



# Post-Fracturing Rock-Fluid Reactions in Sub-Surface Caney Shale of Southern Oklahoma



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U.S. DEPARTMENT OF  
**ENERGY** | Fossil  
Energy  
OFFICE OF OIL & NATURAL GAS



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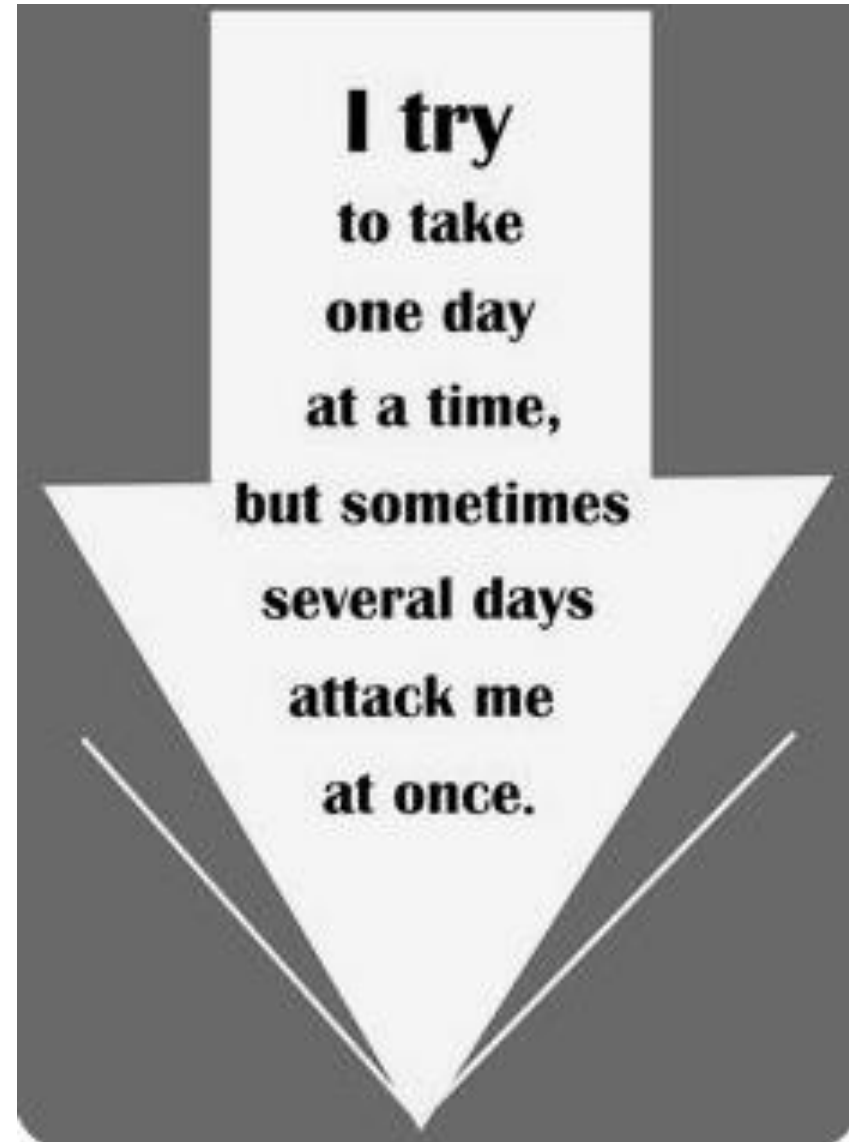
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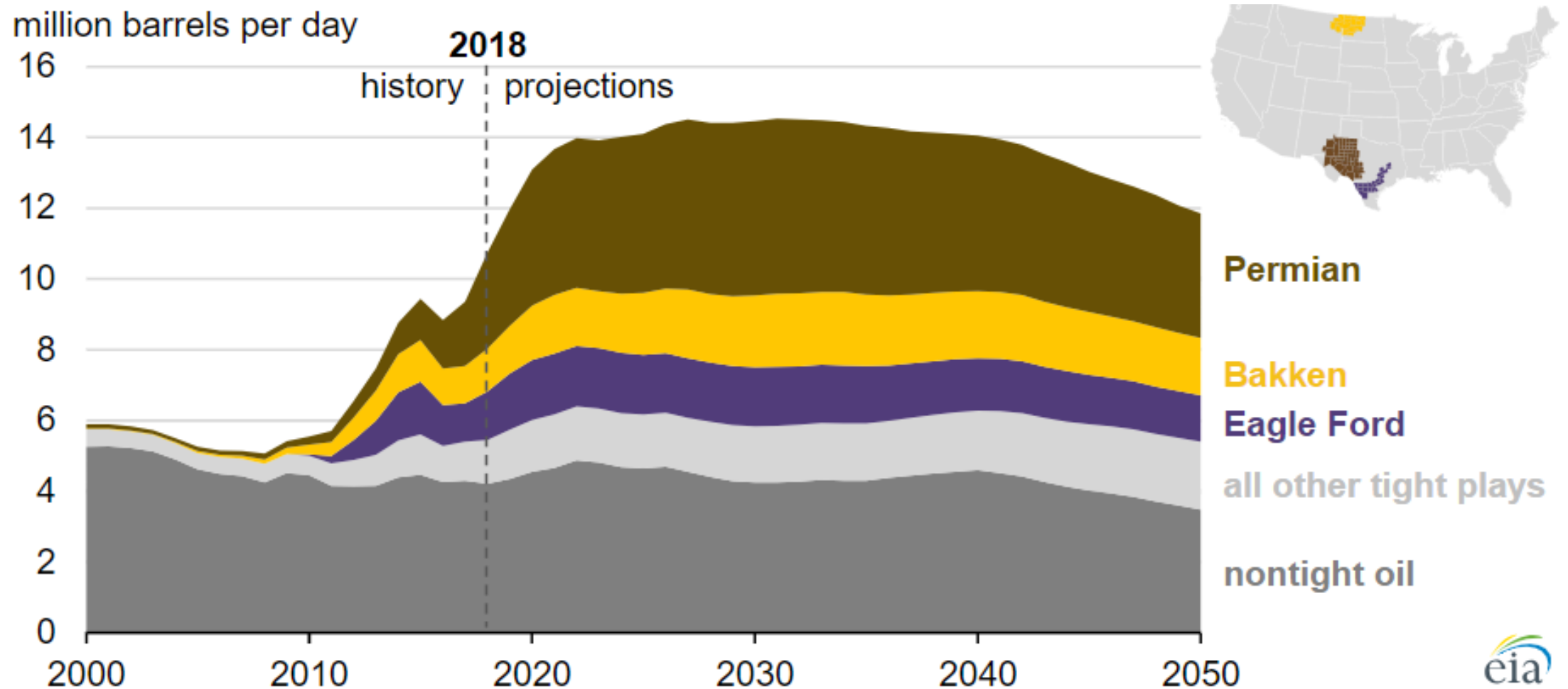
**DOE Award DE-FE0031776 from the Office of Fossil Energy in Partnership with** industry partner, OGS, OSU Geology, OSU Chem. Engineering, University of Pittsburgh, Lawrence Berkeley National Lab and DOE NETL.

# PRESENTATION OUTLINE

- ☐ Overview
- ☐ Problem
- ☐ Objectives
- ☐ Materials and Methodology
- ☐ Results and Discussions
- ☐ Conclusions
- ☐ Plans Going Forward



# OVERVIEW – Conventional versus Unconventional



Contributions from conventional and unconventional sources to total hydrocarbon production in USA

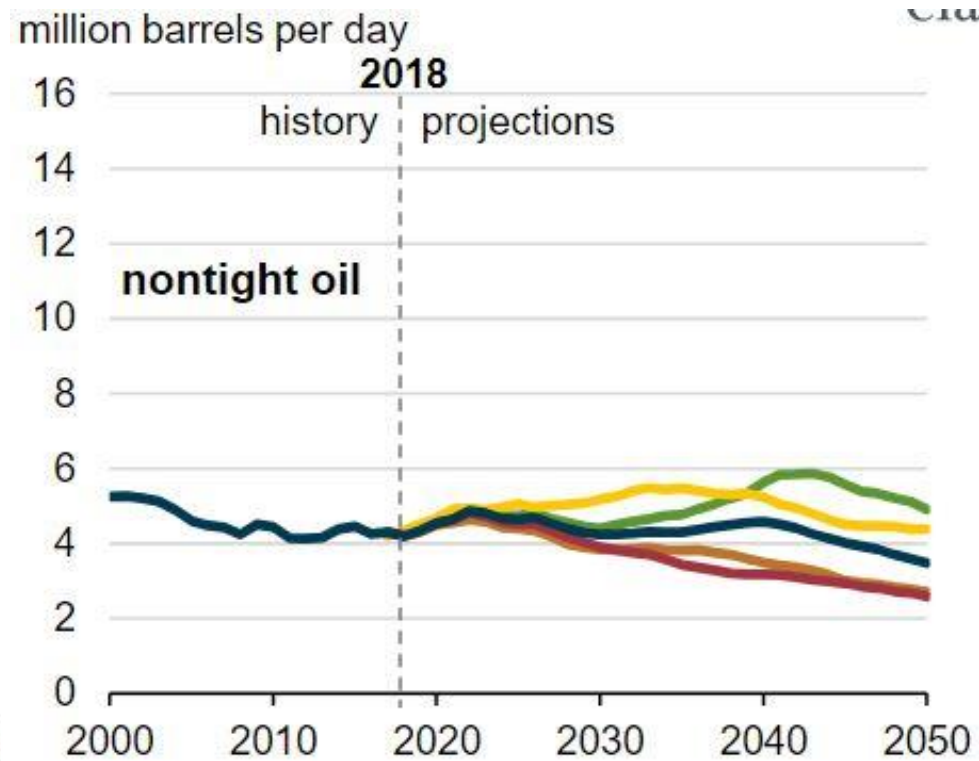
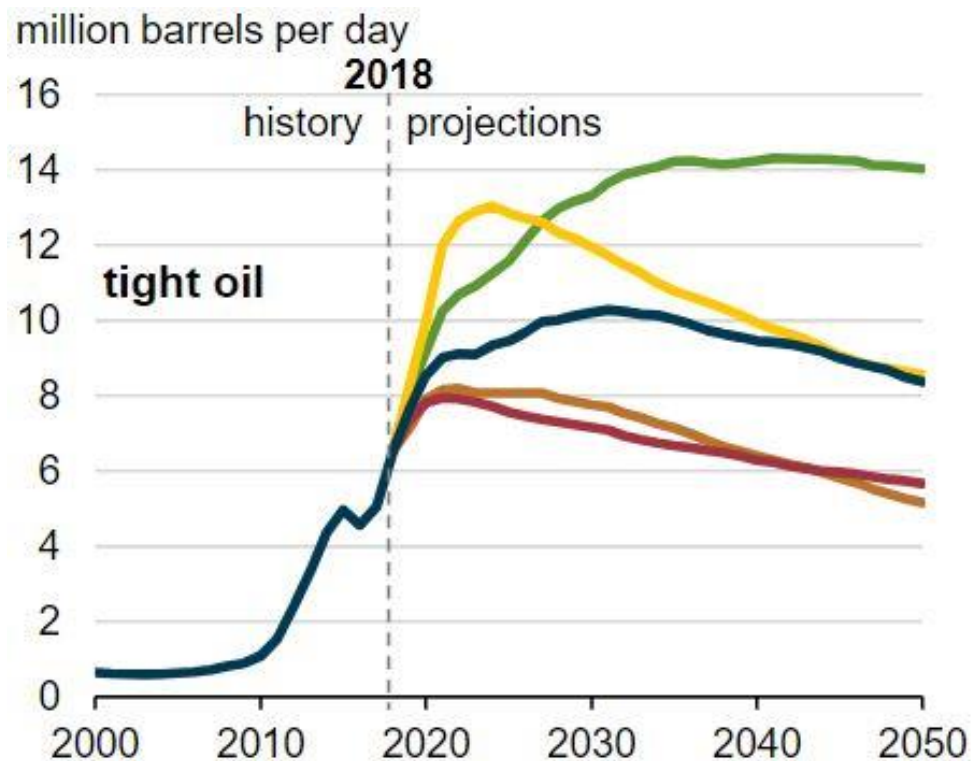
10/22/2024

Source: US Energy Information Administration

# OVERVIEW - PROJECTIONS

Contribution of unconventional hydrocarbon sources to total production is projected to increase

Graphs below show contributions for various scenarios



High Technology  
Development

Low Technology  
Development

High Petroleum  
Prices

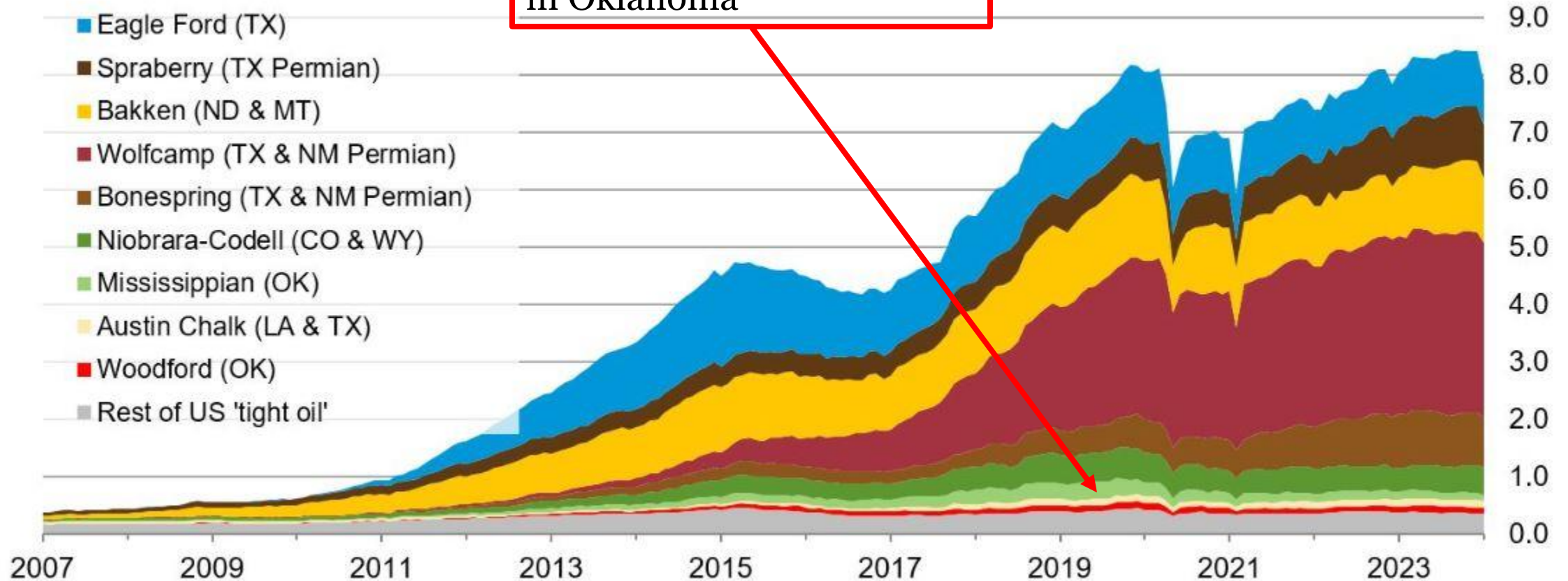
Low Petroleum  
Prices

# OVERVIEW – Caney Shale Contribution

million barrels of oil per day

Caney Shale is categorized under Mississippian Shales in Oklahoma

Source: US Energy Information Administration

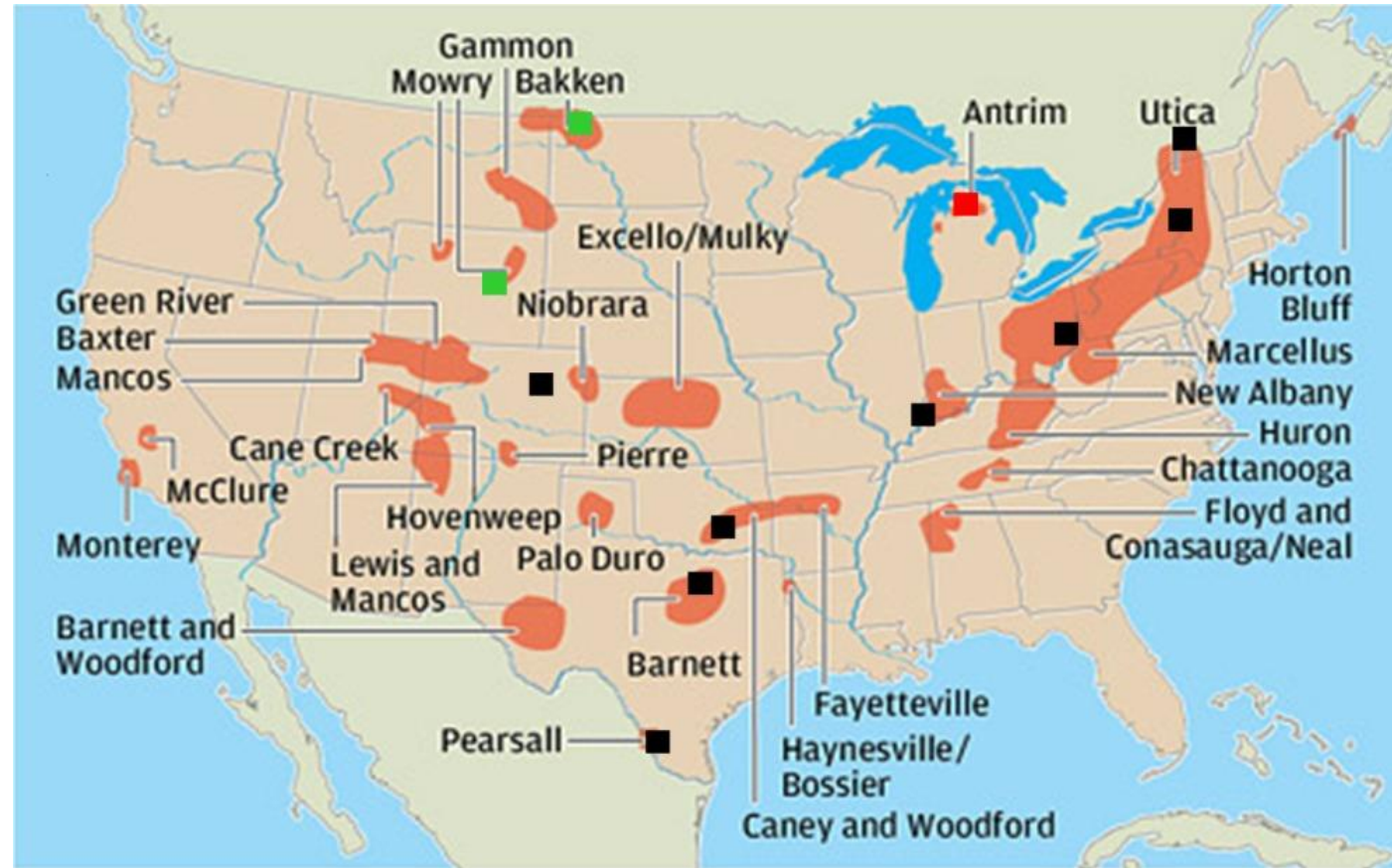


Contributions from various unconventional sources to total unconventional production in USA



# PROBLEM

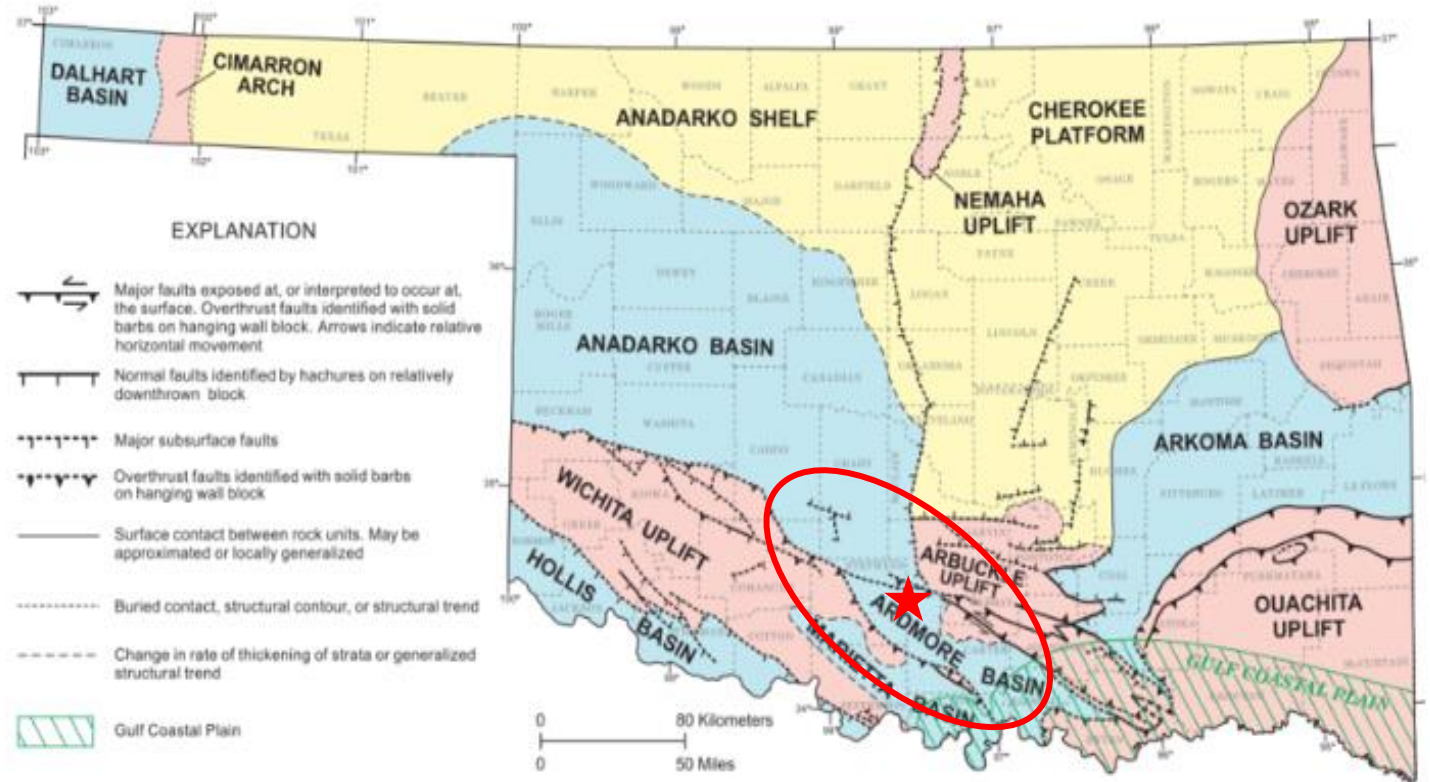
- Recent statistics of unconventional shale reserves in the USA are estimated at approximately, 6 trillion barrels of oil and 495 trillion cubic feet of gas (Farrokhrouz et al., 2022)
- Complex mineralogy and ultra-low permeability of shale reservoir makes development and production of these reservoirs challenging (Swami et al., 2012)
- Current recovery from shale reservoirs is just about 10% of original hydrocarbons in place (Mukhina et al., 2021)
- Current research aims to understand these reservoirs to help create technologies that will enhance recovery



**Locations of unconventional hydrocarbon deposits in the United States of America** ([https://www.ireservoir.com/case\\_shale.html](https://www.ireservoir.com/case_shale.html), accessed on May 12, 2023)

# PROBLEM – Specific Area

- The Caney Shale is located in the Ardmore Basin of South-Central Oklahoma Oil Province (SCOOP)
- It overlies the better-known Woodford Shale which has been the main target of drilling in the area over the years
- The Caney Shale, though replete with hydrocarbons, is characterized by high clay content, complex mineralogy, and ultra-low permeability
- This makes hydraulic fracturing the most viable option in producing from this shale
- This study characterizes the long-term geochemical responses of the Caney Shale after hydraulic fracturing



*Geological map of Oklahoma, showing SCOOP area (red ellipsoid) and well locations (red star) (after Johnson, 2008)*

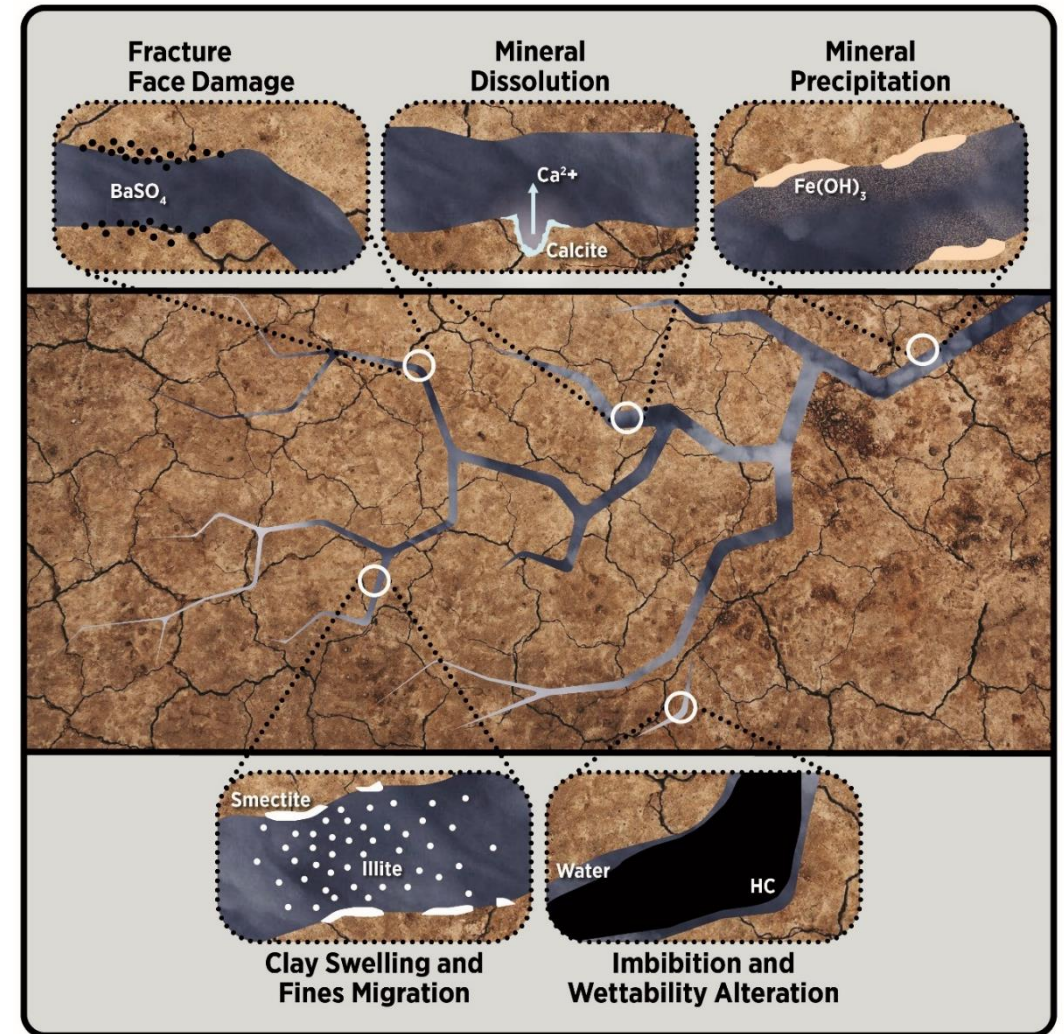


# OBJECTIVES

This work is designed to investigate the impact of geochemical rock-fluid reactions on permeability of Caney Shale

The following sub-objectives culminate in achieving this objective:

1. Evaluating the mineralogy of Caney Shale in South Central Oklahoma Province (SCOOP)
2. Understanding the microstructural configuration and spatial heterogeneity of the Caney Shale
3. To evaluate potential geochemical rock-fluid interactions in Caney Shale
4. To identify the mechanisms controlling geochemical rock-fluid interaction in the Caney Shale and the factors that enhance or reduce these mechanisms
5. To assess the impact of rock-fluid interactions on evolution of petrophysical (permeability and porosity) and mechanical properties of Caney Shale



*Fracture and near-fracture Rock-Fluid Interaction following hydraulic fracturing of reservoir formation*



# MATERIALS AND METHODOLOGY

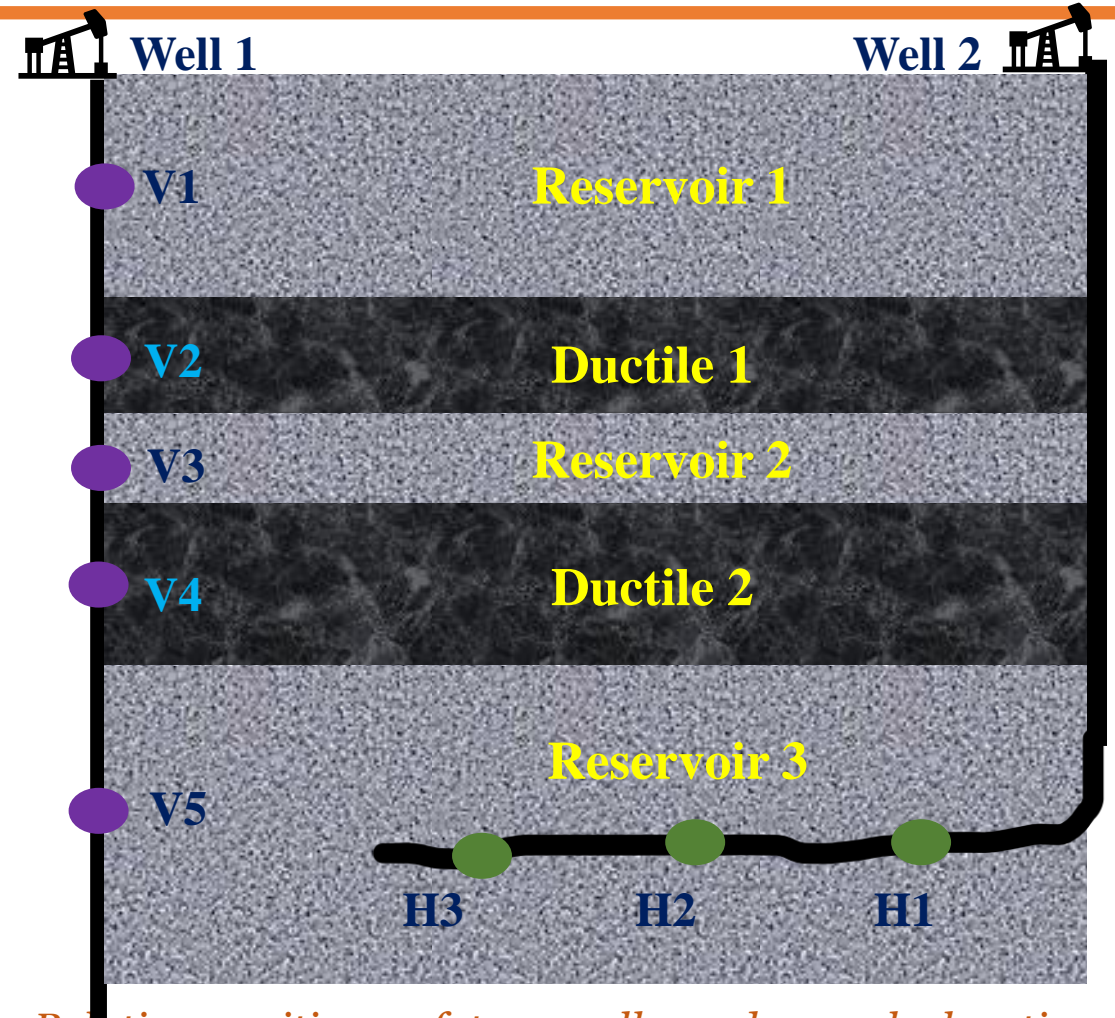
Rock samples used for this experiment are recovered from two different wells as follows:

- Well 1:
  - Vertical well across entire Caney Shale
  - Samples are recovered as cored-rock
- Well 2:
  - Horizontal well drilled within Reservoir 3
  - Samples are recovered as rock-cuttings at 1000ft intervals

Rock samples are prepared and ground into powders with average particle size of 30 $\mu$ m

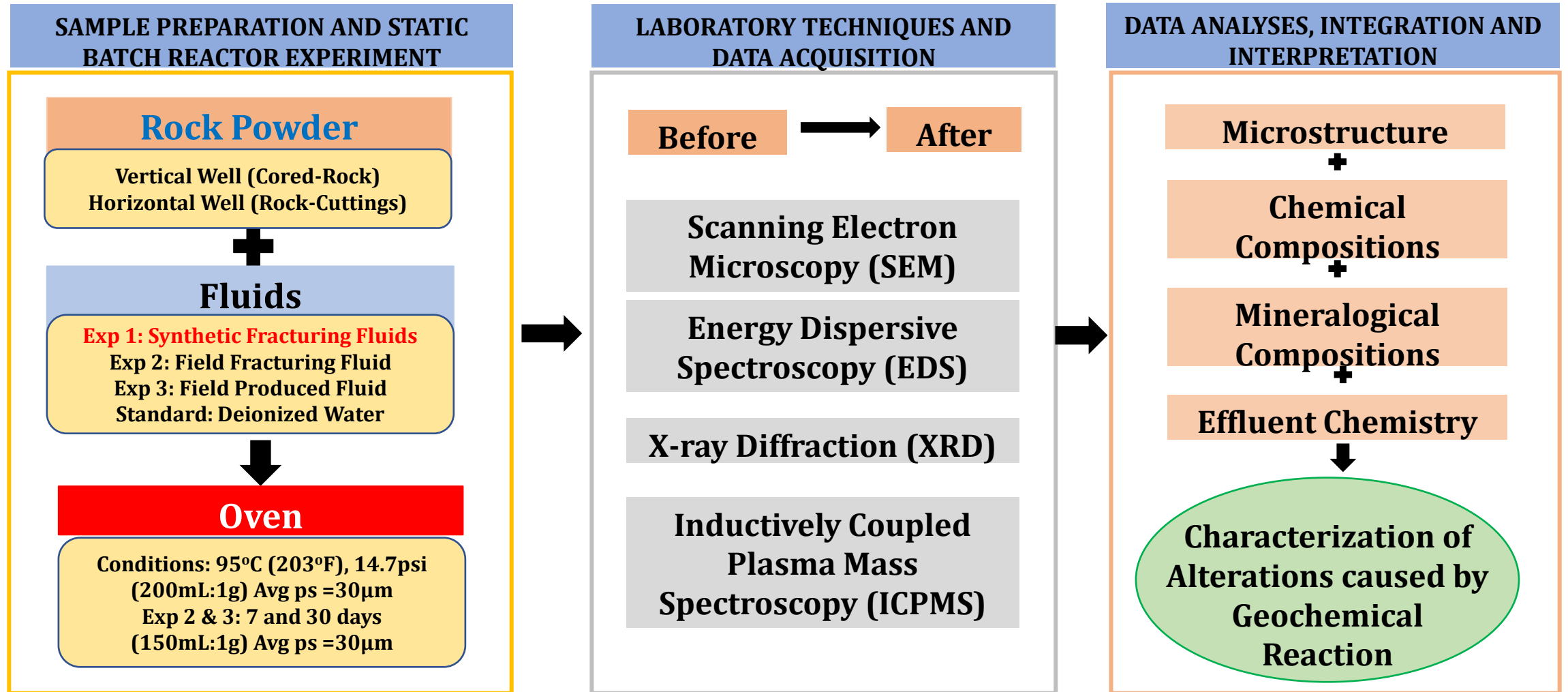
Field Fracturing Fluid and Field Produced Brines recovered from Caney Shale were the main reacting fluids. Deionized water was used as a standard for comparison

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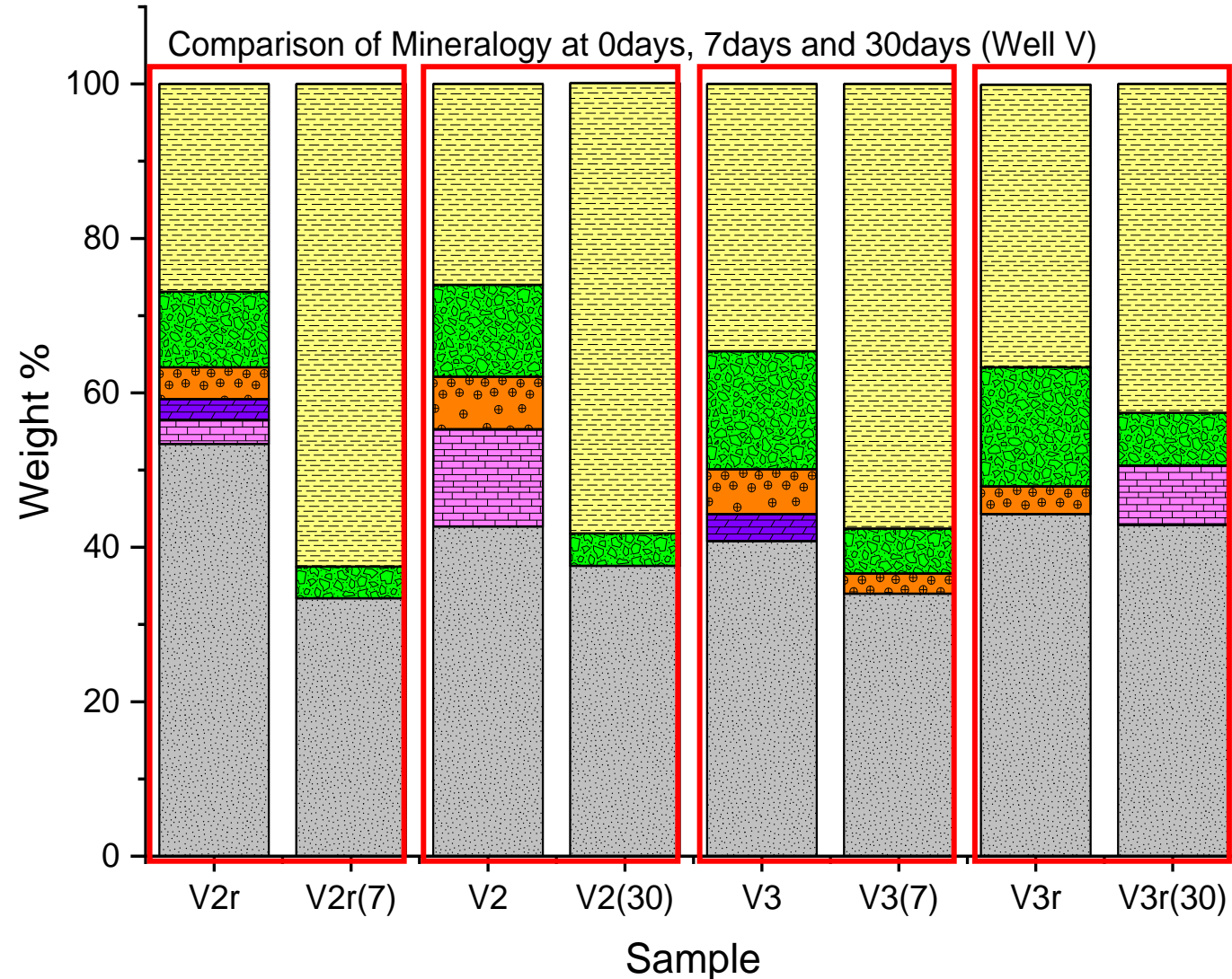
*Relative positions of two wells and sample locations: Samples V1 to V5 are cored-rocks from five (5) zones of the formation. H1 to H3 are rock cuttings spaced 1000ft horizontally at approximately the same vertical depth (Schematic not drawn to scale)*

# MATERIALS AND METHODOLOGY

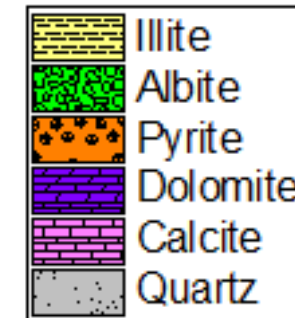


Flow chart of materials and methodology used in preliminary experiments, data acquisition and interpretation

# RESULTS – Mineralogical Alterations of Caney Shale Powders in Field Fracturing Fluids (HF)-XRD analysis



- Pyrite breakdown occurs mostly within the first 7 days of reaction
- The amount of quartz drops after 7 days but remains relatively constant after that.
- Feldspar presence generally shows a downward trend after reaction at both 7 and 30 days
- The amount of illite is increasing continuously at 7 and 30 days.



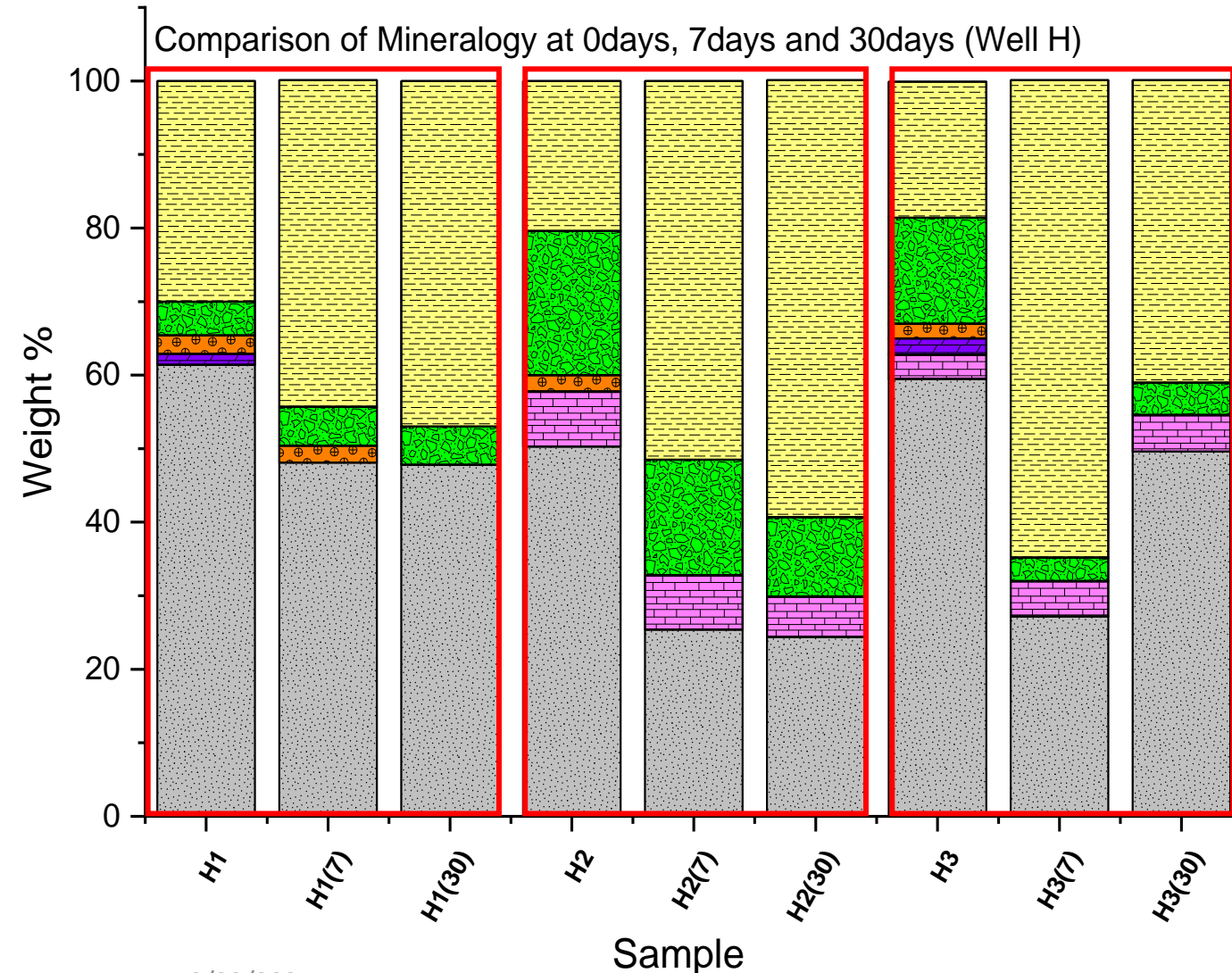
V - Vertical Well

(7) - 7days reaction

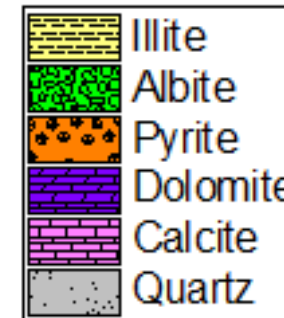
(30) - 30days reaction



# RESULTS – Mineralogical Alterations of Caney Shale Powders in Field Fracturing Fluids (HF)-XRD analysis

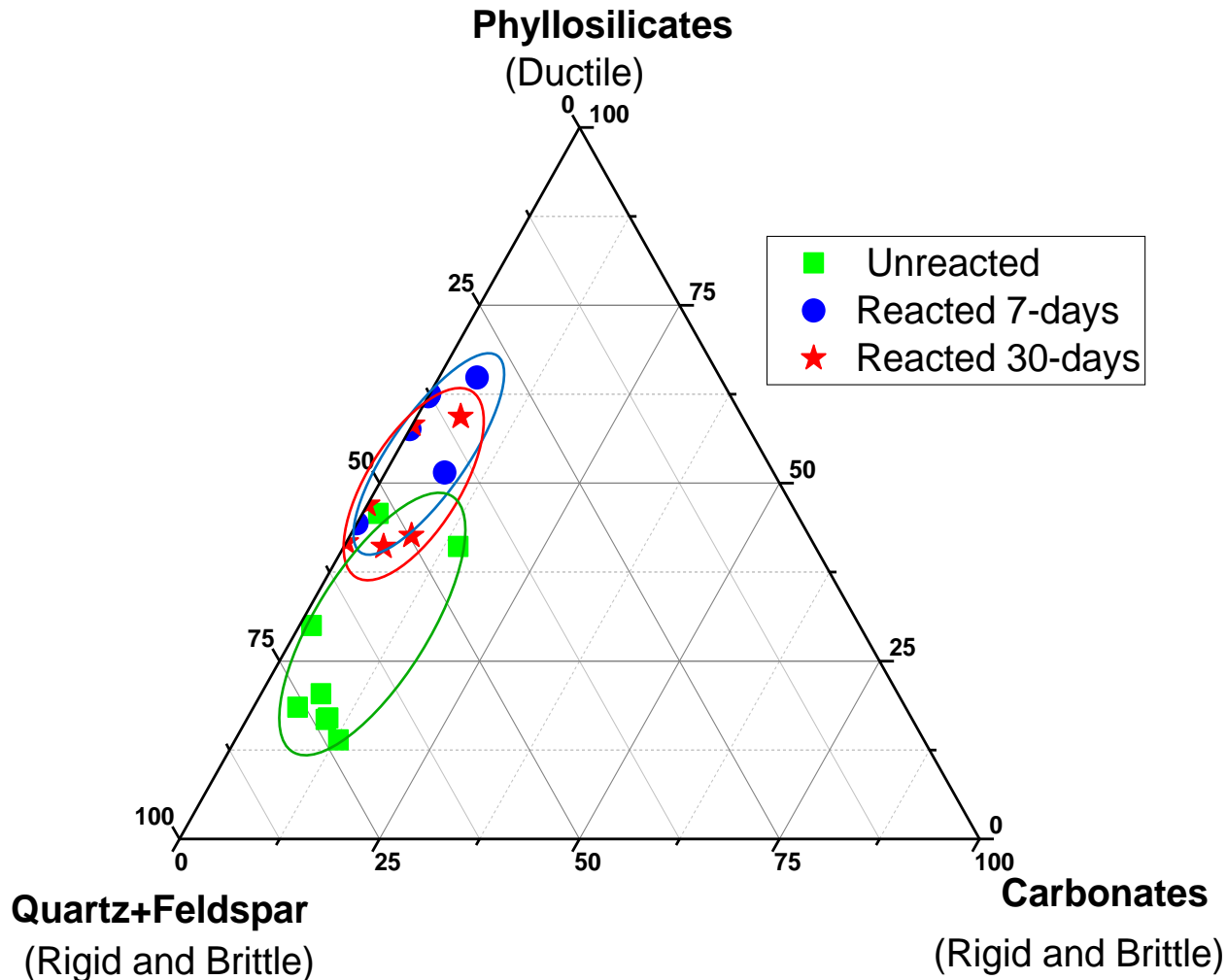


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H - Horizontal Well  
(7) - 7days reaction  
(30) - 30days reaction

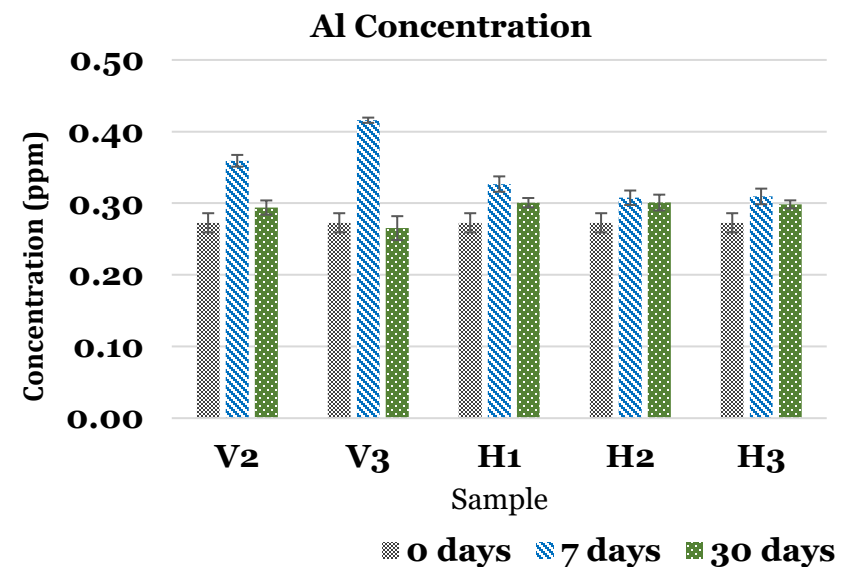
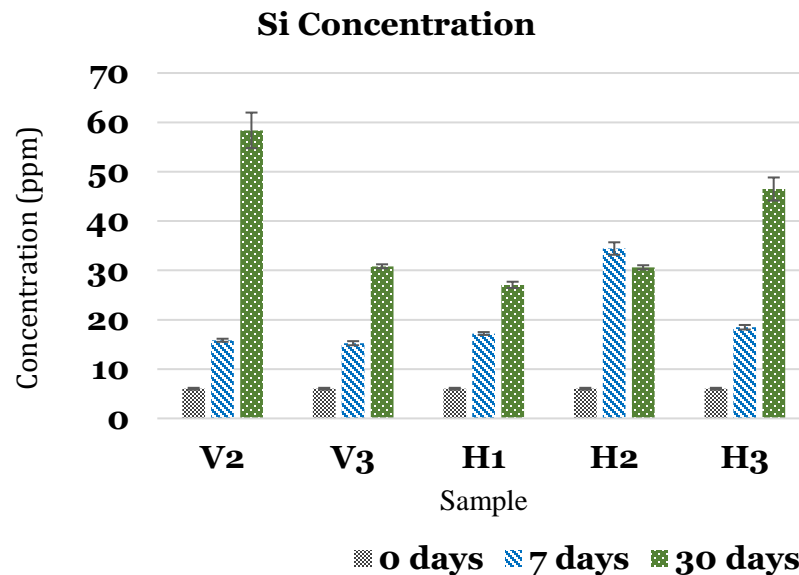
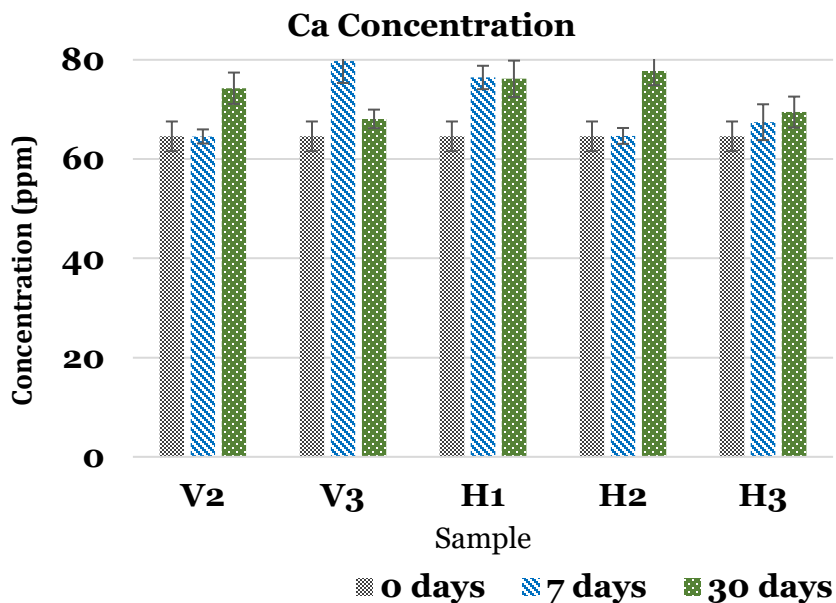
# RESULTS – Big Picture



**Ternary diagram showing Comparison of unreacted samples to 7 days and 30 days reacted samples – Hydraulic Fracturing Fluids**

- The ternary diagram shows the changes in mineralogy that occurred due to geochemical rock fluid interactions
- Mineralogy of rocks are originally closer to quartz, feldspar field which represents the brittle component of the formation
- The breakdown of feldspar, pyrite and carbonates after 7days of reaction shifts the mineralogy towards phyllosilicates
- After 30days of reaction, the mineralogy shifts moderately towards quartz-feldspar field but not enough to regain the original rigid and brittle characteristics
- Shift towards phyllosilicates introduces a ductile character into the rocks

# RESULTS - Elemental Composition of Caney-HF Fluid after Experiment (ICPMS)



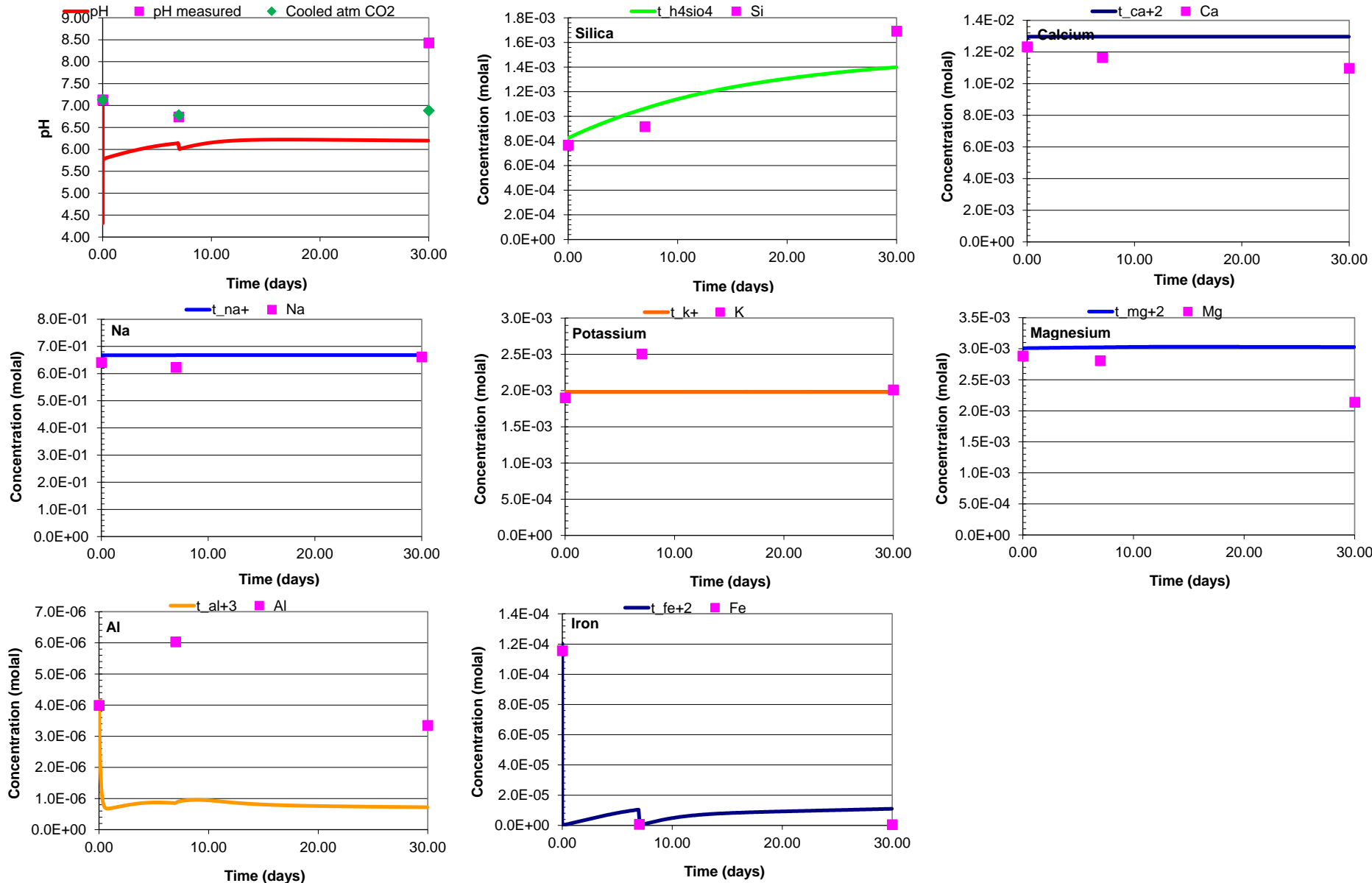
- Ca concentrations relatively stable because, fracturing fluid used for experiment had a circumneutral pH
- Dissolution of pyrite causes transient acidity which initiates dissolution of carbonates
- Cation exchange in clay sites also causes Ca concentration in effluent

- High concentrations of Si observed on the graphs cannot be explained by quartz dissolution at the given conditions
- Dissolution of feldspar contributes to Si concentration in effluent
- Dissolution of biogenic silica could explain high Si concentrations

- Al is mainly from the dissolution of feldspars
- Al entering solution is precipitated at a fast rate – Clays and Al-based minerals
- Similar trends observed for Mg and Fe



# RESULTS – Model of Experiment (TOUGHREACT Simulator with Thermoderm Thermodynamic Database) by LBNL



Modeling of experiment shows most elemental concentrations in effluent matching with ICP-MS results

Due to limitations in complete characterization of rock and fluids, some assumptions were made in the model

These assumptions and limitations of model are captured in the next slide

# RESULTS – Model of Experiment

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The following uncertainties and limitations are worth noting about modeling of experiment:

## **Thermodynamic data/models**

Modeled minerals of mixed composition (e.g. clays) may not have the same composition as in the rock formation

Fluid salinity may exceed the validity range of the implemented ion activity model (extended Debye-Hückel)

## **Reconstruction of the Fracturing compositions**

Anion concentrations computed from assumptions

Organic compounds besides acetate were neglected (unknown potential effects on experimental results)

## **Rock formation mineralogy**

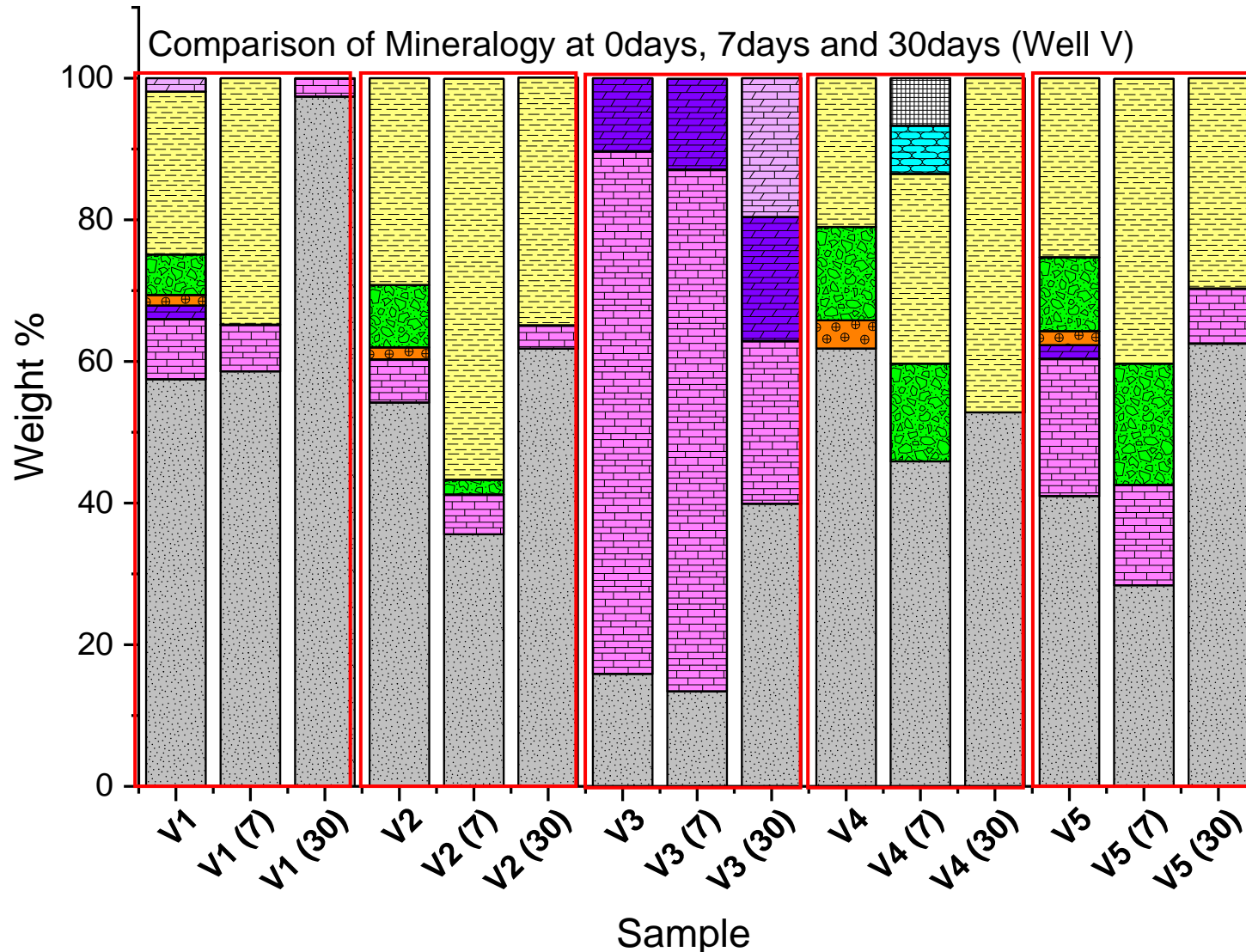
Trace or amorphous minerals (undetected by XRD) impact the system geochemistry – amounts and types were assumed

## **Sampling effects**

Interactions with atmosphere (O<sub>2</sub>, CO<sub>2</sub> impact pH and redox)

Mineral reaction rates (kinetic constants, surface area)

# RESULTS - Mineralogical Alterations in Vertical Well Samples



- Pyrite dissolution occurs within the first 7 days of reaction
- Quartz reduces in the first 7 days but increases between 7 to 30 days whilst carbonate is relatively stable
- Feldspar composition reduces and completely breakdown after 30 days
- Illite composition shows an increasing trend over 7 days but remains relatively the same between 7 days and 30 days

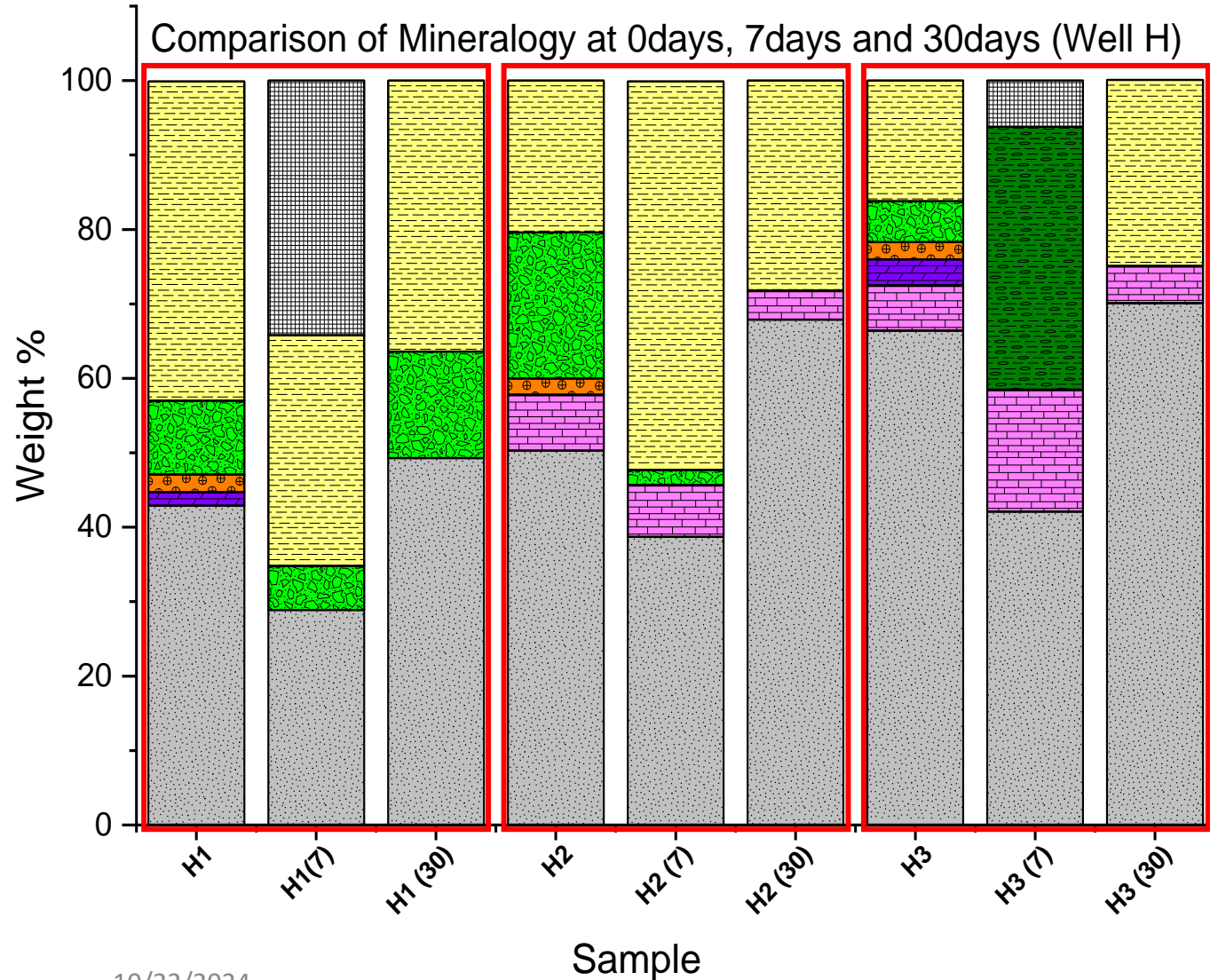
**V – Vertical Well**

**(7) – 7 days reaction**

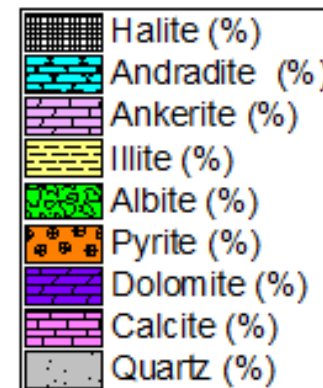
**(30) – 30 days reaction**



# RESULTS - Mineralogical Alterations in Horizontal Well Samples



- Pyrite breakdown occurs within the first 7 days of reaction
- Composition of quartz drops after 7 days but increases between 7 to 30 days
- Feldspar reduces continuously and mostly dissolve or transform by 30 days
- Illite composition shows an increasing trend after 7 days reaction and decreases between 7 and 30 days

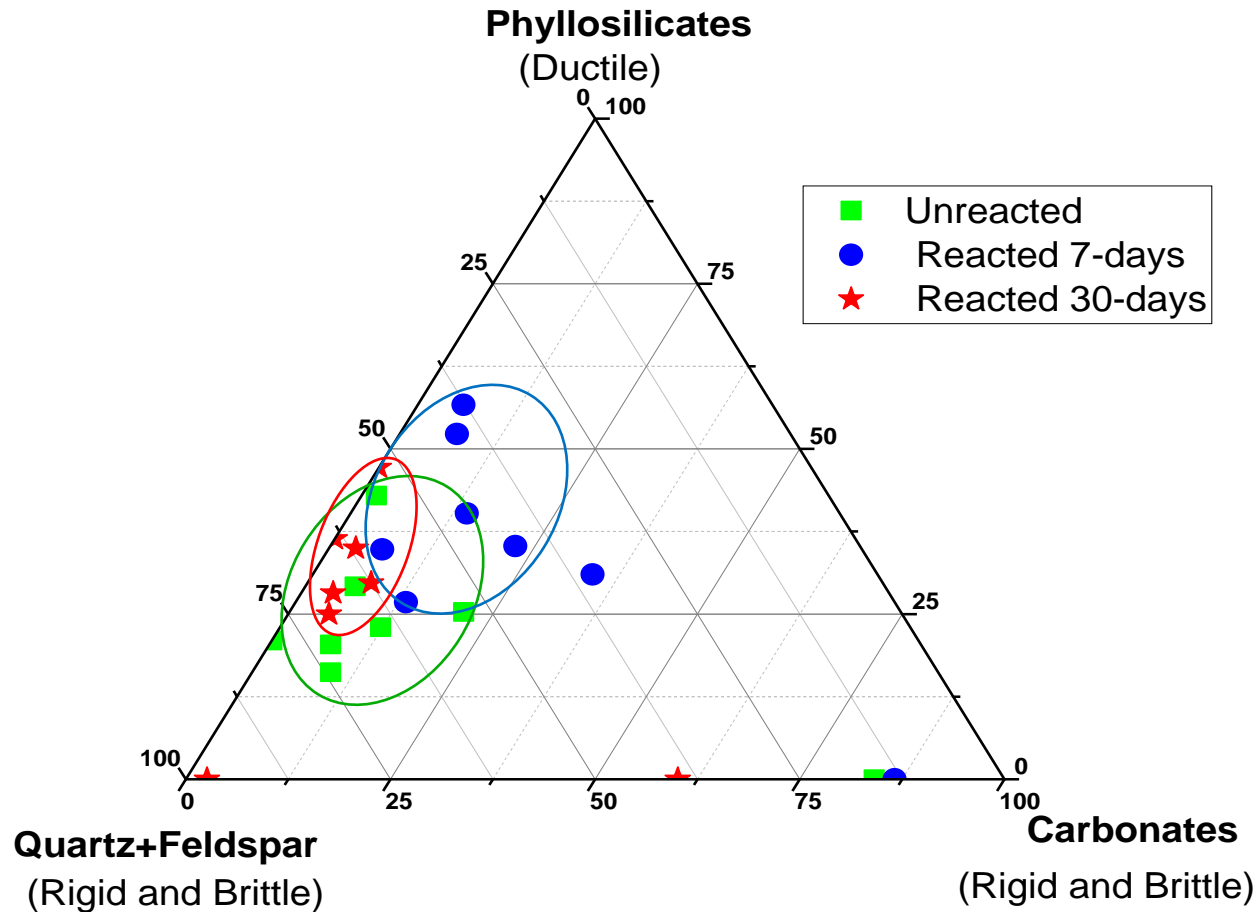


**H – Horizontal Well**

**(7) – 7 days reaction**

**(30) – 30 days reaction**

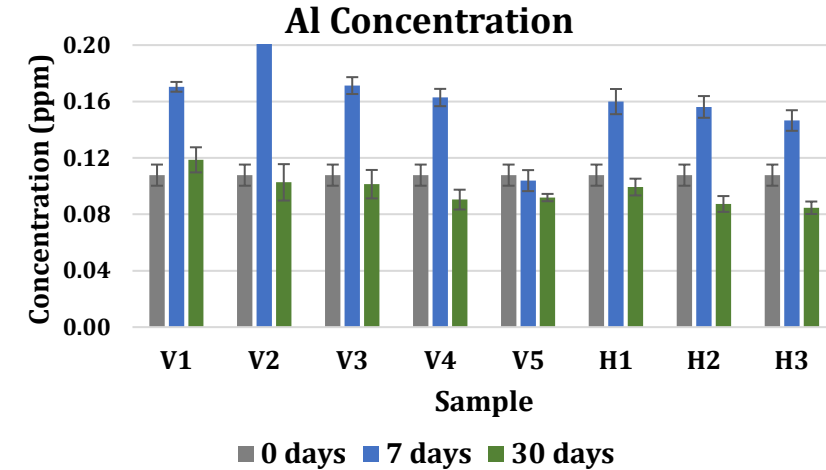
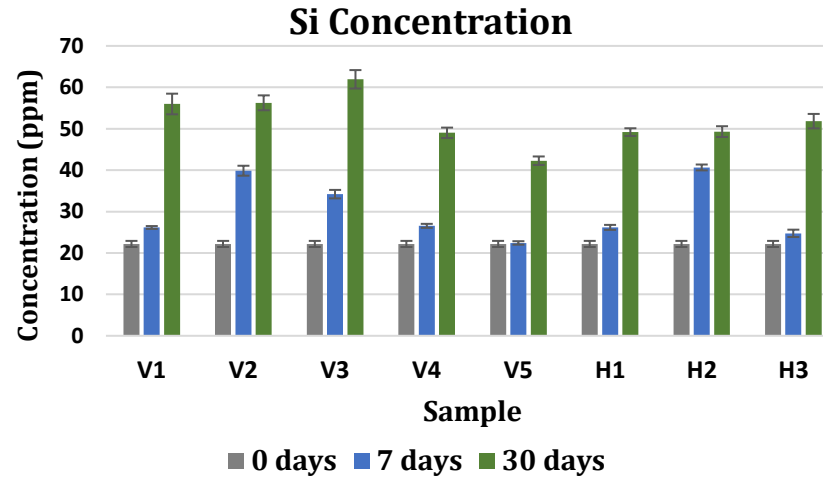
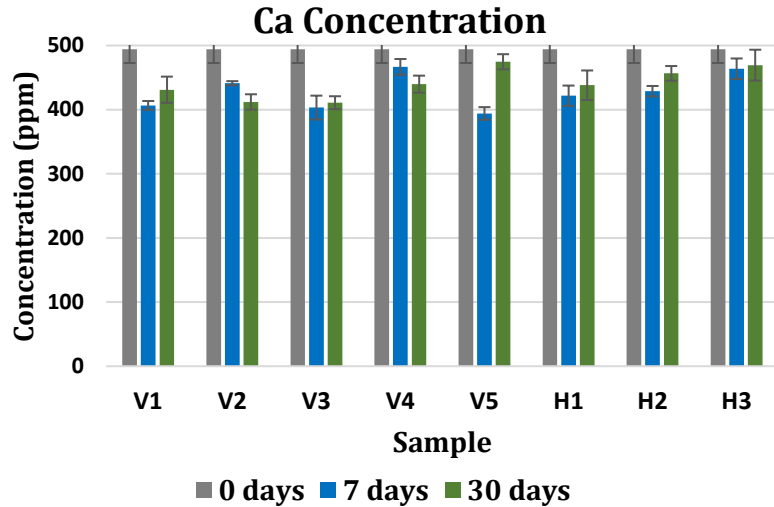
# RESULTS – Big Picture



**Comparison of unreacted samples to 7 days and 30 days reacted samples – Produced Fluids**

- The ternary diagram gives a big picture of impacts of mineralogical changes on rock properties
- Mineralogy of rocks are originally closer to quartz and pyrite, indicating brittleness
- Rock-fluid reaction shifts the samples to phyllosilicate zone, indicating ductility
- Ductility promotes fracture healing thus loss of permeability
- Main reactions that promote shift include:
  - Breakdown of pyrite and microcrystalline quartz
  - Breakdown of feldspar and carbonates
  - Formation of illite

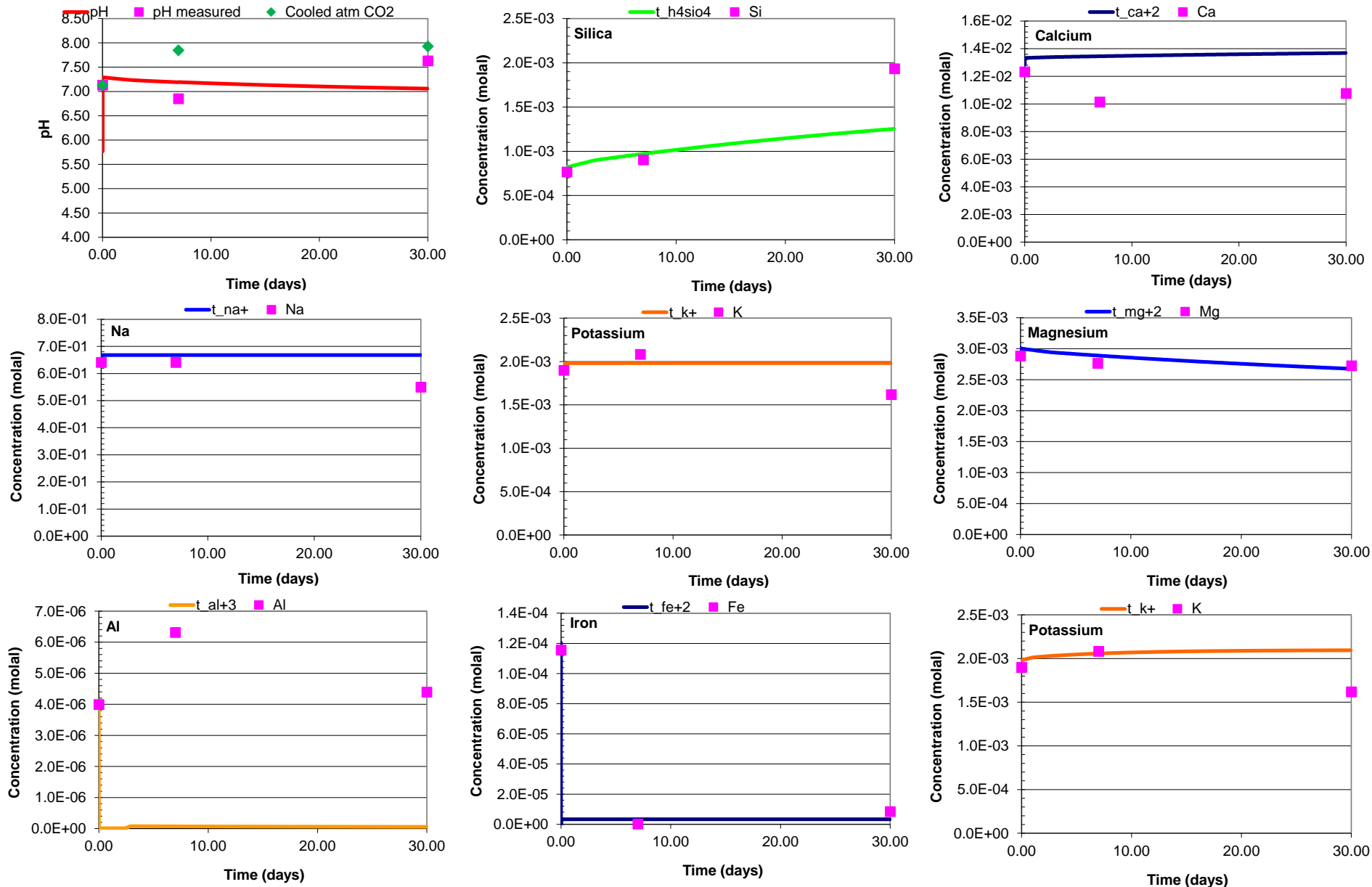
# RESULTS - Elemental Composition of Caney-Produced Fluids after Experiment (ICPMS)



- Due to approximate neutral pH, Ca concentrations relatively stable
- Dissolution of carbonates occur due to transient acidity caused by dissolution of pyrite
- Precipitation or cation exchange in clay sites may lead to Ca uptake from effluent causing decreased Ca concentrations
- The high Si concentrations cannot be explained only by the dissolution of quartz at the experiment conditions
- Dissolved biogenic (microcrystalline quartz) or amorphous silica could explain high silica concentrations
- Dissolution of feldspar contributes to Si concentration in effluent
- Al is mainly from the dissolution of feldspars
- Al concentrations are very low due to uptake from fluid – illite and other Al-based mineral precipitation
- Similar trends observed for Magnesium (Mg) and Iron (Fe)



# RESULTS – Model of Experiment (TOUGHREACT Simulator with Thermoderm Thermodynamic Database) by LBNL



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## **Reconstruction of the Produced Fluid compositions**

Anion concentrations computed from assumptions

Organic compounds besides acetate were neglected (unknown potential effects on experimental results)

## **Rock formation mineralogy**

Trace or amorphous minerals (undetected by XRD) impact the system geochemistry – amounts and types were assumed

## **Sampling effects**

Interactions with atmosphere (O<sub>2</sub>, CO<sub>2</sub> impact pH and redox)

Mineral reaction rates (kinetic constants, surface area)

# DISCUSSION

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Illitization – Increased illite composition due to breakdown of feldspars which provides the necessary elements for illitization. This phenomenon has been observed in earlier studies such as Guven et al., (1982), where they observed that illitization is favored by high Al concentrations at circum-neutral pH. This is similar to conditions of our experiment

Iron Oxides – The breakdown of pyrite and other iron-bearing minerals release mostly, Fe(II) into solution which is subsequently oxidized to Fe(III) oxyhydroxides that block pores within the formation and lead to permeability losses. The breakdown of pyrite in this study points to high probability of iron oxides formation

Fines Migration – Clay fines migration are occasioned by the deflocculation and dispersal of clay minerals. These subsequently aggregate within flow paths to cause significant permeability losses. High amorphous compositions after reaction observed in this study points to possible clay deflocculation

The cumulative impact of reactions described above is the loss of permeability of formation during long-term post-hydraulic fracturing rock-fluid interactions.

# CONCLUSIONS AND RECOMMENDATIONS

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- Carbonates, pyrite, feldspars and clays are susceptible to rapid geochemical reactions
- Oxidation is a major mechanism in rock-fluid interactions, it leads to breakdown of pyrites
- Breakdown of pyrite and other sulfides after exposure to oxygenated fluid leads to generation of acids which cause transient pH reductions, thus catalyzing breakdown of other minerals such as carbonates
- Reactions with fluids lead to increased illite content in rock samples suggesting the shift from initially brittle rock to more ductile rock in the long term
- Deflocculation of clay minerals leads to the generation of fines which can coalesce later within the fracture to cause blockage of pore-throat (Between 7 to 30 days)
- Further work is being done to investigate the cause of illitization observed from XRD measurements

## **Recommendations:**

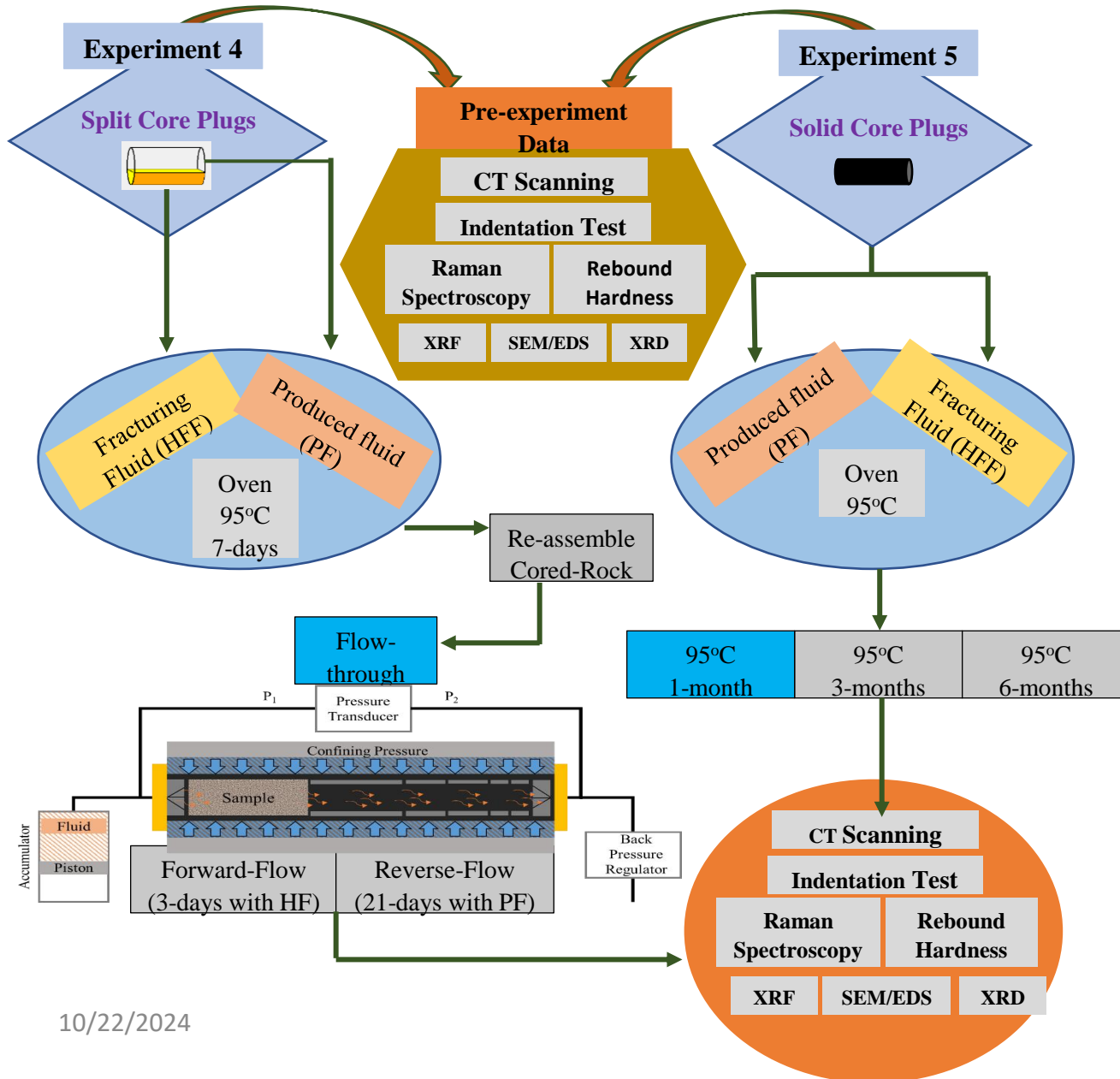
- Longer periods for experiments to help improve model accuracy
- Experiment with cored rock samples over longer periods for better replication of rock-fluid reactions in the subsurface
- Investigate potential illitization and mechanism that may be responsible



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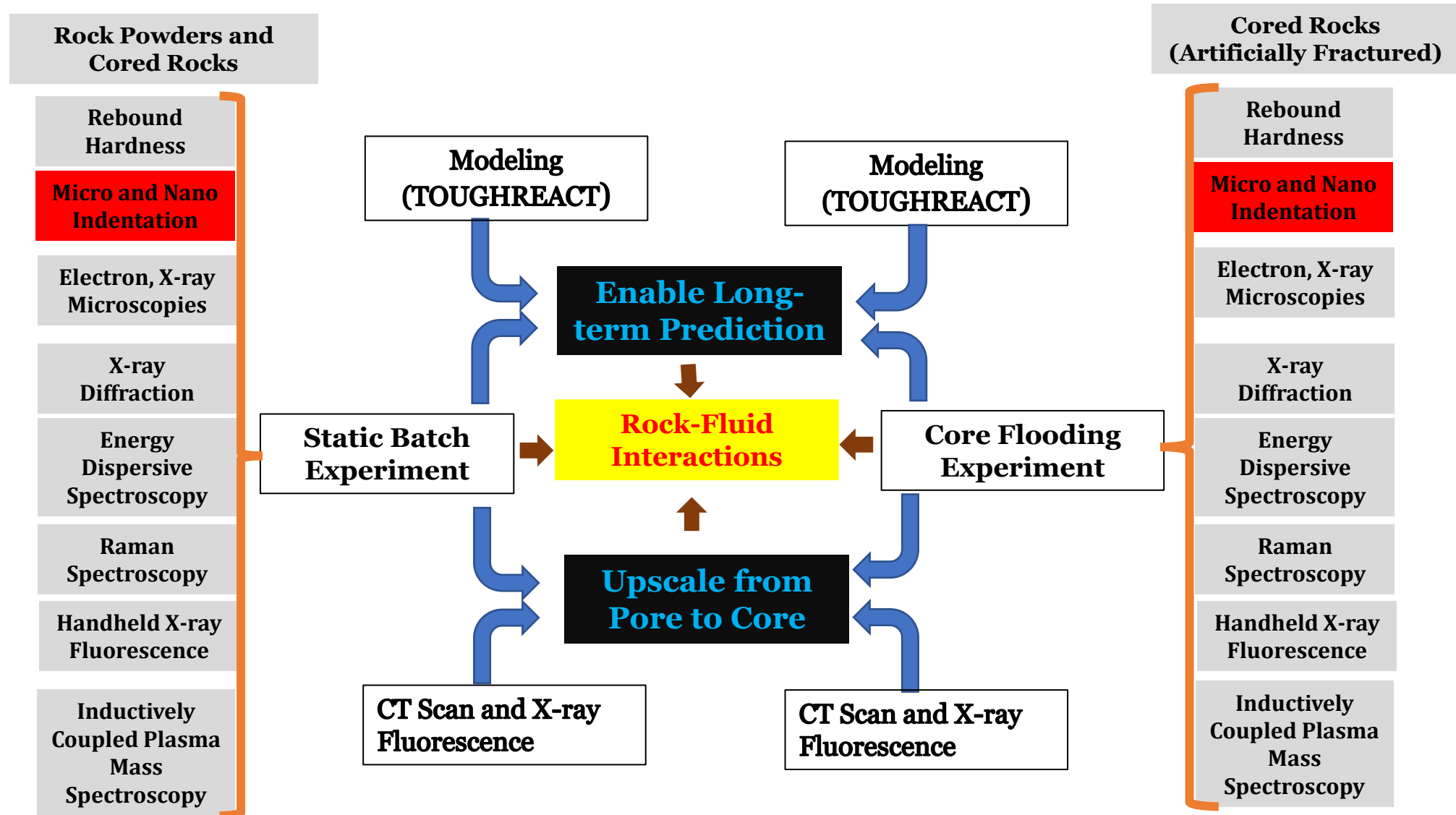
# **PLANS AND WORK CURRENTLY IN PROGRESS**

# WORKFLOW FOR THE REMAINING EXPERIMENTS



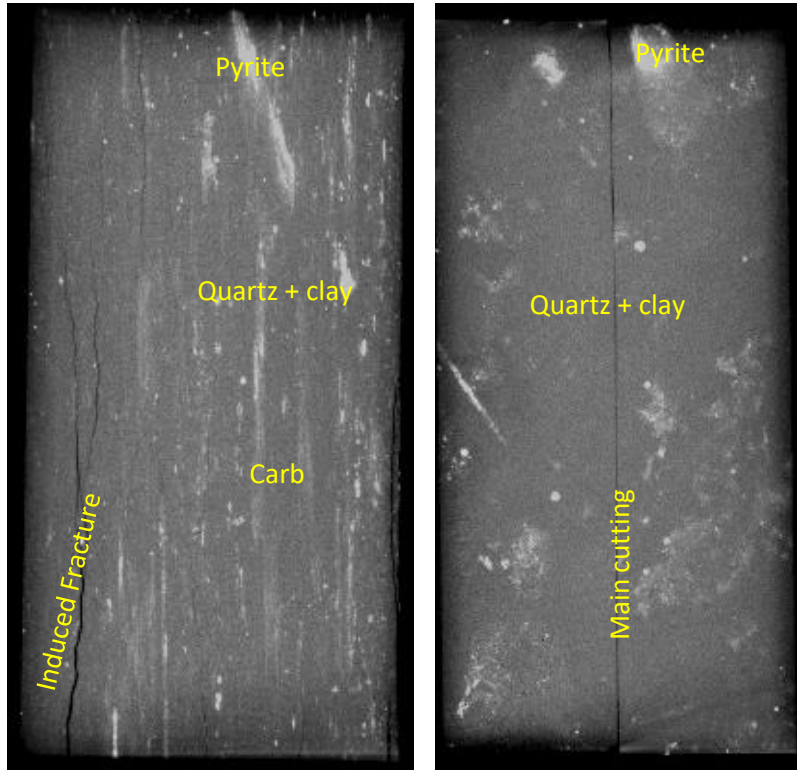
- Experiments designed to complement the initial experiments already undertaken
- Experiments include flow-through experiments and extended static batch reactor experiments with cored rock
- These experiments are designed to be conducted with core-rock samples
- Flow-through experiments will be conducted under dynamic conditions (fluid-flow, temperature, pressure)
- Crucial measurements such as pH will be measured at in-situ temperature and pressure conditions
- These experiments will provide a closer replication of conditions in the subsurface

# METHODOLOGY



Flow chart of overall project direction and protocols established to achieve objectives

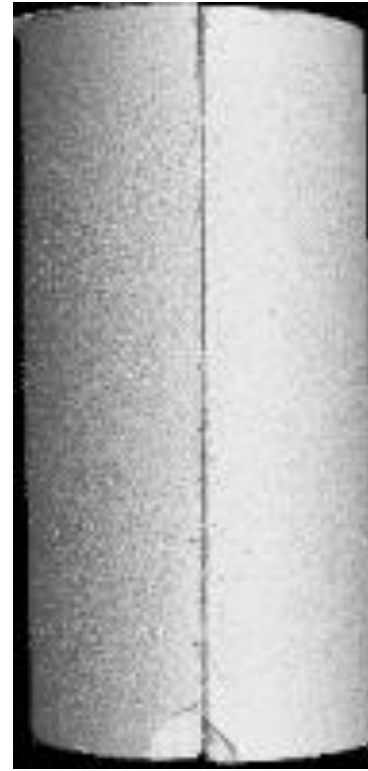
# CT-Scan – Sample D2H



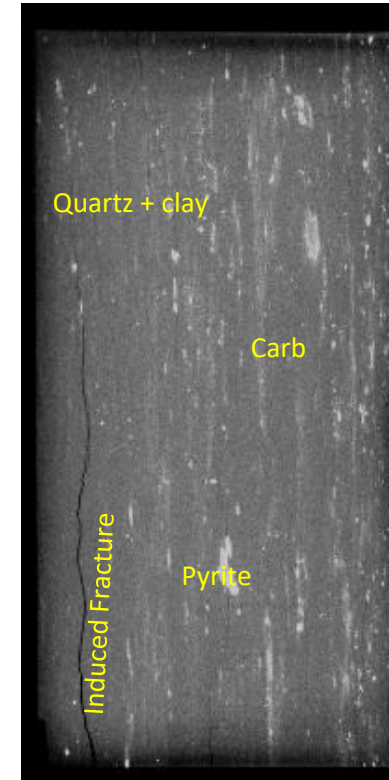
**Front View**

**Side View**

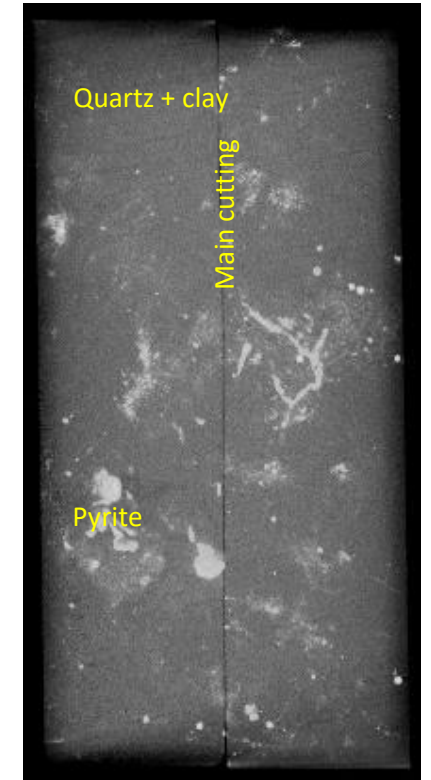
**D2H1**



**Solid View**



**Front View**

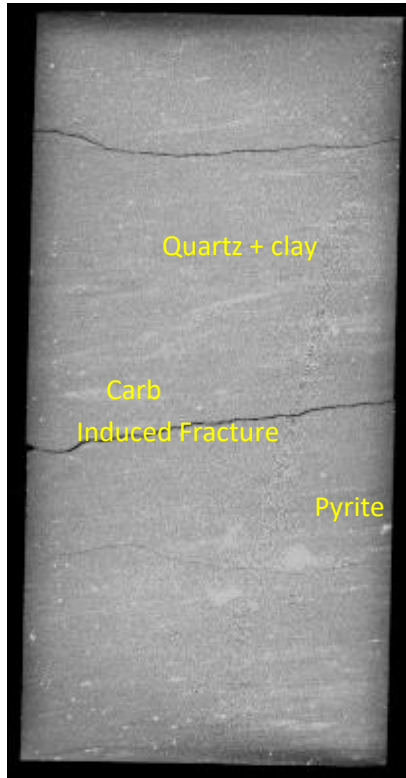


**Side View**

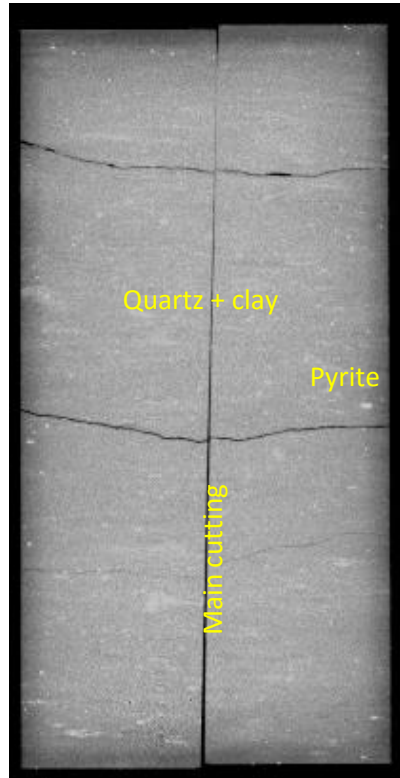
**D2H2**



# CT-Scan – Sample D2V



**Front View**

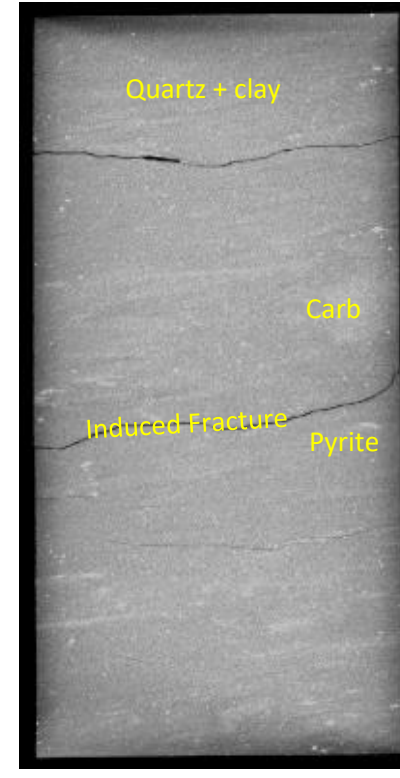


**Side View**

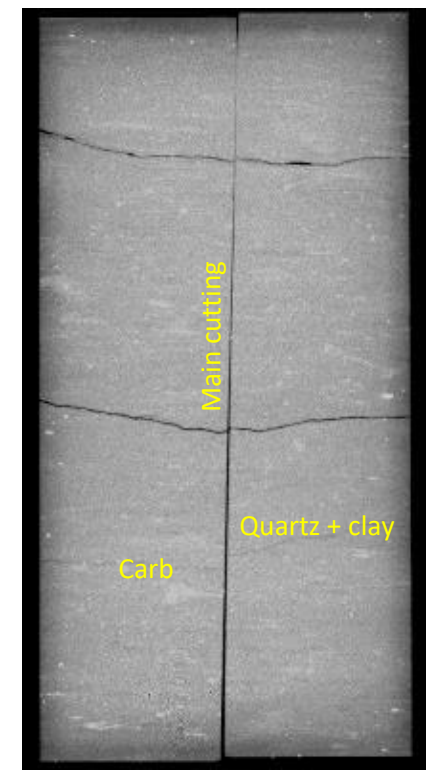
**D2V1**



**Solid View**



**Front View**

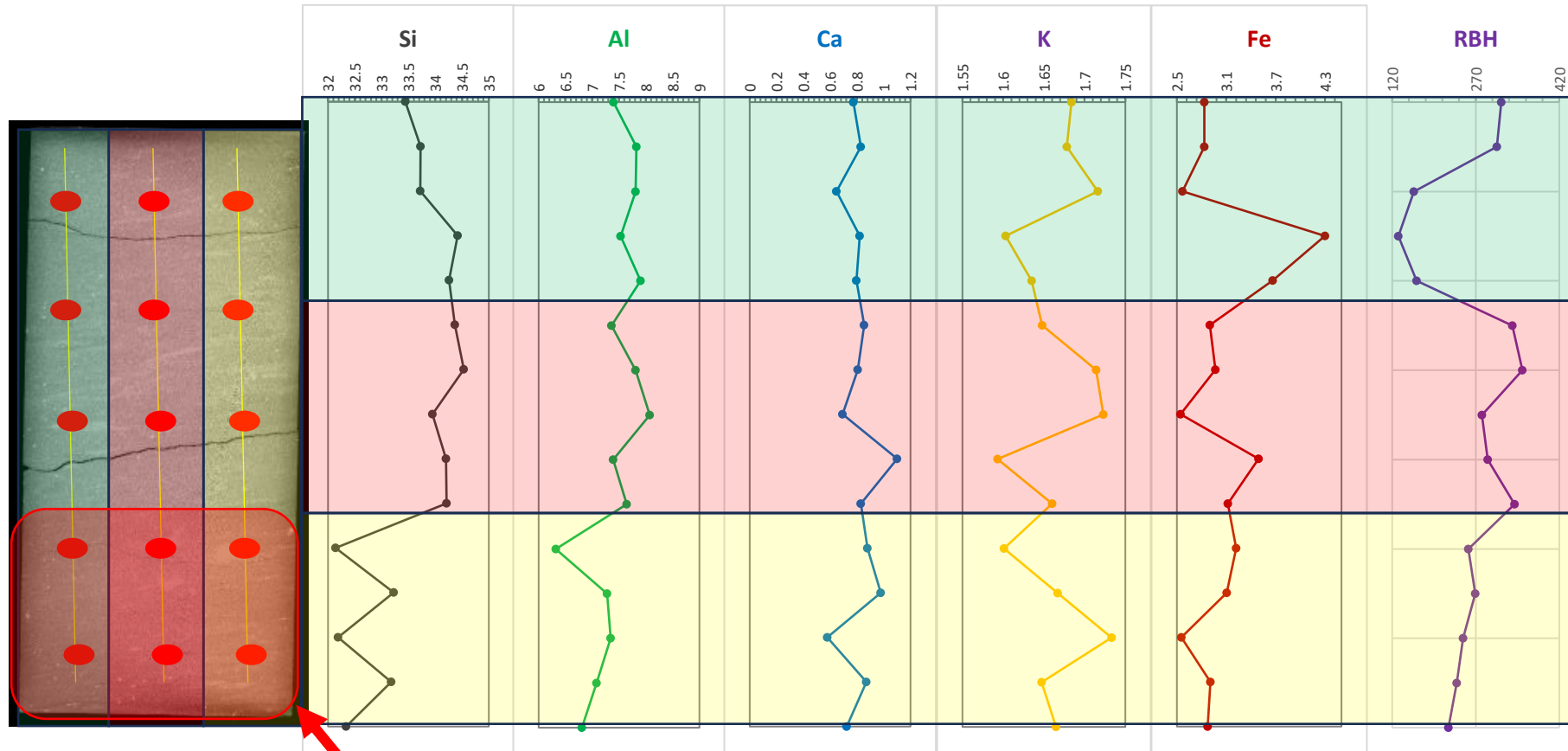


**Side View**

**D2V2**

# Samples (D2V1)

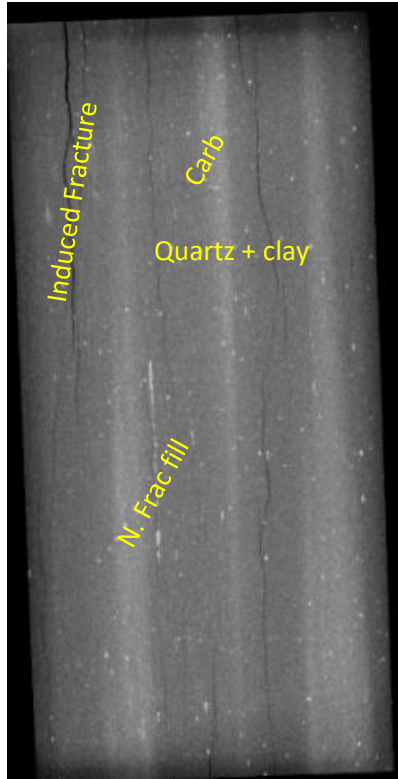
## Combination of CT-Scan, XRF and RBH



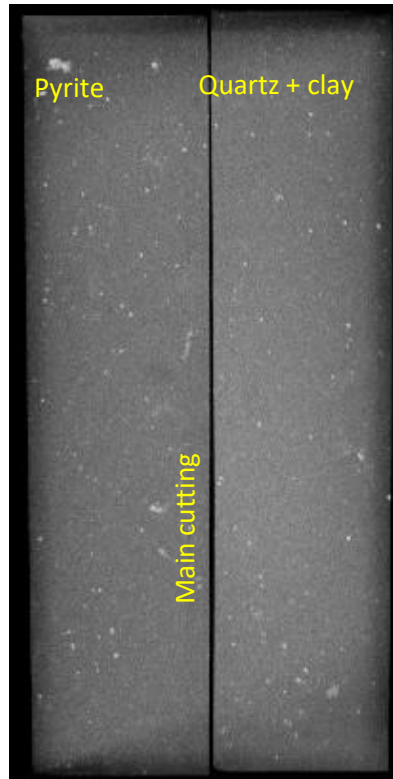
Selected Spot for Raman

- Low Ca throughout
- Si, and Al constant on left side and middle
- Si drops significantly on the right side
- Ca, Si and Fe drops significantly in middle
- Fe drops in middle and right side
- Generally, ductile and more so in right side
- Highest RBH in the middle

# CT-Scan – Sample R<sub>3</sub>H

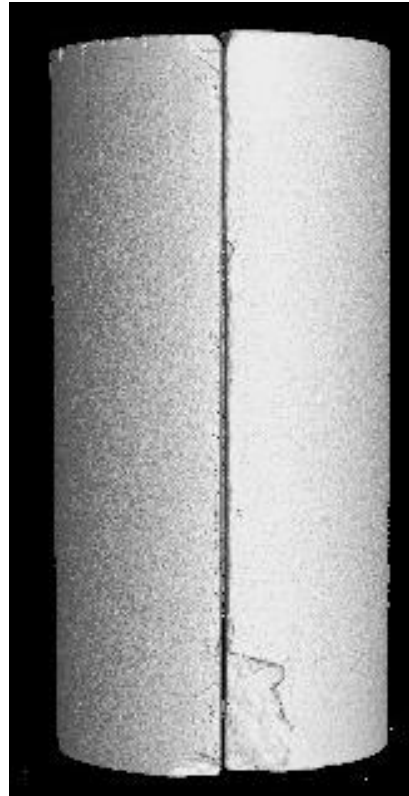


Front View

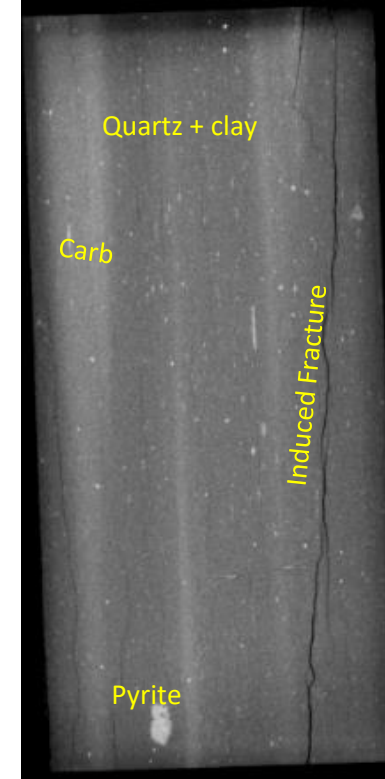


Side View

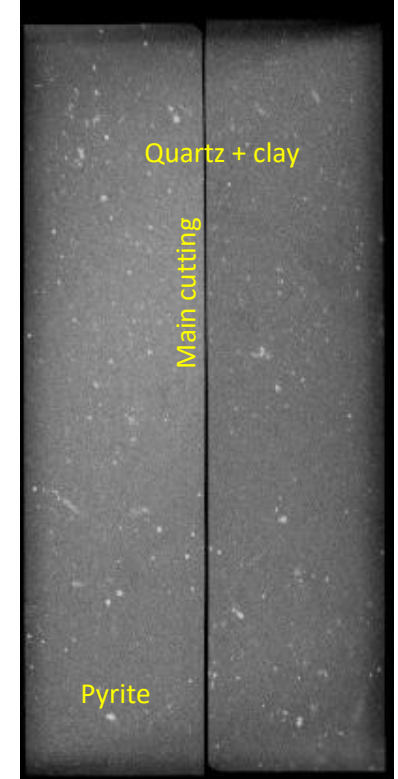
R<sub>3</sub>H1



Solid View



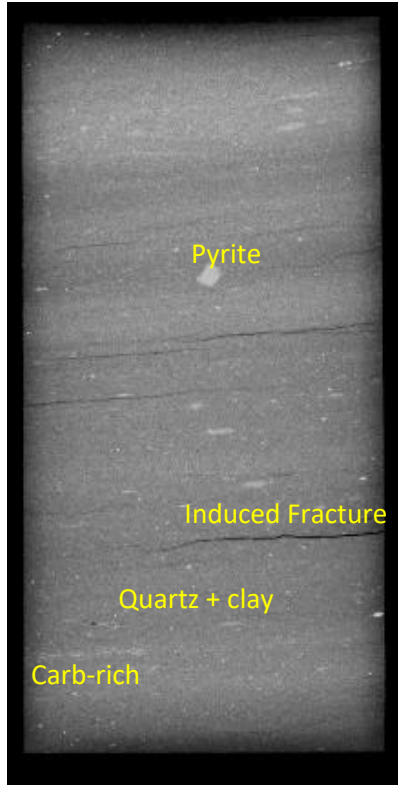
Front View



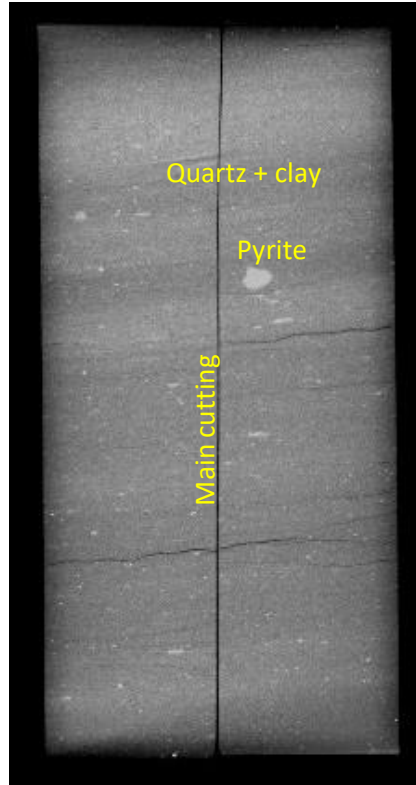
Side View

R<sub>3</sub>H2

# CT-Scan – Sample R3V

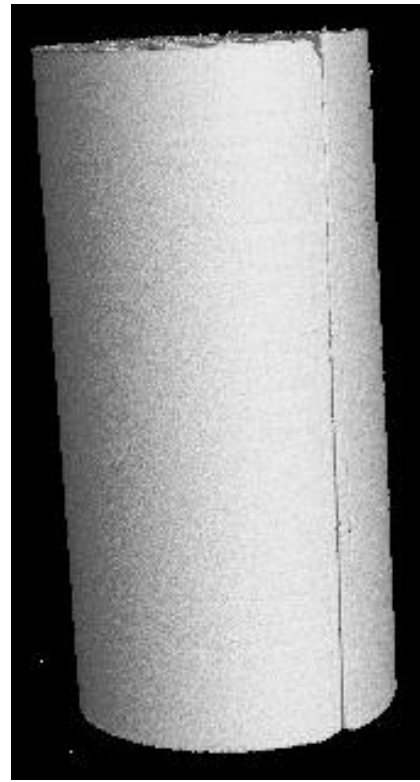


**Front View**

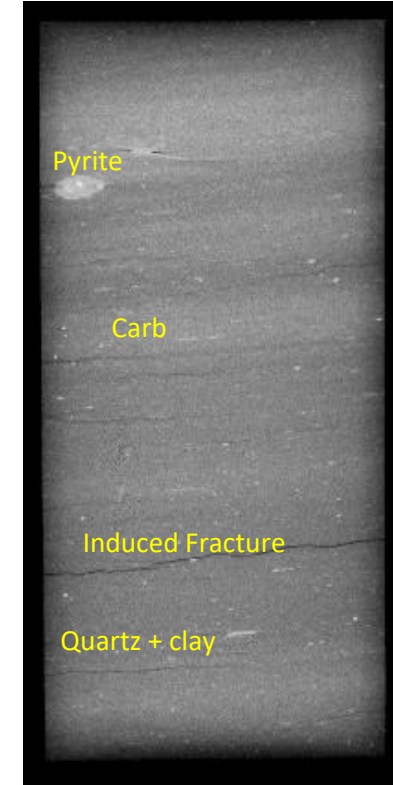


**Side View**

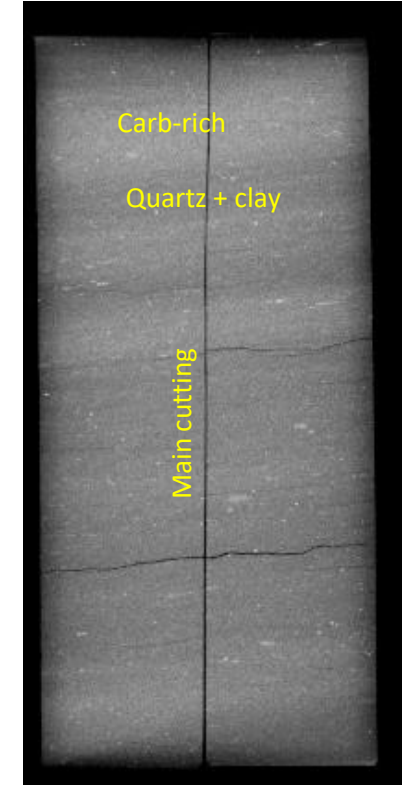
**R3V1**



**Solid View**



**Front View**



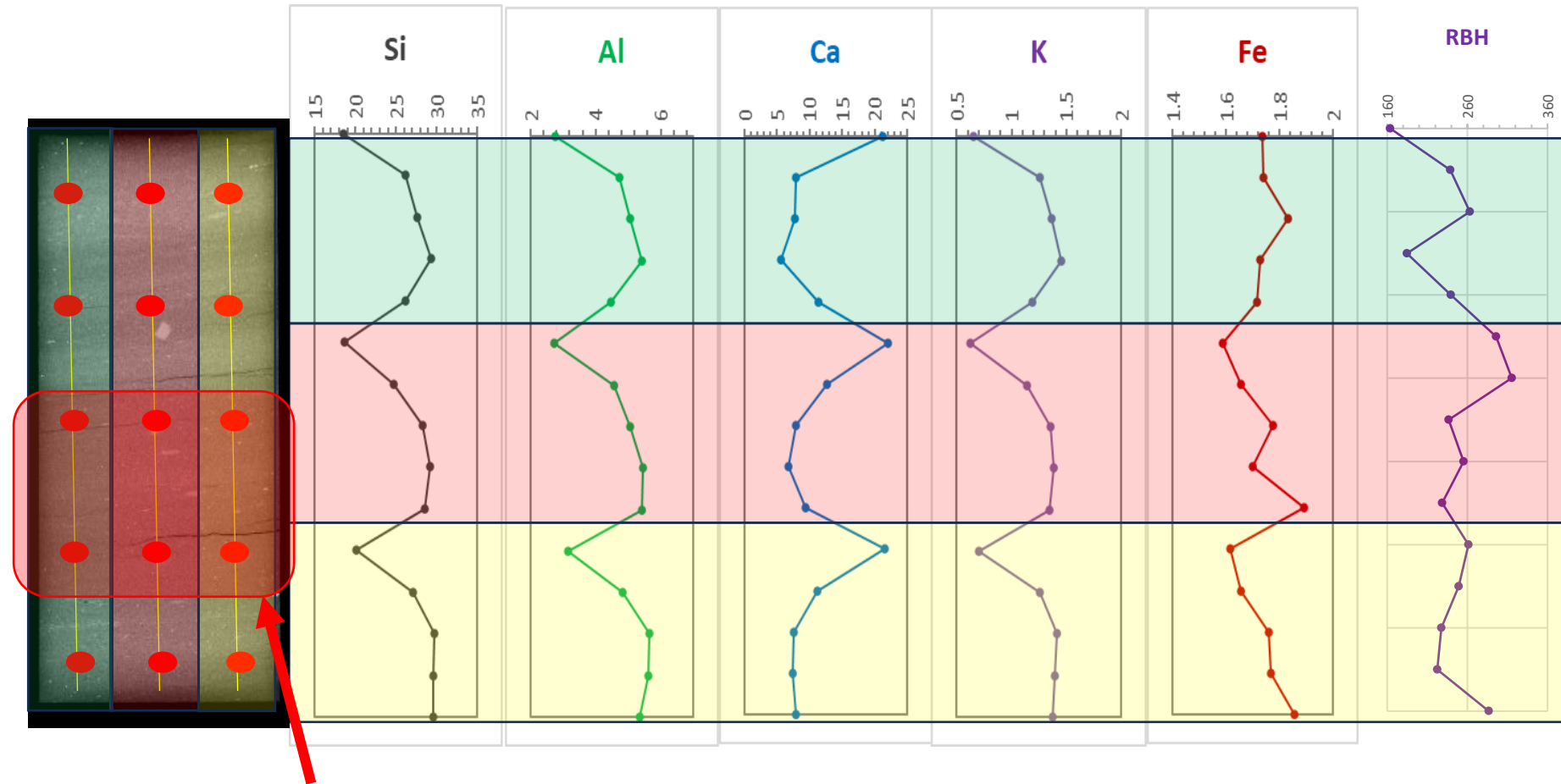
**Side View**

**R3V2**



# Samples (R<sub>3</sub>V<sub>1</sub>)

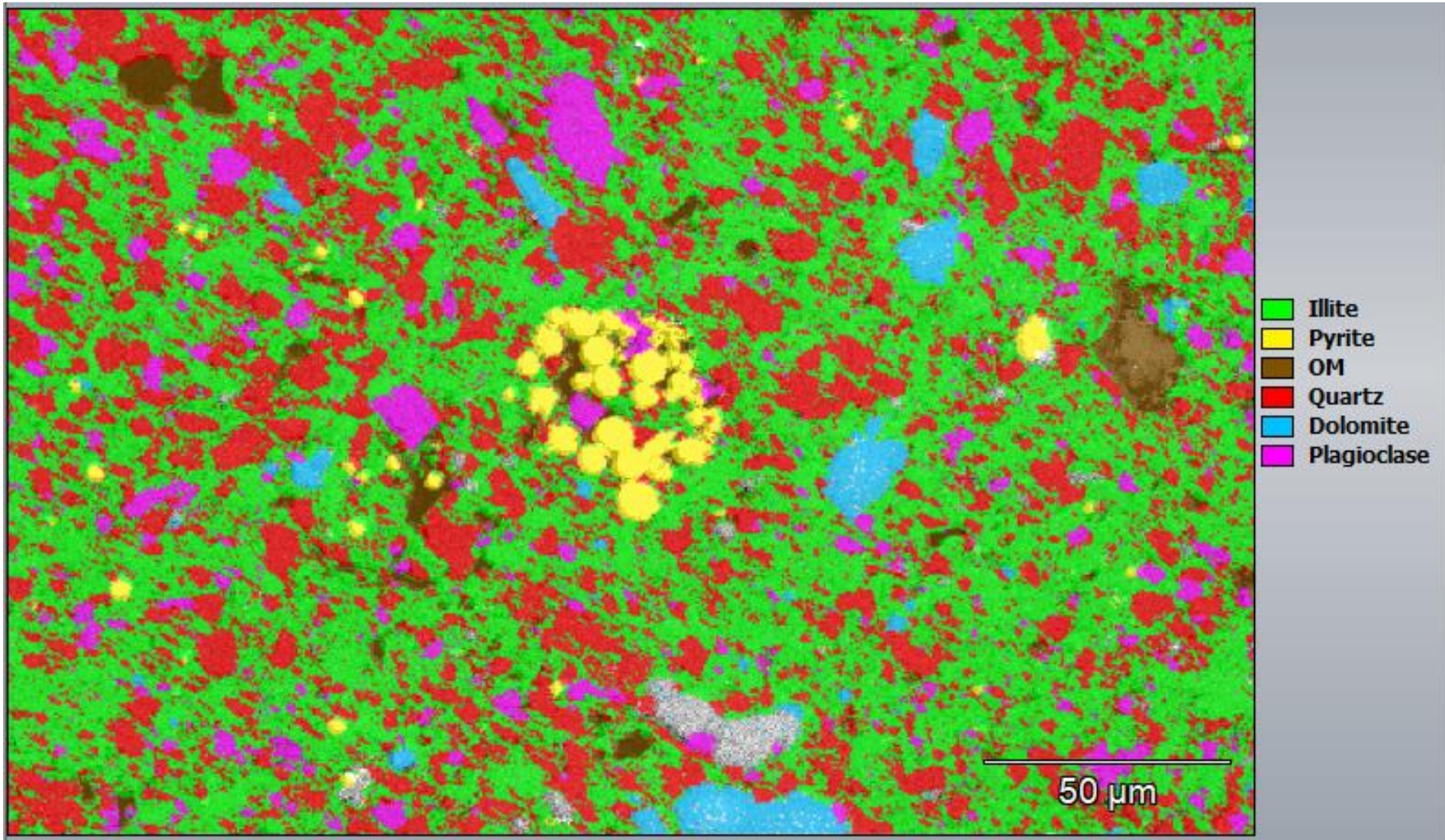
## Combination of CT-Scan, XRF and RBH



Selected Spot for Raman

- Si, Al, and K increase on left side
- Si, Al, and K increase in middle portion
- Si, Al, and K increase on right side
- Fe constant throughout
- High carbonate at top and lower portions
- Generally, grade from brittle to ductile throughout sample
- High RBH in middle

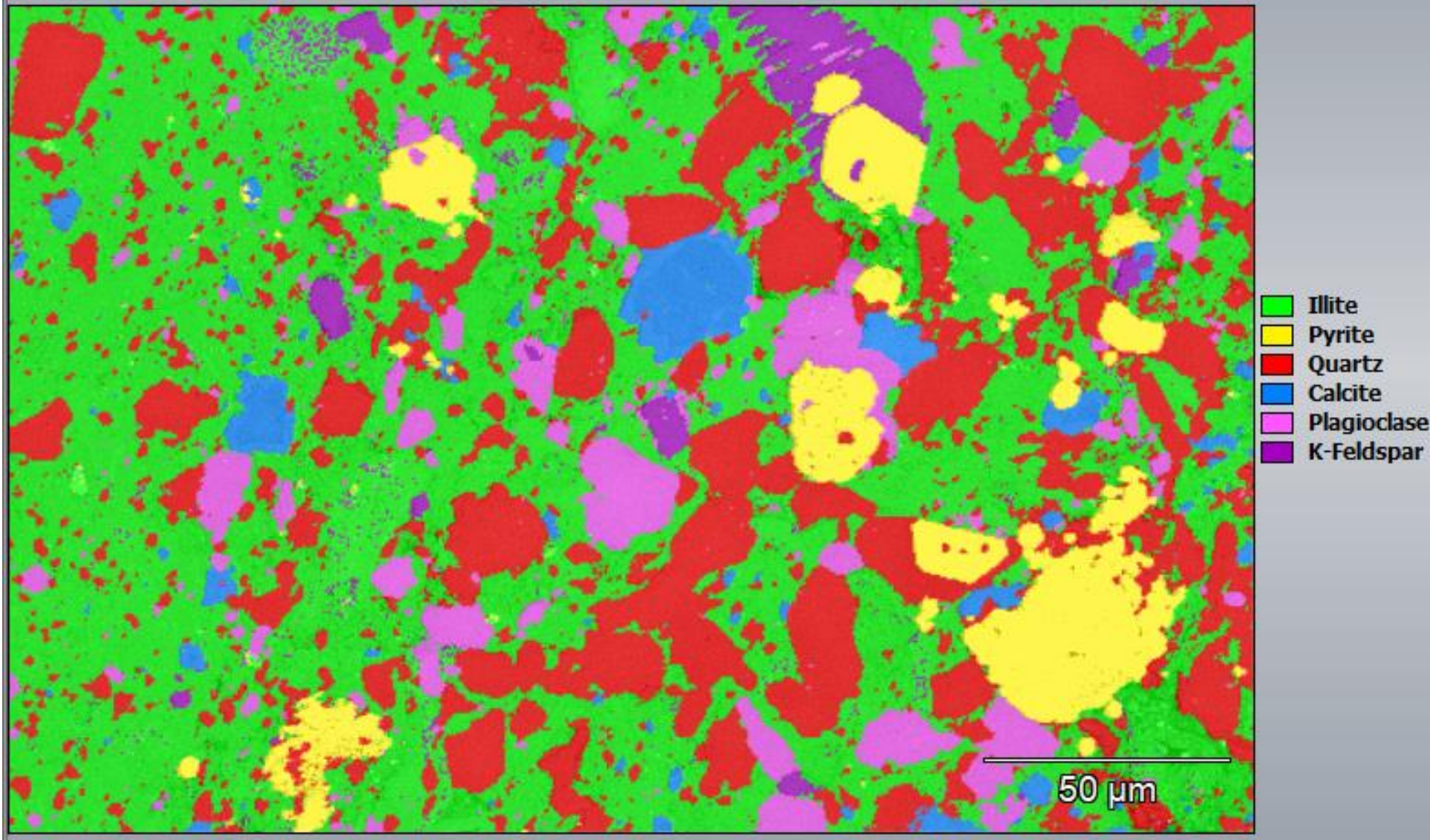
# Samples (D2V)



- High clay content in ductile samples
- Particles of quartz, carbonates and felspars are encapsulated within high amounts of clay matrix
- Pyrite occurs as individual pieces and pyrite framboids in other locations



# Samples (R3V1)



- Reservoir is characterized by large grains
- Relatively Lower clay control on properties as in ductile samples
- Particles of quartz, carbonates and feldspars are surrounded by clays
- Grain-to-grain contacts more prevalent in reservoir

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# THANK YOU

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