Chemical control of fluid flow and contaminant release in shale microfractures

FWP 100211

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SLAC National Accelerator Laboratory and Stanford University

U.S. Department of Energy

National Energy Technology Laboratory

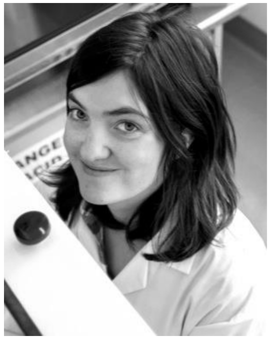
Mastering the Subsurface Through Technology, Innovation and Collaboration:

Carbon Storage and Oil and Natural Gas Technologies Review Meeting

August 16-18, 2016

Team

Harrison



Geochemical modeling

Jew

Experimental geochemistry

Dustin

Experimental geochemistry

Joe-Wong

Experimental geochemistry

Kohli

Geo-mechanics

Kiss

Imaging, CT

"Senior" personnel

Maher

Geochemical modeling

Bargar

Experimental geochemistry

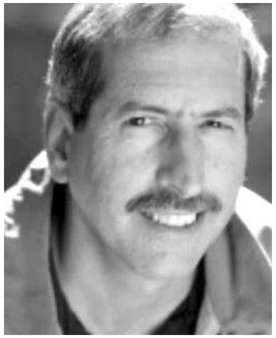
Brown

Experimental geochemistry

Kovscek

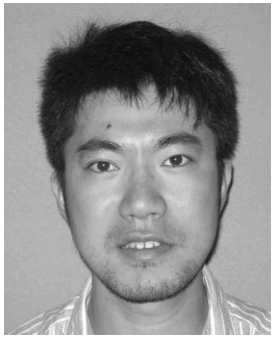
Fluid flow porous media

Zoback



Geo-mechanics

Liu



Imaging, CT

Outline

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- Benefit to program
- Project overview
- Technical
  - Processes and predictions
  - Approach: geochemistry & synchrotron imaging
  - Evolution of fracture surface damage ('skin')
  - Iron chemistry and precipitation
- Accomplishments
- Overarching Summary
- Future Plans
- Synergy opportunities

Benefit to the Program

- **Program goals addressed:**
  - Improve **resource optimization** (unconventional stimulation)
  - Improve **water quality** and **environmental impact**
  - Address **fundamental** subsurface science **knowledge gaps**

- **Benefits to project: fundamental scientific research**
  - Baseline improvements to knowledge base: (i) Identify shale-fluid processes, (ii) quantify rates of reactions, (iii) Characterize physical damage to shale
  - 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.

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Project overview

Project goals: improve knowledge base - critical processes

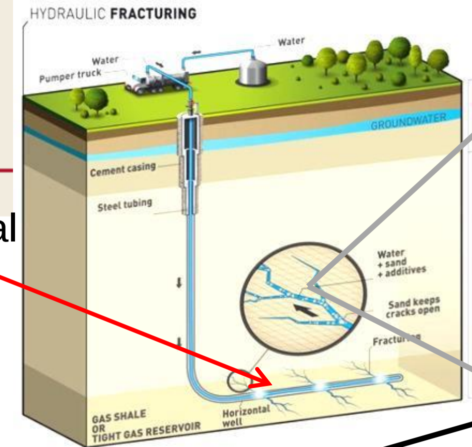
- (i) Identify shale-fluid processes
- (ii) Quantify rates of reactions
- (iii) Characterize physical/chemical damage to shale

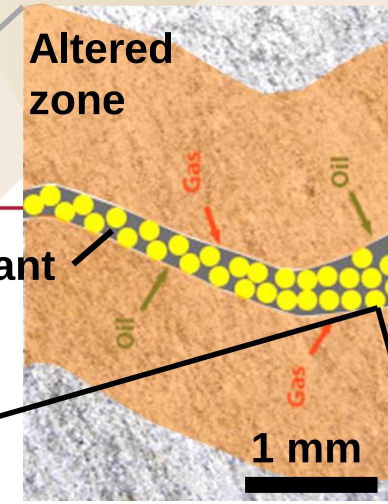
Success criteria:

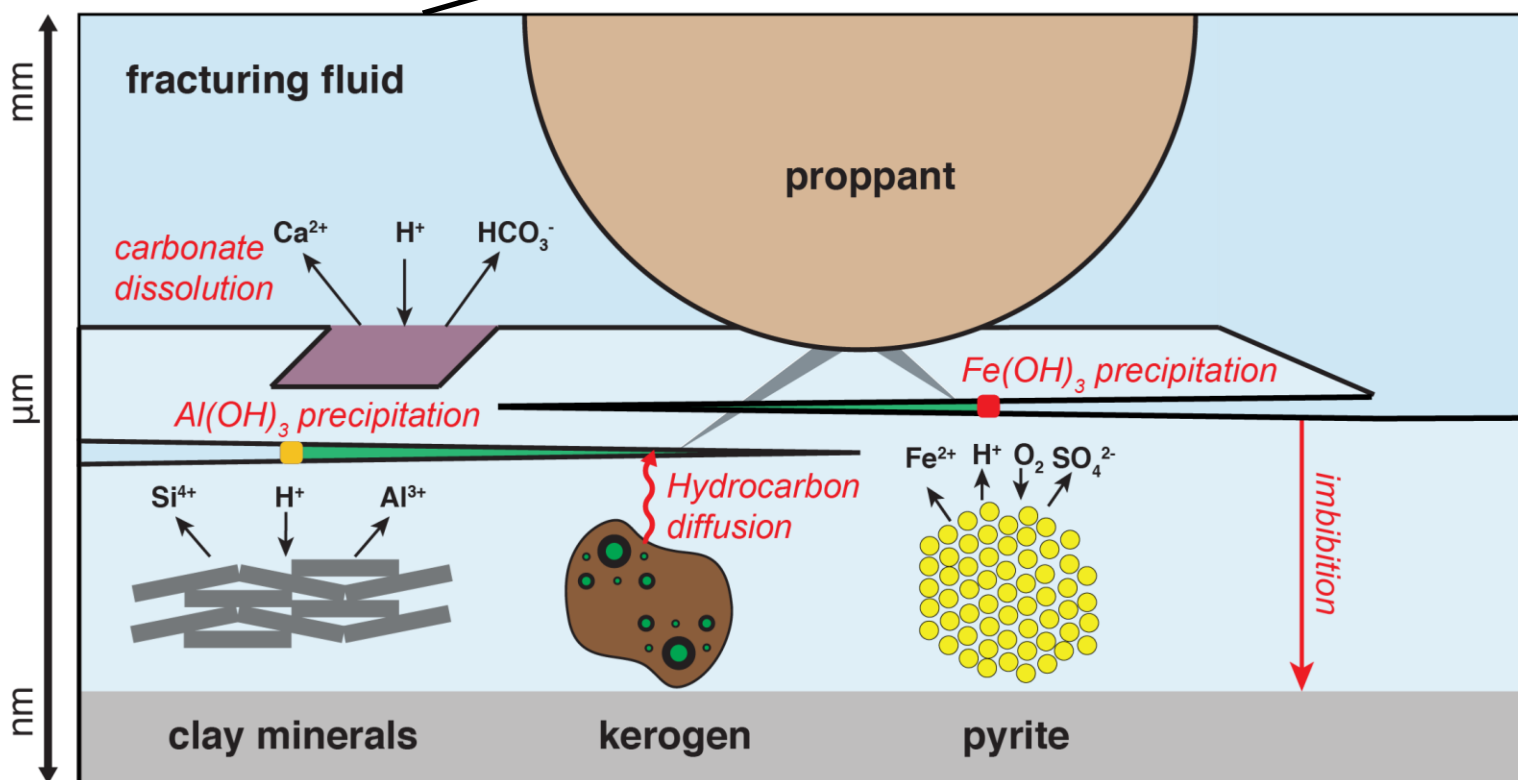
- On-time completion of specific tasks in PMP
- Identification of primary fluid-shale processes
- Identification of damage mechanisms to shale, kerogen
- Development of quantitative reactive transport model
- Presentation of results at national/international meetings
- Publication of 3 peer-reviewed manuscripts in major journals

Project overview

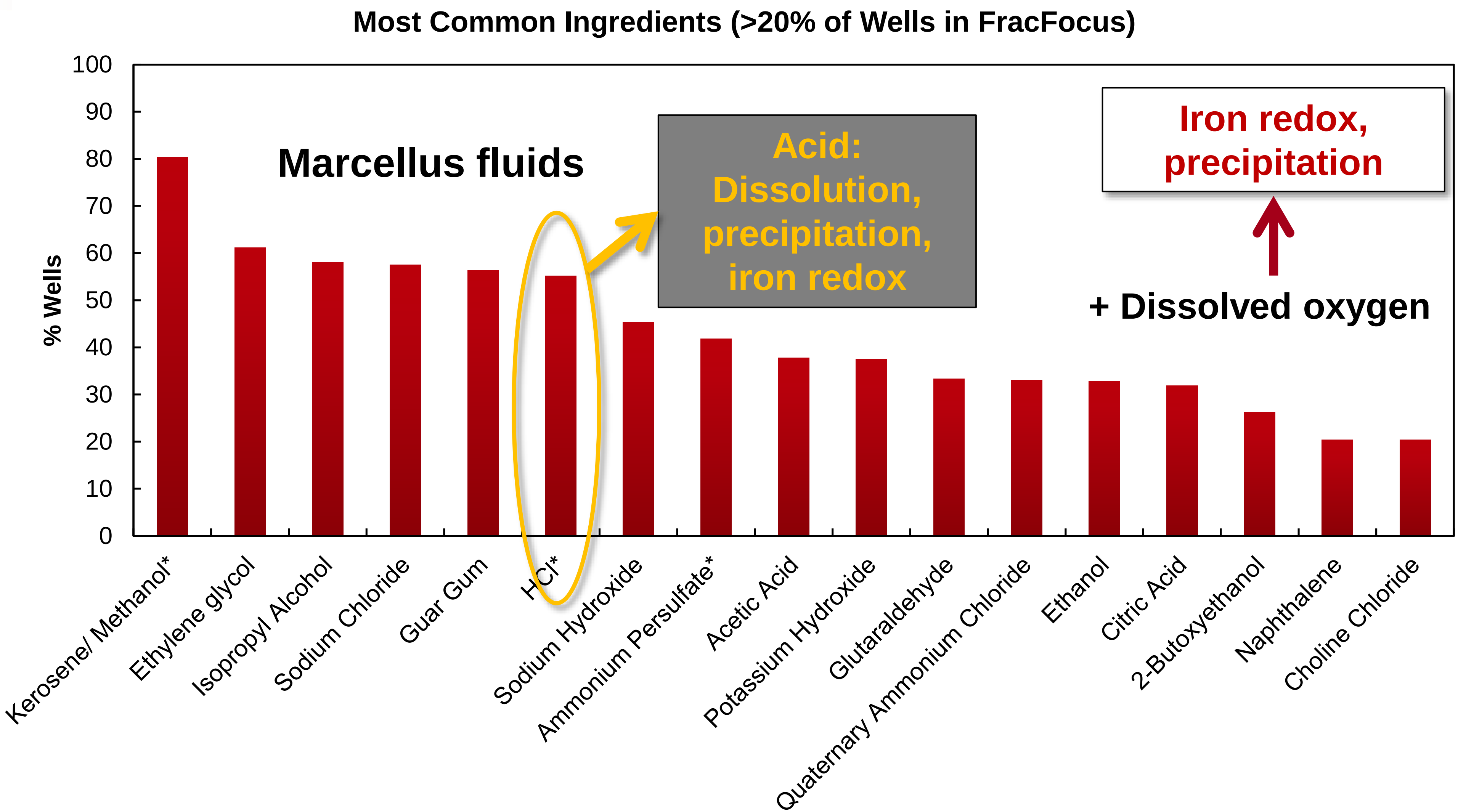
Fluids react strongly with shale





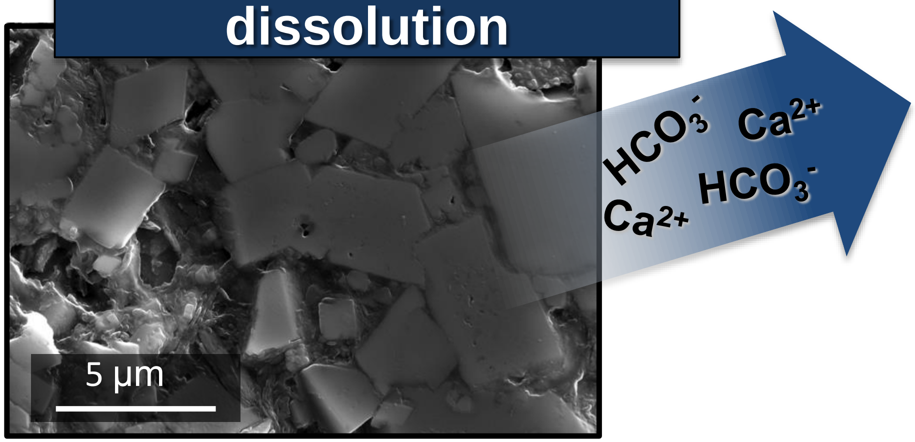


Fracture fluid compositions



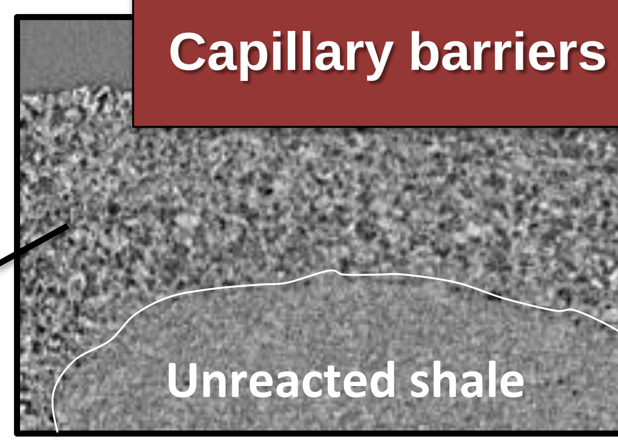
Processes: initial acid injection

Carbonate mineral dissolution



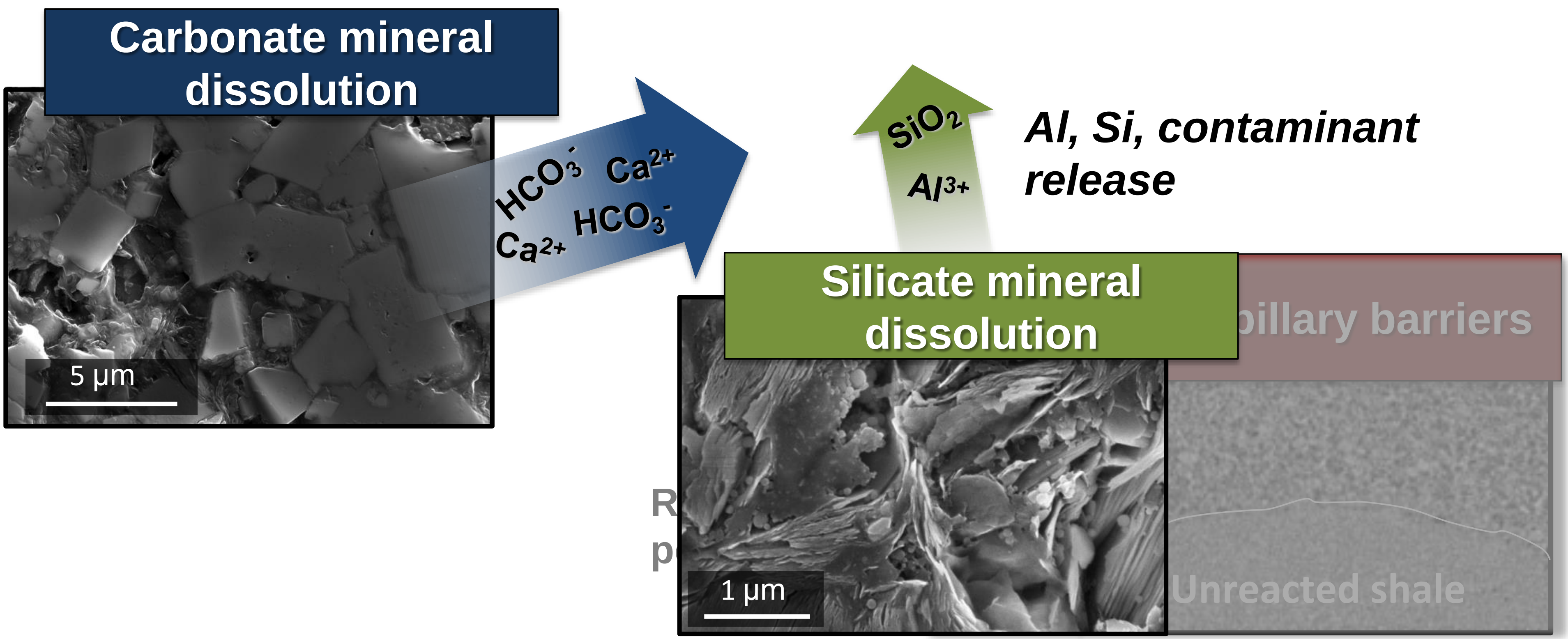
Cation and trace metal release (Ca, U) and alkalinity generation

Capillary barriers

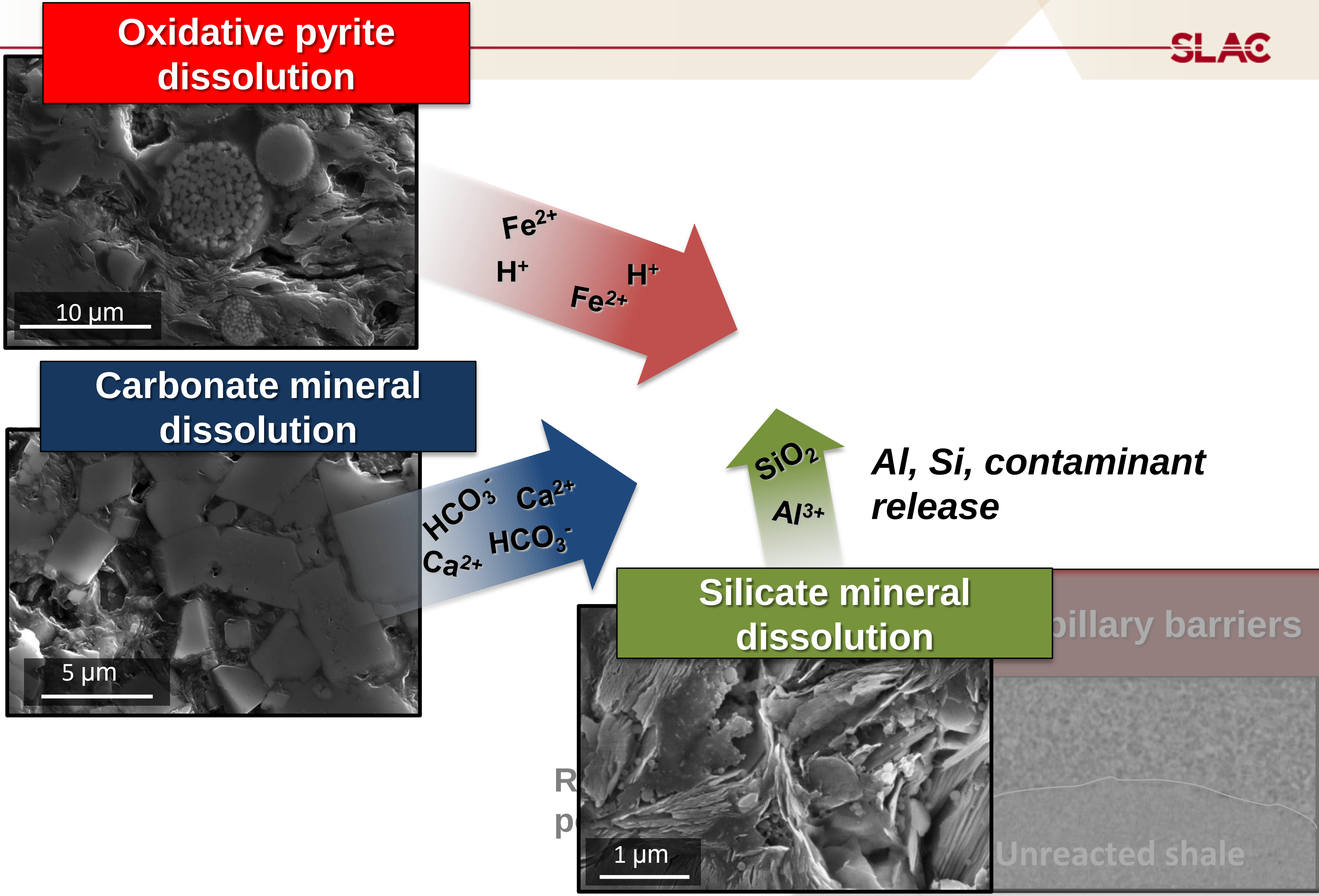


Reacted secondary porosity zone

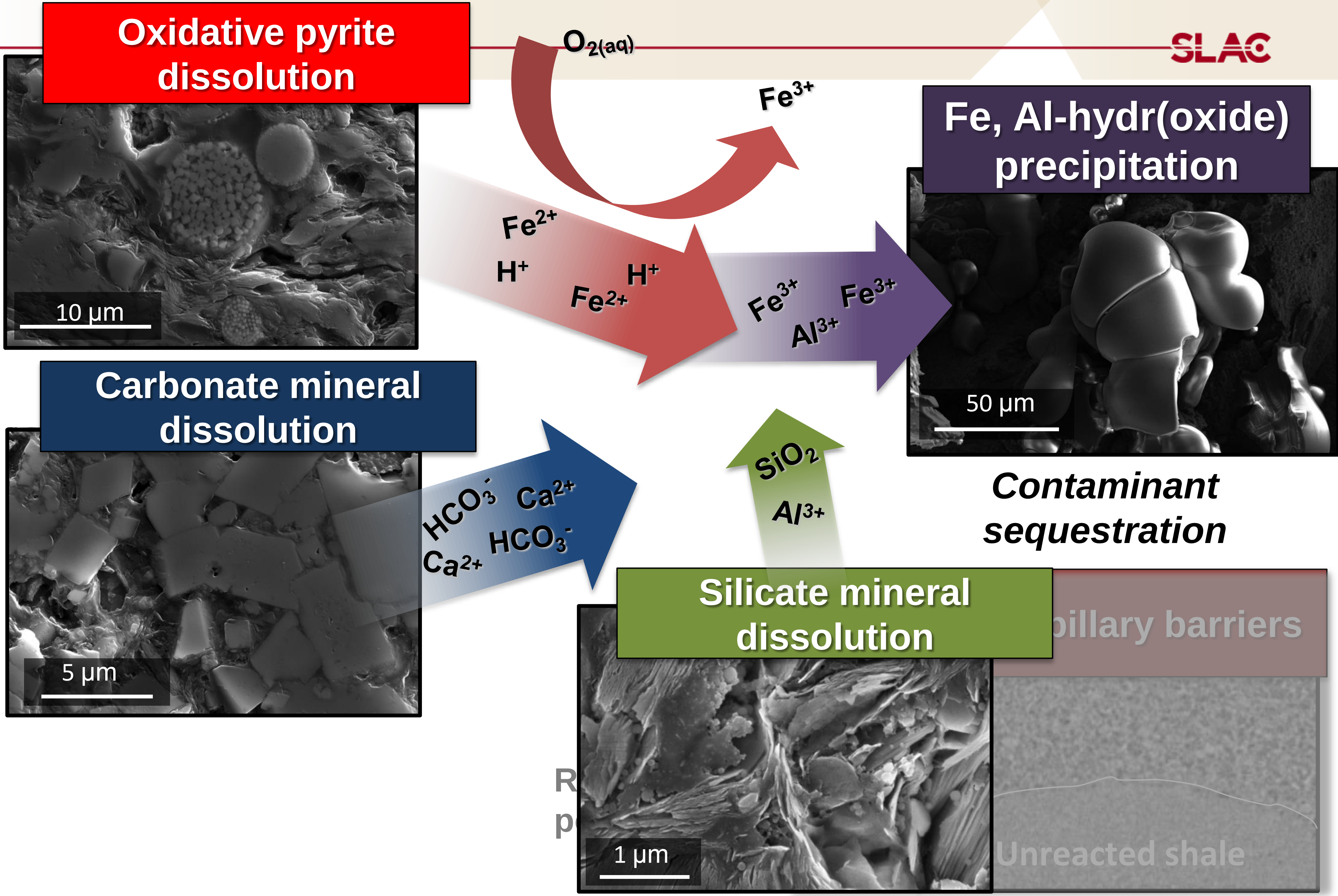
Processes: initial acid injection



Processes: initial acid injection



Prediction: acid neutralization



Positive and negative impacts on transport

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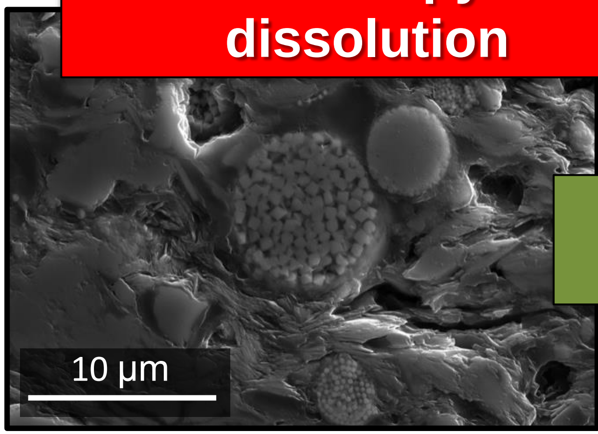
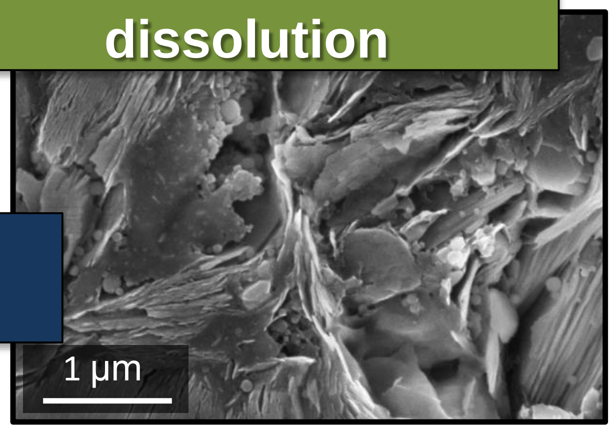
Porosity generation

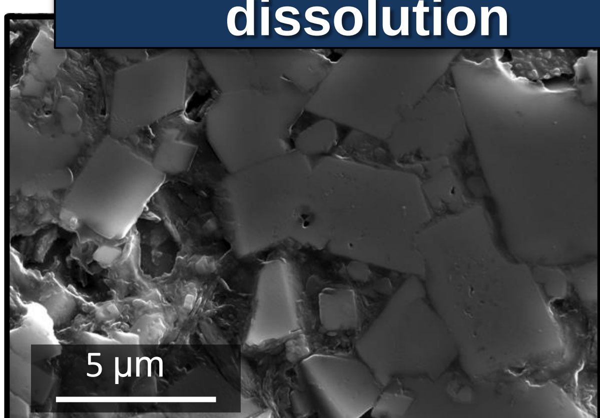
Oxidative pyrite dissolution



Silicate mineral dissolution

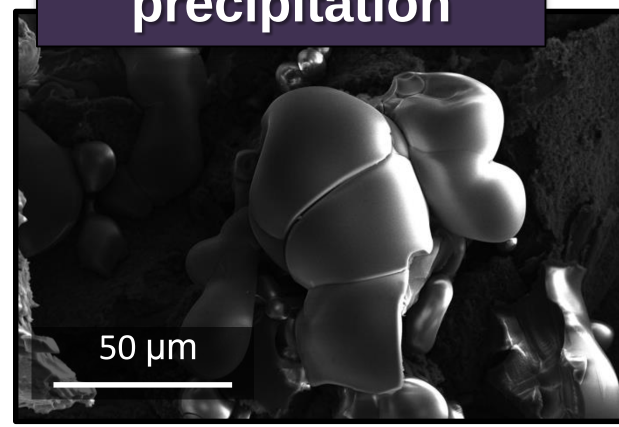


Carbonate mineral dissolution

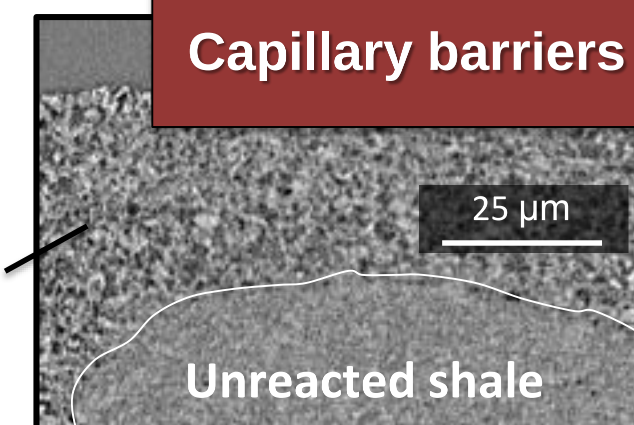


Flow occlusion

Fe, Al-hydr(oxide) precipitation

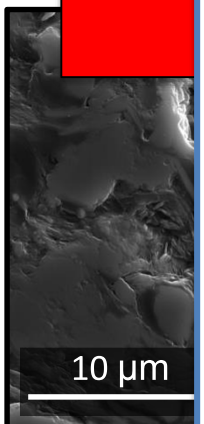


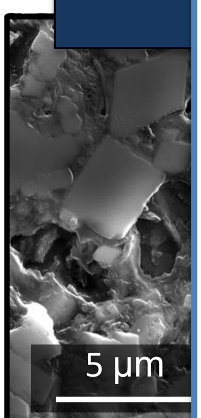
Capillary barriers

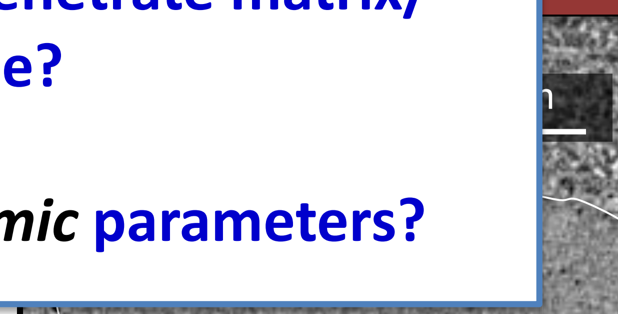


Reacted secondary porosity zone

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 penetrate matrix/ dissolved solids escape?**

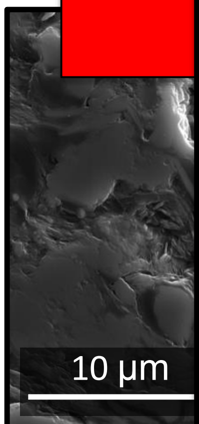
What are the relevant *thermodynamic* parameters?

Positive and negative impacts on transport

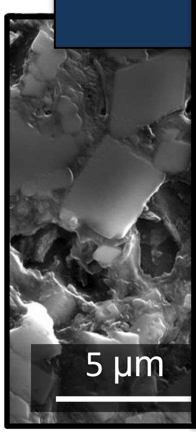
Porosity generation

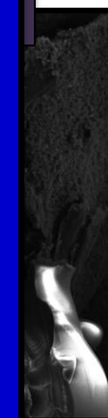
Flow occlusion

Oxidative pyrite

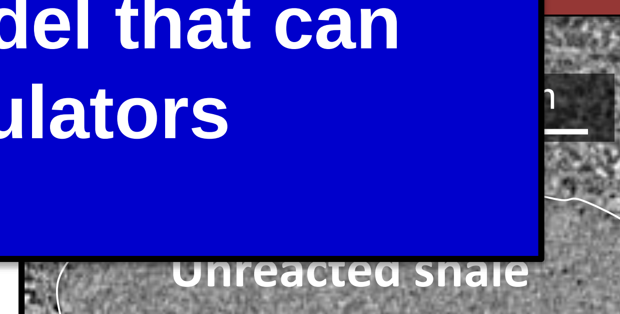


Ca





ers



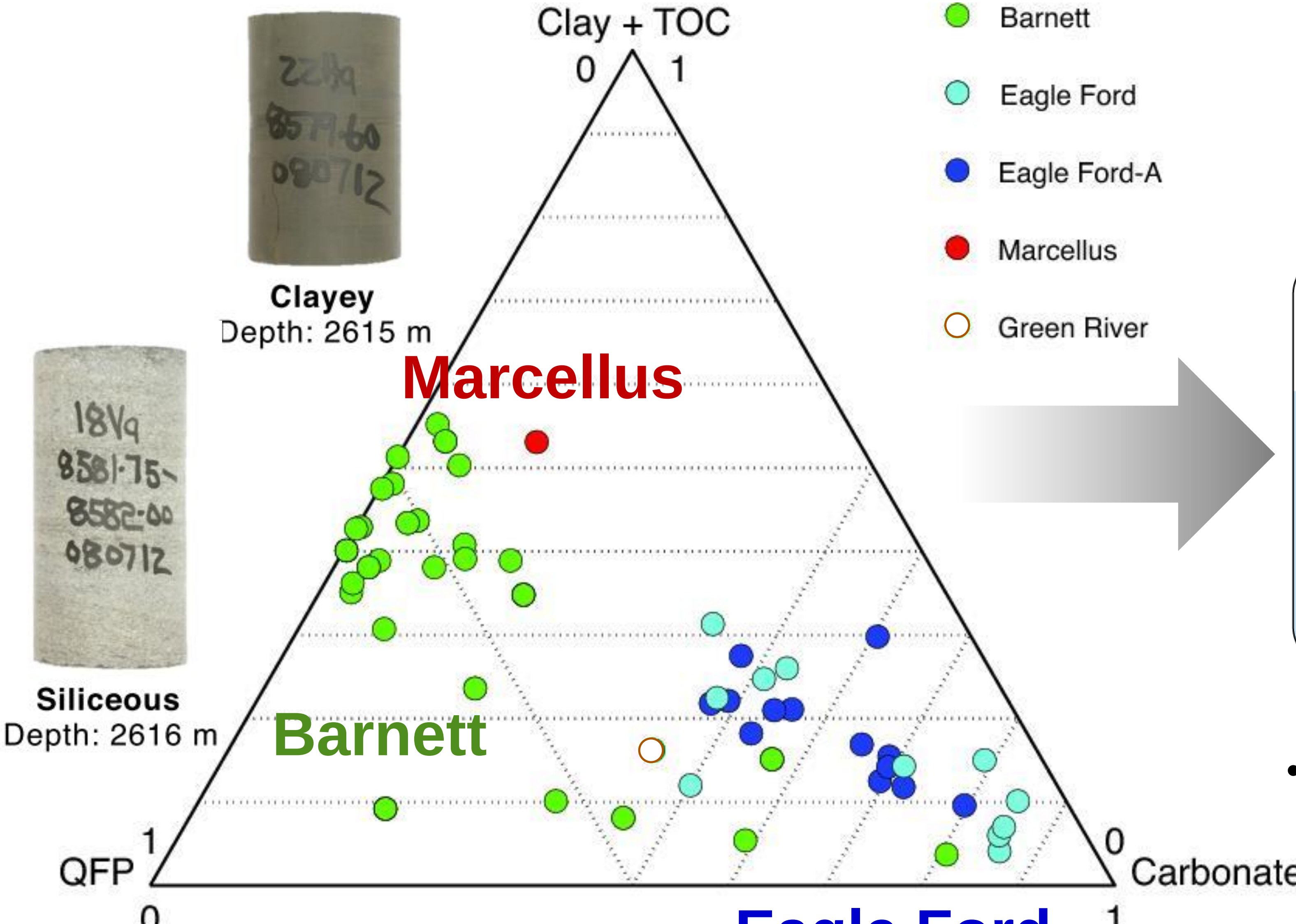
Objectives:

Identify processes, damage to shale

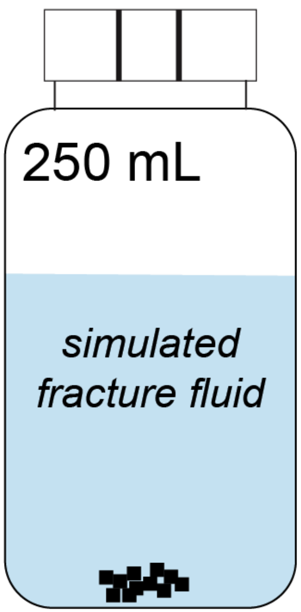
Quantify rates

Develop geochemical model that can inform reservoir simulators

Approach:
Carbonate poor vs. carbonate rich



80°C
pH = 2



- 3 weeks, 3 months, 6 months

Approach: Imaging – spectroscopy – modeling

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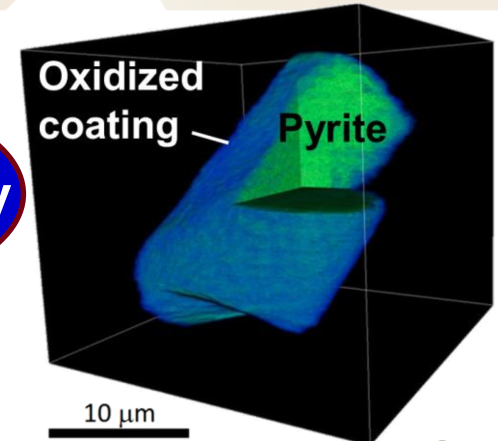
Spectroscopy

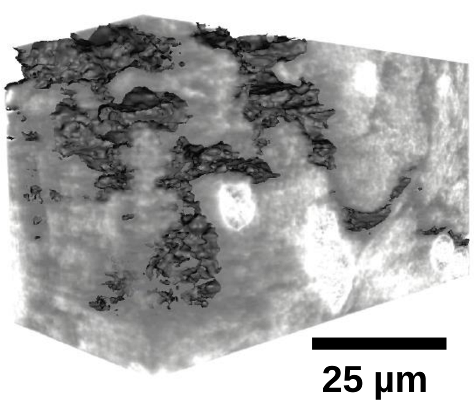


FeS_2
FeOOH

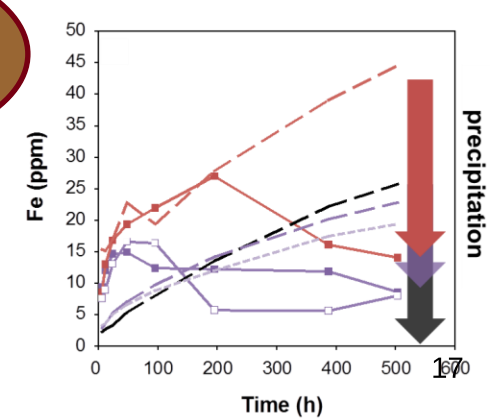
Imaging

Experiments

Modeling



Barnett shale



Synchrotron: unique, time-resolved imaging

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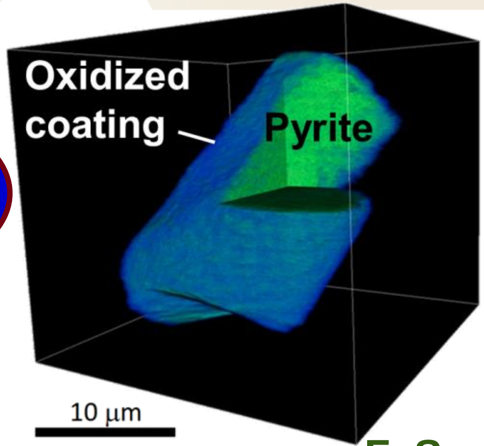
Spectroscopy



FeS_2
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Imaging

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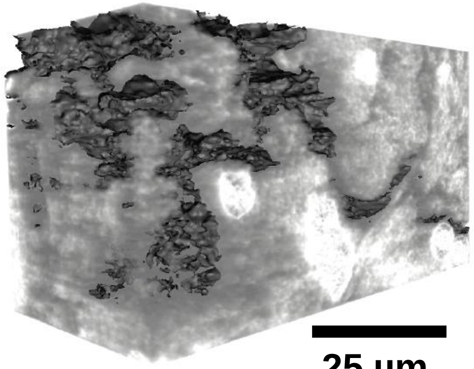
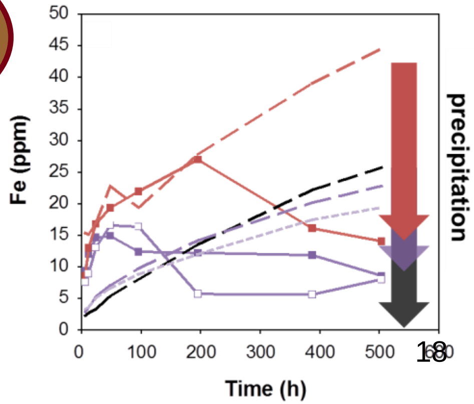


Barnett shale

Modeling



Evolution of fracture surface damage

Types of damage?

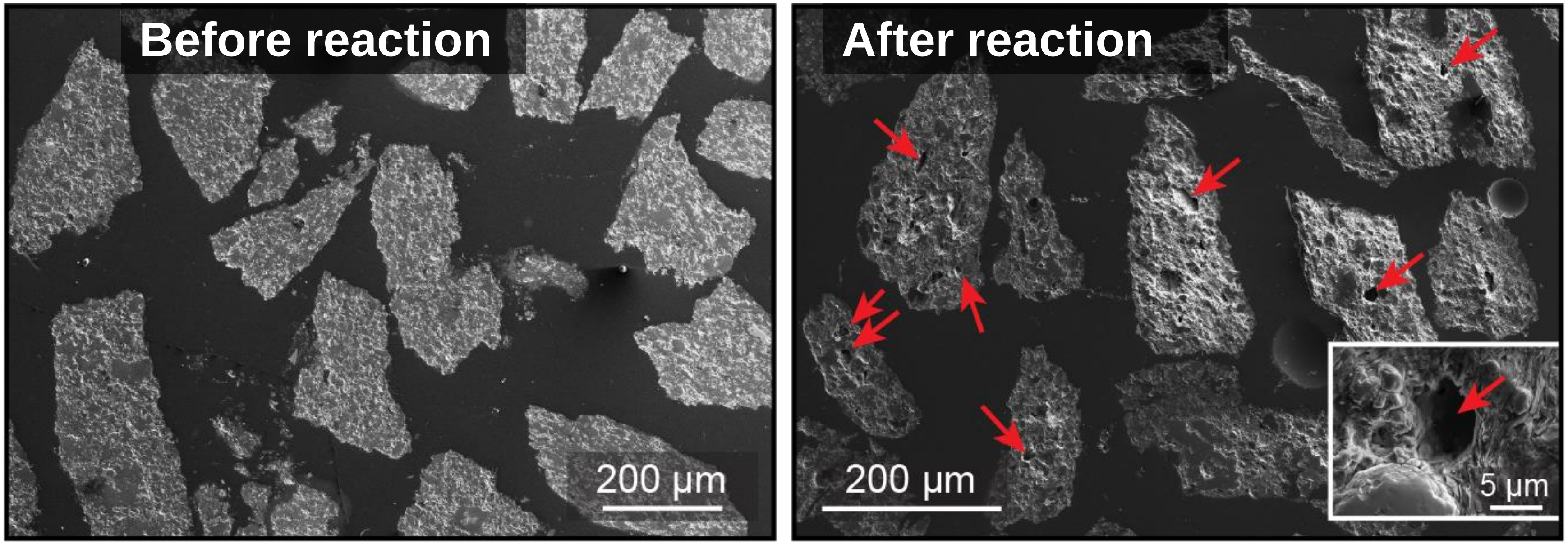
Rates (How fast)?

Implications for flow?

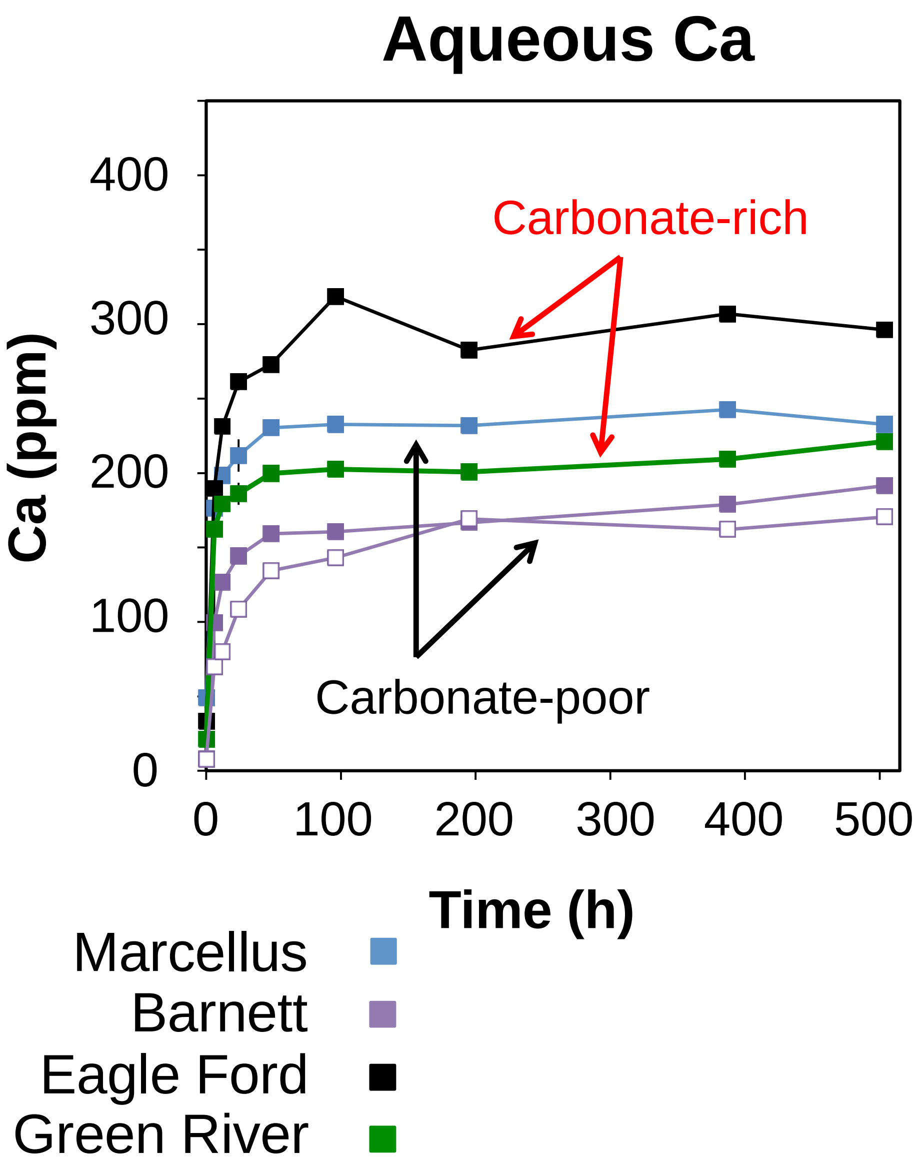
Porosity evolution: dictated by mineralogy

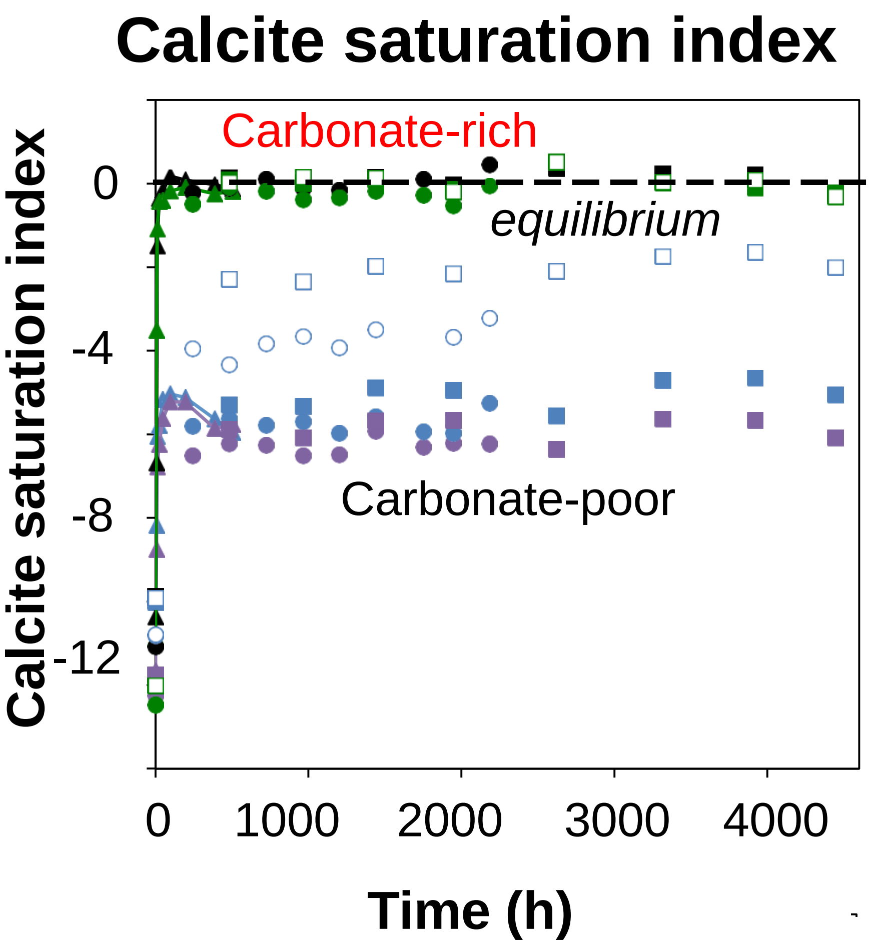
A. Harrison *et al.* (2016) *in submission to Appl. Geochem.*

Carbonate-poor Barnett



Rapid reactions controlled by calcite

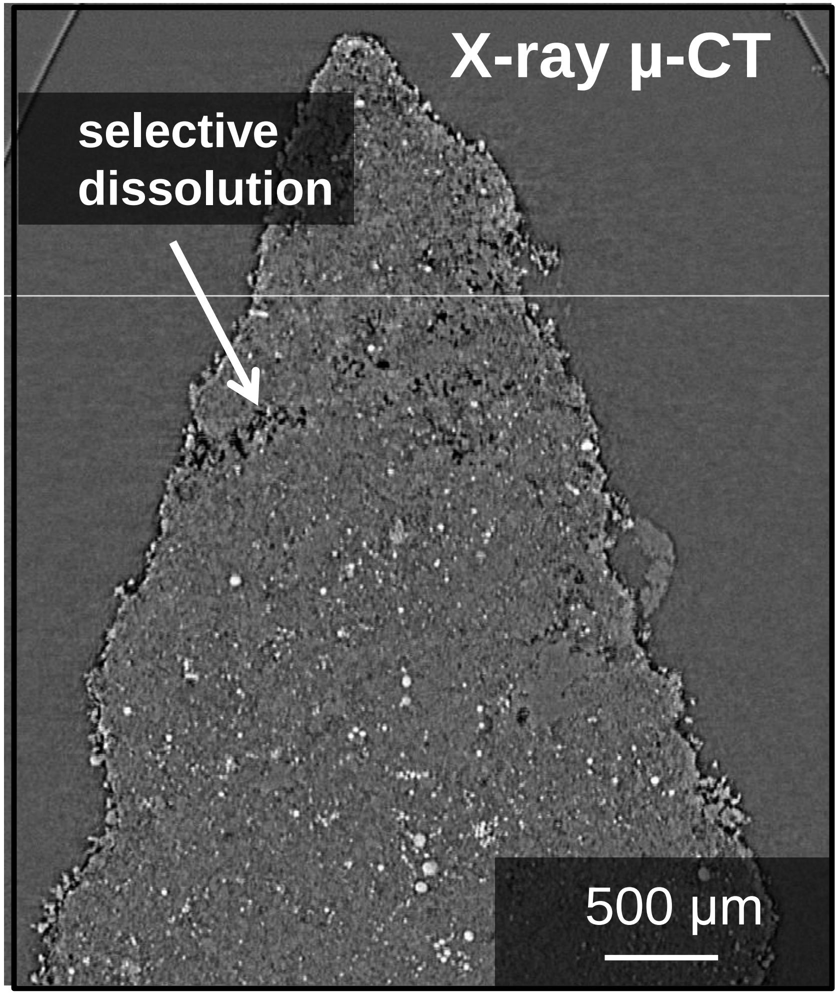




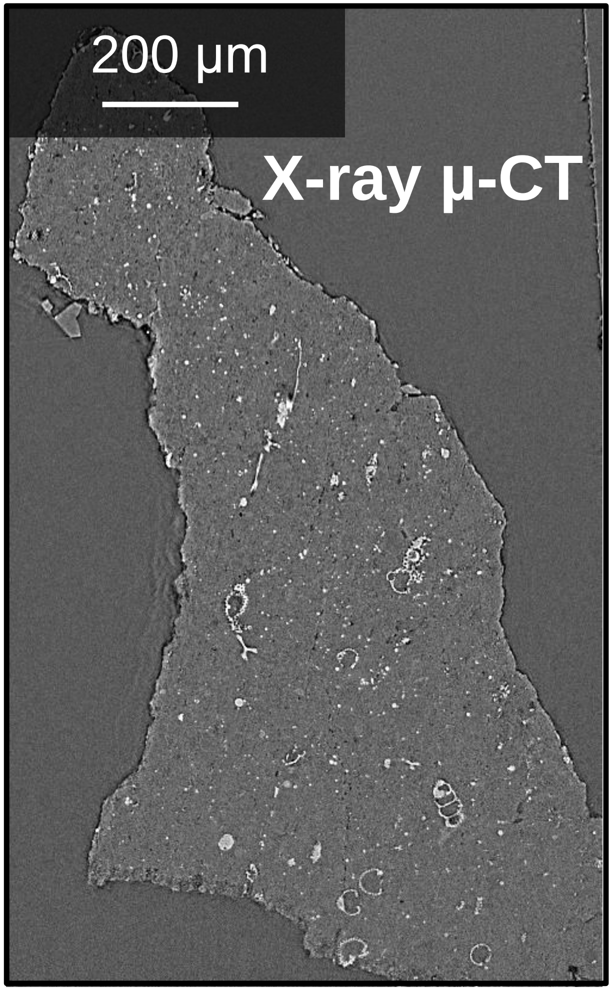
A. Harrison *et al.* (2016) *in submission to Appl. Geochem.*

Physical damage: Secondary porosity

Carbonate-poor Marcellus



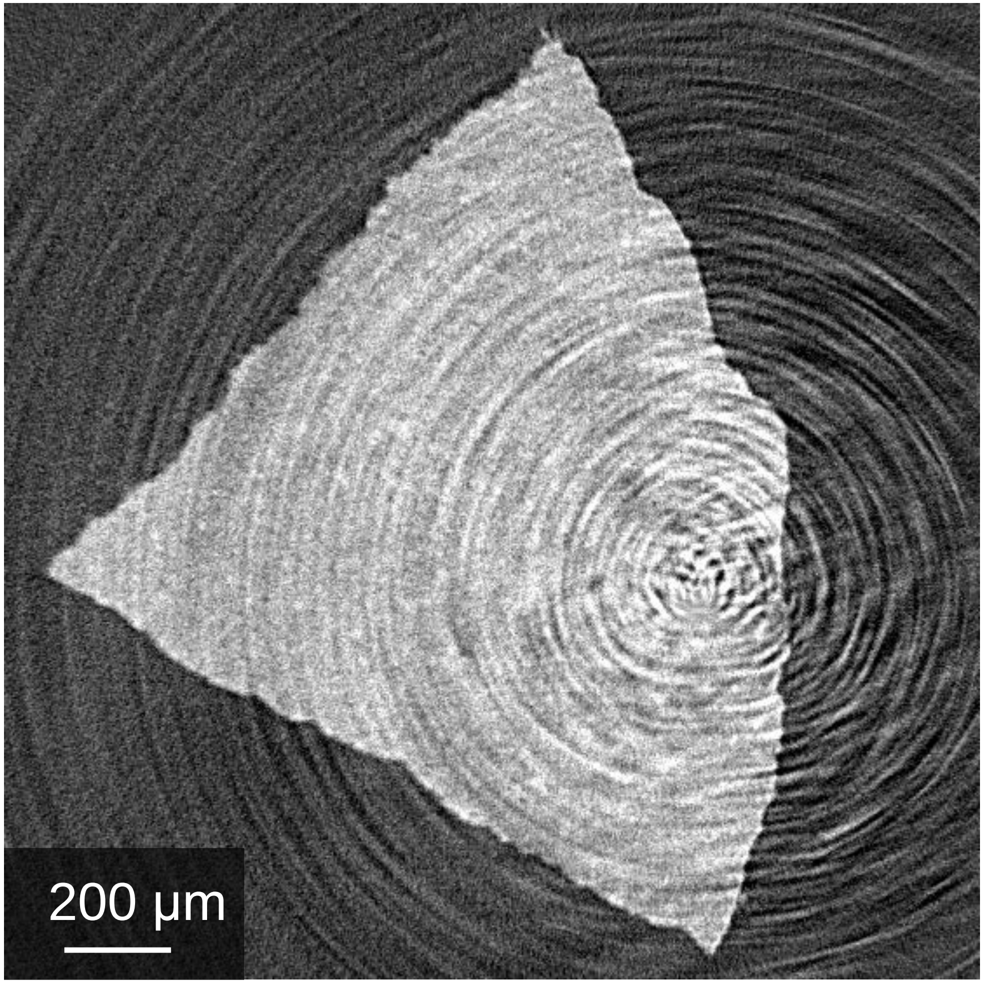
Carbonate-rich Eagle Ford



- **Physical protection of carbonate is important**

Physical damage: Secondary porosity

Carbonate-rich Green River



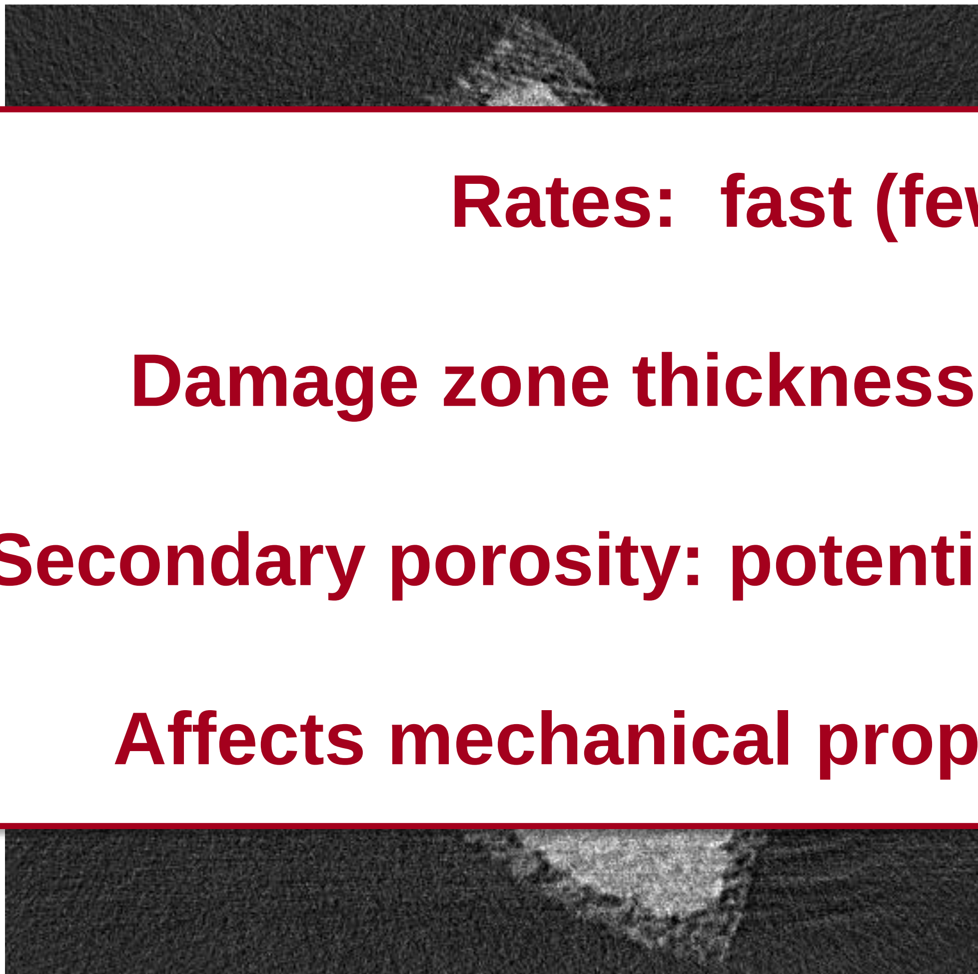
A. Kiss *et al.* (2016) *in preparation*

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

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

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

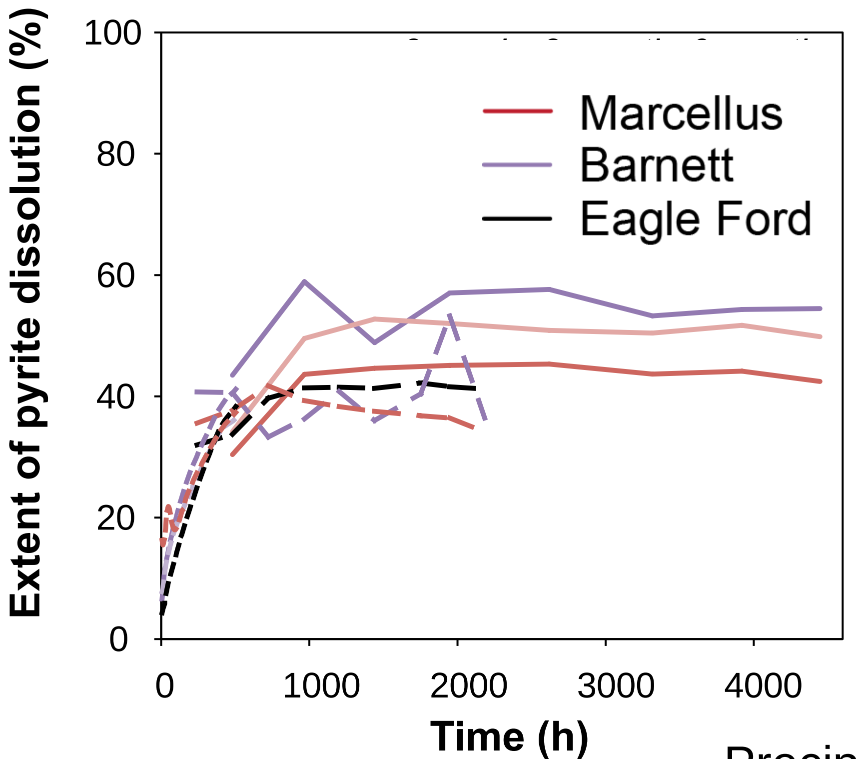
A. Kiss *et al.* (2016) *in preparation*

Iron oxidation / precipitation

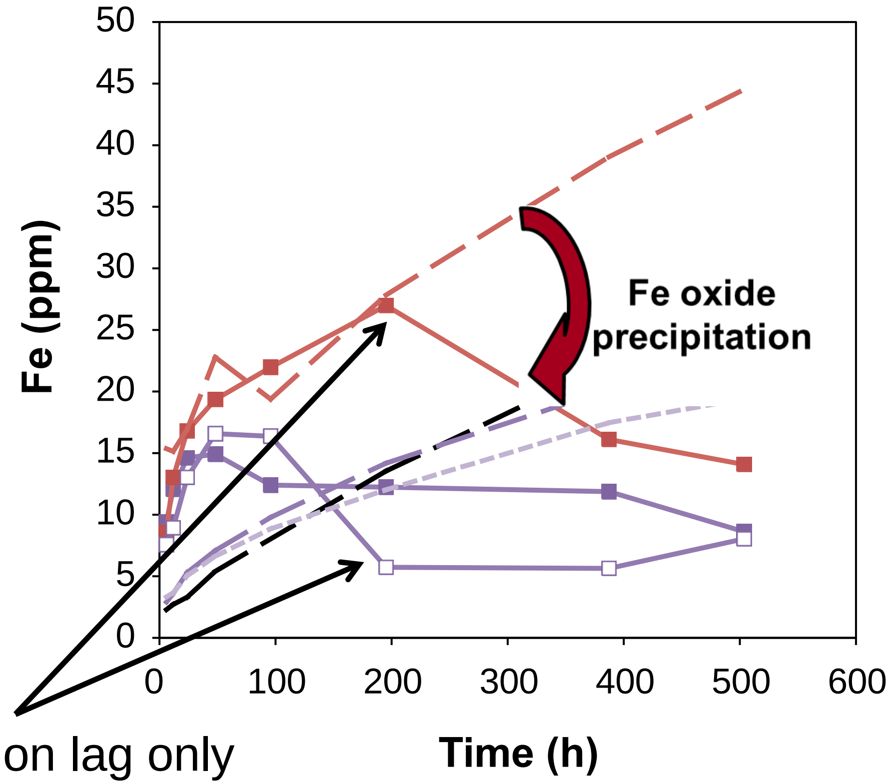
- Under what conditions does iron oxidation occur?
- Rates?
- Where are precipitates localized?
- What phases occur?

Pyrite dissolution

Extent of pyrite dissolution



Evidence for precipitation

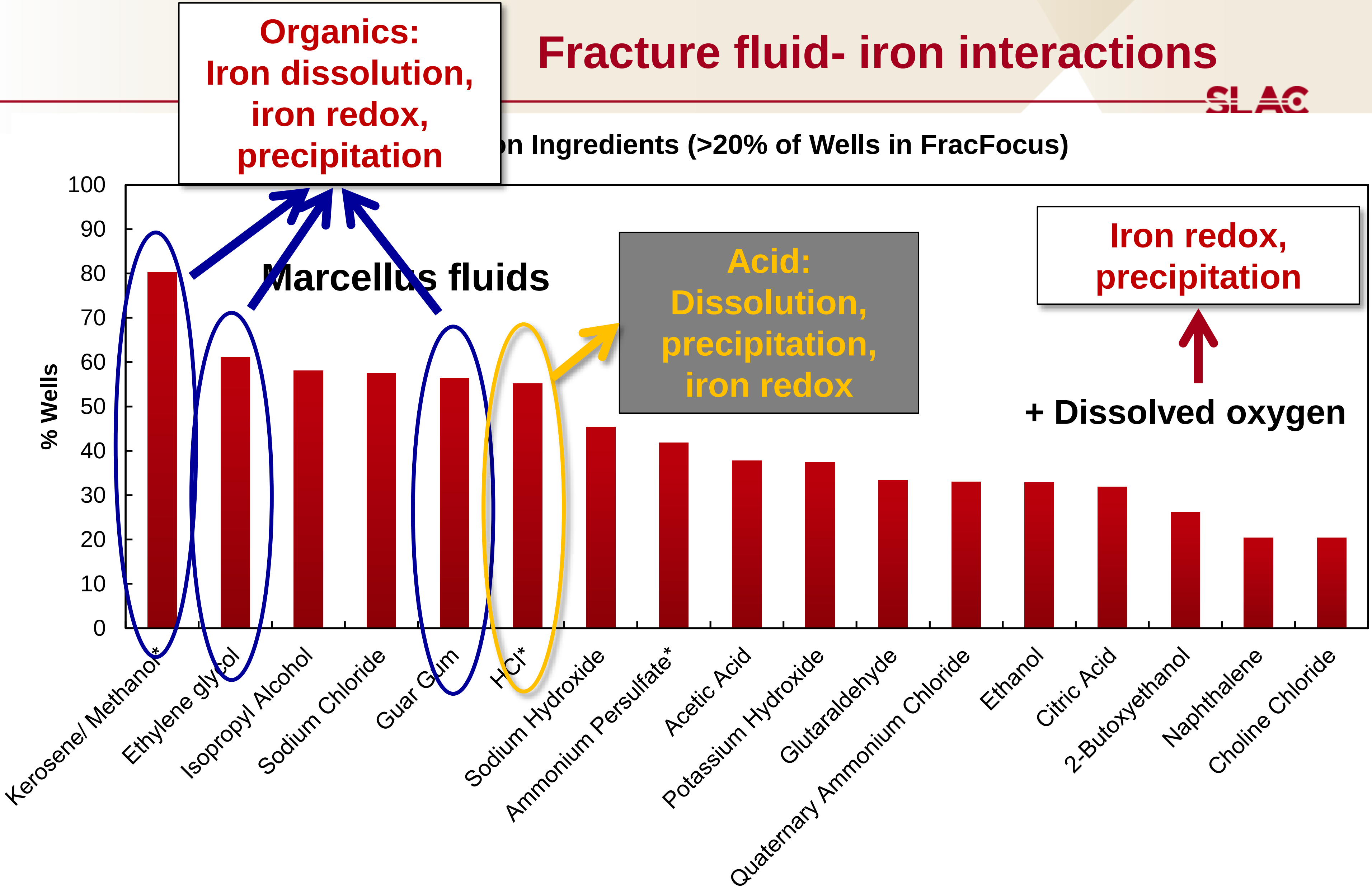


Precipitation lag only for carbonate-poor

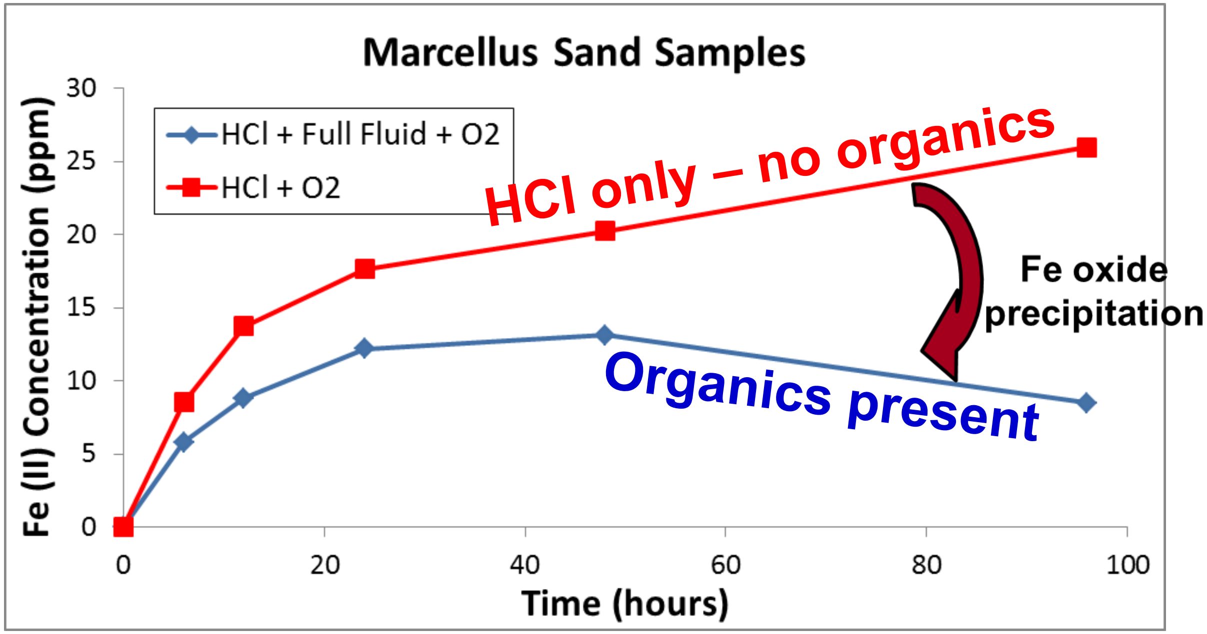
	Marcellus	Barnett	Eagle Ford
Measured			
Stoichiometric			

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

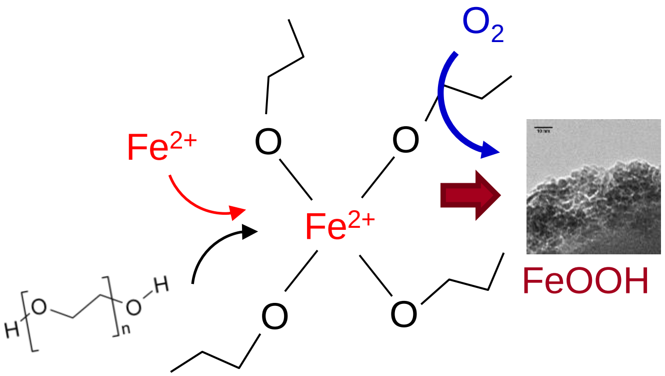
Fracture fluid- iron interactions



Organics in fracture fluid accelerate iron oxidation



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

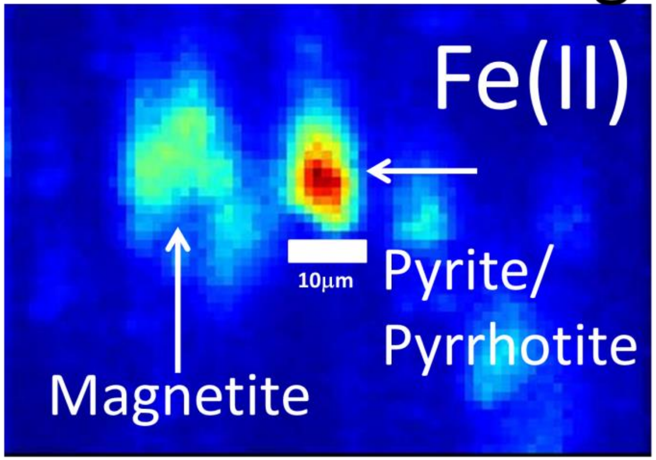


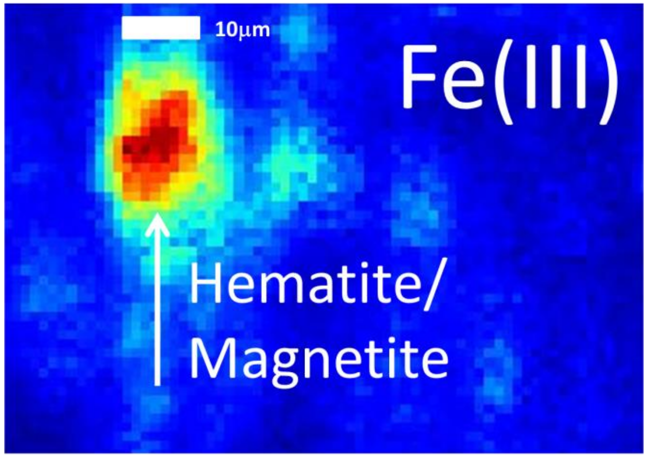
A. Jew *et al.* (2016) *in preparation*

Iron oxides precipitate *in shale matrix*

High carbonate (strong pH buffer)

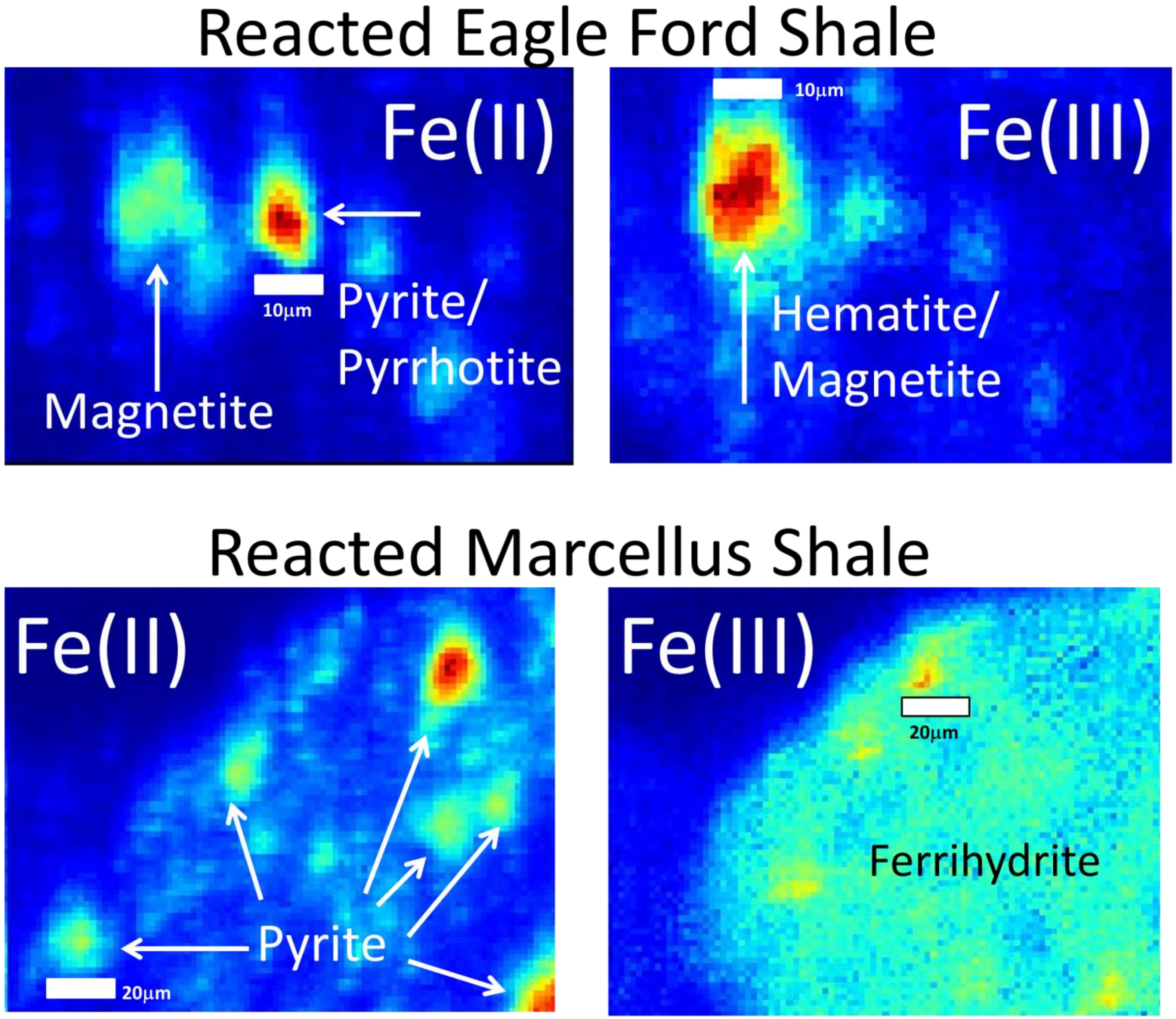
Reacted Eagle Ford Shale





Iron oxides precipitate *in shale matrix*

High carbonate (strong pH buffer)



Low carbonate (poor pH buffer)

pH (carbonate) controls precipitate distribution

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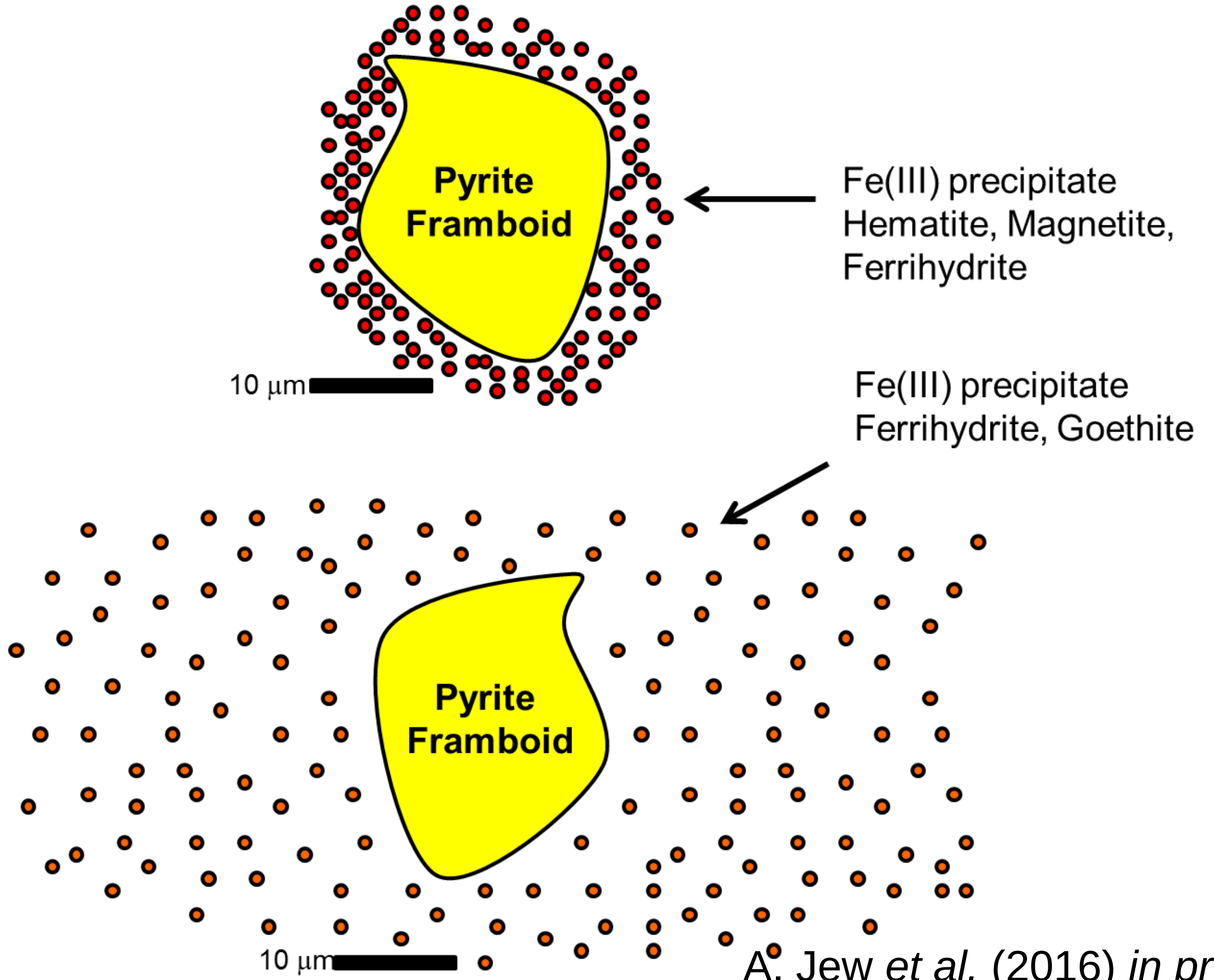
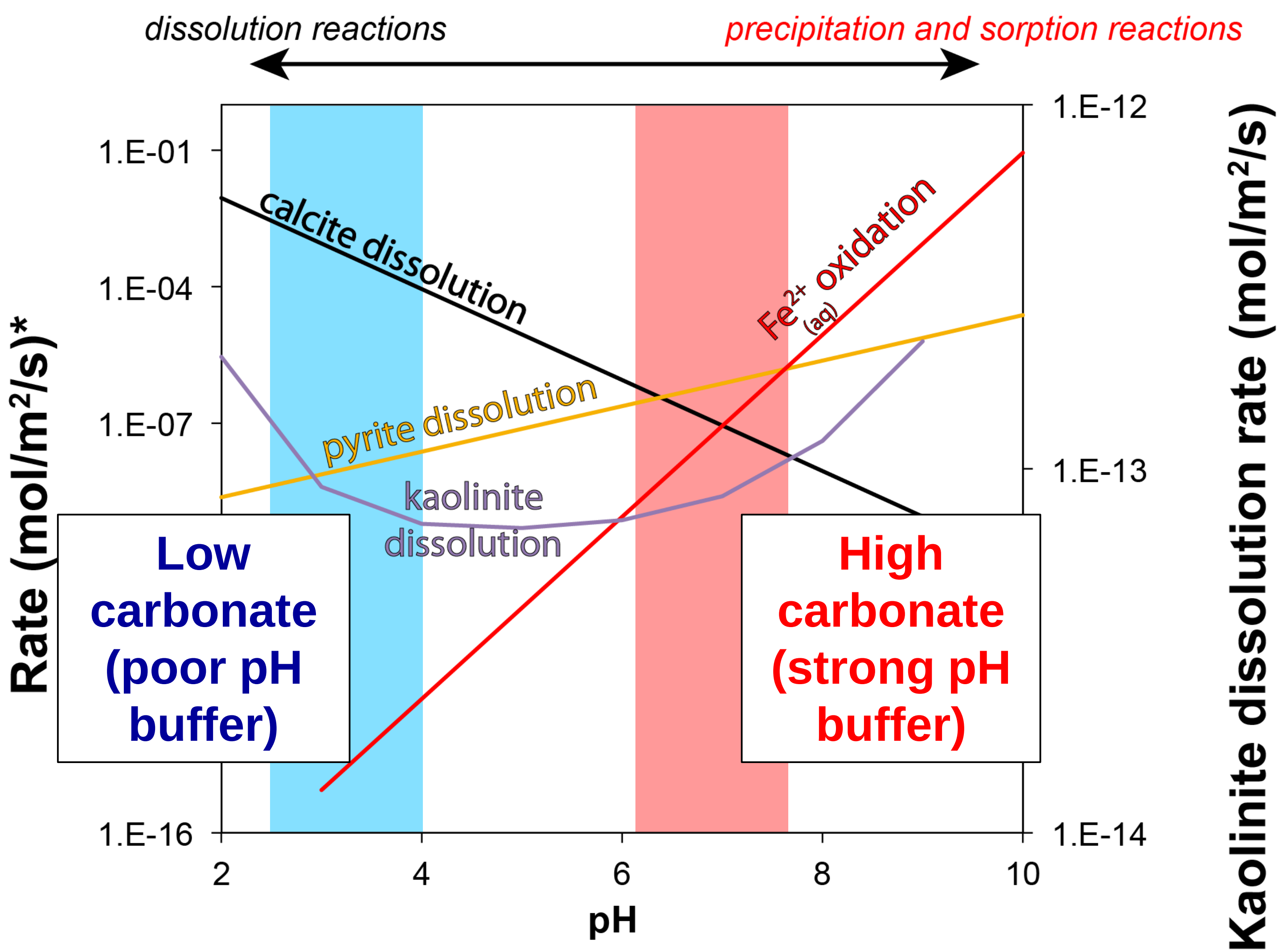
High carbonate (strong pH buffer)

Low carbonate (poor pH buffer)

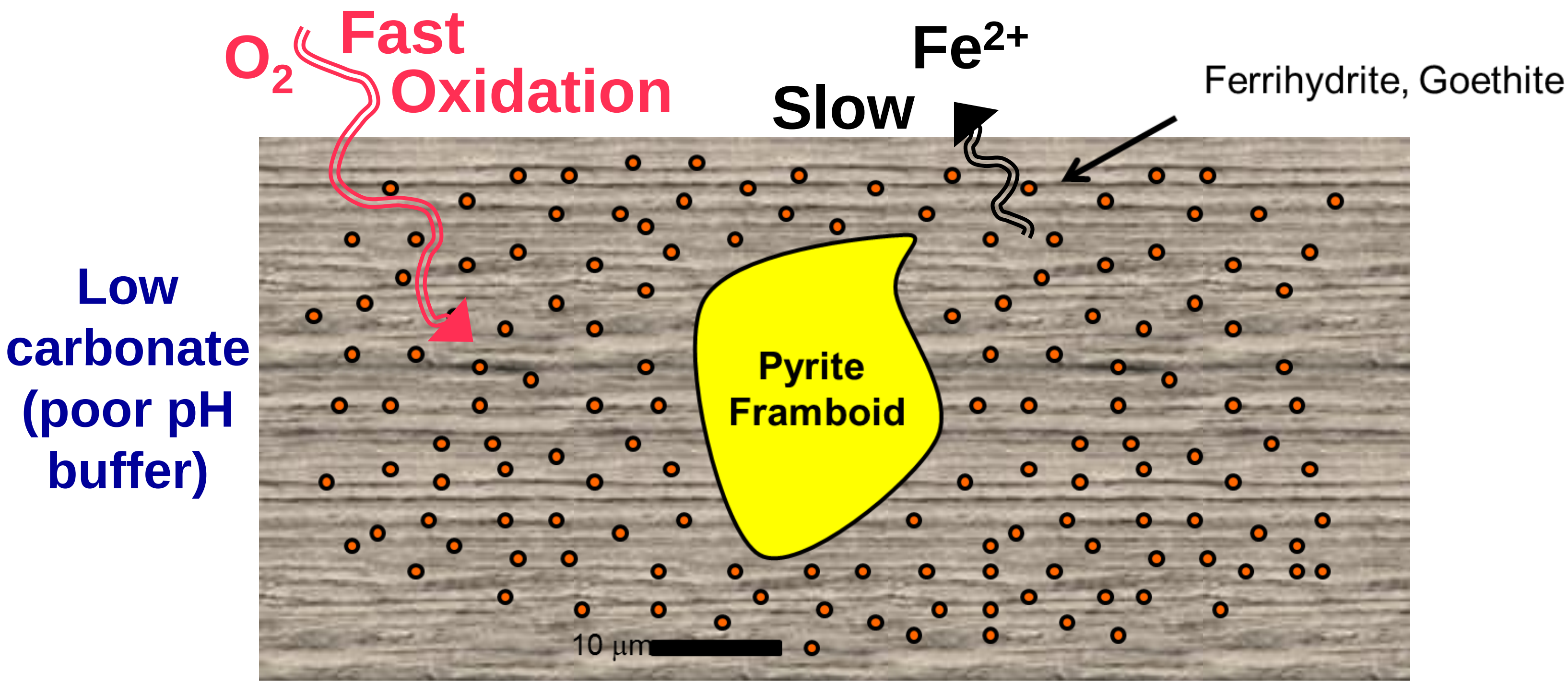


A. Jew *et al.* (2016) *in preparation*

Carbonate controls pH… *and* Fe oxidation rates

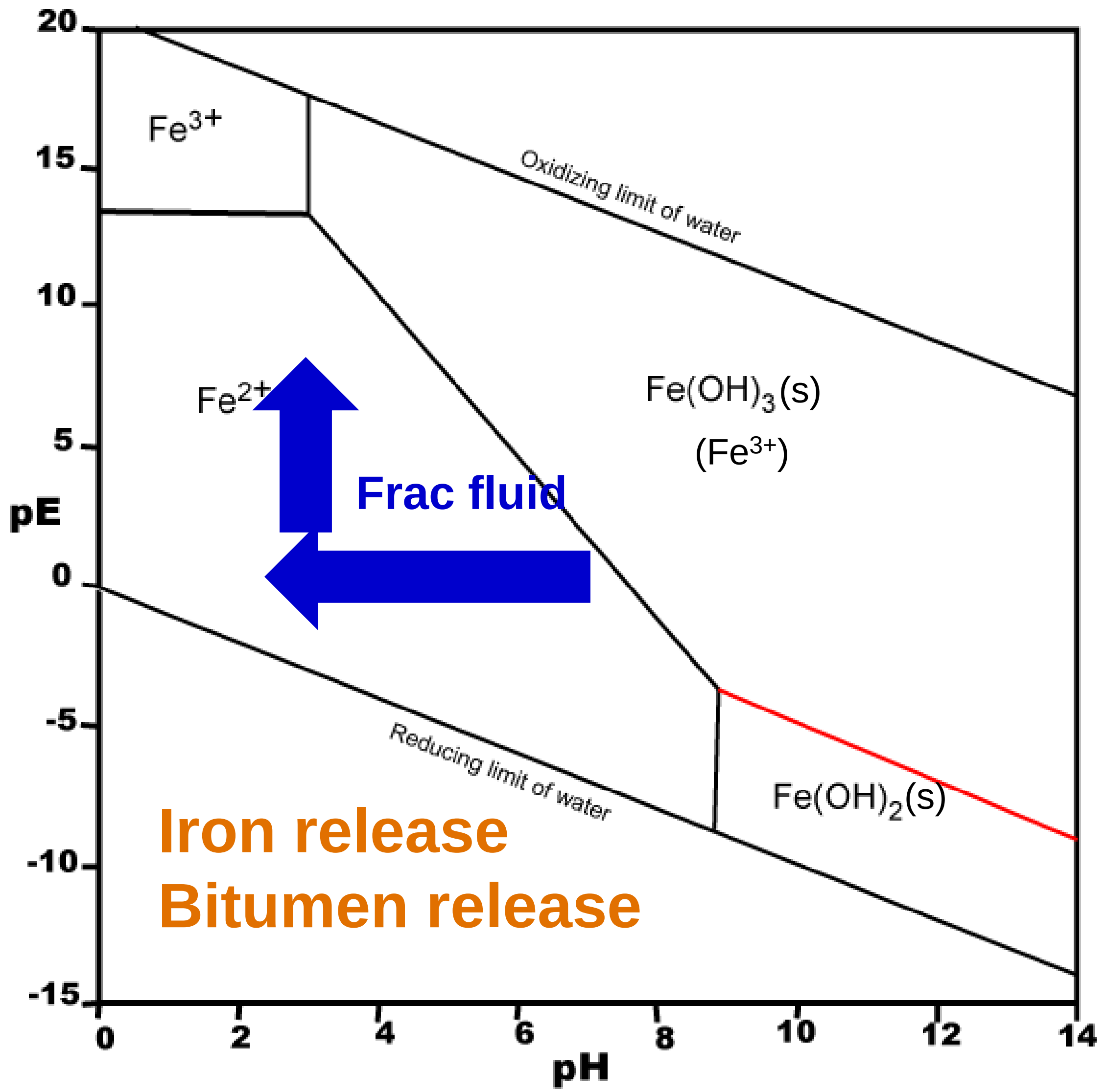


pH (carbonate) controls precipitate distribution

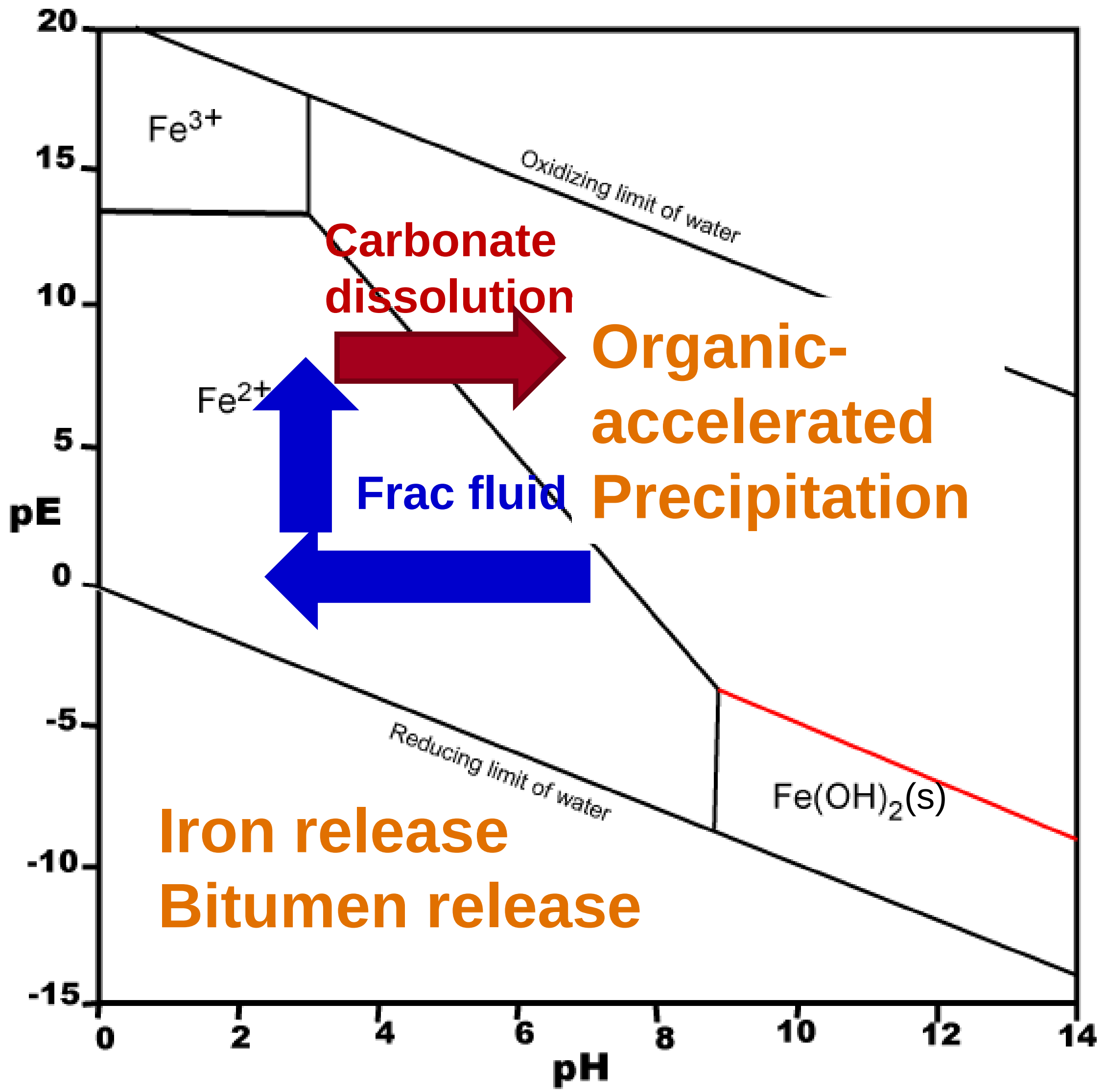


Pulling this together

Chemical model: Iron oxidation and precipitation



Chemical model: Iron oxidation and precipitation



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

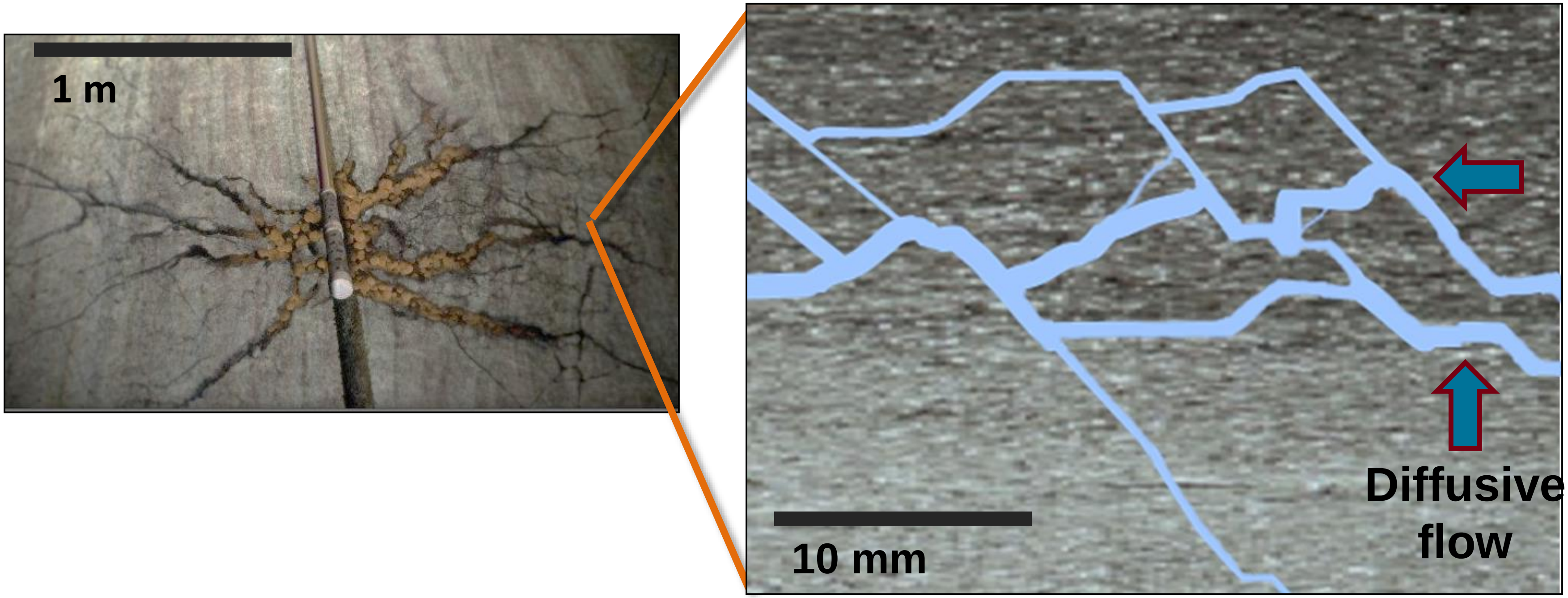
- Dissolution rapidly damages fracture surfaces (hours)
- Mineral precipitation causes matrix damage (days)
- Primary control: pH (carbonate): Rates, extent
- Important secondary controls on rates: Mineral texture, organics

Lessons Learned

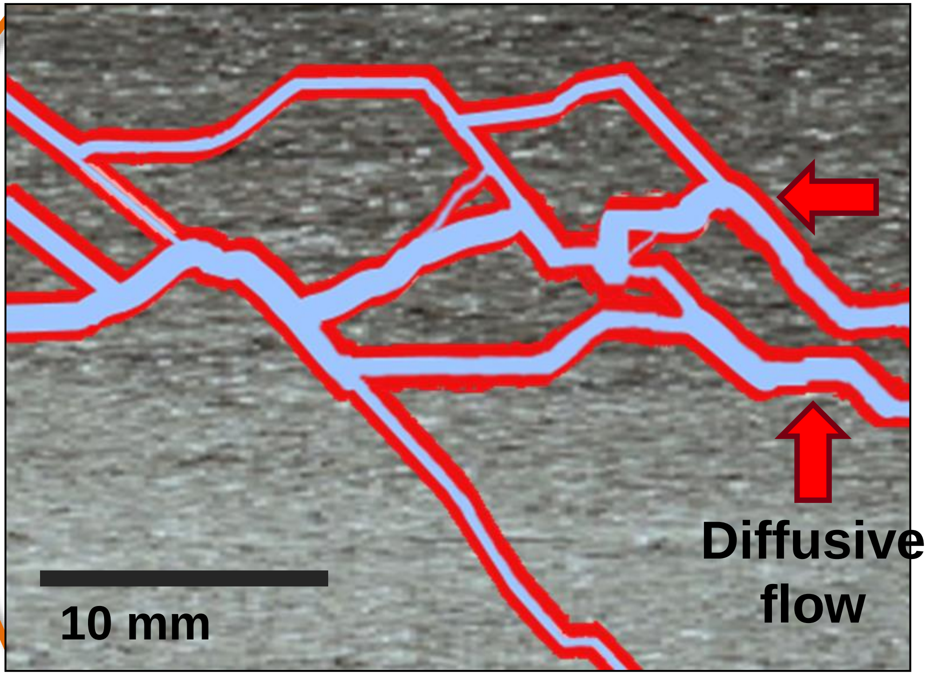
- Rapid formation damage follows fracture fluid everywhere
- Large variations in pH are bad for formations prone to iron scale
- Organic iron control additives should be carefully evaluated
- Shale matrix is important location for mineral precipitation

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

Shale alteration occurs everywhere fluid is imbibed



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

Synergy Opportunities

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COLLABORATIONS:

• **Fracture-scale geochemistry**	**NETL**
• **Field context experiments (MSEEL)**	**NETL**
• **Reservoir-scale simulations**	**LANL**
• **Alternative fracture fluid compositions**	**BHI**
• **Properties of sub-100 nm pores**	

THANK YOU, NETL !

Appendices

Organization Chart, Expertise, and Roles

SLAC director
Chi-Chang Kao

SSRL director
Kelly Gaffney

SSRL Science Director, Co-lead, Chemistry and Catalysis Group
Britt Hedman

Senior Scientist, Research Manager
John Bargar, Geochemistry, Synchrotron-based spectroscopy, imaging

SLAC scientific staff
Postdoctorals (2)

Co-Principle Investigators:

Stanford University

Gordon Brown, Geochemistry

Tony Kovscek, Reservoir engineering, Fluid flow

Kate Maher, Geochemistry, Reactive transport

Mark Zoback, Geomechanics

SLAC

Yijin Liu, CT imaging

Gantt Chart – reproduced from Quarter 7 report (9-30-2016)

Task	Title	Month of project																							
		2015												2016											
	Quarter:	1			2			3			4			5			6			7			8		
	Month:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
		Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept
1	Project management plan																								
	Development and revision	M																							
	Quarterly progress reports				M			M			M			M			M			M			M		
	Annual progress reports													M											
	Final technical report																								
	Ongoing project management																								
2	Mineral-fracking fluid																								
2.1	Initial characterization (XRD)				M																				
2.2	Develop model fracking fluid																								
2.3	Reaction of Fe(II) solution with hydraulic fracturing solution													M											
2.4	Reaction of Fe(II) w/bitumen [Set I]																		M						
2.5	Reaction of Fe(II) w/bitumen [Set II]																			M					
2.6	Characterize Fe solid products																				M				
2.7	Analysis of synchrotron XRF data																		M						
2.8	Analysis of μ-XANES data																		M						
2.9	Analysis of Fe EXAFS data																					M			
2.10	Draft manuscript																						M		
2.11	Manuscript submission																								
3	Kerogen-fracking fluid																								
3.1	Isolation of Green River kerogen (GRK)							M																	
3.2	Short-term GRK experiment															M									
3.3	Intermediate-term GRK experiment											M													
3.4	Long-term GRK experiment														M										
3.5	Isolation of Marcellus kerogen (MK)															M									
3.6	Short-term MK experiment																	M							
3.7	Characterization																				M				
3.8	Draft manuscript																								
4	Whole shale-fracking fluid																								
4.1	Initial characterization							M																	
4.2	Initial 2-wk HCl-only reaction							M																	
4.3	Analysis of reaction products							M																	
4.4	Short-term experiment [I]										M														
4.5	Short-term experiment [II]													M											
4.6	Short-term experiment [III]																				M				
4.7	Intermediate-term experiment											M													
4.8	Long-term experiment														M										
4.9	Characterization																						M		
4.10	Draft manuscript																						M		
4.11	Manuscript submission																								
5	Uranium-fracking fluid																								
5.1	Initial characterization							M																	
5.2	Initial 2-wk HCl-only reaction							M																	
5.3	Analysis of reaction products							M																	
5.4	Short-term experiment										M														
5.5	Short-term experiment [II]															M									
5.5	Short-term experiment [III]															M									
5.6	Intermediate-term experiment											M													
5.7	Long-term experiment														M										
5.8	Uranium Radiography																						M		
5.9	Sequential extractions																						M		
5.10	Characterization																						M		
6	Modeling																								
6.1	Define reactions, Evaluate Thermo data																								
6.2	Initial numerical experiments for experiment design				M																				
6.3	Numerical experiments																M								
6.4	Evaluate models against data																				M				
6.5	Sensitivity analysis																				M				
6.6	Model refinement																						M		
6.7	Complete initial model: secondary porosity simulation																								

Bibliography

Conference poster presentations (*presenting author)

Anna Harrison*, Kate Maher, Adam Jew, Megan Dustin, Andy Kiss, Arjun Kohli, Dana Thomas, Claresta Joe-Wong, Yijin Liu, J.-H. Lim, Gordon Brown Jr., and John Bargar (2016) Physical and chemical alteration of shales during hydraulic fracturing. Presented at the 2016 Goldschmidt Conference, Yokohama, Japan, June 29, 2016.

Megan K. Dustin*, Adam D. Jew, Anna L. Harrison, Claresta Joe-Wong, Dana L. Thomas, Katharine Maher, Gordon E. Brown Jr., and John R. Bargar (2015) Kerogen-Hydraulic Fracture Fluid Interactions: Reactivity and Contaminant Release. American Geophysical Union Fall Meeting, San Francisco, USA, December 14-18.

Anna L. Harrison*, Adam D. Jew, Megan K. Dustin, Claresta Joe-Wong, Dana L. Thomas, Katharine Maher, Gordon E. Brown Jr., and John R. Bargar (2015) A Geochemical Framework for Evaluating Shale-Hydraulic Fracture Fluid Interactions. American Geophysical Union Fall Meeting, San Francisco, USA, December 14-18.

Adam D. Jew*, Claresta Joe-Wong, Anna L. Harrison, Dana L. Thomas, Megan K. Dustin, Gordon E. Brown Jr., Katharine Maher, and John R. Bargar (2015) Iron Release and Precipitation in Hydraulic Fracturing Systems. American Geophysical Union Fall Meeting, San Francisco, USA, December 14-18.

Claresta Joe-Wong*, Anna L. Harrison, Dana L. Thomas, Megan K. Dustin, Adam D. Jew, Gordon E. Brown Jr., Katharine Maher, and John R. Bargar (2015) Coupled mineral dissolution and precipitation reactions in shale-hydraulic fracturing fluid systems. American Geophysical Union Fall Meeting, San Francisco, USA, December 14-18.

Megan K. Dustin*, Adam D. Jew, Anna L. Harrison, Claresta Joe-Wong, Dana L. Thomas, Katharine Maher, Gordon E. Brown Jr., and John R. Bargar (2015) Kerogen-Hydraulic Fracture Fluid Interactions: Reactivity and Contaminant Release. Stanford Synchrotron Radiation Lightsource 2015 User's Meeting, Stanford, USA, Oct 7-9.

Anna L. Harrison*, Adam D. Jew, Megan K. Dustin, Claresta Joe-Wong, Dana L. Thomas, Katharine Maher, Gordon E. Brown Jr., and John R. Bargar (2015) A Geochemical Framework for Evaluating Shale-Hydraulic Fracture Fluid Interactions. Stanford Synchrotron Radiation Lightsource 2015 User's Meeting, Stanford, USA, Oct 7-9.

Seminar and workshop presentations (†invited, *presenting author)

Anna L. Harrison*, Adam D. Jew, Megan K. Dustin, Claresta Joe-Wong, Dana L. Thomas, Katharine Maher, Gordon E. Brown Jr., and John R. Bargar (2015) A Geochemical Framework for Evaluating Shale-Hydraulic Fracture Fluid Interactions. Stanford Center for Secure Carbon Storage Research Seminar, Stanford, USA, October 21.

†John R. Bargar*, Gordon E. Brown, Jr., Megan K. Dustin, Anna L. Harrison, Adam D. Jew, C.M. Joe-Wong, and Katharine Maher (2015) Geochemical control of shale fracture and matrix permeability. Shales without Scales Workshop, Santa Fe, USA, June 10.

†John R. Bargar*, Gordon E. Brown, Jr., Megan K. Dustin, Anna L. Harrison, Adam D. Jew, C.M. Joe-Wong, and Katharine Maher (2015) Geochemical control of shale fracture and matrix permeability. Baker Hughes Incorporated, Tomball, USA, July 14.

Bibliography

List peer reviewed publications generated from the project per the format of the examples below

Journal, one author:

- Gaus, I., 2010, Role and impact of CO_2-rock interactions during CO_2 storage in sedimentary rocks: International Journal of Greenhouse Gas Control, v. 4, p. 73-89, available at: XXXXXXX.com.

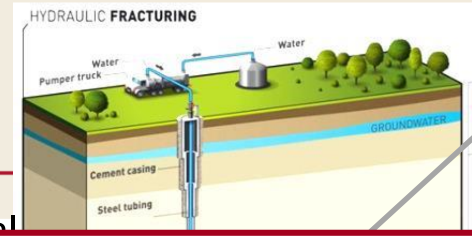
Journal, multiple authors:

- MacQuarrie, K., and Mayer, K.U., 2005, Reactive transport modeling in fractured rock: A state-of-the-science review. Earth Science Reviews, v. 72, p. 189-227, available at: XXXXXXX.com.

Publication:

- Bethke, C.M., 1996, Geochemical reaction modeling, concepts and applications: New York, Oxford University Press, 397 p.

Project overview



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

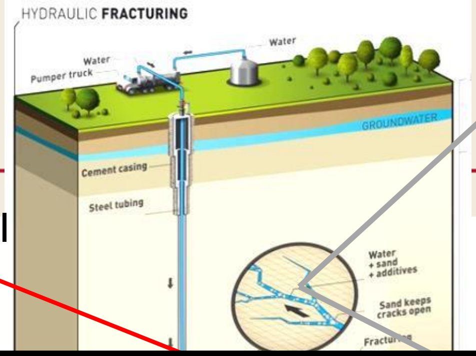
What are *rates* of reactions?; What reactions occur on relevant timescale?

Where will reactions occur? (fracture apertures?, surfaces?, matrix?)

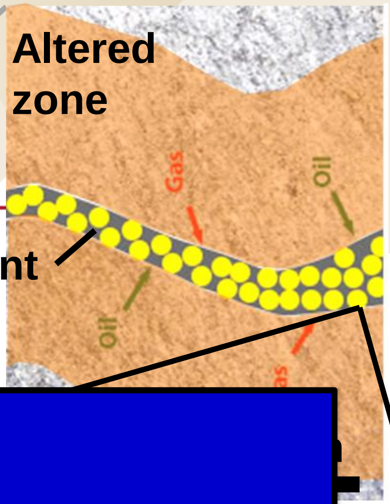
***Transport*: how quickly does fluid penetrate matrix/ dissolved solids escape?**

What are the relevant *thermodynamic* parameters?

Project overview



horizontal well



Fluids ...
with s...

Objectives:

Identify processes, damage to shale

Quantify rates

Develop geochemical model that can inform reservoir simulators

Summary: reaction progress dictated by pH