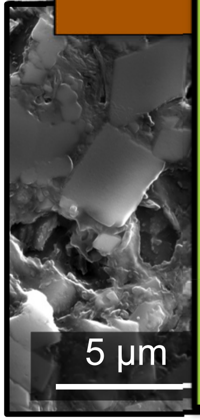
Porosity generation

Flow occlusion

Oxidative pyrite



Ca

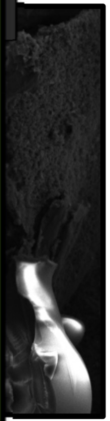


Objectives:

Identify processes, damage to shale

Quantify rates

Develop geochemical model that can inform reservoir simulators



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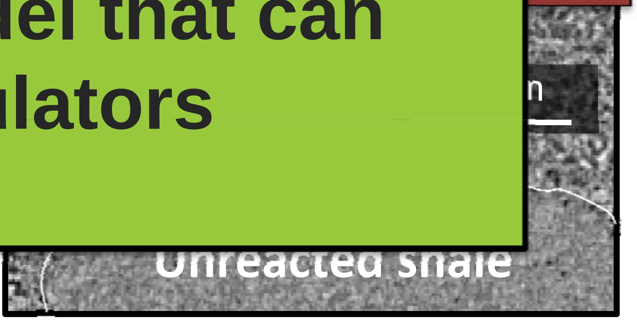
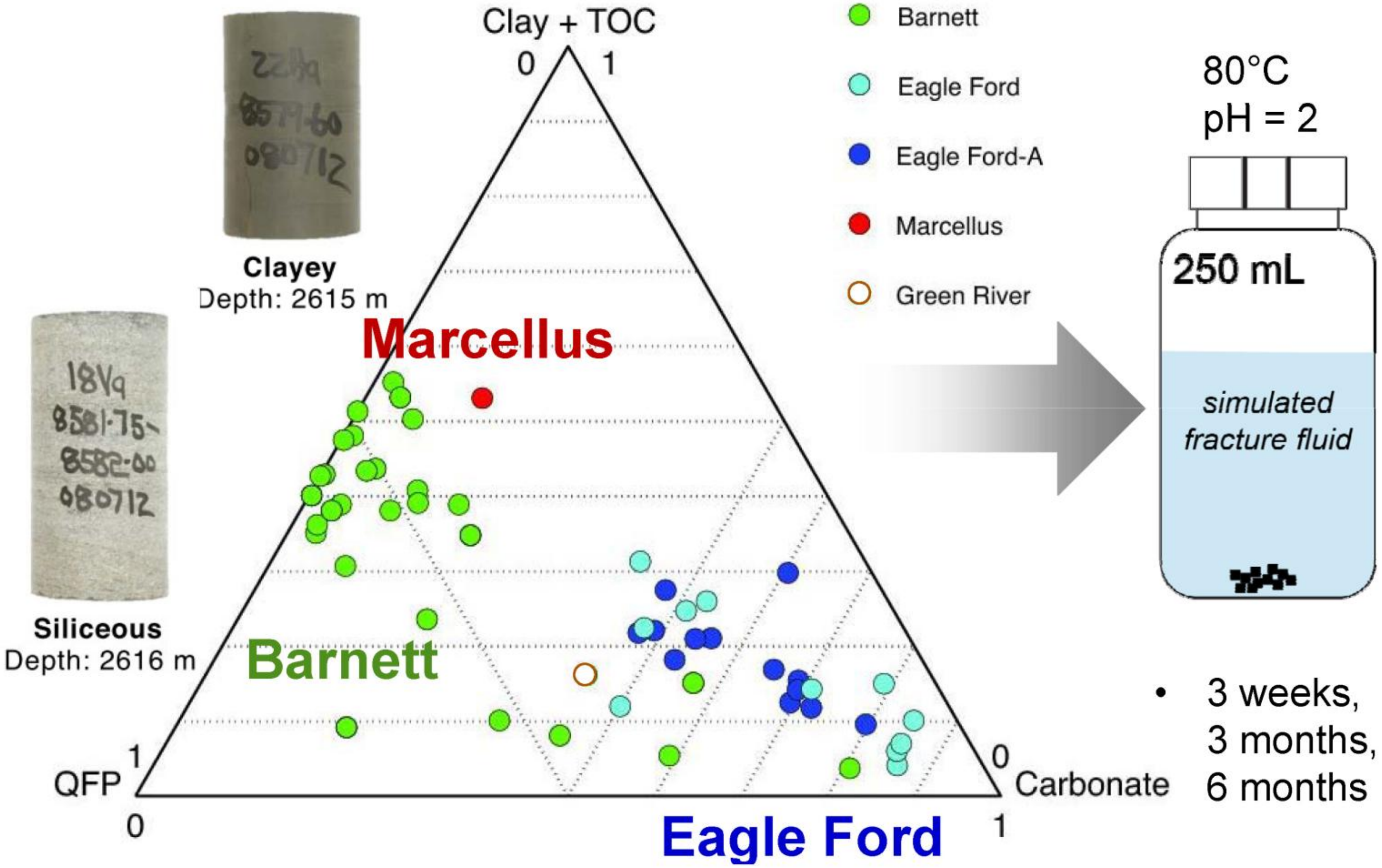


Approach:

Carbonate poor vs. carbonate rich



80°C
pH = 2

- 3 weeks, 3 months, 6 months

Presenter's notes: SLAC has been part of this effort from the beginning and we intend to participate in the funding.

Evolution of fracture surface damage

Types of damage?

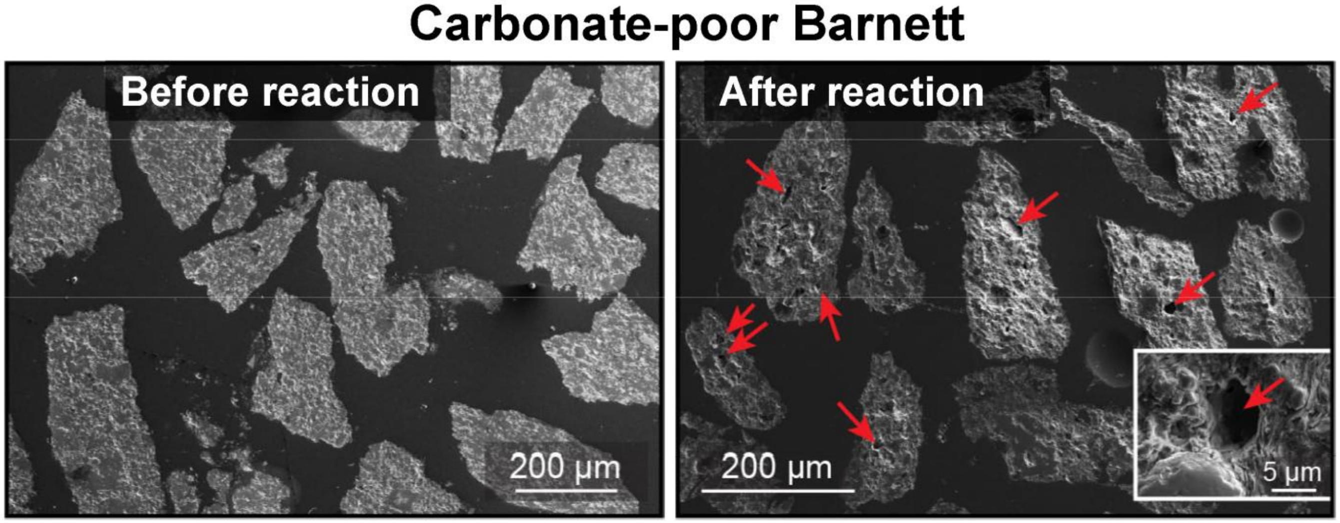
Rates (How fast)?

Implications for flow?

Presenter's notes: Generation of porosity due to selective carbonate dissolution in both carb-rich and carb-poor shales. Distribution of new porosity dictated by pore-scale distribution of carbonate minerals (SEM images after 3 weeks of reaction).

Porosity evolution:

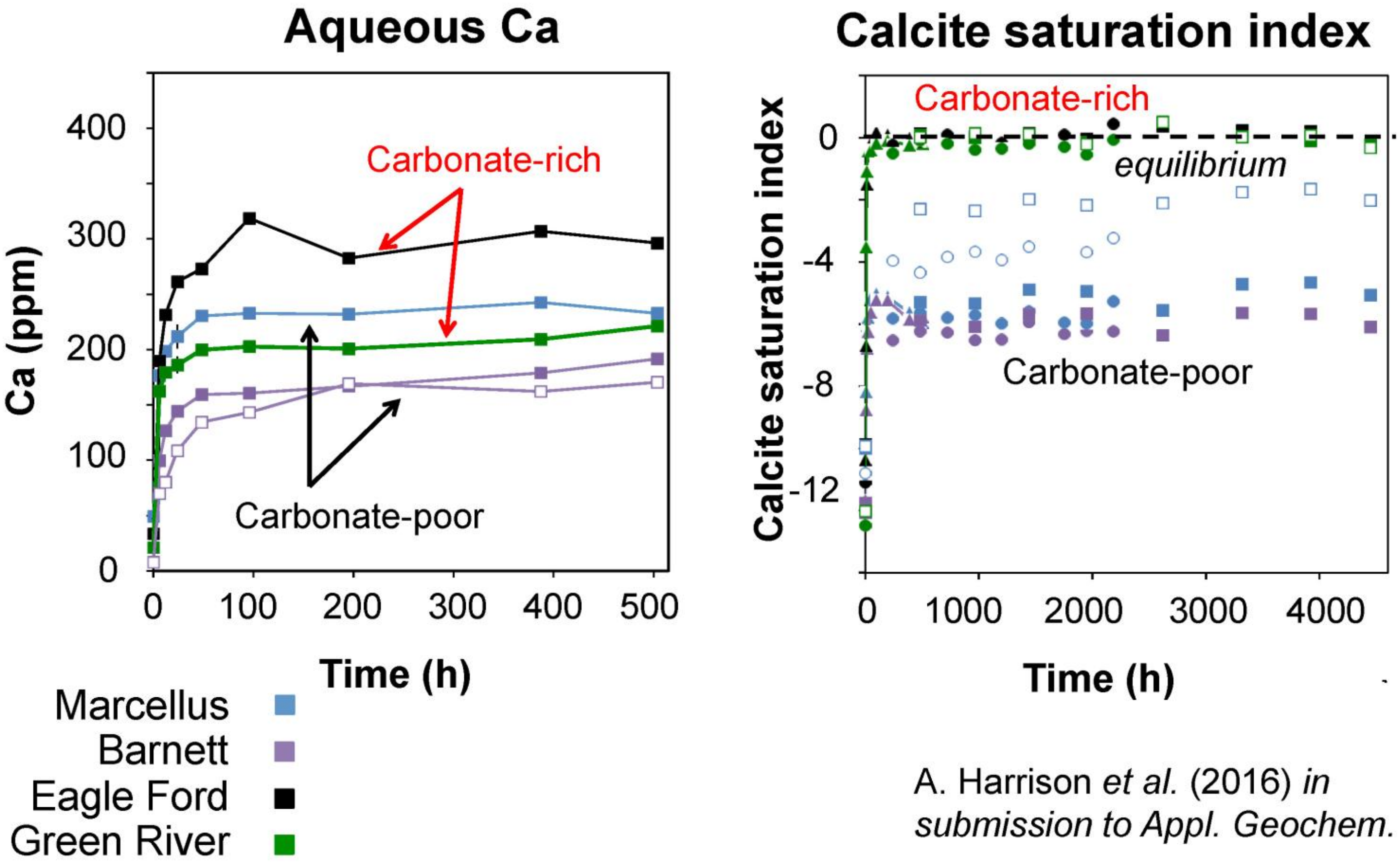
dictated by mineralogy



A. Harrison *et al.* (2016) *in submission to Appl. Geochem.*

Presenter's notes: Fluid composition largely dictated by rapid reaction of calcite – evidenced by rapid release and stabilization of Ca.
In carbonate-rich shales, however, plateau in pH/Catot is due to achievement of equilibrium wrt calcite, while still maintaining at least 70% of initial Ca content. Conversely, plateau is due to near-complete removal of calcite for the carbonate-poor shales; there is insufficient calcite to reach equilibrium.

Rapid reactions controlled by calcite



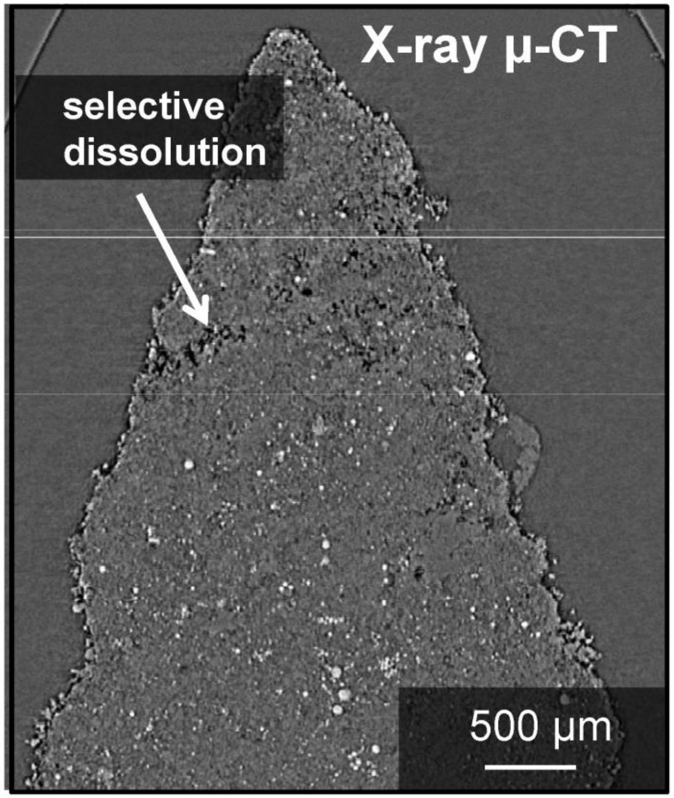
A. Harrison *et al.* (2016) *in submission to Appl. Geochem.*

Presenter's notes: Barnett- Pohang light source data – after 3 weeks of reaction.

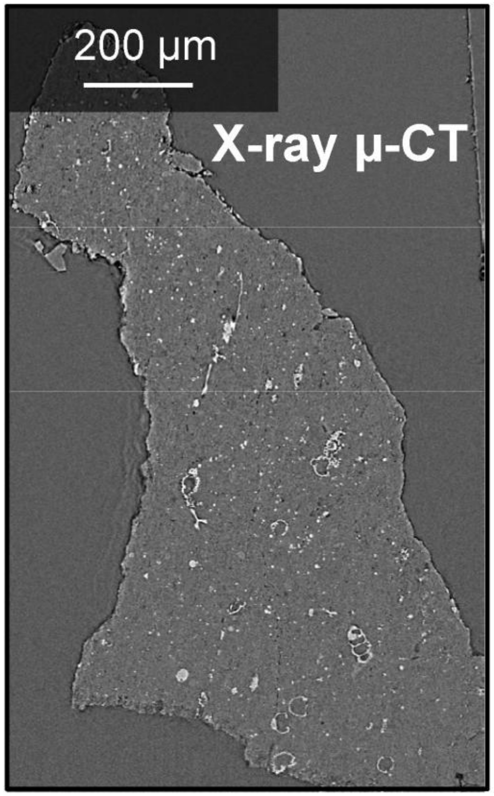
Much more uniform reaction front develops as a consequence of calcite distribution in GR compared to Barnett. Similar generation of discrete porosity observed for Marcellus, and even Eagle Ford. This suggests it is not the abundance of carbonate, but its distribution. In GR, calcite forms somewhat of a cement between nicer crystals of dolomite, quartz, and analcime, whereas in EF it is big chunks, or remnants of shells, that are not necessarily well exposed to the fluid.

Physical damage: Secondary porosity

Carbonate-poor Marcellus



Carbonate-rich Eagle Ford

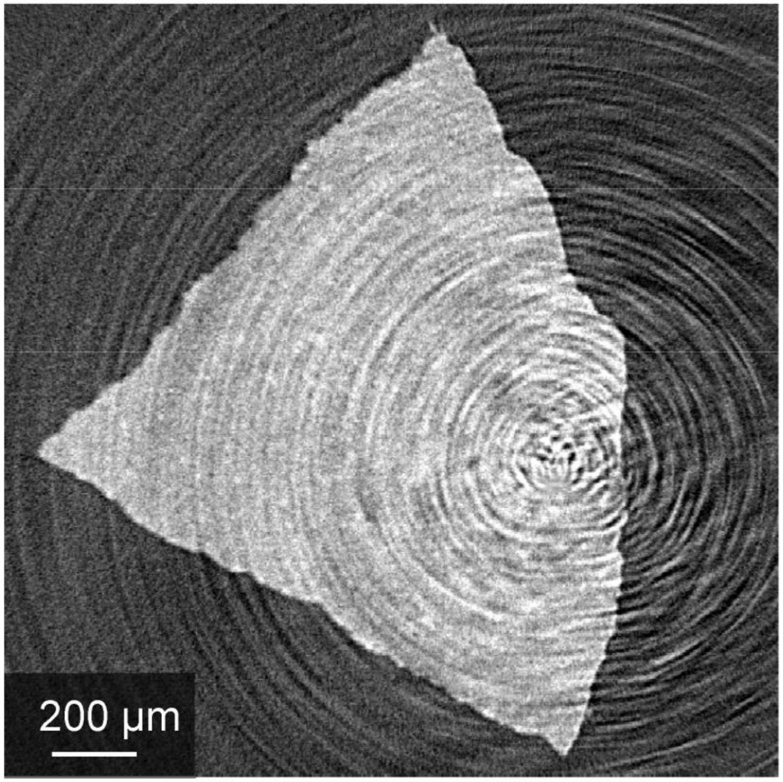


- **Physical protection of carbonate is important**

Presenter's notes: Sample was initially dry; so rxn front is a combination of imbibition and reaction. Collected at SSRL.

Physical damage: Secondary porosity

Carbonate-rich Green River



A. Kiss *et al.* (2016) *in preparation*

Generation of uniform reaction front that propagates approximately proportional to $t^{0.5}$

Green River shale reacted for 5 h at 80 C, imaged at 1 h intervals with synchrotron radiation

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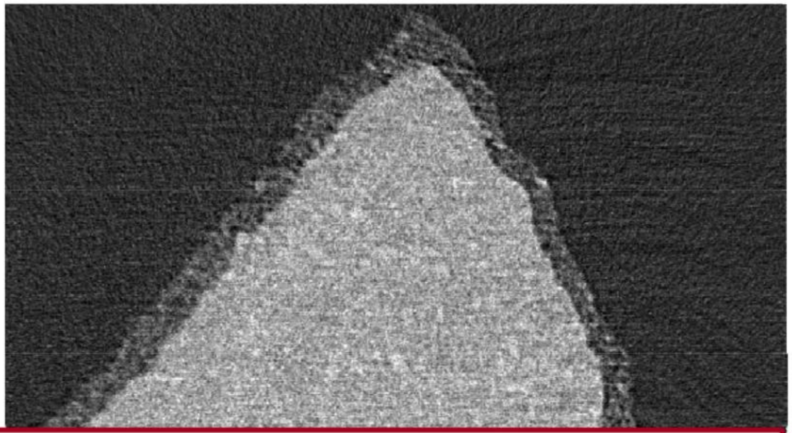
Physical damage: Secondary porosity

Carbonate-rich Green River



Rates: fast (few hours)

Damage zone thickness: approaches mm

Secondary porosity: potential for capillary barrier

Affects mechanical properties of fractures

A. Kiss *et al.* (2016) *in preparation*

Generation of uniform reaction front that propagates approximately proportional to $t^{0.5}$

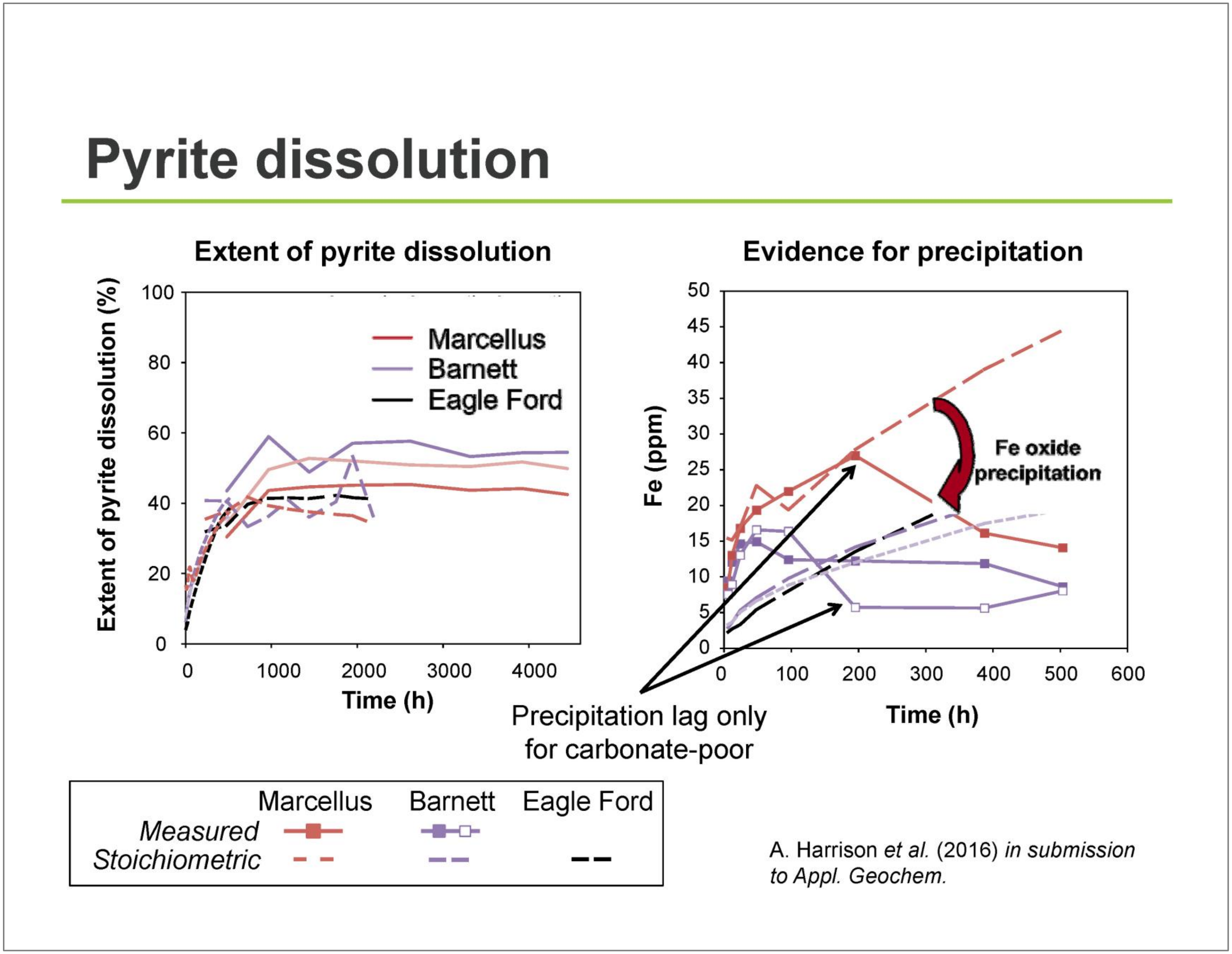
Green River shale reacted for 5 h at 80 C, imaged at 1 h intervals with synchrotron radiation

Presenter's notes: SLAC has been part of this effort from the beginning and we intend to participate in the funding.

Iron oxidation / precipitation

- Under what conditions does iron oxidation occur?
- Rates?
- Where are precipitates localized?
- What phases occur?

Presenter’s notes: Sample was initially dry; so rxn front is a combination of imbibition and reaction. Collected at SSRL.



Pyrite dissolution

Extent of pyrite dissolution

Evidence for precipitation

Precipitation lag only for carbonate-poor

	Marcellus	Barnett	Eagle Ford
Measured	■	■□	
Stoichiometric	– –	– –	– –

A. Harrison *et al.* (2016) *in submission to Appl. Geochem.*

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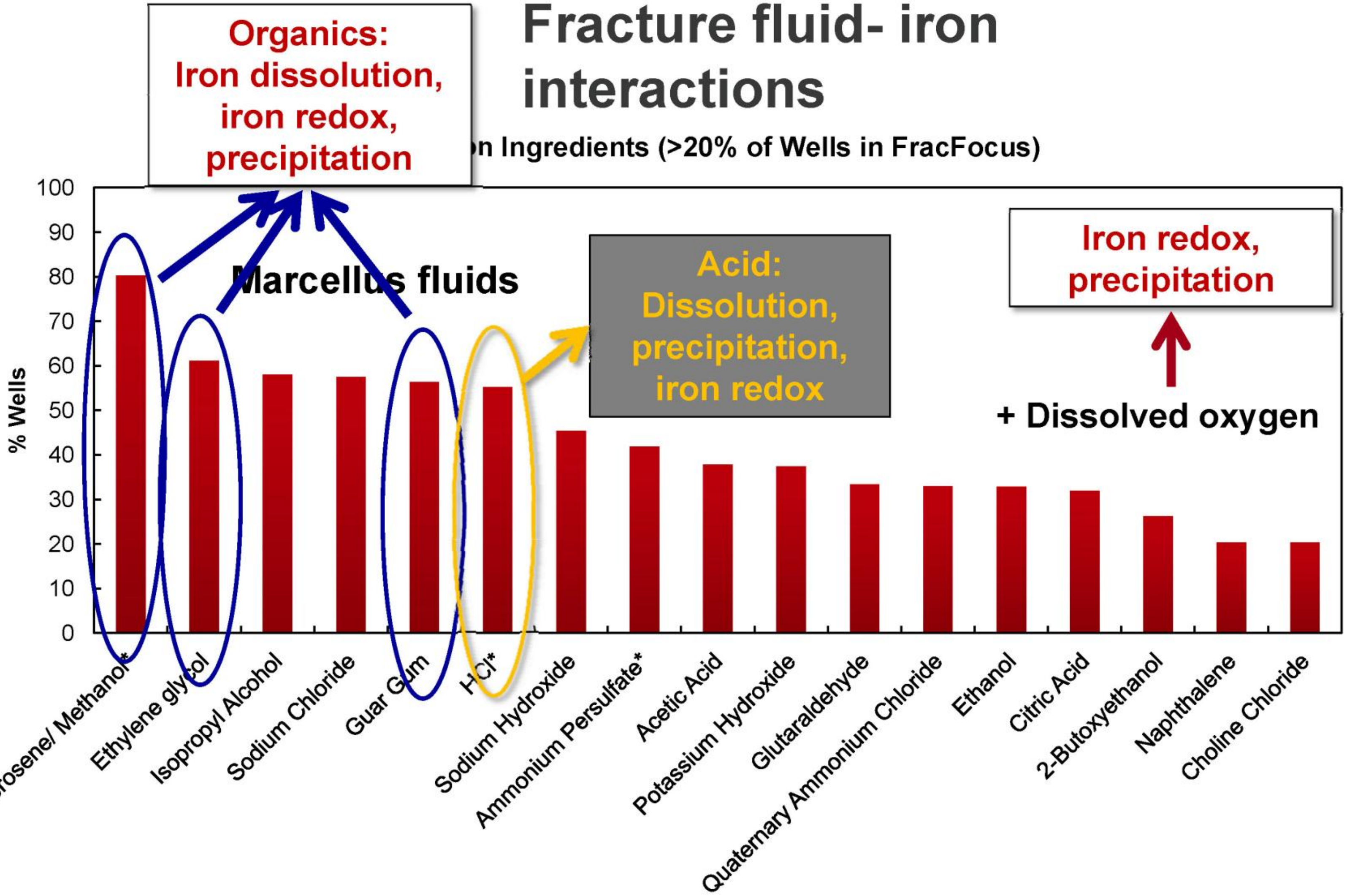
Fracture fluid- iron interactions



Organics:
Iron dissolution,
iron redox,
precipitation

Marcellus fluids

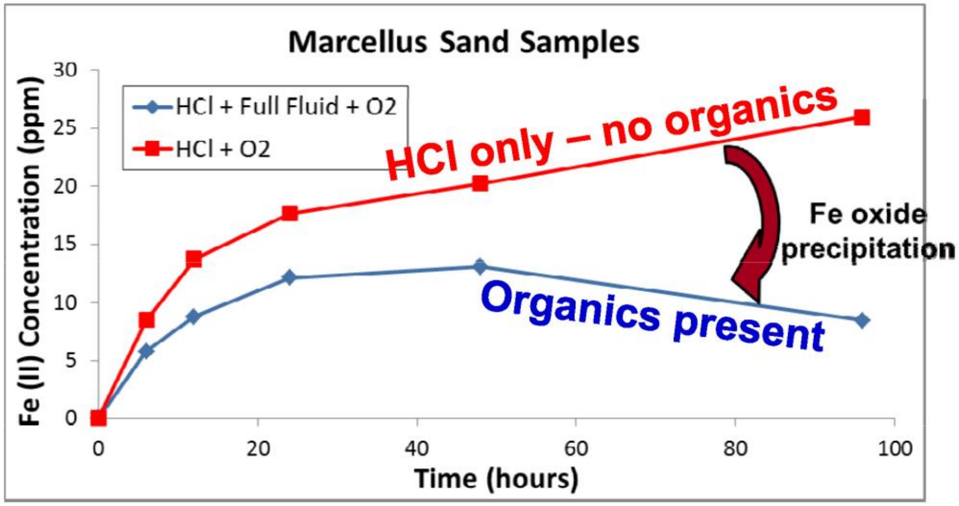
Acid:
Dissolution,
precipitation,
iron redox

Iron redox,
precipitation

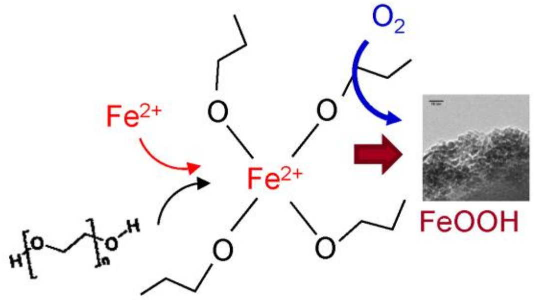
+ Dissolved oxygen

Presenter's notes: Organics in fracture fluid accelerate iron oxidation.

Organics in fracture fluid accelerate iron oxidation



Fracture fluid accelerates iron oxide precipitation – ***opposite of intended effect of "iron control" additives.***



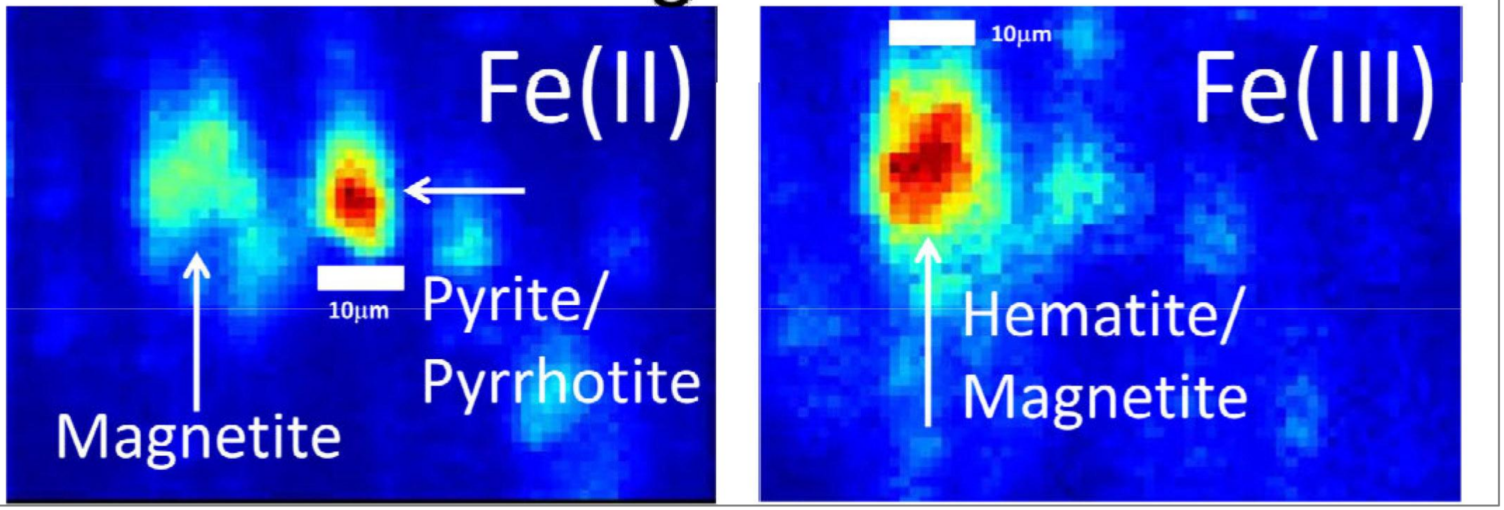
A. Jew *et al.* (2016) *in preparation*

Presenter's notes: We have to use a SR microprobe to do this cuz electrons don't penetrate, aren't sensitive enough, don't give speciation.

Iron oxides precipitate in shale matrix

High carbonate (strong pH buffer)

Reacted Eagle Ford Shale

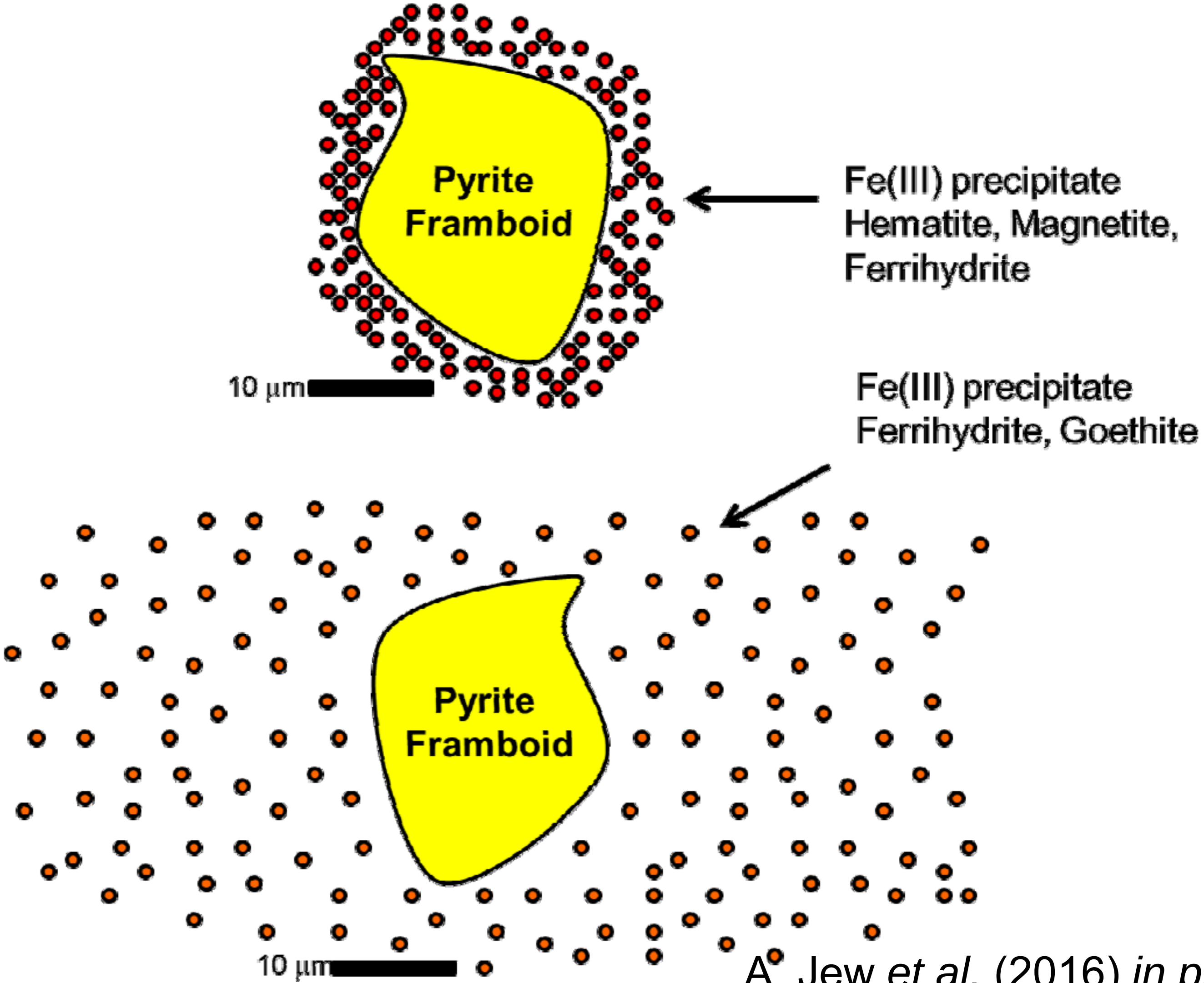


Presenter's notes: We have to use a SR microprobe to do this cuz electrons don't penetrate, aren't sensitive enough, don't give speciation.

pH (carbonate) controls precipitate distribution

High carbonate (strong pH buffer)

Low carbonate (poor pH buffer)



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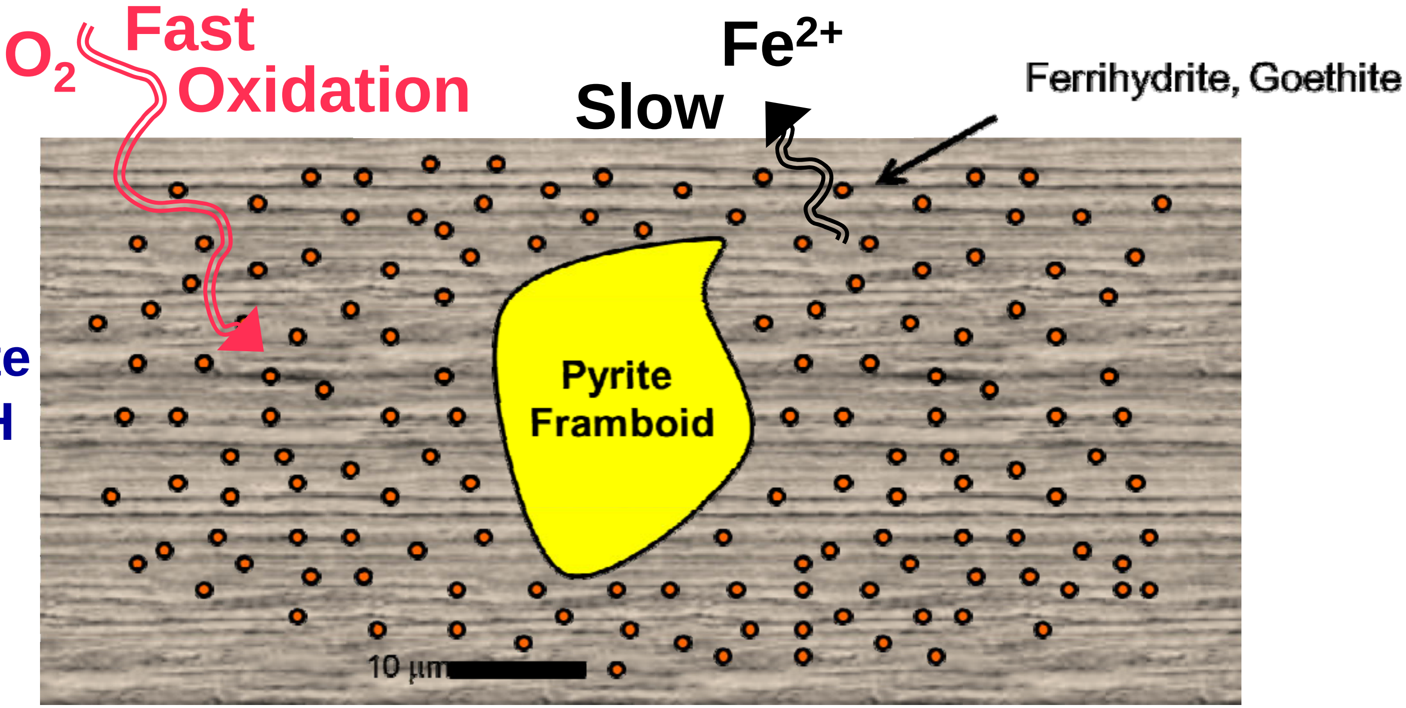
pH (carbonate) controls precipitate distribution

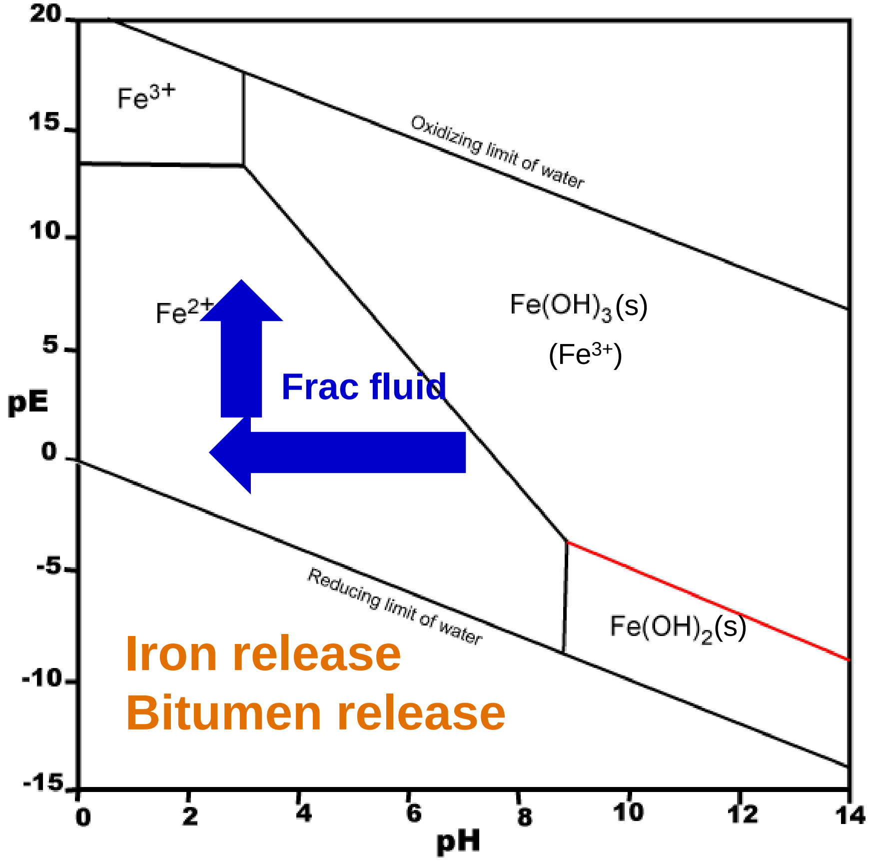
Low carbonate (poor pH buffer)



Pulling this together

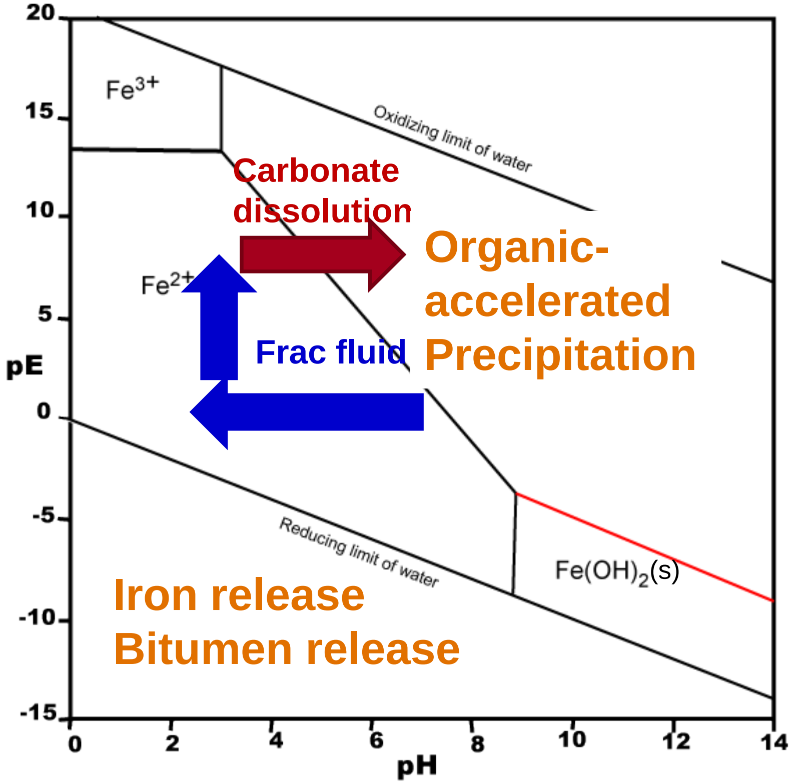
Presenter’s notes: SLAC has been part of this effort from the beginning and we intend to participate in the funding.

Chemical model: Iron oxidation and precipitation



Presenter's notes: Marcellus specific Fe-bearing minerals: Fe-bearing dolomite: 0.2 wt%; siderite: 0.5 wt%; pyrite: 4.6 wt%; ankerite (basically dolomite with Fe, Mn, Mg solid solution): 0.5%; Fe-bearing chlorite: 4.2 wt%.

Chemical model: Iron oxidation and precipitation



Carbonate dissolution

Organic-accelerated Precipitation

Frac fluid

Iron release

Bitumen release

Presenter’s notes: Marcellus specific Fe-bearing minerals: Fe-bearing dolomite: 0.2 wt%; siderite: 0.5 wt%; pyrite: 4.6 wt%; ankerite (basically dolomite with a Fe, Mn, Mg solid solution): 0.5%; Fe-bearing chlorite: 4.2 wt%.

Accomplishments to date

Advanced knowledge baseline in following areas:

- ✓ **Identified key processes / regimes**
- ✓ **Quantified reaction rates**
- ✓ **Characterized physical/chemical damage**
- ✓ **Quantitative geochemical model**
- ✓ **Concept model for iron behavior**
- ✓ **Concept for kerogen behavior**
- ✓ **Constraints on U behavior**
- ✓ **Presented results at national/international meetings**
- ✓ **3 Manuscripts in submission/preparation**

Summary and conclusions

Conclusions

Dissolution rapidly damages fracture surfaces (hours)

Mineral precipitation causes matrix damage (days)

Primary control: pH (carbonate): Rates, extent

Important secondary controls on rates: Mineral texture, organics

Summary and conclusions

Conclusions

Dissolution rapidly damages fracture surfaces (hours)

Mineral precipitation causes matrix damage (days)

Primary control: pH (carbonate): Rates, extent

Important secondary controls on rates: Mineral texture, organics

Lessons Learned

Rapid formation damage follows fracture fluid everywhere

Large variations in pH are bad for formations prone to iron scale

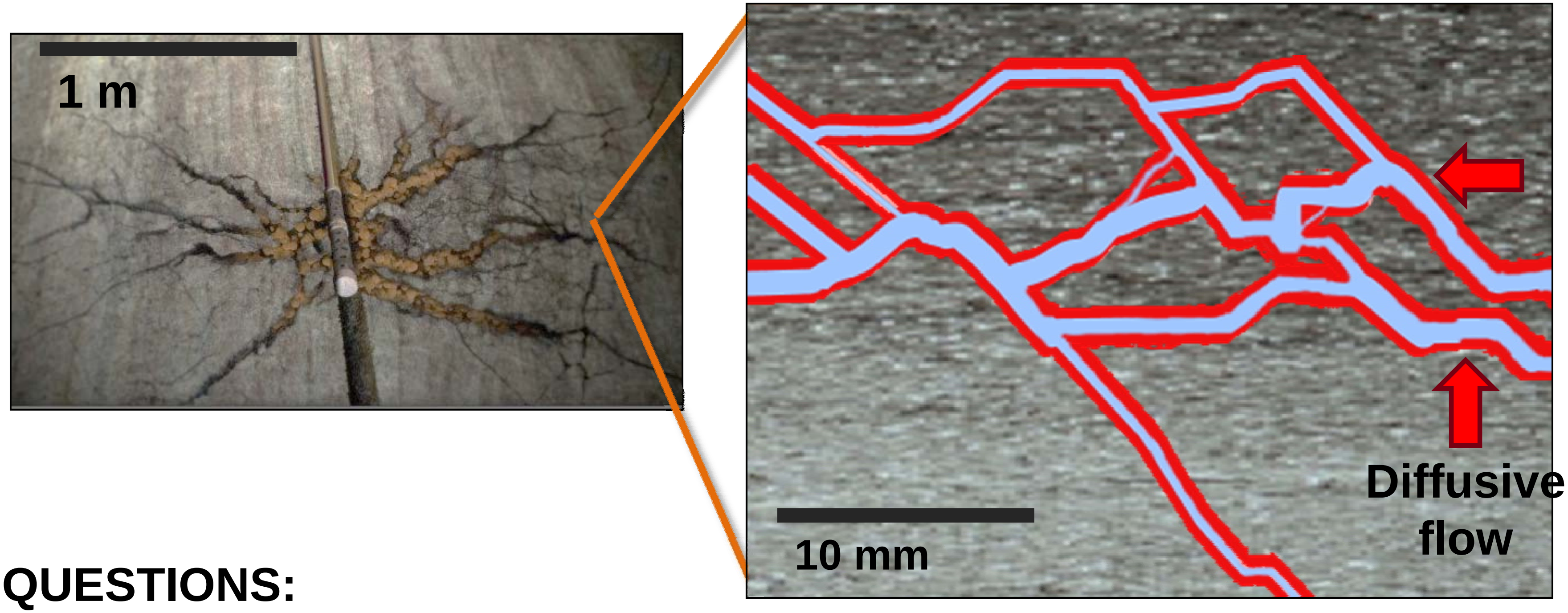
Organic iron-control additives should be carefully evaluated

Shale matrix is important location for mineral precipitation

Looking forward: New model for damage zone (‘skin’)

Presenter’s notes: SLAC has been part of this effort from the beginning and we intend to participate in the funding.

Damage zone ('skin')



QUESTIONS:

- What is the impact of damage zone on production?
- How to minimize?

OBJECTIVES:

- Image/model geochemistry and flow in damage zone
- Assess reservoir-scale impact on gas/fluid flow