



GEOCHEMICAL COMPOSITIONAL CHANGES DUE TO FRACTURING FLUID INTERACTION WITH CANEY SHALE, SOUTH CENTRAL OKLAHOMA, USA



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PRESENTATION OUTLINE

- ❑ Introduction
- ❑ Objectives
- ❑ Materials & Methods
- ❑ Results
- ❑ Conclusions and Recommendations

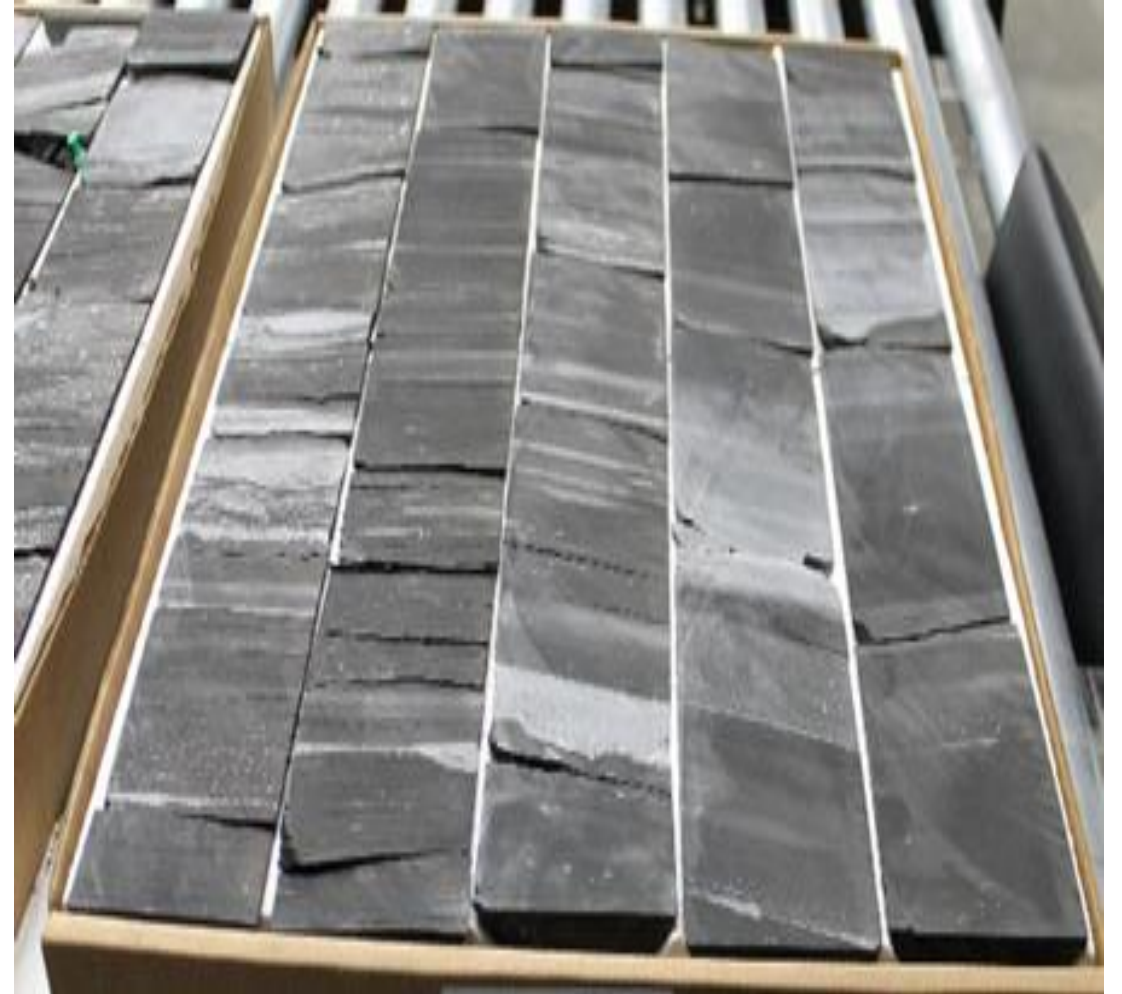
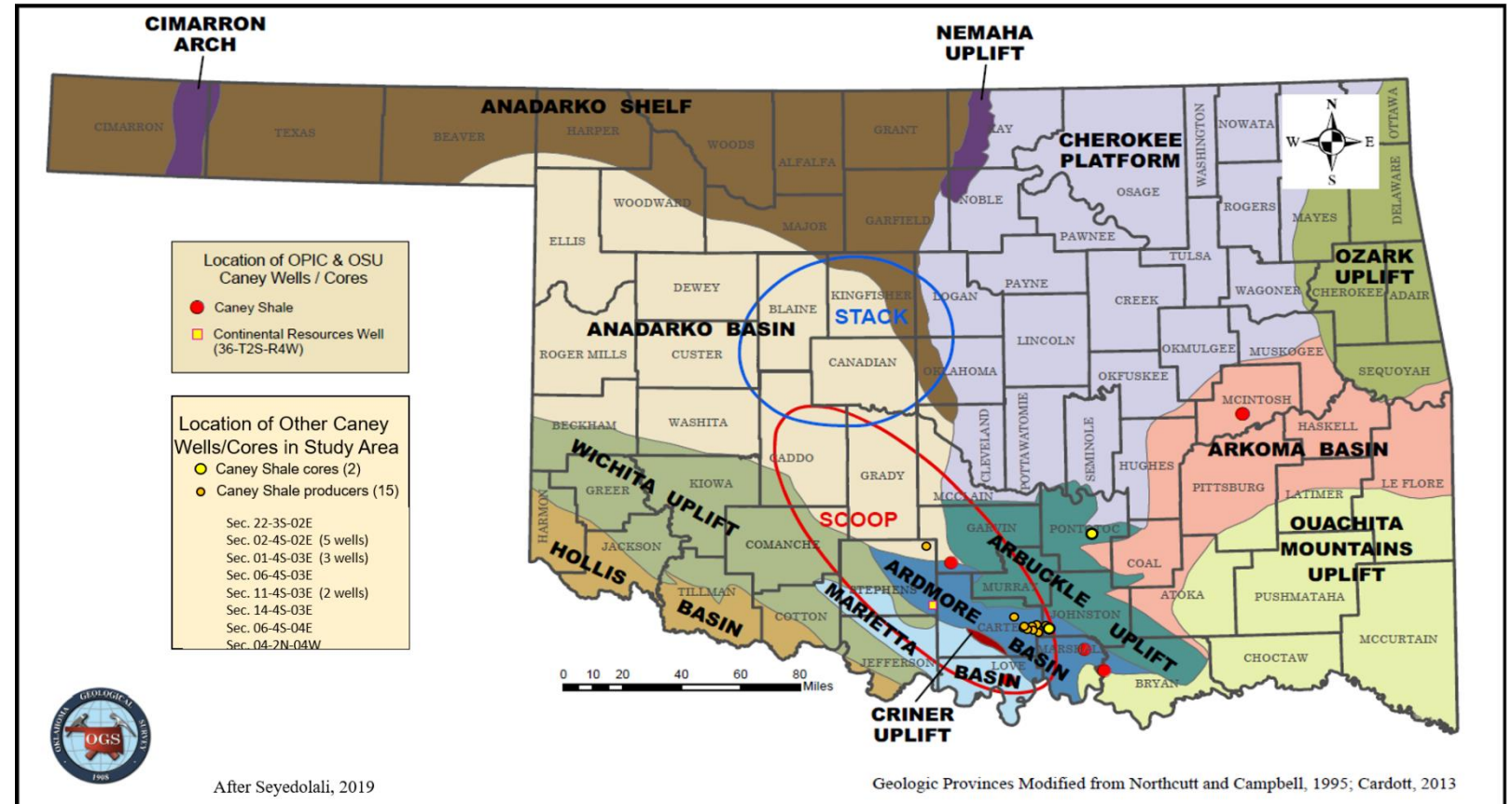


Figure 1: Caney core on display at workshop in OKC, February 2020. This was recovered from over 650ft interval of drilled well

INTRODUCTION

- The Caney shale is a promising unconventional reservoir located in South-Central Oklahoma Oil Province (SCOOP)
- It overlies the Woodford Shale, which is more brittle and has been the target of drilling over the years
- Although the Caney shale contains recoverable amounts of hydrocarbons, it has historically been considered a seal or source rock
- Relatively less work has been done to fully characterize the geochemical responses of the formation to HFFs for this area

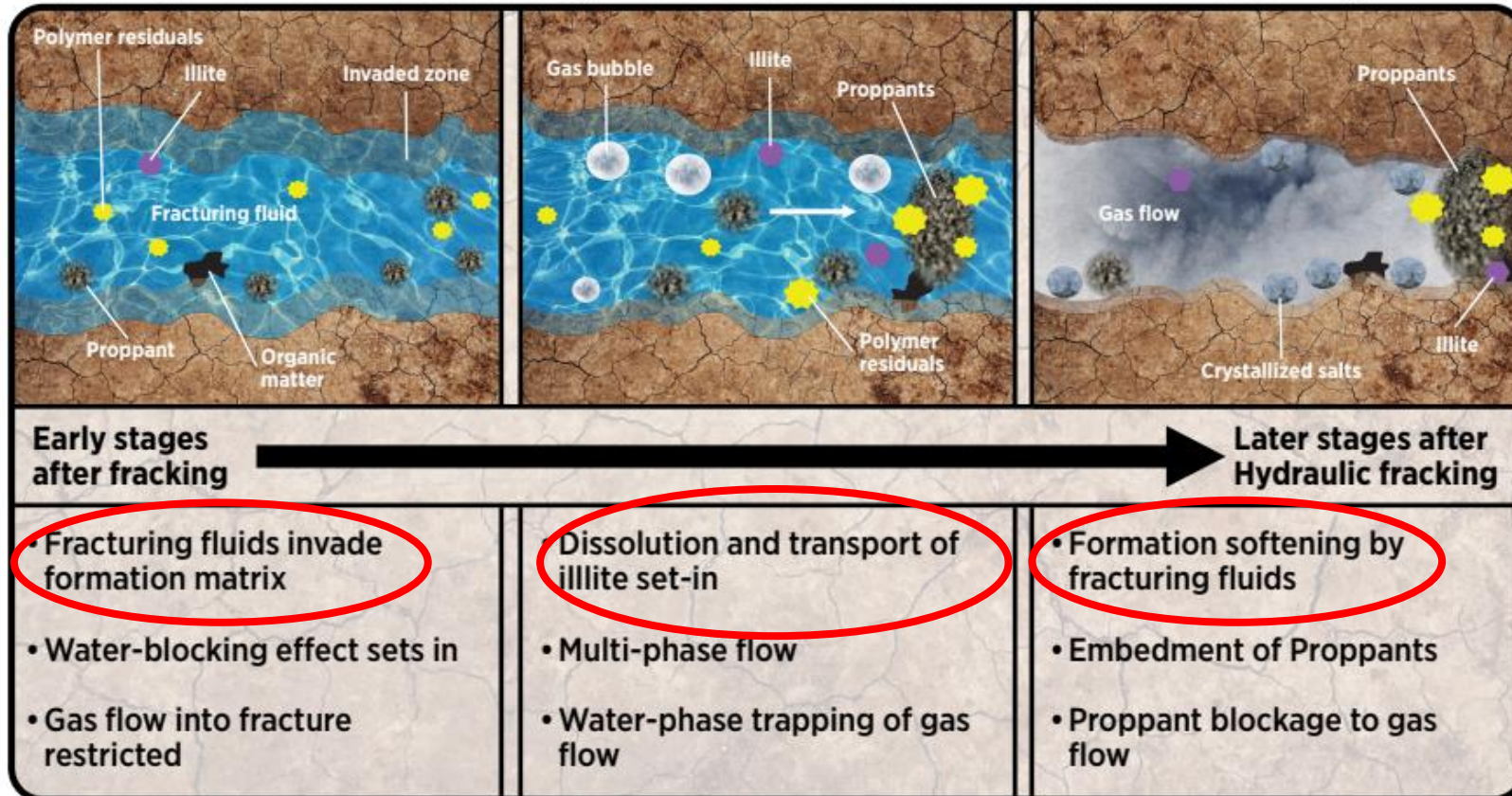


OBJECTIVES

Investigate Rock-HFF interactions relative to:

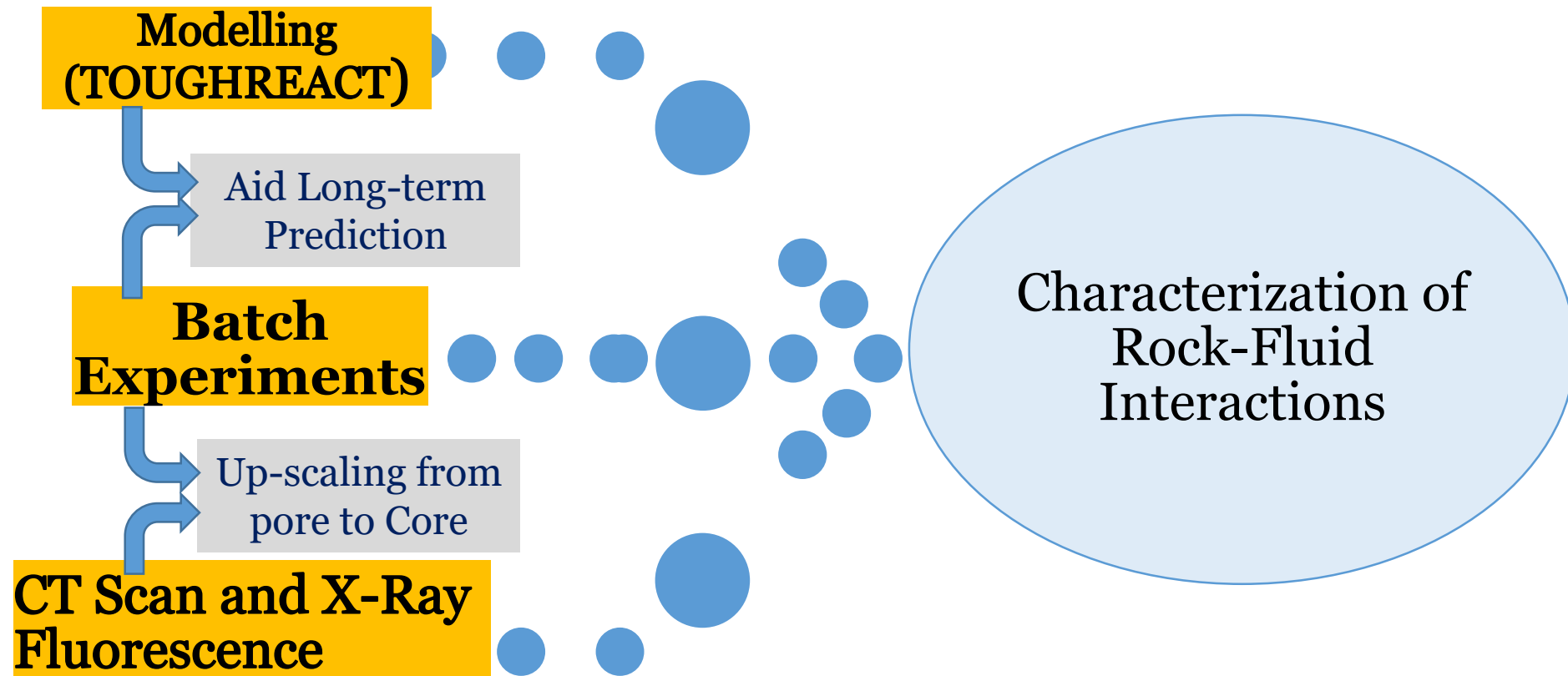
- Dissolution and precipitation of minerals
- Clay swelling and Migration of fines
- Petrophysical Impact of Rock-Fluid Interactions

Fracture and near-fracture clay-fluid reactions after hydraulic fracturing



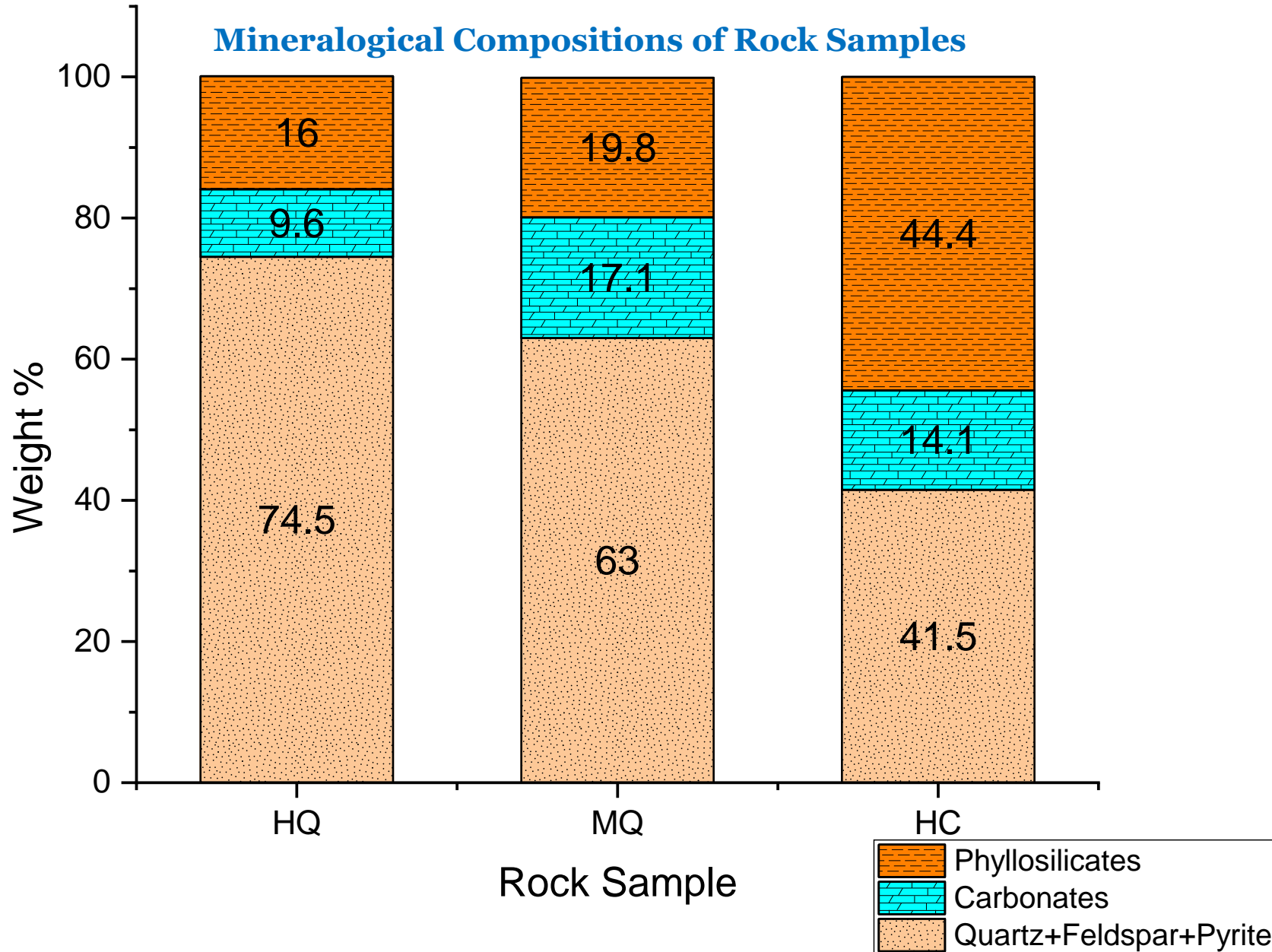
MATERIALS AND METHODS

Experimental and Simulation Design



MATERIALS AND METHODS

Mineralogical Compositions of Rock Samples



Fluids Used:

- Deionized Water (Base, pH~7)
- 2% Potassium Chloride Solution (pH~4)
- 0.5% Choline Chloride Solution (pH~4)

Rock Samples Designation:

- HQ – High Quartz
- MQ – Medium Quartz, Carbonate and Clay
- HC – High Clay

MATERIALS AND METHODS

Static Batch Experiments

- Static batch experiments at temperature of 95°C and atmospheric pressure
- Designed to mimic shut-in period
- Initial fluid to rock powder ratio of 200mL/g (140mL: 0.7g)
- Sampling undertaken on days 1, 3, 7, 14 and 28 (~10ml each sampling)
- Sampling period approximately 10 minutes

Modelling

- Simple geochemical model of the batch reactor experiment was constructed and modelled using TOUGHREACT, a numerical simulation program
- Assumptions in model included:
 - No fluid flow or chemical transport
 - Constant temperature and chemical reactions occur with kinetic rates
 - Fluid/Rock Powder ratios changed over time due to sampling

MATERIALS AND METHODS

X-Ray Diffraction (XRD)

- Mineralogical compositions of samples

Scanning Electron Microscopy (SEM)

- Dissolution and precipitation patterns

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

- Elemental analysis of effluent

Computed Tomography

- Voxel resolution for scans was 0.43 x 0.43 mm in the XY plane and 0.5 mm along the core axis
- 3D volumes are re-sliced along the XZ axis and used as image log

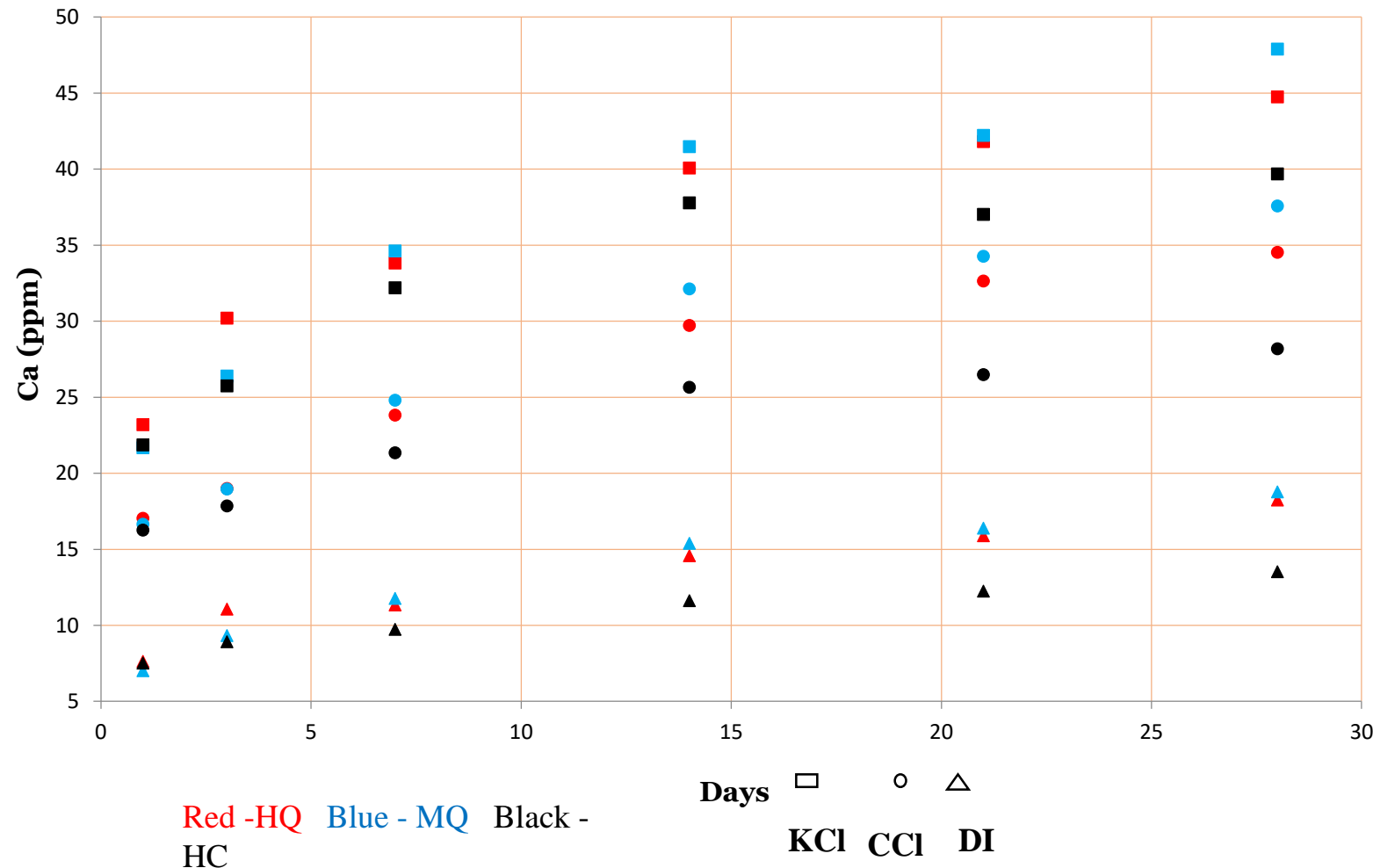
X-ray Fluorescence

- To measure relative elemental abundances along core z-axis
- Mining-Plus suite was run at 6 cm resolution for 60 seconds of exposure time per beam through the entire 650 feet of core

RESULTS

In general, fluid composition is the main driving force for dissolution and precipitation kinetics in rock-fluid interaction for the Caney shale

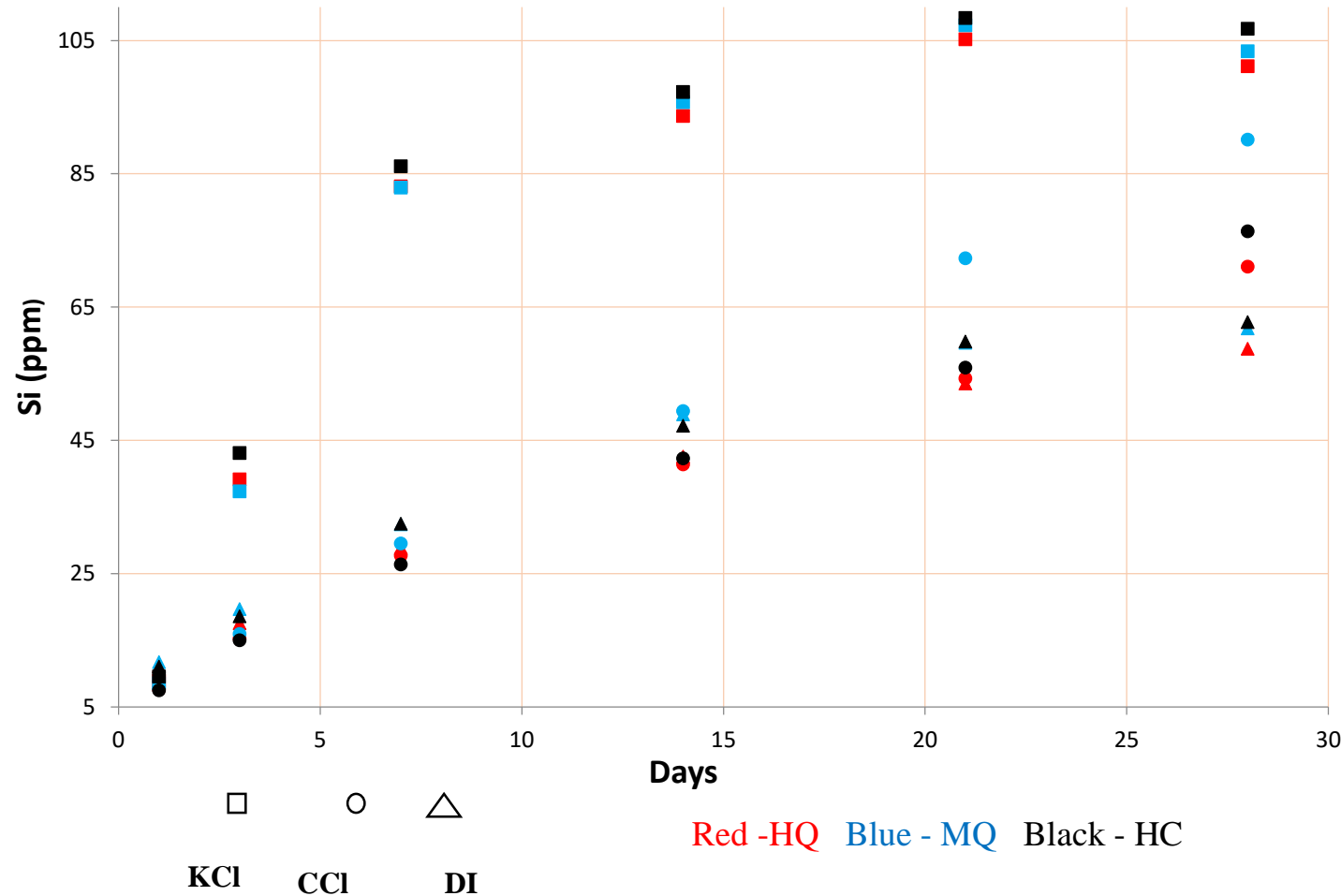
Ca-Rich Minerals Dissolution by Rock Type and HFF



- **HC has least Ca concentration for each fluid**
- **Clay reduces the dissolution of carbonates**
- **Lag in dissolution of carbonates in MQ compared to HQ due to higher clay content in MQ**
- **KCl dissolves carbonates more relative to other fluids for all the rock types**
- **Ability of KCl to stabilize clay allows more fluid to dissolve carbonate minerals**

RESULTS

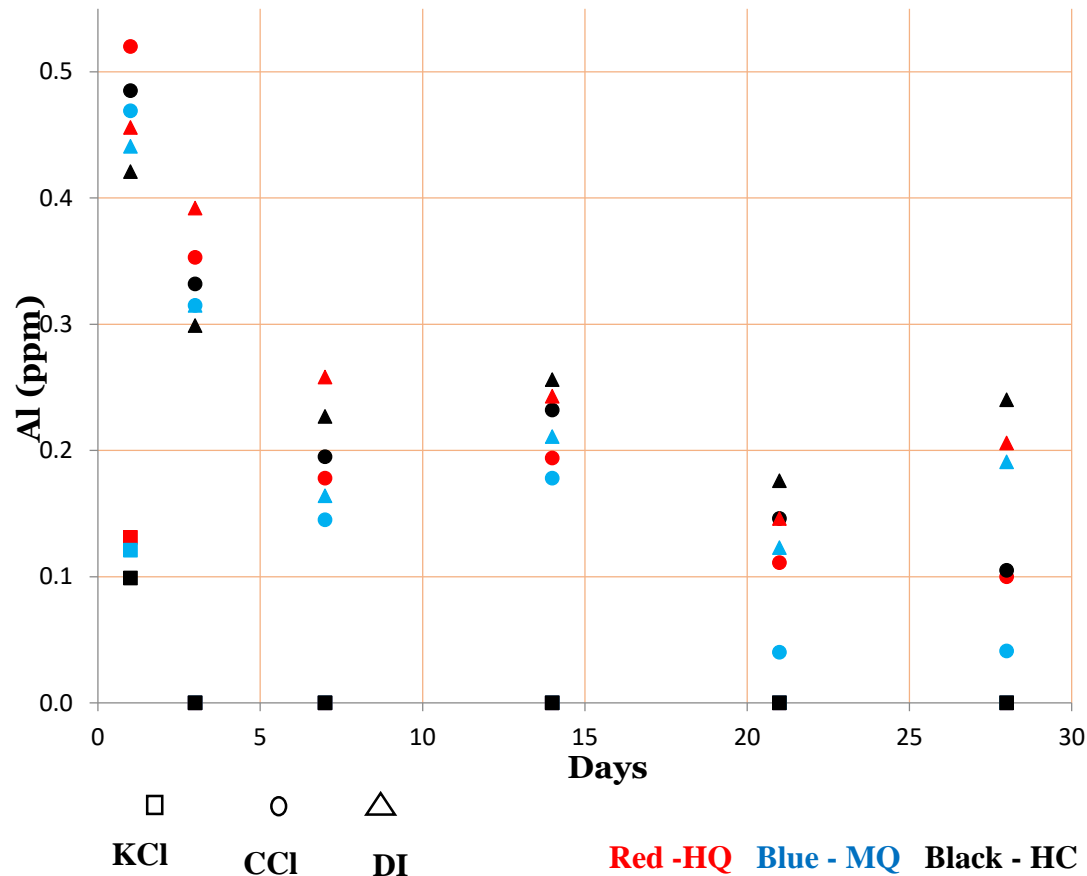
Si-Rich Minerals Dissolution by Rock Type and HFF



- Higher Si concentration in effluent
- HC and MQ samples having higher Si concentration than HQ
- An indication Si in solution is not from dissolution of quartz
- Si may be from clay sites or from less stable SiO polymorphs
- KCl produces more Si in solution relative to other fluids for all the rock types
- Ability of KCl to stabilize clay prevents further elemental exchange between fluid clay sites thus released Si remains in solution

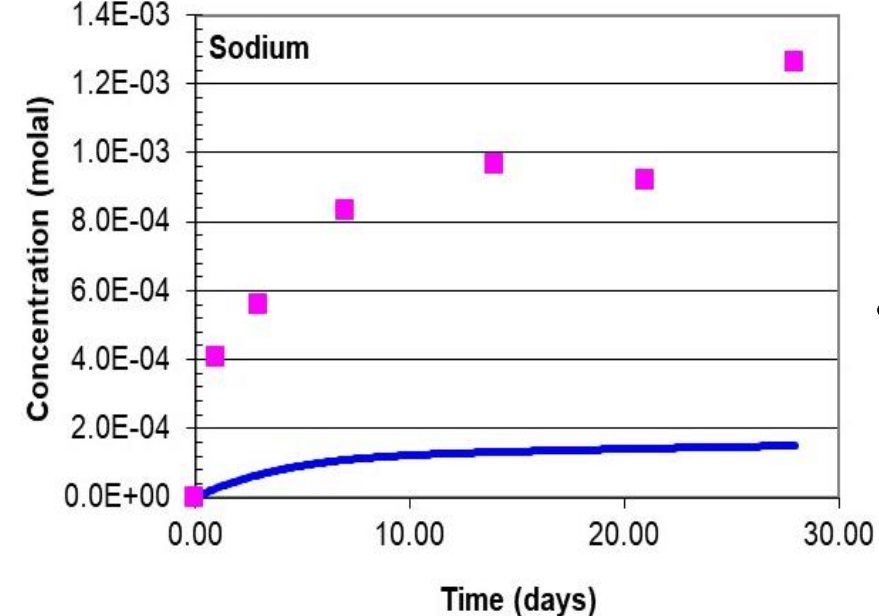
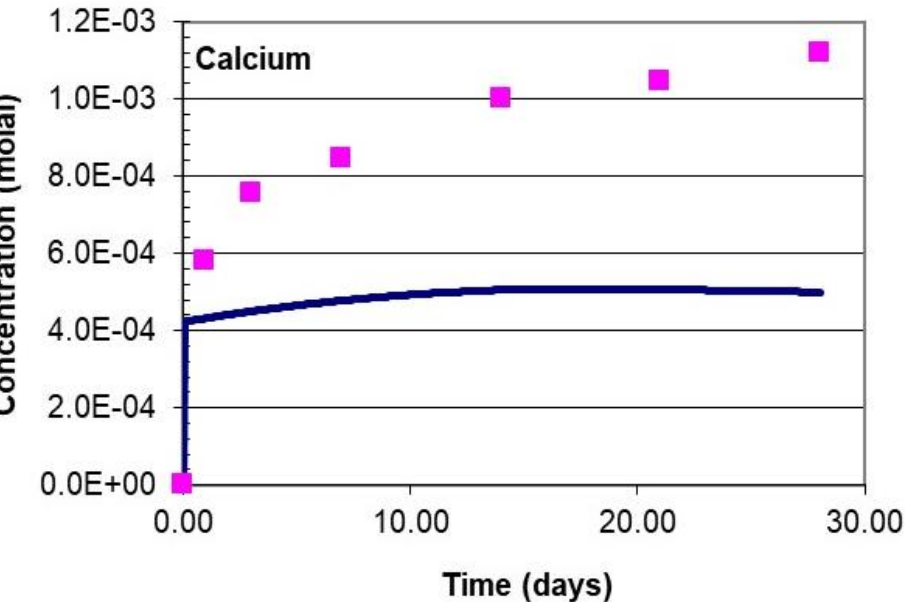
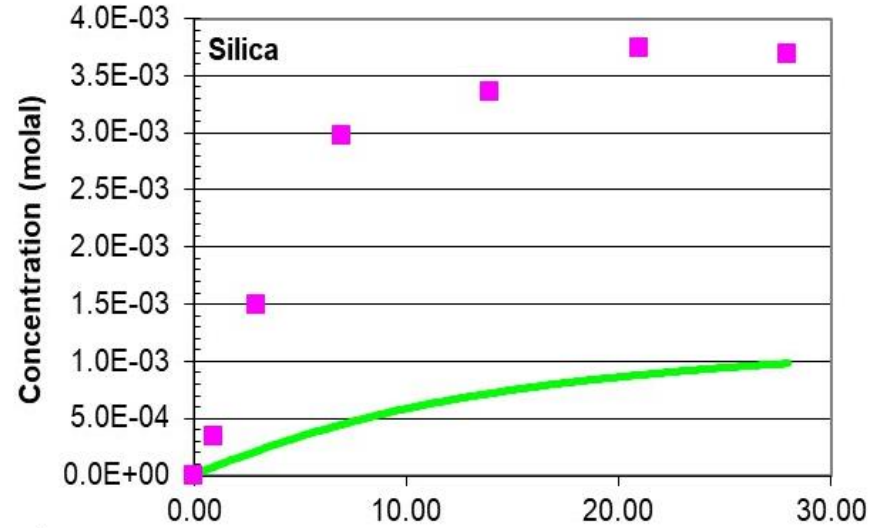
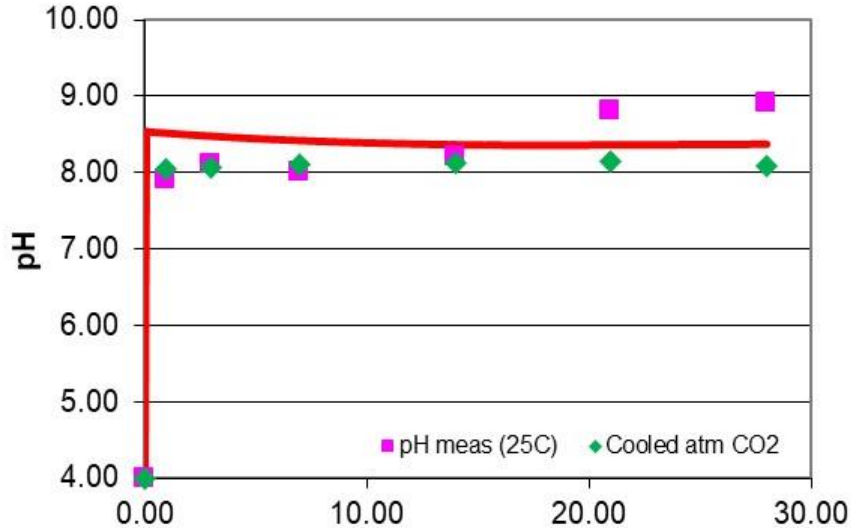
RESULTS

Al-Rich Minerals Dissolution by Rock Type and HFF



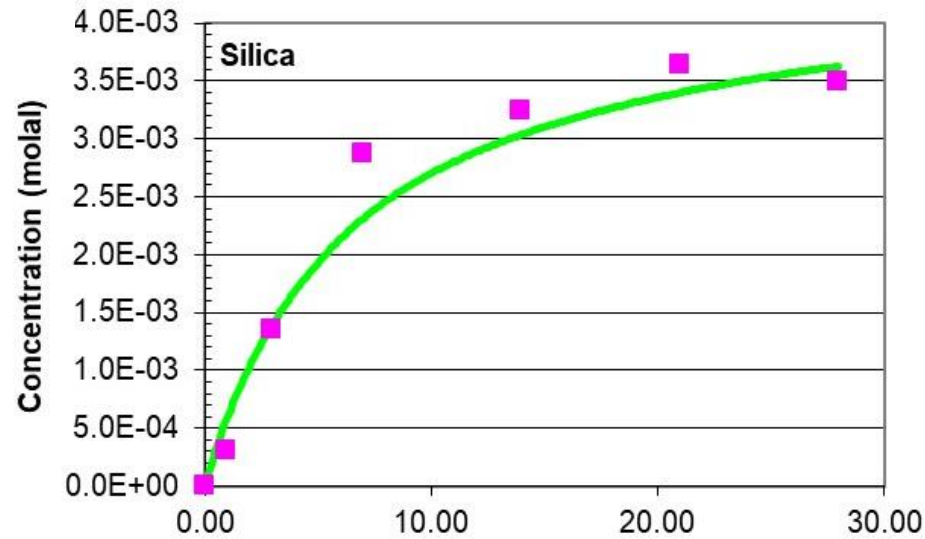
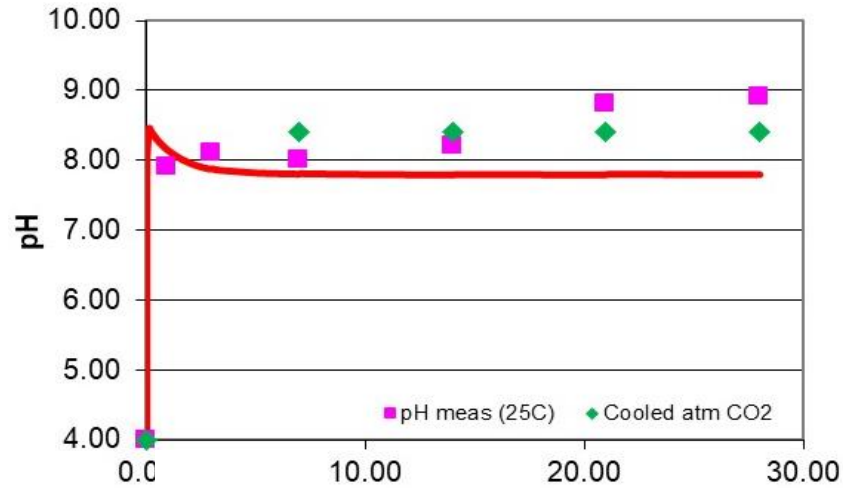
- Al and Mg are the only elements to show sharp drop in elemental concentrations with time
- The amount of Al released in solution is very low compared to Si or Ca
- The main dynamic causing very low Al concentration in sample is still under investigation
- Aluminium decrease could be caused by ion exchange at clay sites or precipitation of Al-based minerals

RESULTS – Initial Modelling versus Experimental Results



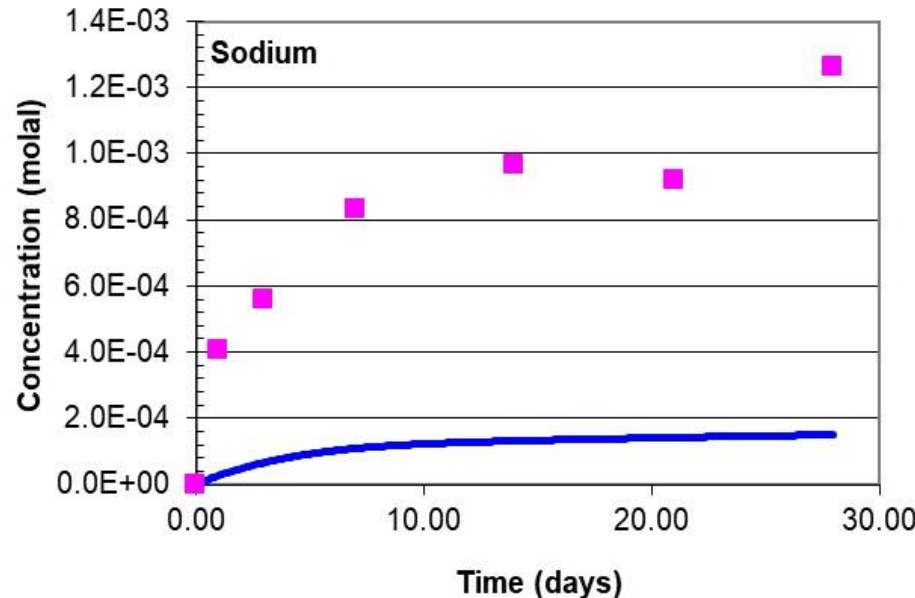
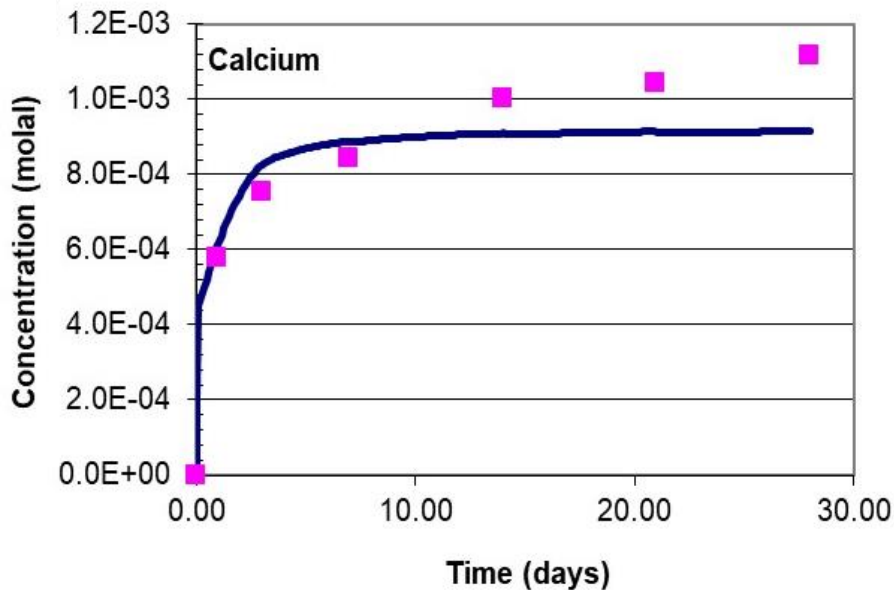
- In this experiment, all assumptions were regarded except the period of sampling
- When sampling is not considered, only pH values of modelling are in consonance with experimental information
- There are significant variations in modelled and experimental information

RESULTS – Subsequent modelling versus Experimental Results



In this experiment, all assumptions were regarded including the period of sampling. Assumption was that during sampling, extra atmospheric oxygen is introduced into the sample.

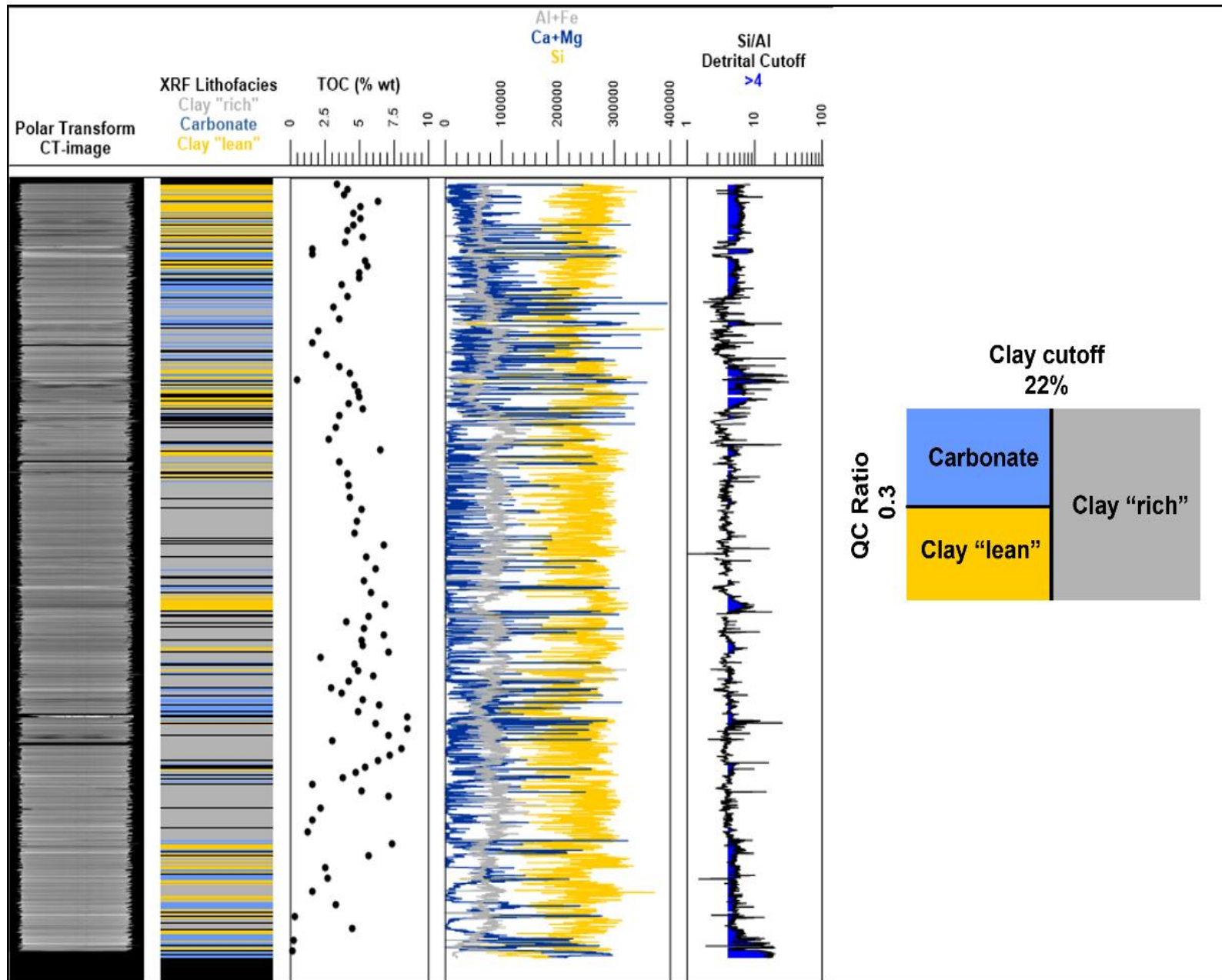
When sampling is considered, almost all values of modelling are in consonance with experimental information except Sodium.



Variations in modelled and experimental information is almost insignificant.

Sodium exchange at clay sites during experiments far exceeds what model data provides thus the variation.

RESULTS



Three informal Divisions based on XRF results:

- Upper Caney shows decreased Si concentration through heavily bioturbated intervals and Al and Fe rich intervals (Clay and Carbonate Rich Zone)
- For the middle Caney, Al and Si concentrations remain consistent whilst Ca is low (Quartz-rich shale zone)
- In the lower Caney, sharp increase in Ca is observed whilst Al and Si constant (Carbonate zone followed by High Quartz Shale)

CONCLUSIONS AND RECOMMENDATIONS

Conclusions:

- Carbonates and Clays are more susceptible to geochemical reactions whilst Quartz is relatively unaffected by reactions
- High Si concentration in effluent are from Si adsorbed on clay surfaces and from less stable silica polymorphs
- Increasing clay composition of samples adversely impact the dissolution of quartz and carbonate minerals
- KCl and CCl stabilized clay minerals and promotes dissolution of quartz and carbonates
- KCl effected greater stabilization of clay minerals thus leaving initially leached elements in solution, therefore higher concentrations

Greater stabilizing effect of potassium chloride may be explained by the greater ability of potassium cations to exchange for cations in clay interlayers and locking of the interlayers from further interaction with surrounding fluids

Recommendations:

- Working on improving geochemical and physical characterization of the rocks and fluid samples for modelling in our next work
- Longer periods for experiments to determine the time limits of KCl and CCl effectiveness in preventing adverse clay-fluid reactions especially considering pH values continued increasing throughout the experiment

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REFERENCES

1. Dove, P.M. 1995. Kinetic and thermodynamic controls on silica reactivity in weathering environments, in: White, A.F. and Brantley, S.L. (eds). *Chemical Weathering Rates of Silicate Minerals*. pp. 235–290.
2. Knauss, K.G., and T.J. Wolery. 1988. The dissolution kinetics of quartz as a function of pH and time at 70 C. *Geochim. Cosmochim. Acta* 52, 43–53.
3. Olabode, A.O. 2017. Diagenesis and Formation Stress in Fracture Conductivity of Shaly Rocks; Experimental-Modelling Approach in CO₂-Rock Interactions.
4. Tester, J.W., W.G. Worley, B.A. Robinson, C.O. Grigsby, and J.L. Feerer. 1994. Correlating quartz dissolution kinetics in pure water from 25 to 625C. *Geochim. Cosmochim. Acta* 58, 2407–2420.

THANK YOU