Annual Report and 4th Quarter Research Performance Progress Report

Project Title: Chemical control of fluid flow and contaminant release in shale microfractures

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1. EXECUTIVE SUMMARY

This project is studying fundamental shale-fracture fluid reactions that alter shale permeability and drive the release of inorganic contaminants, such as uranium, to the environment. Little is known in detail about these reactions, yet they have the potential to clog shale fractures and pores and facilitate proppant embedment and fracture closure, all of which attenuate hydrocarbon production. Shale-fracture fluid systems are being characterized using a combination of laboratory, synchrotron, and electron microscopy techniques. We are using the obtained information to develop geochemical and reactive transport models to quantitatively understand observed shale-fracture fluid interactions and provide improved predictive capability as to the likely reactions to occur for a given shale composition. Fundamental new knowledge provided by this program supports the ability to predict the evolution of shale permeability, mineralogy, and fracture behavior over time during hydraulic fracturing. The combination of fundamental knowledge and predictive capability ultimately will lead to improved fracture fluid compositions and unconventional stimulation techniques, and better assessment and limitation of environmental impacts.

We have identified 3 sets of results from our research activities over the past year that have good prospects to be developed into 3 manuscripts. In order to be successful in producing these papers, we are focusing our research activities on measurements that are required for the manuscripts. We are reducing scope in areas of the project that do not contribute to these manuscripts (*e.g.*, by cutting back on pure mineral–fracture fluid reactions). We are also identifying scientific questions that represent high-value research targets but fall beyond the scope of the current project (*e.g.*, linking geochemical models from the current project to whole-rock permeability measurements and systematic imaging of porosity evolution to develop a comprehensive model of geochemical controls over bulk-scale permeability). These subjects are of potential interest for a renewal grant, if such an opportunity were to occur.

In the past year, we made 9 presentations (3 invited) at national scientific/industrial venues (*cf*., Appendix A). Research from this project was featured as the lead article in the NETL fall 2015 E&P Newsletter.

Science and technology highlights for FY2015. Experiments were performed in FY2015 to understand fundamental geochemical controls on reactions between fracture fluids and economically important shales (Marcellus, Barnett, Eagle Ford), and in Green River shale, a kerogen-rich oil shale that provides a useful contrast to the others. Experimental conditions were simplified to permit identification and characterization of specific geochemical reactions occurring between shale and fracture fluids. Five key observations and technical developments have emerged from this work.

- **Controlling role of carbonate on geochemical processes.** Carbonate dissolution plays multiple and crucial roles controlling not only porosity in shales following reaction with fracture fluids, but also the evolution of geochemical reactions. Hydraulic stimulation practices typically are initiated with injection of acid, which attacks minerals, particularly carbonates. Our work shows that the relative abundance of carbonate is a crucial control over the subsequent geochemical and physical changes that occur in the shale. Carbonate-rich shales rapidly buffered solution pH without significantly depleting the buffering capacity of the matrix (*i.e.*, the carbonate content). In contrast, carbonate-poor, clay-rich shales had insufficient carbonate to titrate pH back up to non-acidic values. The lower pH in these systems may encourage further dissolution of silicate minerals, but limits precipitation of secondary phases. These findings will be incorporated into a manuscript on geochemical modeling of fracture fluid-shale interactions.

- **Fracture fluid organic constituents and bitumen dramatically accelerate Fe(II) oxidation**. Hydrochloric acid injected into shales in the initial stages of stimulation liberates iron [as Fe(II)]. When oxidants such as O_2 are present in fracture fluid, Fe(II) can be oxidized and precipitated as insoluble Fe(III). Our research suggests that this process is strongly accelerated by the abundant organic compounds present in fracture fluid. This observation leads to several questions, including: (1) Which component in fracture fluid is responsible for enhanced Fe(II) oxidation?; (2) What is the mechanism by which the organics enhance Fe(II) oxidation?; and (3) What levels of oxygen are required to facilitate Fe(II) oxidation? To address these questions, a new set of short-term experiments are being performed to systematically investigate oxidation of aqueous Fe(II) in the presence of extracted bitumen and fracture fluid organics in reactors lacking shales at different concentrations of DO. Preliminary results suggest that the bitumen also accelerates oxidation of aqueous Fe(II), implying that the presence of organic fracture fluid additives facilitates extraction of bitumen from the shales and thus indirectly enhances oxidation. We are planning to publish a (second) manuscript detailing our findings in this system.
- **Limitations on uranium release.** Uranium (U) is released following exposure to fracture fluids. U release is fastest at the low pH conditions caused by hydrochloric acid. Dissolved U concentrations exhibited steady-state values after just a few days, and slowly declined over 3 months, indicating that total uranium release to produced waters is fundamentally limited by loss mechanisms such as incorporation into solid phases. It is hypothesized that U released to solution is hosted in carbonates, which have been shown to contain U in Marcellus shale (*e.g.*, Phan et al., 2015). Thus, U release in the short term is likely to be controlled by the extent of carbonate dissolution. These hypotheses are being tested in our modeling program. The research results will be incorporated into the afore-mentioned geochemical modeling manuscript.
- **Surprising reactivity of kerogen.** Although kerogen is typically considered to be relatively unreactive, it was found to release significant amounts of metals and alkaline elements, including Fe, Li, Mn, Cu, Zn, Rb, and Ba. Accumulation of these elements within kerogen may be an artifact of the extraction process or may reflect the true composition of this organic material. If the latter is true, then our observations reflect an important contribution to the kerogen literature. We are conducting a post-reaction analysis of the solids to identify the sources of these metals. In addition to these findings, we have observed that reaction of kerogen with fracture fluid alters the molecular structure and composition of kerogen. Imbibition of fracture fluids into shales implies that kerogen can be altered at some distance from fracture surfaces. The alteration of organic functional groups is likely to affect shale wettability and thus alter transport of both hydrocarbons and hydraulic fracture fluid in the subsurface. We are planning to develop a manuscript around these results.
- **Technique development: Computed tomography and model integration.** In a separate (non-NETL) research grant, we are developing advanced nano- and microscale computed x-ray tomography (CT) methods for geochemical applications. X-rays can penetrate relatively

large distances (millimeters) in rock. Consequently, **X-ray CT can nondestructively image internal structure within *the same sample* before and after reaction with fluids, and image fluid movement within shales**. These capabilities are not provided by any other technique including focused ion beam scanning electron microscopy (FIB-SEM), which destroys the sample during image acquisition. Moreover, X-ray CT can be combined with X-ray absorption spectroscopy to analyze metal oxides and sulfides inside the rock. Thus, X-ray CT techniques should be highly valuable to studying fracture fluid-shale interactions inside shales at the scale of individual pores and would substantially advance our ability to model geochemical reactions at the pore scale. Performing such measurements requires method development, which is the focus of this parallel research project. The goal is to develop a research "pipeline" capability to use nano and μ-CT to study structural changes in shale.

In a leveraging effort, we are using x-ray CT imaging to characterize altered shales reacted with fracture fluid for 3 weeks in this NETL project. Samples of shales were imaged using X-ray μ-CT before and after exposure to fracture fluid. Preliminary analysis shows extensive alteration of porosity over an approximately 40 μm thick surface zone **(Figure 1)**. Similarly, nano-CT data reveal changes in pore structure at the nano-scale **(Figure 2)**. The alteration of porosity at the fluid-shale interface is likely to expected to influence transport of hydrocarbons and contaminants. These data demonstrate feasibility to characterize internal shale structure/mineralogy of individual samples at the pore-scale before and after reaction with fracture fluid. We are now poised to integrate this capability with geochemical modeling.

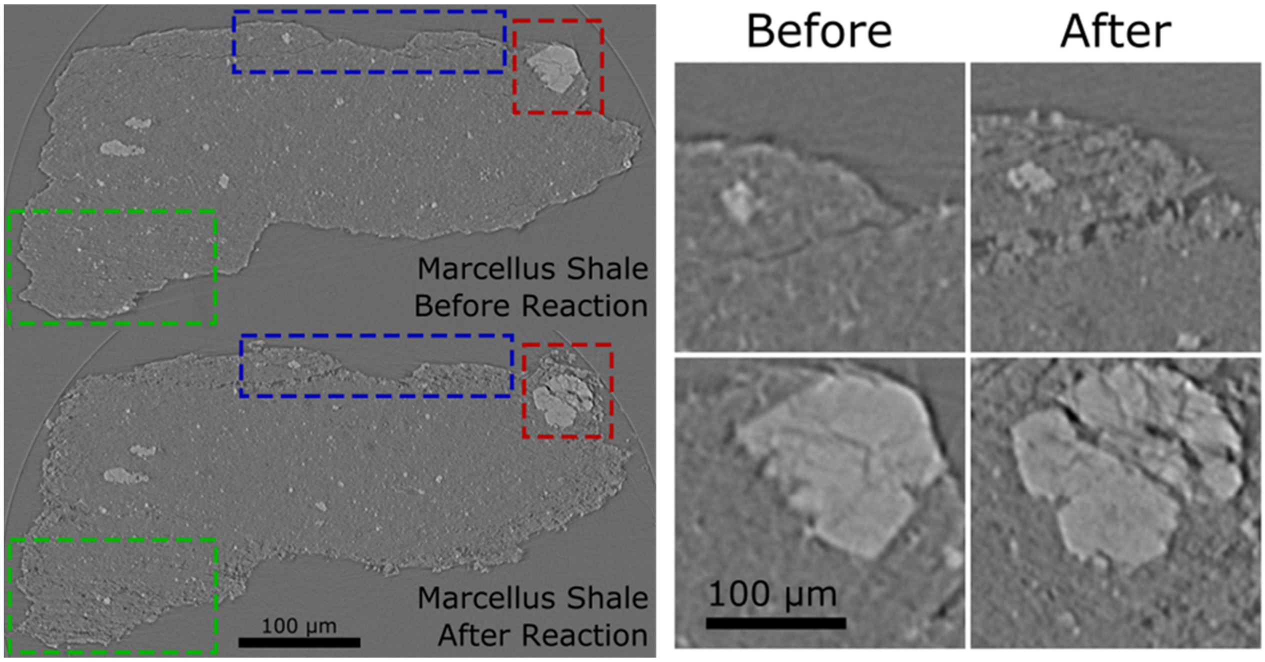


Figure 1. Left panel: Micro X-ray computed tomographic (CT) slice reconstruction of a piece of Marcellus shale pre- and post-reaction with hydraulic fracture fluid for 3 weeks. Right-hand panel: enlargements of detail in regions of interest in the blue and red dashed boxes.

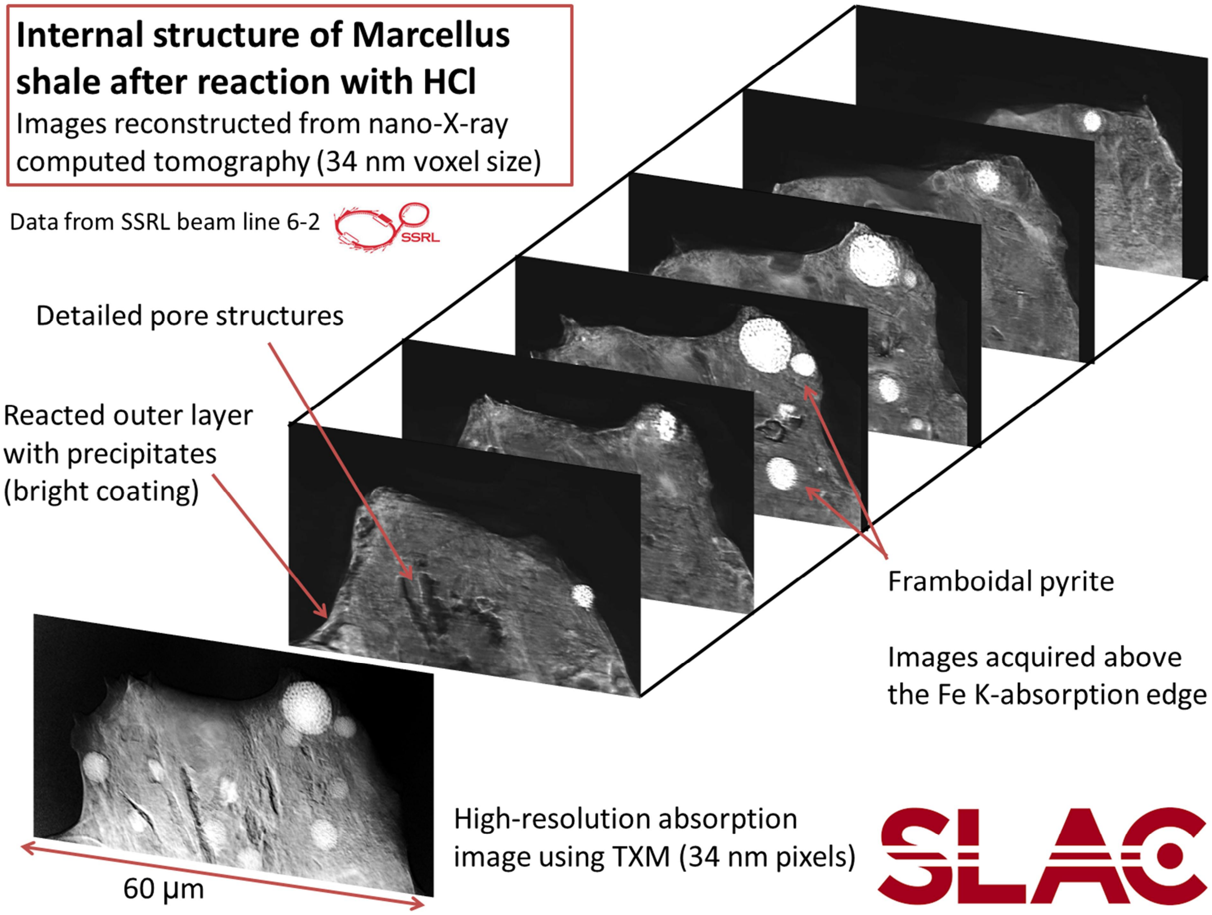


Figure 2. Nano x-ray computed tomographic (CT) slice reconstructions of different elevations through a piece of Marcellus shale following reaction with HCl.

Problem statement. Current fracture technologies recover less than 30% of natural gas and less than 5% of oil from unconventional source rocks (shales). The introduction of fracture fluids into shales has the potential to initiate myriad geochemical reactions that can drive mineral dissolution, oxidize organic and inorganic species, release metals, and precipitate solids (e.g., iron or Al oxides, carbonates, and sulfates). For example, oxygen dissolved in fracture fluid is expected to oxidize pyrite (abundant in shales), releasing insoluble Fe^{3+} and leading to the formation of iron (hydr)oxide coatings that can reduce shale permeability (**Figure 3**). Oxidation reactions also can release arsenic, selenium, and uranium into flowback water, creating the potential to introduce contamination into shallow groundwater aquifers or surface waters. The extent to which these metals reach the surface will also depend on reaction-induced porosity changes. Moreover, dissolution weakens both fracture surfaces proppant grains compressed against them. This process leads to embedment of proppant grains (**Figure 3**) and collapse of fractures, with severe consequences for hydrocarbon production.

In spite of the intrinsic reactivity of fracture fluid towards shale, there is a dearth of studies that have investigated basic fluid-rock geochemical processes occurring in fractures and shale pores. The present research program is addressing the need for fundamental scientific investigation.

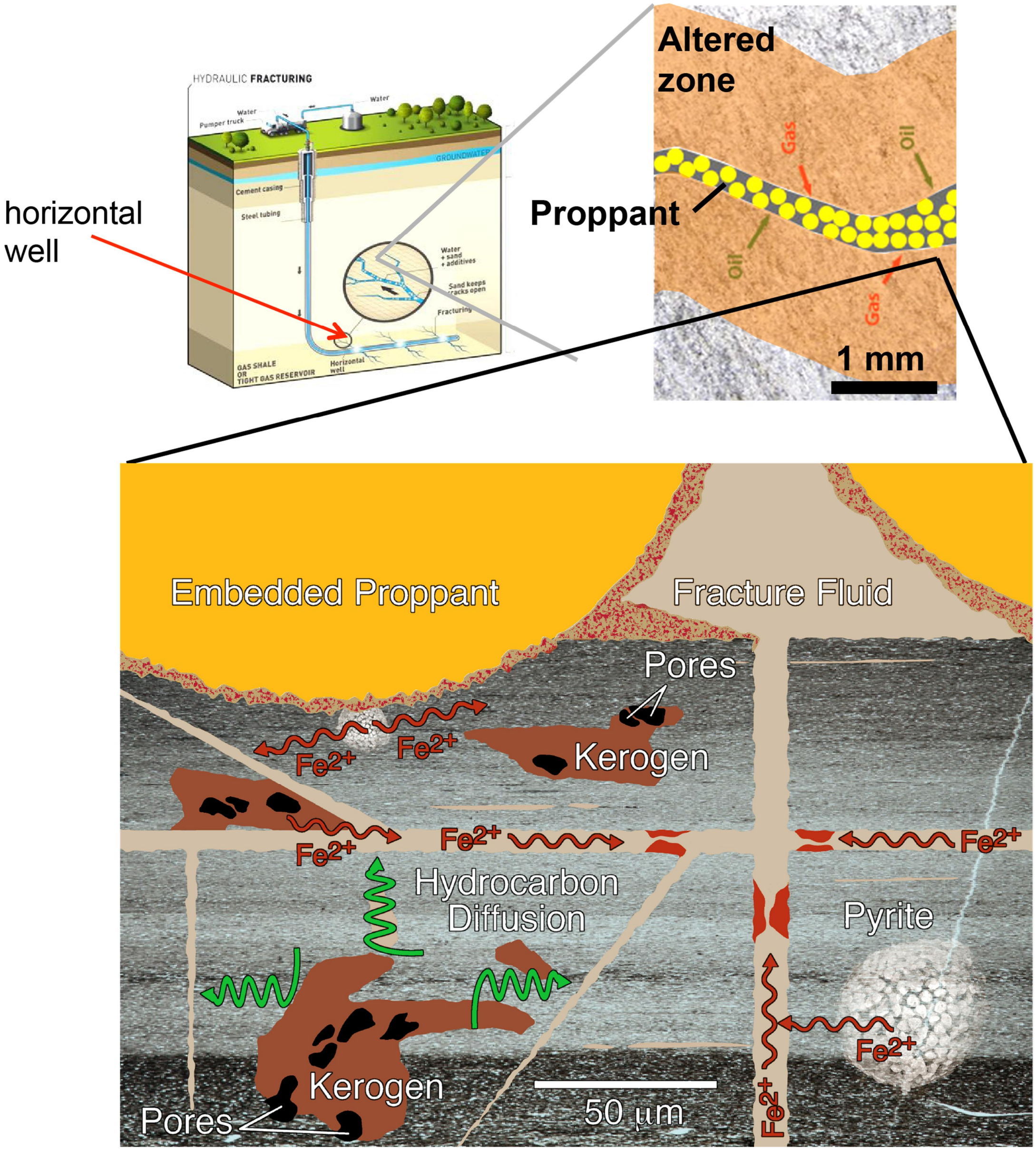


Figure 3. Conceptual model of altered (damaged) zones marginal to propped fractures in hydraulically fractured shales. Fracture fluid-shale reactions can drive iron redox cycling, precipitation of fracture-clogging minerals, shale weakening, and release of contaminants such as uranium.

2. GOALS AND OBJECTIVES

The objectives of this research program are to characterize products (dissolved and solid phases) formed by the reaction of fracture fluids with shale minerals and kerogen and to assess the compositions and morphologies of coatings and aperture-clogging precipitates at spatial scales down to that of individual fracture coatings (*i.e.*, down to the nm level). In addition, we will characterize the impact of fracture fluid-rock interactions on uranium mobilization from shales as a proxy for toxic redox-active trace metal and radionuclide mobilization.

During the first year of the project, we initiated the science program, completed key characterization steps, and observed novel and sometimes unexpected phenomena. We have identified key sets of results that be further examined with the intent to publish them. To be successful in these efforts, we have prioritized the experimental program to focus predominantly on measurements and analyses that will generate these specific manuscripts. These priority areas and manuscripts are identified in the task descriptions below.

The project is subdivided into a management task (Task 1) and five research tasks. The experimental approach is designed to systematically probe fracture fluid reactions with the primary constituents of shales, including Fe(II) (Task 2), and kerogen (Task 3). These results are being used to understand the products formed when whole shales react with fracture fluids (Task 4). Uranium release following reaction of shales with fracture fluids is being assessed in Task 5. A geochemical fluid-shale reaction model is being developed during Task 6 to improve quantitative prediction of shale-fluid reaction products under varied shale compositions and chemical conditions.

3. TECHNICAL HIGHLIGHTS, RESULTS, AND DISCUSSION

Accomplishments during the fourth quarter (*i.e.*, the period under review) built upon the cumulative accomplishments of the prior 3 quarters. Important progress included the following:

Task 2

1. Extraction of bitumen from Marcellus and Green River shale for Fe oxidation experiments
2. Completion of preliminary $Fe(II)_{(aq)}$ experiments with combinations of hydraulic fracture solution and extracted bitumen at low and neutral pH

Task 3

3. Completion of intermediate-term (3-month) fracture fluid-kerogen reactions using kerogen extracted from Green River shale. (Marcellus kerogen is also being studied), subsequent solution-phase analyses and characterization of the reacted kerogen
4. Initiation of Marcellus kerogen isolation (completing at the time of writing)
5. Ongoing FTIR analysis of reacted kerogen and shales to determine changes to mineral phases and organics in samples

Tasks 4 and 5

6. Completion of short-term (3-week) reactors with inert (Ar) headspace and intermediate-term (3-month) reactors with O_2-bearing headspace that investigated fracture fluid-shale reactions using shales from a variety of locations (Marcellus, Eagle Ford, Barnett, and Green River). Shales were exposed to a fracture fluid formulation representative of that used for the Marcellus shale

7. Characterization of products from short- and intermediate-term fluid shale reactions using a combination of scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and energy dispersive spectroscopy (EDS). The surface area and pore size distribution of initial shales and products from the intermediate-term reactors were also determined using gas adsorption.
8. The evolution of fluid composition with reaction progress (*e.g.*, cation concentrations, pH) for the short-term inert headspace and intermediate-term reactors was measured.

Task 6

9. Speciation calculations of experimental fluid chemistry to help determine which primary phases are likely dissolving and what secondary precipitates are stable under the observed experimental conditions.
10. Refinement and application of geochemical model to inform interpretation of experimental results.
11. Preliminary application of experimentally-calibrated models to 1-dimensional simulations of reactive transport.

Task 1. Project management. See sections 4 (risk analysis), 5 (milestone status), and 6 (schedule status).

Task 2. Fe(II) and bitumen reactions with fracture-fluid

To date, our results have reproducibly shown that hydraulic fracture fluids, and in particular their organic constituents, dramatically accelerate oxidation of Fe(II) and simultaneously drive the release of bitumen from shales. As described below, these behaviors dominate iron redox chemistry and are potentially important to the formation of fracture-clogging Fe(III) hydroxide precipitates. In contrast, the pure mineral-fracture fluid reactions that were proposed in the original project plan have been evaluated as relatively less important based on the relatively low reactivity of particularly silicate mineral phases. Subsequently, we have prioritized the Fe(II)-bitumen-fracture fluid system as a target for a manuscript and have suspended action on pure mineral-fracture fluid experiments except in the case that they support one of the three manuscript priority topics.

Progress in the 4th quarter. Experiments investigating the effect of the hydraulic fracture solution and shale samples have shown that Fe-cycling in these systems is complex. The experiments have shown that HCl is necessary for the release of Fe into solution, but has also shown that HCl is an inhibitor to Fe oxidation. Fe oxidation experiments using the fracture fluid with HCl and 36 ppm $FeCl_2$ in solution resulted in no detectable oxidation of Fe(II) nor precipitation of Fe(III)-bearing phases over a 2-week period. This result appears at first to contradict the Fe oxidation seen in the whole shale-fracture solution reactors throughout this project. Since bitumen release from the shales was visually observed less than 24 hours after the start of the experiments, it was hypothesized that the addition of bitumen in the reactors was responsible for Fe oxidation and precipitation in the reactors. A preliminary set of experiments using bitumen extracted from the Marcellus and Green River shales during kerogen isolation in conjunction with the hydraulic fracture solution, both with and without HCl, were completed.

Results. Bitumen was extracted from both the Marcellus and Green River shales as a by-product of the kerogen extraction used in Task 3. Significant quantities of bitumen from both source rocks was extracted using a 3:1 toluene/methanol mixture in a Soxhlet reactor. The extracted bitumen from the Marcellus and Green River shales differs significantly in both physical character and chemical behavior in the Fe oxidation experiments.

The Green River bitumen is highly hydrophobic and extremely asphaltine rich with the consistency of tar. Though the Marcellus bitumen does contain asphaltine material, the overall bitumen is more hydrophilic in comparison to Green River and was easy to disperse into the Fe oxidation reactors. Dynamic light scattering of unfiltered Marcellus bitumen at a concentration of ~40 ppm bitumen indicated a wide range of particle sizes ranging from 38-395 nm in particle diameter. Green River bitumen was so hydrophobic that dynamic light scattering was not possible. Bitumen reactors without HCl show that the bitumen from both Marcellus and Green River can readily oxidize iron in solution. The Marcellus bitumen without HCl oxidized 26% of the Fe(II) within 48 hours, initially 35 ppm Fe(II), with the majority of the precipitated Fe-(oxy)hydroxides being trapped in a 0.22 μm syringe filter. Conversely, when HCl was included in the reactor, less than 1.5% of the Fe was oxidized. Similar to the Marcellus bitumen, the Green River bitumen reactor readily oxidized Fe with nearly 38% of the Fe oxidizing and precipitating. Hydrochloric acid had strong impact on Fe oxidation for the Green River bitumen with only 6% of the Fe oxidizing throughout the experiments. Similar to the hydraulic fracture solution experiments, HCl significantly inhibited Fe oxidation.

For comparison, a reactor with hydraulic fracture solution and no HCl showed significant oxidation of Fe over a 48 hour period with ~41% of the total Fe being oxidized. Since one of the primary purposes of the ethylene glycol is for Fe control, at neutral pH this additive is not effective at Fe control. Based on the results thus far (**Figure 4**), low pH is the greatest inhibitor of Fe oxidation. Since Fe oxidation is effectively halted in the hydraulic fracture solution only and bitumen only reactors, it is important to determine if the two components in tandem can override the inhibition of Fe oxidation caused by the low pH and explain why Fe-(oxy)hydroxide precipitation is seen in our low pH shale reactors (Marcellus pH 3.8 and Barnett pH 3.2). For Marcellus bitumen with hydraulic fracture solution, 13.8% (with HCl) and 18.4% (without HCl) of the Fe oxidized in the reactors. In comparison, for Green River bitumen with hydraulic fracture solution, 16.6% (with HCl) and 17.2% (without HCl) of the Fe oxidizing in the reactors. These results show that even at low pH, ~3.2, the combination of bitumen and hydraulic fracture solution is capable of oxidizing a significant amount of Fe in a short time period, 48 hours for these experiments.

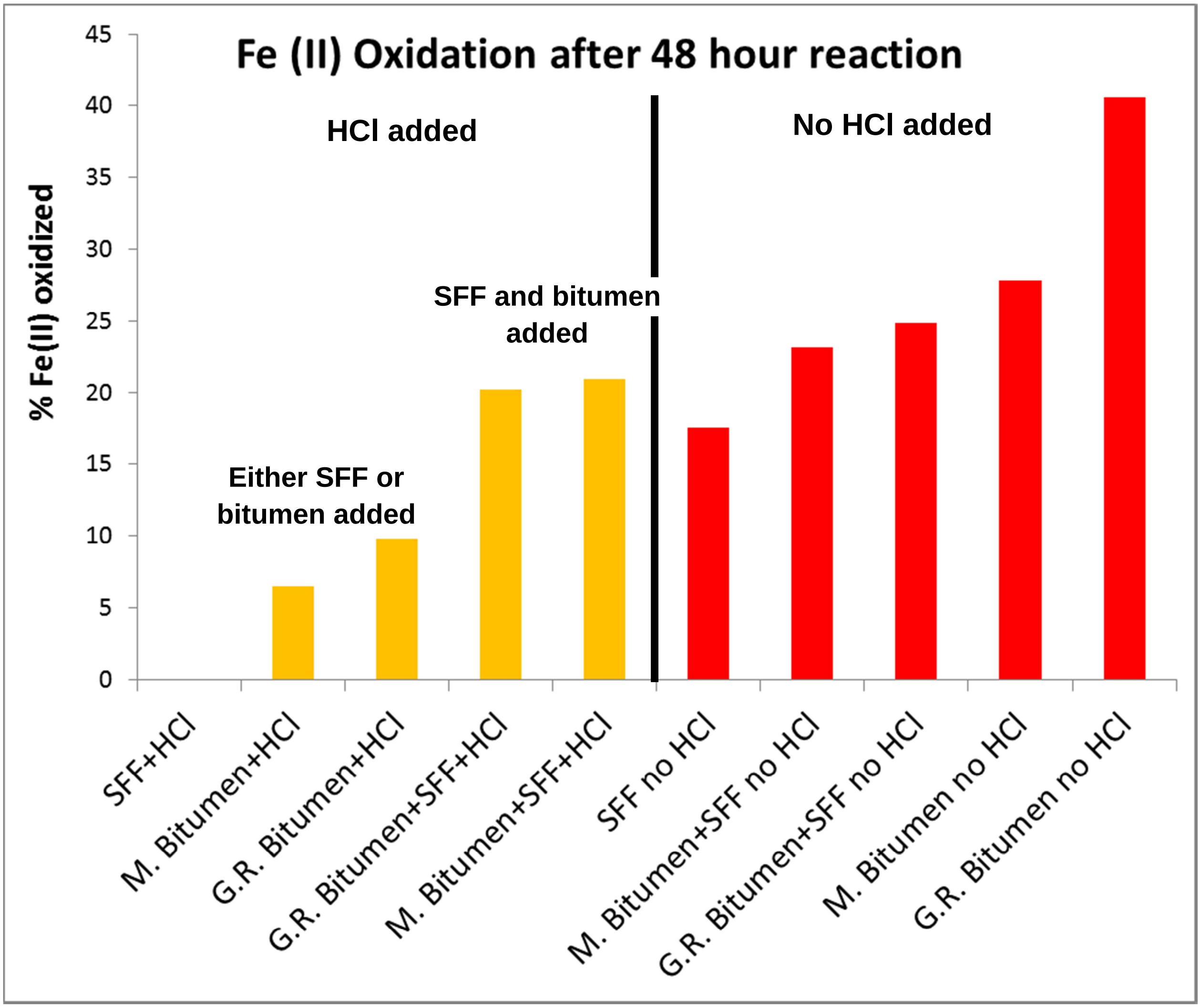


Figure 4: Impact of acidity, simulated fracture fluid (SFF), and bitumen on oxidation of dissolved Fe(II) after 48 hours reaction in the absence of shale surfaces. The pH of reactors with HCl was 2.1 ± 0.1 for and 6.8 ± 0.2 for reactors without HCl. Starting Fe(II) concentration, added as $FeCl_2 \cdot 4H_2O$, was 35 ppm. Reactors were open to the atmosphere and incubated in the dark at 80^oC.

The majority of the Fe-(oxy)hydroxides formed in these reactions are larger than 220 nm in diameter. That, coupled with the fact that the majority of the bitumen released from the oil/gas shales is larger than 220 nm in diameter, suggests that both of these types of particles can have a significant impact on porosity in the subsurface. Because of this potential, Task 2 of the project will be shifted towards Fe oxidation and bitumen chemistry in the subsurface.

Planned Experiments.

The preliminary results have shown that the hydraulic fracture solution is not capable of oxidizing Fe at low pH, but it is capable of extracting bitumen from the rocks. The combination of bitumen and hydraulic fracture solution can significantly accelerate oxidation of Fe in solution at low pH. To focus on this part of the subsurface chemistry, we propose to investigate which of the chemical additives from the hydraulic fracture solution is responsible for the release of bitumen into solution. Additionally, a more refined set of experiments with the bitumen in which O_2 is varied is required. These experiments will range from 1) no O_2 in solution or headspace, 2) O_2 in solution with Ar headspace, and 3) fully open to the atmosphere. These experiments will determine the impact of O_2 on Fe oxidation in the presence of hydraulic fracture solution and bitumen. Following experiments, identification of the types of Fe precipitates formed will be done along with identifying the sizes of the mineral precipitates.

The preliminary tests on the effect of extracted bitumen on Fe oxidation have shown that the bitumen released from the shale by the hydraulic fracture solution has the potential of being important to Fe-(oxy)hydroxide production. The large particle size of both the bitumen and Fe-precipitates coupled with the short time period required for oxidation and precipitation suggests they have the potential to clog nano- and micro-pores and inhibit production of hydrocarbons.

Manuscript Plans. We will produce a manuscript focused on the oxidation of Fe released from oil/gas shales due to the presence of hydraulic fracture solution. The manuscript will present for the first time the importance of bitumen extracted from the rock on not only the potential occlusion of pores by the bitumen itself, but also from the formation of Fe-(oxy)hydroxides due to the presence of bitumen. Tentatively the manuscript will be titled: The Importance of Bitumen Derived from Oil/Gas Shales on the Oxidation and Precipitation of Iron during Hydraulic Fracturing. This manuscript will illustrate that Fe controlling agents added to the hydraulic fracture solutions in a laboratory setting do not work in real world settings due to the unforeseen Fe oxidation potential of bitumen extracted from the rocks by the organics injected into the subsurface. Additionally, this manuscript will attempt to determine if enough bitumen and Fe-(oxy)hydroxide is produced to completely explain the significant drop off of production from fracturing wells following the initial 6-months of operation.

Task 3. Kerogen-fracture fluid interactions

Kerogen is an important shale component because it is the source of shale hydrocarbons. It is also mechanically incompetent and thus may contribute to fracture development. By definition, kerogen should not dissolve into fracture fluids. However, kerogen does contain elevated concentrations of redox-sensitive heavy metal(loids), which accumulate in organic matter. Redox-sensitive refers to the ability for metals to gain or lose electrons. Electron-rich ions, such as Fe^{2+}, U^{4+}, and sulfide (S^{2-}), are said to be “reduced”. Electron-poor ions, such as Fe^{3+}, U^{6+}, and sulfate (SO_4^{2-}) are said to be “oxidized”. These redox-active toxicants can be released into fracture fluids and formation waters following contact with oxygen or other oxidants, which are introduced by hydraulic fracture fluids.

Kerogens from Marcellus and Green River shales are being extracted and reacted with fracture fluids in this portion of the project, which is aimed at determining the chemical and structural changes of kerogen that occur in shales in contact with fracture fluids. Marcellus is being used because it is economically important and contains more kerogen than the other unconventional shales being used in this project (Eagle Ford and Barnett). It represents a more thermally mature kerogen. Green River shale contains more thermally immature kerogen and thus provides a useful contrast to help understand the impact of maturity on kerogen reactivity with fracture fluid. Green River shale is highly enriched in kerogen and therefore was used to develop and test our kerogen extraction and characterization procedures.

Progress in the first 3 quarters. A method for isolating high purity kerogen was adapted and used for preparing Green River kerogen. Isolated kerogen has been reacted with hydraulic fracture fluid for various durations, 3 week, 3 month, and 6 month time frames, with the short and intermediate reactors completed on June 16 and August 3, respectively. Solutions and gas samples were collected at regular time intervals. All analyses are complete for solutions collected from both short and intermediate term reactors. Analyses of the kerogen solids are in progress. Isolation of kerogen from the Marcellus shale is near completion, and experiments will begin in the present quarter.

Progress in the 4th quarter. Analyses of both sampled solutions and reacted solids have continued in quarter 4, and the intermediate term kerogen reactor was completed on August 3. Analyses of solution samples for both the short and intermediate term reactors have been completed, including inductively coupled plasma optical emission and mass spectrometry (ICP-OES; ICP-MS), ion chromatography (IC), total organic carbon and nitrogen (TOC; TN), gas chromatography (GC) to obtain pO_2 values. Solid kerogen from the short term reactor has now been analyzed by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR), to be followed shortly by X-ray fluorescence (XRF) and X-ray diffraction (XRD). Kerogen from the intermediate term reactor has been imaged with SEM to understand its general morphology, with the chemical analyses to be completed in the upcoming weeks.

Table 1. Task 3 objectives for quarter 4:

Goal	Status
Short-term (3 week) reaction of kerogen with hydraulic fracture fluid	Complete
Intermediate-term (3-month) reaction of kerogen with hydraulic fracture solution	Complete
Initiation and sampling of kerogen reaction with hydraulic fracture solution for time frame of 6 months	In Progress
Extraction of kerogen from Marcellus Shale	In Progress
X-ray absorption spectroscopy (C and Fe K-edges)	Completed
Ferrozine assay (Fe^{2+} and Fe_{tot} concentrations)	Completed
ICP-OES and ICP-MS for total metal concentrations	Completed
XRF analysis of post-reaction kerogen	In Progress
FTIR analysis of post-reaction kerogen	Completed
XRD analysis of post-reaction kerogen	In Progress
SEM analysis of post-reaction kerogen	Completed

Results. FTIR spectroscopy was used to measure kerogen before and after reaction with fracture fluid to assess changes in the organics. These measurements demonstrate the loss of multiple peaks after reaction, indicating a change in surface functional groups **(Figure 5)**. There is also significant release of N to solution, not seen in any of the bulk shale reactors, indicating the N-containing functional groups may be influential in reaction. Alteration of organic matter in this way may affect shale wettability, known to be strongly affected by which organic functional groups are present. This would consequently alter transport of both hydrocarbons and hydraulic fracture fluid through the shale matrix. Solution analyses of both the short and intermediate term reactors indicate the release of high concentrations of Si, Fe, Li, Al, Cu, Zn, Rb, and Ba into solution, an additional indicator of kerogen reactivity (**Figures 6A-C**). Ba behavior is particularly notable because it is a proxy for radioactive Ra. These findings raise the prospect that kerogen may contribute significantly to TDS, contaminant, and radioactivity loads in produced waters. Additional analyses of the reacted solids will clarify the source of these elements and help constrain mobility. Solute release from isolated kerogen is higher than from the bulk shale parent material. This effect is attributed to complexation of metals by the relatively abundant organic ligands in the isolated kerogen.

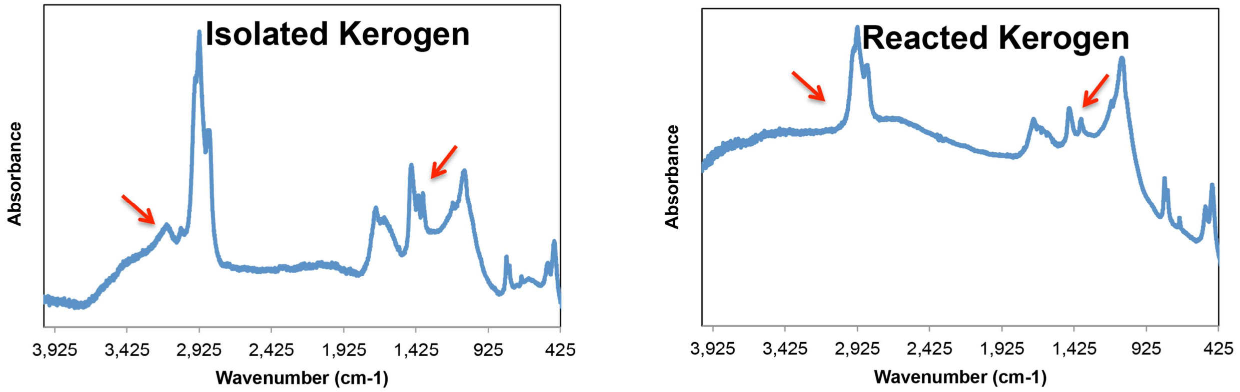


Figure 5. Fourier transform infrared (FTIR) spectra of Green River kerogen before and after short term reaction with hydraulic fracture fluid. Arrows indicate the locations of peaks that have been lost after reaction with fracture fluid.

Planned experiments. Kerogen is currently being extracted from Marcellus shale following protocols learned from our initial Green River shale kerogen experiments and will be reacted with fracture fluid to determine the chemical effects of hydraulic fracture fluid on a more thermally mature and aromatic-rich kerogen. These experiments will be conducted for 3 weeks. Each sampling point will include collection of solution for measuring dissolved metal and anion concentrations and total organic carbon and nitrogen content. The Marcellus derived kerogen (pre- and post-reaction) and the Green River derived kerogen (post-reaction) will be analyzed using FTIR, STXM, and C XAS to determine changes to the solid state Fe and organics caused by the hydraulic fracture solutions.

Manuscript Plans. There are relatively few published studies on potential kerogen reactivity, primarily because kerogen is considered to be largely inert. Studies detailing kerogen's potential for reaction and alteration in the presence of oxidizing hydraulic fracture fluids are needed. The planned manuscript will detail the successful isolation of high purity kerogen (both Green River and Marcellus), its potential for metal release to solution and implications for contaminant mobility, and the differences in surface functional groups before and after reaction with hydraulic fracture fluid. This effort will utilize the data collected from ICP-MS, ICP-OES, IC, GC, TOC/TN, XRD, XRF, SEM, FTIR, STXM, and XAS. In order to have a complete data set and present a compelling argument for reactivity, more FTIR, STXM, and C XAS data will be required. These analyses are currently being prioritized. This manuscript will tentatively be submitted in April 2016 to either *Chemical Geology* or *Energy and Fuels*. This work resulted in one poster presentation at the Stanford Synchrotron Radiation Lightsource 2015 User's meeting (Dustin et al.; Appendix A), and one poster to be presented at the upcoming American Geophysical Union 2015 Fall Meeting in December (Dustin et al.; Appendix A).

Task 4. Whole shale-fracture fluid interaction

This module investigates the impact of fracture fluids on bulk shale samples with emphasis on studying alteration of shale surfaces and coating development as a function of shale composition. Economically important shales from different geological environments representing a wide range of clay, carbonate, and kerogen contents were reacted with fracture fluid in batch reactors at reservoir-representative temperature: Marcellus, Eagle Ford, Barnett, and Green River. Changes in both fluid and solid composition were tracked to gauge reaction progress and inform geochemical models.

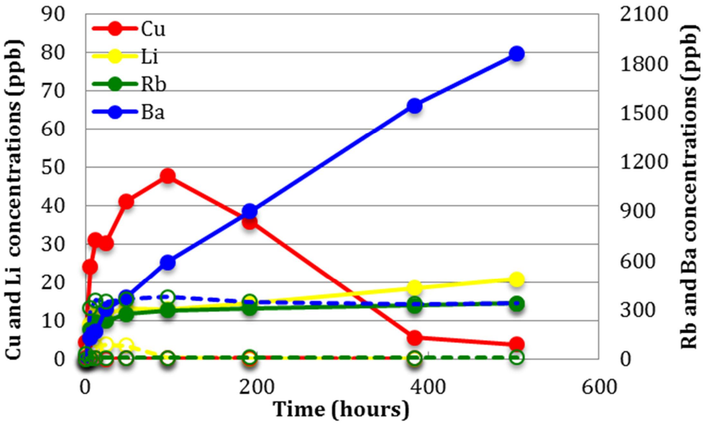


Figure 6A. Concentrations of Cu, Li, Rb, and Ba released to solution from extracted Green River kerogen (solid lines with filled circles) as a function of time in the short short-term experiments. For comparison, Cu, Li, Rb, and Ba release from bulk Green River shale is shown in dashed lines and open circles.

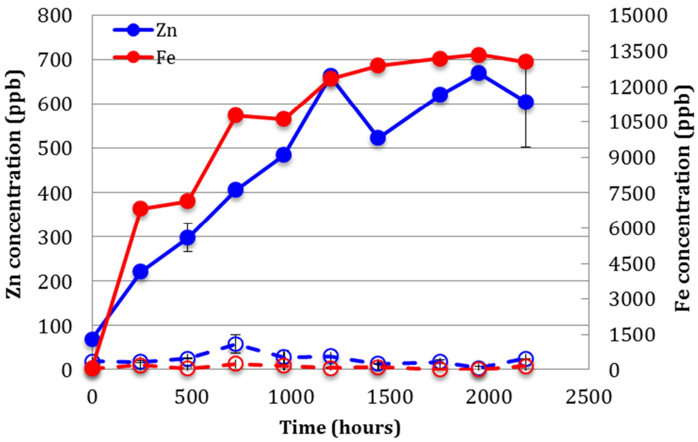


Figure 6B. Concentrations of Zn and Cu released to solution from extracted Green River kerogen (solid lines with filled circles) as a function of time in the short short-term experiments. For comparison, Zn and Cu release from bulk Green River shale is shown in dashed lines and open circles.

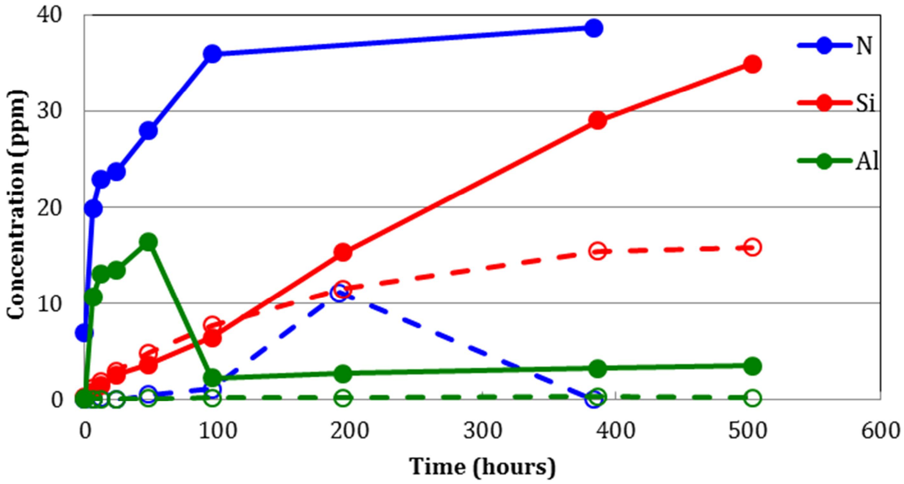


Figure 6C. Concentrations of N, Si, and Al released to solution from extracted Green River kerogen (solid lines with filled circles) as a function of time in the short short-term experiments. For comparison, N, Si, and Al release from bulk Green River shale is shown in dashed lines and open circles.

Progress in the first 3 quarters. A series of experiments containing shales of different initial mineralogical composition exposed to hydraulic fracture solution were conducted. This included completion of short-term (3 week) and intermediate- (3 month) experiments, and commencement of long-term (6 month) experiments. Approximately 1 g of pulverized (150 – 250 µm) and whole (~0.4 cm^3) samples of each of four different shales were reacted with 200 mL of fracture fluid at 80°C in glass serum vials at circum-atmospheric pressure. All reactors also contained a single piece of Al_2O_3, a relatively inert mineral to serve as a substrate for precipitation of secondary phases. The fracture fluid composition was representative of that used in fracture operations at the Marcellus shale, and comprised ethylene glycol, polyethylene glycol, guar gum, kerosene, 2-ethylhexanol, glycol ether, and hydrochloric acid (HCl). In order to isolate the effects of the organic fracture fluid additives versus HCl, a subset of experiments was conducted using pulverized Marcellus shale exposed to 1) fracture fluid without HCl, 2) HCl only, and 3) de-

Table 2. Task 4 objectives for quarter 4:

Goal	**Status**
Complete short-term reactions with inert headspace	Complete
Intermediate- and long-term shale-fracture fluid experiments	Complete and in progress
Analysis of aqueous chemical data with ICP-OES, ICP-MS, and TOC	In progress
Characterize reacted solids using XRD, SEM, FTIR, BET, FIB-SEM, EDS, and gas adsorption pore-size analysis	In progress

ionized water for 3 weeks. Gas and solution samples were removed and reactor pressure was measured periodically for all experiments. All solid products were collected and dried under vacuum following completion of the experiments, and were characterized using SEM and EDS. Fluid pH was measured immediately following sampling, as was the aqueous Fe speciation for the short-term experiment (ferrozine method). Other cation concentrations were analyzed following completion of the experiment using ICP-OES and ICP-MS for analysis of major and trace elements, respectively. Anion and total organic carbon concentrations have been determined using ion chromatography and combustion catalytic oxidation analysis, respectively for the short-term experiments. Gas samples from the short and intermediate-term experiments were analyzed using gas chromatography.

Several experimental problems were encountered, including gas exchange between the reactors and laboratory air, which altered the redox conditions. This was addressed by conducting an additional set of experiments employing reactors with thicker butyl rubber stoppers that provided a better barrier between the reactors and the laboratory air. The data collected from the experiments that allowed gas exchange are nevertheless useful, as they provide an oxygen-rich end-member to compare to subsequent experiments with inert (low O_2) headspace. An additional set of experiments is planned that will include O_2 initially in the headspace, but will employ the thick stoppers such that the volume of O_2 available for reaction is limited, and well known.

Progress in the 4th Quarter.

Completion of short-term (3 week) batch shale-fracutre fluid reactor experiments with inert headspace, and completion of intermediate (3 month) batch shale-fracture fluid reactor experiments. Long-term (6 month) batch shale-fracture fluid reactor experiments will be completed shortly after submission of this report (Nov 5, 2015). Inert headspace reactors included approximately 1 g of pulverized (150 – 250 μm) Marcellus shale reacted with fracture fluid at 80°C in glass serum vials with an inert argon (Ar) gas headspace. A single reactor contained an O_2-bearing headspace (laboratory air) for comparison, but was isolated from the atmosphere such that the volume of O_2 available for reaction was limited, in contrast to short-term experiments conducted during quarter 3 and the intermediate and long-term reactors, which permitted some exchange with the laboratory atmosphere, and therefore partial replenishment of O_2. The intermediate- and long-term reactors comprised pulverized or whole (3-10 mm) pieces of Marcellus, Eagle Ford, Green River, or Barnett shale. The fracture fluid composition is representative of that used in fracture operations at the Marcellus shale, and contained ethylene glycol, polyethylene glycol, guar gum, kerosene, 2-ethylhexanol, glycol ether, and hydrochloric acid (HCl). The goal of the inert headspace reactors was to assess the role of O_2, which is present in hydraulic fracture fluids, in metal release and precipitate formation. Gas and solution samples were removed and reactor pressure was measured periodically for all experiments. All solid products were collected and dried under vacuum following completion of the experiments.

Analysis of experimental run products from intermediate-term experiments and short-term inert headspace experiments. Fluid pH was measured immediately following sampling, as was the aqueous Fe speciation for the inert headspace experiment (ferrozine method). Other cation concentrations were analyzed using ICP-OES and ICP-MS for analysis of major and trace elements, respectively, for the intermediate-term experiments. Analysis of anion and total organic carbon concentrations using ion chromatography and combustion catalytic oxidation analysis, respectively, was completed for the intermediate-term experiments and is underway for the short-term inert headspace reactors. Gas samples were analyzed for CO_2 and O_2 partial pressure using gas chromatography at Lawrence Berkeley National Laboratory.

Analysis of solid experimental run products for chemical and morphological changes is well underway and includes XRD, XRF, FTIR, BET surface area analysis, and pore size distribution by gas adsorption. Surface sensitive techniques to explore the morphology, distribution and composition of surface precipitates include SEM with energy dispersive spectroscopy (EDS) and focused ion beam (FIB) milling. In addition, tomography measurements of samples of each shale type before and after reaction with fracture fluid for three weeks were collected at the Pohang Light source to reveal changes in morphology and porosity.

Results. Aqueous chemistry data revealed unique behavior for the carbonate-rich shales, Green River and Eagle Ford, in contrast to the clay-rich shales, Barnett and Marcellus. Carbonate-rich shales rapidly buffered solution pH to circum-neutral conditions without substantially depleting the buffering capacity of the rock (*i.e.,* the carbonate mineral content). Although the carbonate content is nearly completely stripped from the clay-rich shales, as inferred by mass balance calculations **(Figure 7)**, the solution pH remains acidic. This has important implications for reservoir evolution over time, namely 1) the maintenance of acidic conditions will encourage further dissolution of the silicate minerals that comprise the majority of the clay rich shale, and 2) an acidic pH may reduce Fe(II) oxidation rates and inhibit precipitation of Fe(III)-hydroxides. In addition, the selective removal of carbonate minerals was found to generate large (~5 μm diameter) pores **(Figure 8)**, which is likely to increase shale permeability. Tomography data col-

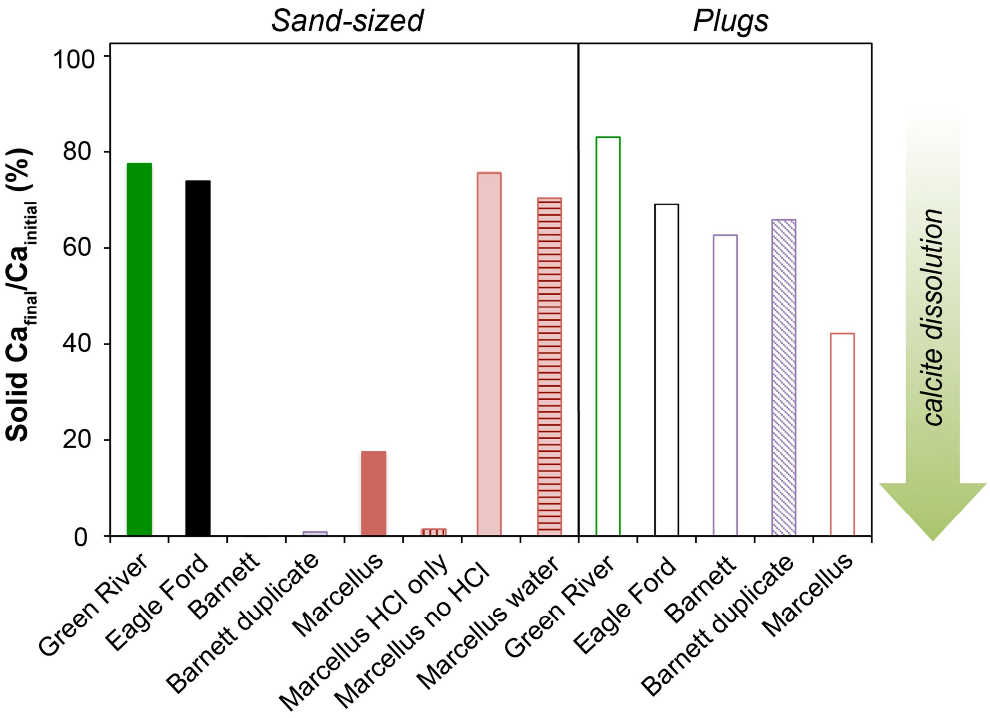


Figure 7. Ca mass balance in short-term shale experiments with O_2-bearing headspace. Ca is treated as a proxy for calcite [$CaCO_3$] dissolution. Mass balance is calculated using X-ray fluorescence data for initial materials and aqueous Ca concentrations at the conclusion of the experiments.

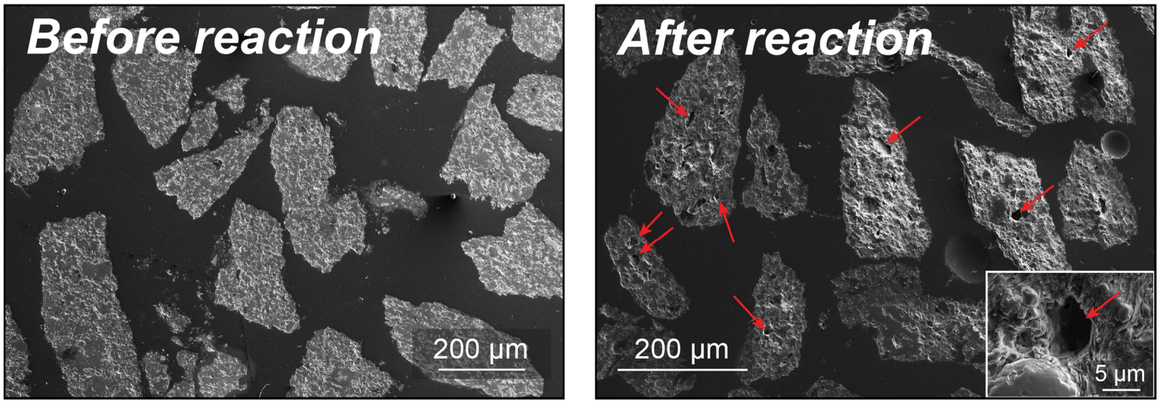


Figure 8. Scanning electron micrographs of sand-sized Barnett shale before and after three weeks of reaction with fracture fluid. Red arrows indicate pores generated following reaction.

lected at the Pohang Light Source revealed that porosity was generated in shales of all types, but was most significant for the Green River and Marcellus **(Figures 1 and 9)**. Similarly, an increase in porosity in the 5-30 nm pore size range was found following reaction for the Barnett and Eagle Ford shales as measured using N_2 gas adsorption. On the other hand, observation with SEM and EDS analysis indicates that Al-bearing precipitates were present in the majority of the reactors after 3 months, indicating that porosity may be lost depending on the location of such precipitates in the subsurface. Although the net effect of these mineral dissolution-precipitation reactions on porosity is unclear, it is evident that fracture fluids are likely to influence porosity and permeability in the subsurface and thus hydrocarbon and contaminant release. These findings highlight the need to couple pore-scale measurements to changes in whole-rock permeability.

Analysis of the samples collected from the inert headspace reactors is still in progress, but results obtained thus far reveal that availability of O_2 is a strong control on reaction progress. Gas chromatography analysis indicated that the headspace had ≤5% O_2, compared to ~20% O_2 initially present in the reactors with laboratory air. With less O_2 available to drive oxidation reactions, no Fe(III)-bearing precipitates were visible, nor was significant Fe(II) oxidation evident based on Ferrozine analysis, in contrast to the previous experiments that allowed minimal O_2 exchange with the laboratory air. The implication is that the extent of pore-clogging precipitates formed in the subsurface will strongly depend on the oxidation capacity of the fracture fluid relative to the reductive capacity of the host shale. Nevertheless, depending on the relative rates of reaction and fluid flow, even a small amount of oxygen could lead to localized formation of oxidized precipitates that significantly impact permeability. For example, if reaction rates were rapid relative to fluid flow, precipitates would be concentrated in the vicinity of the point of injection and along fracture interfaces; even small changes in porosity at these interfaces could have a strong influence on permeability.

Key outcomes. 1) Reaction progress was strongly dependent on shale composition. Carbonate-rich shales rapidly buffered solution pH without depleting buffering capacity whereas carbonate-poor, clay-rich shales had insufficient carbonate to recover pH to non-acidic values. The lower pH in these systems may encourage further dissolution of silicate minerals, but limit precipitation of secondary phases. 2) The extent of reaction was strongly dependent on fluid composition; experiments that lacked hydrochloric acid exhibited little dissolution, whereas significant mineral dissolution occurred in reactors with acid. Moreover, the presence of the organic additives in the fracture fluid was found to influence iron redox chemistry and encourage precipitation of secondary Fe-hydroxides. 3) Mineral dissolution induced by interaction with fracture solutions can increase porosity, though the presence of secondary phases (*e.g.*, Al-hydroxides) provides the potential for porosity reduction.

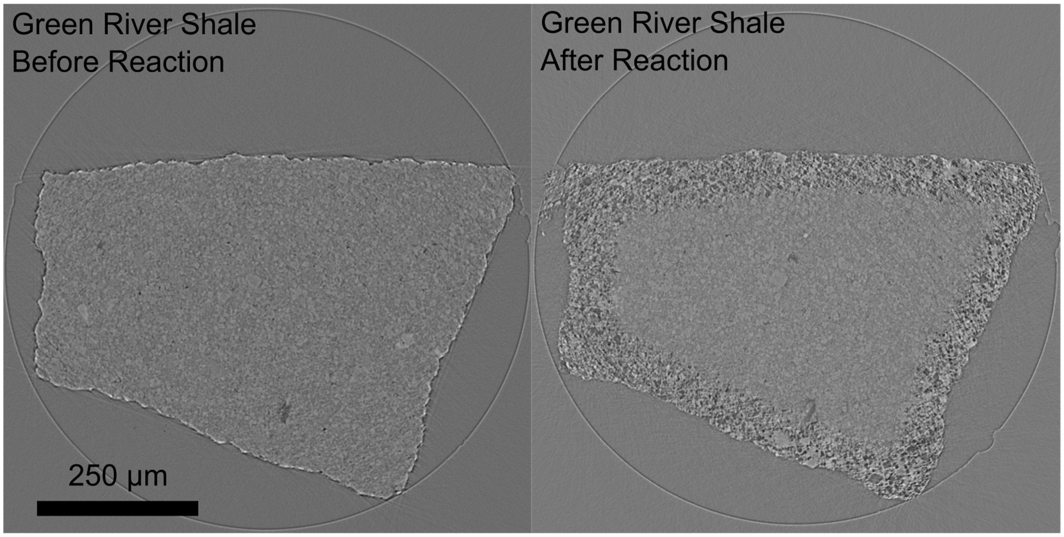


Figure 9. Micro X-ray computed tomographic (CT) slice reconstruction of a piece of Green River shale pre- and post-reaction with hydraulic fracture fluid.

Planned experiments. An additional set of short-term reactors with O_2-bearing headspace (laboratory air) using reactors that are completely sealed from the atmosphere and each shale type are required to complete a manuscript and are scheduled to begin at the time of writing. The goal of these experiments is to quantify the extent of oxidation induced in the shales with a known volume of oxygen to improve prediction of reaction progress for given redox conditions and to help better quantify the extent of reservoir oxidation that will be incurred upon injection of fracture fluids in the subsurface.

Manuscript plans. Task 2 will generate a manuscript tentatively titled "A geochemical framework for evaluating shale-hydraulic fracture fluid interactions" to be submitted to *Chemical Geology* or *Environmental Science & Technology*. This work resulted in one poster presentation at the Stanford Synchrotron Radiation Lightsource 2015 User's meeting (Harrison et al.; Appendix A), and one poster to be presented at the upcoming American Geophysical Union 2015 Fall Meeting in December (Joe-Wong et al.; Appendix A).

Task 5. Uranium-fracture fluid interactions.

Oxygen present in fracture fluids is expected to oxidize relatively insoluble U^{4+} to U^{6+}, which is relatively soluble and mobile in water. For this reason, oxidation of shale has the potential to mobilize significant concentrations of uranium. The purpose of this task is to examine uranium speciation and release from shales in response to reaction with fracture fluids.

Activities during the performance period. Whole-shale experiments for this task are the same as those for Task 4 (same samples and treatments, followed by different analyses). Marcellus samples, which are relatively enriched in uranium (55 mg/kg) compared to the other samples, have been reacted in the experiments described in Task 4.

Table 3. Task 5 objectives for quarter 4:

Goal	**Status**
Analysis of U concentrations from fluid-shale reactions using ICP-MS	Complete

Results. Reactions of the Marcellus shale with hydraulic fracture solution indicate that HCl is the largest factor in the release of U into solution (**Figure 10**). Though significant U is released in the hydraulic fracture solution reactors, ~55 ppb, these concentrations are similar to the HCl only control reactor. In the presence of HCl, total U concentrations climbed rapidly during the early stages of the reaction **(Figure 10)**. Though the release of U from intact shale pieces was slower than the sand sized shale, total U concentrations did rise to a concentration of ~36 ppb U in the short-term reactors. This initially rapid U release is consistent with the liberation of U from the solid phase due to the rapid dissolution of carbonate minerals, which are known to contain U in Marcellus shale (Phan et al., 2015). Mass balance calculations based on solution chemistry and initial bulk U concentrations in the solids measure with XRF indicate that up to ~25% of the solid phase U was leached to solution during the initial rapid reaction. Sequential extractions should reveal whether this mass of U is present in the carbonate minerals, and thus confirm this hypothesis.

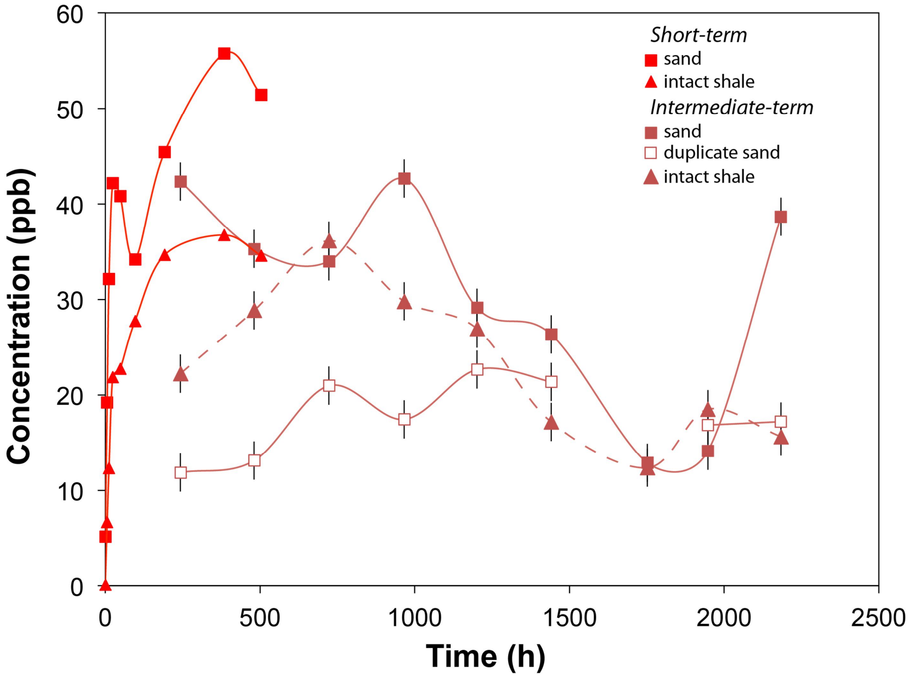


Figure 10. Uranium concentration versus time in the short and intermediate-term shale-fracture fluid experiments with O_2-bearing headspace.

Interestingly, U concentrations were observed to decline after ~50 days in the intermediate-term experiments **(Figure 9)**. The mechanism behind this decline remains unclear; it may be attributable to adsorption of U to the surfaces of precipitates, precipitation of U-bearing phases, or reduction of aqueous U^{6+}. Geochemical modeling revealed that uranium-bearing minerals are typically not saturated in bulk solution in our experiments, suggesting the decrease in U concentration over time is not attributable to precipitation of U phases. Analysis of the solid samples post-reaction by XAS should permit determination of the oxidation state and phase of the solid-phase U and help elucidate the mechanism by which U is removed from solution.

Planned experiments: Work by Phan *et al.* (2015) focused on selective chemical extractions of Marcellus shale samples from the southern portion of the Marcellus region. Since there is a significant difference in mineralogy and organics in the Marcellus shale depending on the region, doing a similar sequential extraction for the U is necessary to extend the speciation information beyond what we have been able to ascertain using XAS techniques. Currently, the linear combination fitting of the U L_{III}-edge XANES data indicates that the U is present as U(IV) oxides, presumably uraninite, in the Oatka Creek Member of the Marcellus. Phan *et al.* state that the majority of the U in their samples is in the silicate phases. If the U is bound in the silicate structures as U(IV) bound to oxygen, then the XAS analysis would make differentiating between uraninite and the U-silicate difficult. Reaction of shale with low-pH fracture fluid preferentially dissolves carbonate (*cf.*, section 6). We expect that the pool of carbonate-associated U(IV) in the shale should also be lost, leaving behind U(IV) dominated by other binding mechanisms (*e.g.*, U(IV) associated with clays or present as the mineral uraninite, UO_2). We can assess this change in the pool of uranium present in the shale using chemical extractions that remove U(IV) from shales starting with the most weakly bound forms (*e.g.*, cation-exchangeable U(IV) adsorbed to minerals surfaces), and proceeding sequentially to attack more recalcitrant forms (*e.g.*, U(IV) structurally hosted in silicates or uraninite). We propose to use chemical extractions to determine if there are any changes to the dominant chemical form (speciation) of U(IV) in the solid after reaction with fracture fluid.

Task 6. Geochemical and transport modeling.

Geochemical modeling is being performed to support 2-D and 3-D representations of fractured shale in order to make predictions about the coupling between redox reactions, uranium transformations and transport of fracture fluids. The model is presently being evaluated and calibrated using the incoming experimental data to provide a platform for future work coupling transport and geochemical processes.

Progress in the first 3 quarters. To develop a framework for prediction and evaluation of our experimental studies, we used the multicomponent reactive transport code Crunch Flow (Steefel et al., 2014) to develop a set of mixed kinetic-equilibrium reaction path calculations that include shale mineralogy, aqueous species and secondary mineral phases likely to form when shales interact with oxidized fracture fluids. An example of the solid phases used in our calculations for the Marcellus shale is shown in **Table 5**. Thermodynamic data is from the EQ3/EQ6 database and the kinetic data (including rate constants, activation energies and any dependence on aqueous species) were compiled and evaluated using the compilation of Palandri and Kharaka (2004). Initial development of the geochemical model began in quarter 1, but modeling activity did not progress during the 2nd quarter due to the departure (in late December) of the postdoctoral fellow who was working on this task. A new postdoctoral fellow was hired in mid-April and took over this task.

After initial simulations to help guide the design of our experimental program, modeling efforts have now been focused on simulations of our experimental conditions with the aim of reproducing observed trends in aqueous chemistry and changes in mineralogy. Reproduction of experimental trends is achieved largely through alteration of reactive surface areas in the model, upon which mineral dissolution-precipitation rates depend, as this is a key uncertainty in our systems. Mismatch between modeled and experimental data also provide important insights as to what reaction pathways are missing from our current conceptual framework of shale hydraulic-fracture fluid interactions. This allows us to better target our experiments to investigate these missing processes. Presently, our models are able to reproduce certain aspects of the aqueous chemistry quite well, in particular the reaction rates of calcite [$CaCO_3$], however reproduction of the observed Fe dynamics remains a challenge. Experiments focused on measurement of the kinetics of aqueous Fe(II) oxidation in the presence of organic fracture fluid components and bitumen (*cf.*, Task 2) will help remove some of the ambiguity in these simulations which at present suffer from numerous unknown variables (dissolution rates of multiple Fe-bearing phases, secondary phase precipitation rates, and aqueous oxidation rates).

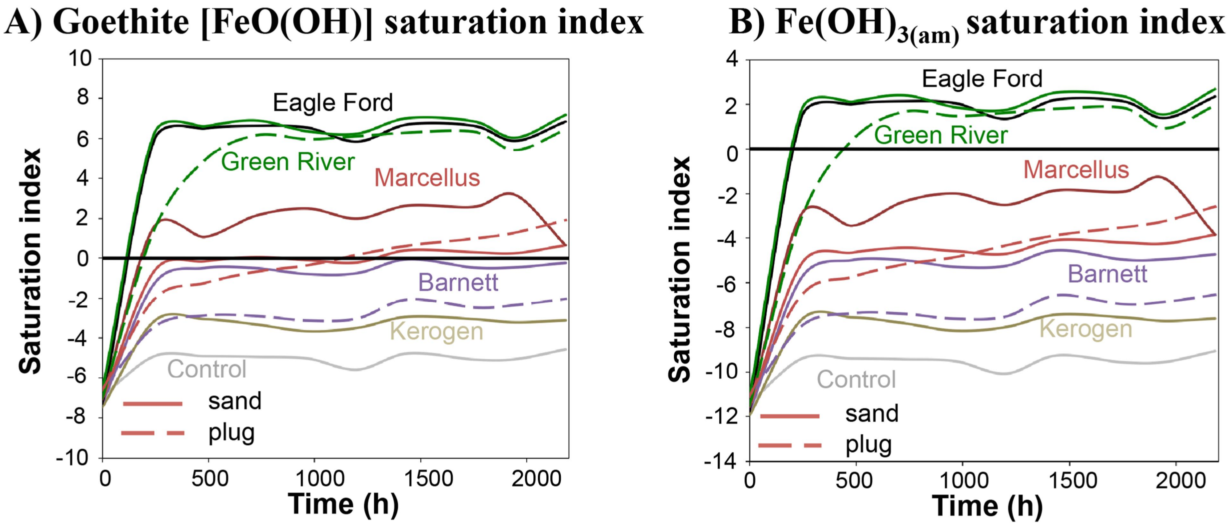
By modeling our experimental conditions, we were also able to identify an issue with our experimental setup, namely the replenishment of depleted O_2 in our reactors from the ambient laboratory atmosphere. Subsequent experiments are being conducted to address this experimental issue and determine the extent to which it impacted our results (Task 4). This finding highlights the model's utility for informing the interpretation of experimental results.

Progress in the 4th Quarter. The modeling framework developed in quarters 1 and 3 using the multicomponent reactive transport code Crunch Flow (Steefel et al., 2014) is being refined and calibrated as more experimental results become available. A reaction network has been constructed for each of the four shale samples based on their initial mineralogy, and experimental conditions are simulated. As an example, the reactions considered during reaction of the Marcellus shale are listed in **Table 5**.

Speciation calculations were conducted for the short-term and intermediate term experiments with O_2-bearing headspace using the geochemical model PHREEQC (Parkhurst and Appelo, 2013) and measured cation and anion concentrations and pH values. These speciation calculations reveal that gibbsite [$Al(OH)_3$] is supersaturated in the majority of the experiments, consistent with the observation of Al- and O-bearing secondary phases with SEM/EDS. In addition, these calculations reveal that goethite [$FeO(OH)$] is near or equilibrium or supersaturated in most experiments, whereas amorphous $Fe(OH)_3$ is only supersaturated in reactors with the carbonate-rich Green River or Eagle Ford shales **(Figure 11)**. This highlights the importance of initial shale composition, as the higher pH maintained by the carbonate-rich shales in comparison to the clay-rich shales will not only influence the type (and morphology) of secondary Fe phases formed, but will determine whether or not they precipitate as Fe-hydroxides are not stable at low pH.

The reaction rates employed in the geochemical model were further refined using new experimental results, namely anion concentrations from the short-term experiments and solution chemistry from the intermediate-term experiments. The models are not yet able to reproduce observed trends in aqueous Fe concentrations, however, due to the large number of variables influencing Fe dynamics: dissolution rates of primary Fe-bearing phases, precipitation rates of secondary Fe-bearing phases, and kinetics of aqueous oxidation. Nevertheless, the models are able to reproduce observed trends in Ca and pH fairly well, which are strongly governed by calcite dissolution – one of the key reactants.

Finally, modeling efforts are currently in progress to account for the observed differences in behavior between the "sand" and "plug" sized shales. This will provide insight as to the influence of diffusive transport limitations on reaction rates.



A) Goethite [FeO(OH)] saturation index

B) $Fe(OH)_{3(am)}$ saturation index

Figure 11. Saturation index of goethite (A) and amorphous $Fe(OH)_3$ (B) in the intermediate-term bulk shale-fracture fluid experiments with O_2-bearing headspace as calculated using measured aqueous chemistry data and PHREEQC (Parkhurst and Appelo, 2013).

Table 4. Task 6 objectives for quarter 4.

Goal	**Status**
Continue model development using incoming experimental data	In progress
Use model to inform experimental interpretations	In progress
Extension of batch model to 1-dimension	In progress

In order to assess how a reaction front might propagate into the shale matrix in the subsurface, the experimentally calibrated reaction rates for the Barnett shale were applied in simulations with 1-dimensional transport across a fracture-matrix interface. The results of these simulations revealed that *the rate of propagation of the reaction front, and therefore the proportion of rock influenced by the fracture fluid is determined by the rate of transport in the shale matrix, rather than the kinetics of mineral reactions*, as indicated by the sharp nature of the reaction fronts **(Figure 12)**. However, this model does not yet take into account the impact of changing porosity on diffusivity. Nevertheless, these simulations allow us to start making first order interpretations regarding reaction front propagation in the shale matrix and reveal the extent of porosity change that may be expected across this interface. Images such as those in **Figure 1** will provide useful constraint on these calculations. **The implication of the simulations conducted thus far is that porosity reduction due to secondary phase precipitation is likely to occur in a narrow layer adjacent to the fracture-matrix interface**, the thickness of which will be dictated by the rate of supply of reactants to the fracture surface.

Key outcomes. 1) Our models are able to reproduce reaction rates of certain minerals in our experiments quite well. 2) Intriguingly, the agreement between experimental and model-predicted aqueous Fe behavior remains poor. This highlights the complexity of the Fe dynamics in these environments, and reinforces the importance of careful reactive transport model calibration and development; our best approximation based on reaction rate laws reported in the literature is insufficient to capture reaction progress in the complex shale-fracture fluid system. This is attributed in part to the dearth of information regarding chemical interactions between organic hydraulic fracture fluid additives and inorganic minerals. The specific mismatch between modeled and experimental results will provide insight as to how these fracture fluid additives alter reaction progress relative to that predicted based on known thermodynamic and kinetic constraints. 3) Speciation calculations reveal that the presence and type of Fe-bearing precipitates formed will be strongly dependent on the initial composition of the shale, in particular the abundance of carbonate minerals.

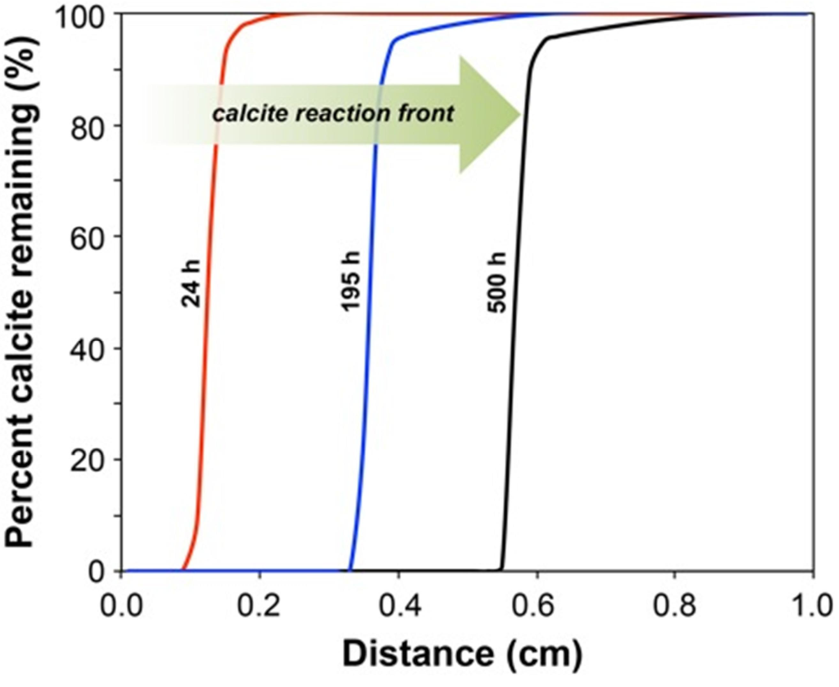


Figure 12. Modeled calcite dissolution reaction front propagation for Barnett shale using preliminary experimentally calibrated reaction rates. The vertical “jump” in each curve gives the physical location of the reaction front along a 1-dimensional transect in a model shale. The front gives the location where calcite content drops from 100 to 0% across a very narrow distance. This sharp demarcation of the reaction front indicates that the rate of reaction front propagation is limited by the rate of transport of reactants and products to and from the reaction front. That is, upon arrival of reactants to the calcite surface, the mineral dissolves rapidly.

Manuscript plans. The geochemical modeling will be included in manuscripts generated with results from Task 2 (aqueous Fe oxidation experiments) as well as Task 4 (bulk shale-fracture fluid interactions). A poster on this subject was presented at the 2015 SSRL users meeting and another will be presented at the upcoming American Geophysical Union 2015 Fall Meeting in December (*cf.*, Appendix A, Harrison et al.).

Table 5. Heterogeneous kinetic reactions included in geochemical models.

Primary minerals	
Mineral	**Reaction**
Quartz	$SiO_2 \rightarrow SiO_{2(aq)}$
Microcline	$KAlSi_3O_8 + 4H^+ \rightarrow Al^{3+} + K^+ + 2H_2O + 3H_2O$
Albite	$NaAlSi_3O_8 + 4H^+ \rightarrow Al^{3+} + Na^+ + 2H_2O + 3H_2O$
Calcite	$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$
Dolomite	$CaMg(CO_3)_2 + 2H^+ \leftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$
Siderite	$FeCO_3 + H^+ \leftrightarrow Fe^{2+} + HCO_3^-$
Pyrite	$FeS_2 + H_2O \rightarrow 0.25H^+ + 0.25SO_4^{2-} + Fe^{2+} + 1.75HS^-$
Chlorite (Mg,Fe)	
Clinochlore	$Mg_5Al_2Si_3O_{10}(OH)_4 + 16H^+ \leftrightarrow 2Al^{3+} + 3SiO_{2(aq)} + 5Mg^{2+} + 12H_2O$
Daphnite	$Fe_5Al_2Si_3O_{10}(OH)_4 + 16H^+ \leftrightarrow 2Al^{3+} + 3SiO_{2(aq)} + 5Fe^{2+} + 12H_2O$
Illite	$K_{0.6}(H_3O)_{0.4}Al_{1.3}Mg_{0.3}Fe_{0.1}Si_{3.5}O_{10}(OH)_2 \cdot H_2O + 8H^+ \leftrightarrow 0.25Mg^{2+} + 0.6K^+ + 2.3Al^{3+} + 3.5SiO_{2(aq)} + 5H_2O$
Kaolinite	$Al_2Si_2O_5(OH)_4 + 6H^+ \leftrightarrow 2Al^{3+} + 2SiO_{2(aq)} + 2H_2O$
Secondary minerals	
Mineral	**Reaction**
$Fe(OH)_3$	$Fe(OH)_3 + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O$
Goethite	$FeO(OH) + 3H^+ \leftrightarrow Fe^{3+} + 2H_2O$
Gypsum	$CaSO_4 \cdot 2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$
Jarosite	$KFe_3(SO_4)_2(OH)_6 + 6H^+ \leftrightarrow K^+ + 2SO_4^{2-} + 3Fe^{3+} + 6H_2O$
$SiO_{2(am)}$	$SiO_{2(am)} \leftrightarrow SiO_{2(aq)}$
Gibbsite	$Al(OH)_3 + 3H^+ \leftrightarrow Al^{3+} + 3H_2O$

4. RISK ANALYSIS

Task 1. Project management plan

Summary description: The Recipient shall work together with the NETL project manager to maintain and update the project management plan (PMP) originally submitted at FWP approval (and formatted in accordance with the guidance provided by NETL).

Project management risks: Post-doctoral departures mid-term, increased risk from short-duration of project, and user facility access risks.

Project resource limitation risks: publication risk

Mitigation:

(i) *Publication risk*. Time was not allocated in the original project scope to write manuscripts because 18-months were required to complete the experimental effort. For this reason, we are requesting a no-cost extension of the project.

Publication risk is a concern because it undermines recruiting and retention efforts and decreases the scientific stature of the home institution and funding agency. Additional risks to publications include (a) departures of post-doctoral fellows prior to completion of manuscripts, (b) failure to complete experiments on the proposed timeline, and (c) insufficient quality of experimental results for publication.

Mitigation: Request no-cost extension of project to end of FY2016. In addition, to address (a), post-doctoral scholars are presently outlining the intended manuscripts and experiments and data collection are being specifically targeted to fill gaps in the current data set to allow for manuscripts to be written. In addition, writing of manuscripts is scheduled to begin prior to the end of the project timeline (and post-doctoral departures) in order to maximize the amount of writing completed while the project is still active and the research group is intact. To address (b), the experimental plan has been refined such that only the key experiments required to produce the desired manuscripts will be conducted (*e.g.*, pure mineral experiments were excluded from Task 2). Moreover, the majority of the planned experiments has either been completed, or is already underway. Finally, to address (c), analysis of the experimental results has been ongoing throughout the project to ensure that the data produced is of value, and the experimental designs are sufficient to produce the necessary quality of data. For example, the experimental design for Task 4 experiments has been altered in order to better constrain the O_2 available for reaction. The coincidence of experiments and analysis permits rapid adjustment of experimental protocols to ensure the data produced are relevant and of good quality.

(ii) *Post-doctoral departures mid-term*. Post-doctoral researchers may depart the project mid-term, creating new recruiting needs and pushing back critical path.

Mitigation: (a) maintain communication with post-doctoral researchers to discover departures as soon as possible, (b) initiate recruiting efforts as soon as possible to fill vacancies, (c) redirect graduate students and remaining staff to maintain critical-path progress during vacancies.

(iii) *Increased exposure to risks in (i) due to short project duration.* The short project duration decreases the time available to respond to the above risk. *Mitigation*: (a) Emphasize initial planning, (b) Emphasize project management for on-time progress, and (c) actively prioritize experimental plans to target most promising research directions.

(iv) User facility access risk. Obtaining access to user facilities such as ALS (advanced light source) requires long lead-times, typically 6 months. *Mitigation*: (i) leverage existing facility access proposals on other projects to initiate measurements at user facilities, (ii) use alternative characterization techniques if necessary.

Task 2. Fe(II) and bitumen reactions with fracture-fluid

Summary description: Research for this task has been refocused on assessing rates of aqueous Fe(II) oxidation in the presence of hydraulic fracture fluid additives and the bitumen inherent to the shales. Preliminary results demonstrate that the combination of bitumen and hydraulic fracture solution can accelerate Fe(II) oxidation compared to solutions lacking these organics. As the kinetics of aqueous Fe oxidation is one of the main unknowns in the reaction network, which hinders modeling and prediction of reaction progress, these experiments are viewed as a key step towards better understanding the controls on reactions in these environments. Mineral reaction kinetics are comparatively better understood.

Technical risks: Oxidation reactions in experiments lacking organic constituents will be too slow to quantify on a reasonable experimental time scale.

Mitigation: Reported values for Fe(II) oxidation in solutions lacking organic constituents under abiotic conditions will be compiled and an expected rate for the experimental pH will be extrapolated.

Task 3: Kerogen-fracture fluid interactions

Summary description: High purity kerogen will be isolated from Marcellus and Green River shales. The isolated kerogen will be reacted with fracture fluid for varying lengths of time following the procedure described in Task 2.

Technical risks: (a) Failure to isolate high-purity kerogen from Marcellus shale due to low initial abundance in bulk shale and high proportion of pyrite, a largely recalcitrant phase. In such a case, the metal release data from the experiments for the Marcellus kerogen will not be useful, due to contributions from the incompletely removed pyrite. (b) Delays during the isolation procedure will inhibit manuscript preparation, as the planned manuscript will contrast the behavior of Green River versus Marcellus shale.

Mitigation: (a) To remove pyrite, we will use a ZnCl2 density separation method, which will not damage organics. In any case, useful data can still be collected with respect to changes in organic functional groups and thus wettability of the kerogen. Thus, in the event of poor isolation procedures, the manuscript will focus primarily on differences in the behavior of organics between the two kerogen types, and metal release from the Green River only. (b) To avoid delays, prioritize the isolation activities.

Task 4: Whole shale-fracture fluid interactions

Summary description: This module investigates the impact of fracture fluids on whole shales with emphasis on identifying the key reactions that could driving porosity/permeability changes and metal release.

Technical risks: Insufficient abundance of secondary Fe-bearing precipitates to analyze.

Mitigation: Geochemical modeling of aqueous chemical data collected during the experiments will allow assessment of the secondary phases that are most likely to have precipitated in the experiments. This modeling coupled with morphological information collected using SEM will help narrow down the types of precipitates that may be present even if they cannot directly be analyzed using XRD or FTIR.

Task 5: Uranium-fracture fluid interactions

Summary description: A subset of the unreacted and reacted shale samples produced in task 4 will be analyzed by sequential extraction to identify the specific mineral hosts in the shale and evaluate the risks of release based on observed reaction rates of these host minerals.

Technical risks: Sequential extractions may not produce sufficient U concentrations to unambiguously identify mineral hosts for U.

Mitigation: Use data published in the literature on Marcellus shale from different locations that details the typical proportions of U hosted in specific mineral phases (*e.g.*, Phan et al., 2015).

Task 6: Geochemical modeling to describe interactions between fracture fluid and shale

Summary description: A geochemical model will be developed to describe interactions between the key components of fracture fluid and shale. Researchers will develop and evaluate a thermodynamic database with components representative of those found in fracture fluid. Forward models of experiments assisted researchers in evaluating the optimal conditions for the experiments (initially) as well as the kinetics and equilibrium points. Ultimately, the calibrated model can be used to evaluate 2-D and 3-D representations of fractured shale in order to make predictions about the coupling between redox reactions, uranium transformations and transport of fracture fluids. The model will be evaluated and calibrated using the experimental data providing a platform for future work linking transport and geochemical processes.

Technical risks: The occurrence of numerous coupled reactions numerous and the complex composition of shales and fracture solutions may impede determination of unique solutions to describe reaction paths.

Mitigation: Experiments in Task 2 have been refocused to ascertain rates of aqueous Fe(II) oxidation/Fe(III)-bearing precipitate formation in the presence of bitumen and both organic and inorganic fracture fluid additives. Incorporation of these experimentally determined rates will help minimize the number of tunable parameters in the models, permitting development of more unique solutions, and thus more robust predictive capability.

5. MILESTONE STATUS

Activity and milestones	Verification method†	Planned Milestone Date	Actual completion or status*
Task 1. Project management			
Development of PMP	D	10-1-14	10-1-14
Quarterly research performance reports	D	8-30-15‡	8-30-15
Annual research performance report	D	10-31-15	--
Final technical report	D	5-15-16	--
Task 2.			
Isolation of bitumen	C	4-30-15	3-31-15
Develop model fracture fluid recipe	D	1-15-15	1-15-15
Reaction of Fe(II) solution with hydraulic fracture solution	C	10-15-15	10-20-15
Reaction of Fe(II) with hydraulic fracture solution and/or bitumen	R	3-31-16	To start Q5
Characterization of alterations to bitumen and hydraulic fracture solution during Fe(II) oxidation	FTIR	3-31-16	To start Q5
Characterization of Fe reaction products	XRD, FTIR	3-31-16	To start Q5
Complete initial draft of Fe(II)-bitumen manuscript	M	7-31-16	To start Q5
Submission of Fe(II)-bitumen manuscript	M	9-30-16	To start Q7
Task 3.			
Isolation of kerogen from Green River (GR) shale	K	4-30-15	3-31-15
Completion of short-term fluid- GR kerogen reactions	C	6-30-15	6-16-15
Completion of intermediate-term GR kerogen reactions	SS, G	8-31-15	9-3-15
Isolation of kerogen from Marcellus shale	S	9-30-15	In Progress
Completion of long-term GR kerogen fluid-kerogen reactions	SS, G	11-30-15	In progress
Completion of short-term fluid- Marcellus kerogen reactions	C	12-15-15	To start Q5
Characterization of samples, solute data	So, XPS, SEM, EDS	3-31-16	In progress
Complete initial draft of kerogen reactivity manuscript	M	9-30-16	To start Q7
Tasks 4 and 5.			
Initial characterization of shales	XRD, XRF	4-30-15	3-31-15
Initial short (2 week) reaction with HCl-only	S	4-30-15	3-31-15
Analysis of reaction products from initial reaction	So	4-30-15	3-31-15
Completion of short-term fluid-shale reactions	So, XPS, SEM, EDS	6-30-15	6-16-15
Completion of short-term fluid-shale reactions with closed headspace	S	10-31-15	In Progress
Completion of intermediate-term reactions	SS, G	8-31-15	9-3-15
Completion of long-term fluid-shale reactions	SS, G	11-30-15	In progress
Characterization of shale samples, solute data	So, XPS, SEM, EDS	3-31-16	In progress
Characterization of uranium samples	R	3-31-16	To start Q5
Complete initial draft of manuscript	M	2-1-16	To start Q5
Submission of manuscript	M	3-31-16	To start Q6

Task 6.			
Complete initial modeling for experiment design	P	1-31-15	1-31-15
Completion of numerical experiments	P	12-31-15	In progress
Evaluate models against experimental data	P	12-31-15	In progress
Complete initial draft of manuscript	M	2-1-16	To start Q5
Submission of manuscript	M	3-31-16	To start Q6

[†] Verification methods: D**,** Documentation provided to project managers; S, Samples harvested; C, complete; R, characterization results in-hand; K, extracted kerogen available; P, simulation results plotted; XRD, X-ray diffraction data collected; XRF, X-ray fluorescence data collected; SEM, scanning-electron microscopy data collected; SS, solute samples collected; So, solute data collected; G, gas samples collected; XPS, X-ray photoelectron spectroscopy data collected; EDS, energy dispersive spectroscopy data collected; M, manuscript in-hand.

* Status as of Oct 30, 2015.

[‡] Future quarterly report dates: in 2015: Oct 30; in 2016: Jan 30

6. SCHEDULE STATUS

As described above, we are (re)focusing our research activities on measurements that are required for the manuscripts in order to be successful in publishing papers. Consequently, we are strategically reducing scope in areas of the project that do not contribute to these manuscripts, notably in Task 2.

As noted in Section 4 (Risk Analysis), the original 18-month scope of the project does not leave time to complete manuscripts writing, revision, and submission. We are requesting a no-cost extension of the project through the end of FY2016 to provide time to complete these critical subtasks.

The project management plan and milestone log have been update to include manuscript writing and submission goals.

Other significant changes are as follows:

(ii) Task 2. As described in Section 3, the pure-mineral/fracture fluid reactions have been removed from the project management plan in order to allocate resources to investigate the impacts of organic fracture additives and bitumen on the kinetics of aqueous Fe(II) oxidation. The aqueous experiments are of short duration (<1 week), and can therefore easily be conducted within the timeframe of the project. A manuscript-writing subtask has been added to the project.

(iii) Task 3. A manuscript-writing subtask has been added to the project.

(iv) Task 4. and Task 6. A new set of reactors will be initiated using improved seals and O_2-bearing headspace in order to study shale-fracture fluid reactions in closed headspaces, which will allow oxygen to be consumed throughout the experiment due to reaction with shale minerals, and permit better constraint on the evolving redox conditions in the reactors. These reactors are also more representative of conditions expected at field scale. A manuscript-writing subtask has been added to the project.

The postdoctoral leading the modeling effort and in charge of writing the manuscript for this task will formally leave the project on Dec 31, 2015. She will continue to work on this manuscript under fellowship funding provided by NSERC (Canada).

(v) Task 5. In order to evaluate the source of U released into solution, sequential extractions of the Marcellus shale will be conducted to identify the mineral hosts for U in the initial materials and reconcile observed trends in U release with reaction rates of specific minerals.

Project timeline from the Project Management Plan. “M” denotes milestones.

Task	Title	Month of project																							
					2015												2016								
		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								
	Annual progress reports													■ M											
	Final technical report																		■ M						
	Ongoing project management	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■						
2	Mineral-fracking fluid																								
2.1	Initial characterization (XRD)	■	■	■	M																				
2.2	Develop model fracking fluid	■	■	■																					
2.3	Aqueous Fe(II) oxidation experiments													■	■	M									
2.4	Characterization														■	■	■	M							
2.5	Draft manuscript															■	■	■	■	■	■	■	M		
2.6	Manuscript submission																						■	■	M
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																				■	■	■	■	M
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								■	■	M														
4.5	Short-term experiments with closed headspace (Ar and O2)												■	■	■	M									
4.6	Intermediate-term experiment							■	■	■	■	M													
4.7	Long-term experiment							■	■	■	■	■	■	■	■										
4.8	Characterization									■	■	■	■	■	■	■	M								
4.9	Draft manuscript														■	■	■	M							
4.1	Manuscript submission																	■	■	M					
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 experiments with closed headspace (Ar and O2)												■	■	■	M									
5.6	Intermediate-term experiment							■	■	■	■	M													
5.7	Long-term experiment							■	■	■	■	■	■	■	M										
5.8	Sequential extractions															■	■								
5.9	Characterization									■	■	■	■	■	■	■	■	■	M						
5.1	Draft manuscript														■	■	■	M							
5.11	Manuscript submission																	■	■	M					
6	Modeling																								
6.1	Define reactions, Evaluate Thermo data	■	■																						
6.2	Initial numerical experiments for experiment design		■	■	M																				
6.3	Numerical experiments and sensitivity analysis							■	■	■	■	■	■	■	■	■	M								
6.4	Evaluate models against data										■	■	■	■	■	■	■	■	M						
6.5	Draft manuscript														■	■	■	M							
6.6	Manuscript submission																	■	■	M					

7. COST STATUS

Cost Plan/Status

asesline Reporting Quarte		Year 1	Start: 9/1/14 End: 9/3			Year 2	Start: 10/1/14 End: 9/30/15			Year 3	Start: 10/1/15 End: 3/31/16		
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Baseline Cost Plan													
Federal Share	Task 1					$ 2,709	$ 3,195	$ 4,744	$ 14,453	$ 8,846	$ 8,846	$ 8,846	$ 8,846
	Task 2					$ 5,743	$ 6,773	$ 10,058	$ 30,641	$ 14,941	$ 12,105	$ 12,105	$ 12,105
	Task 3					$ 4,931	$ 5,815	$ 8,635	$ 26,305	$ 10,292	$ 10,292	$ 10,292	$ 10,292
	Task 4					$ 5,743	$ 6,773	$ 10,058	$ 30,641	$ 12,165	$ 12,165	$ 12,165	$ 12,165
	Task 5					$ 5,743	$ 6,773	$ 10,058	$ 30,641	$ 12,165	$ 12,165	$ 12,165	$ 12,165
	Task 6					$ 2,221	$ 2,620	$ 3,890	$ 11,852	$ 5,964	$ 5,964	$ 5,964	$ 5,964
Non-Federal Share													
Total Planned Costs (Federal and Non-													
Cumulative Baseline Cost		$ -	$ -	$ -	$ -	$ 27,091	$ 59,040	$106,484	$251,017	$315,390	$376,927	$438,464	$500,000
Actual Incurred Costs													
Federal Share	Task 1					$ 2,709	$ 3,195	$ 4,744	$ 14,453				
	Task 2					$ 5,743	$ 6,773	$ 10,058	$ 30,641				
	Task 3					$ 4,931	$ 5,815	$ 8,635	$ 26,305				
	Task 4					$ 5,743	$ 6,773	$ 10,058	$ 30,641				
	Task 5					$ 5,743	$ 6,773	$ 10,058	$ 30,641				
	Task 6					$ 2,221	$ 2,620	$ 3,890	$ 11,852				
Non-Federal Share													
Total Incurred Costs - Quarterly													
Cumulative Incurred Cost		$ -	$ -	$ -	$ -	$ 27,091	$ 31,949	$ 47,444	$144,533	$ -	$ -	$ -	$ -
Variance													
Federal Share	Task 1	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ 8,846	$ 8,846	$ 8,846	$ 8,846
	Task 2	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ 14,941	$ 12,105	$ 12,105	$ 12,105
	Task 3	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ 10,292	$ 10,292	$ 10,292	$ 10,292
	Task 4	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ 12,165	$ 12,165	$ 12,165	$ 12,165
	Task 5	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ 12,165	$ 12,165	$ 12,165	$ 12,165
	Task 6	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ 5,964	$ 5,964	$ 5,964	$ 5,964
Non-Federal Share		$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Total Variance - Quarterly		$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Cumulative Variance		$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ 64,373	$125,910	$187,446	$248,983

Collaborative Leveraging. The project effort is being supported by 2 collaborating postdoctoral fellows (Andrew Kiss, and Arjun Kohli, SLAC), and 3 graduate students in the groups of Gordon Brown and Kate Maher (Stanford): Megan Dustin, Claresta Joe-Wong, and Dana Thomas. We also have unfunded collaborations with Dr. Mark Zoback (Stanford) and Dr. Tracy Bank (University at Buffalo).

8. CONCLUSIONS

We have performed a series of novel experiments in which isolated kerogen, Fe(II), or whole shales were reacted with fracture fluid of varied composition, providing unprecedented new views of geochemical reactions occurring between shale and fracture fluids. Overall reaction progress was found to be strongly dependent on shale mineralogy. Carbonate-rich shales (Eagle Ford and Green River) rapidly buffered solution pH from acidic to near-neutral values (*i.e.*, to pH ~7). In contrast carbonate-poor, clay-rich shales (Marcellus and Barnett) experienced total near-depletion of carbonate and incomplete restoration of pH, leaving pore waters in the acidic range. The status of pH is critical to subsequent system behavior, as pH was found to be a master variable (**Figure 13**). Lower pH encourages further dissolution of silicate minerals, and release of U(VI) and Fe(II), but inhibits precipitation of Fe(III) oxyhydroxides and secondary aluminosilicate phases. In contrast, at near-neutral pH, organic fracture fluid additives and bitumen enhance oxidation of aqueous Fe(II), leading to precipitation as Fe(III)-(oxy)hydroxides. Preliminary experiments indicate this may be an indirect effect due to greater bitumen extraction from the shales in the presence of the organic fracture fluid additives.

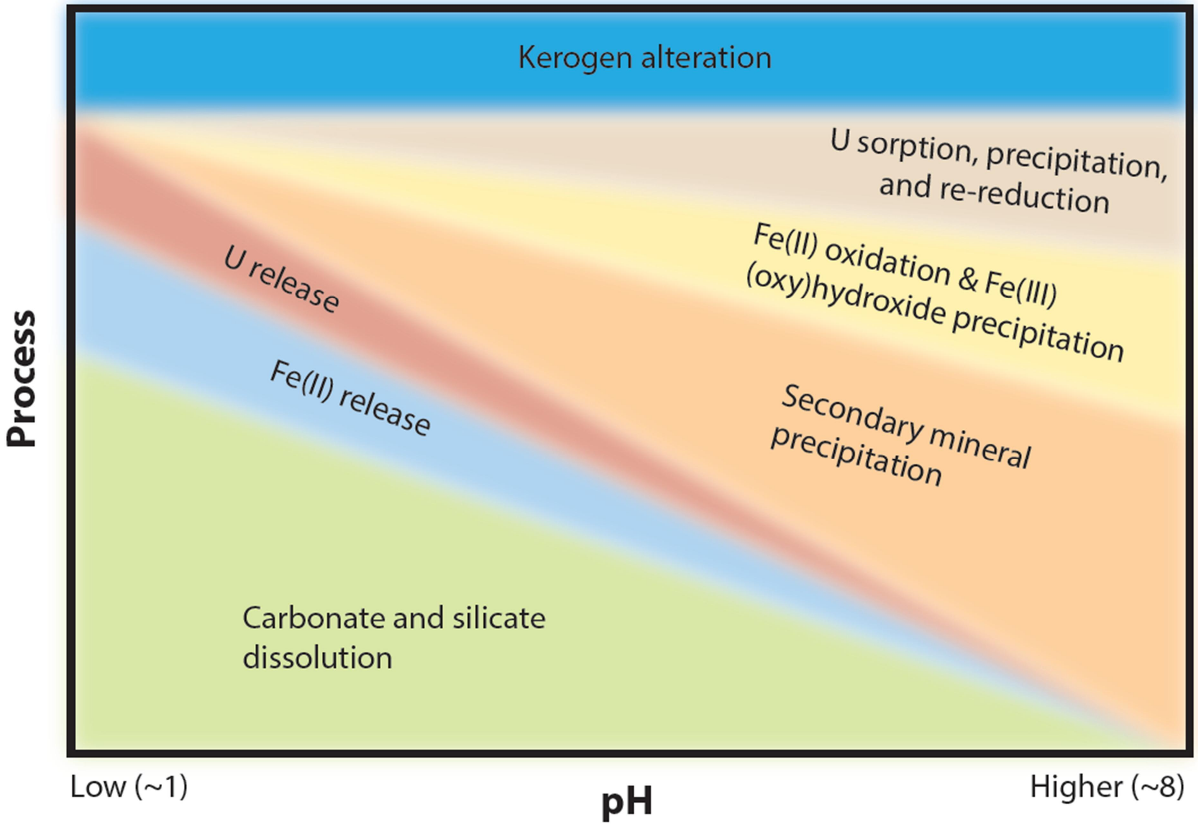


Figure 13. Effect of pH on relative importance of geochemical processes (vertical axis) occurring when shale comes into contact with fracture fluid. At low pH, geochemical reactions are dominated by dissolution and metal release. At near-neutral pH, mineral precipitation and Fe(II) oxidation are important. Kerogen alteration occurs at all pH values.

Uranium (U) is released following exposure to fracture fluids, driven most strongly by the low pH conditions caused by hydrochloric acid. It is hypothesized that the U release is attributable to dissolution of carbonates. Sequential extractions to identify the mineral-hosts of U in the shales are planned to confirm the source of the released U.

Although kerogen is typically considered relatively unreactive, a significant amount of metal release from isolated kerogen was observed. In addition, observed changes in organic functional groups using FTIR and N release to solution indicate that N-containing functional groups were altered by exposure to fracture fluids. The alteration of organic functional groups is likely to affect shale wettability and thus alter transport of both hydrocarbons and hydraulic fracture fluid in the subsurface.

Imaging using scanning electron microscopy and X-ray micro- and nano-computed tomography, in addition to pore size distributions determined with gas adsorption all indicate that shale porosity is altered following interaction with hydraulic fracture fluids. In particular, selective dissolution of carbonate minerals generates porosity at the fluid-shale interface. However, the observation of secondary phases in the reactor experiments indicates that porosity clogging is possible, depending on the spatial distribution of these reactants in the subsurface. This alteration of porosity at the fluid-shale interface is likely to strongly influence transport of hydrocarbons and contaminants.

APPENDIX A. Deliverables

*Conference poster presentations (*presenting author)*

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.