**Characterization of Marcellus Shale and Huntersville Chert before
and after exposure to hydraulic fracturing fluid via feature
relocation using field-emission scanning electron microscopy**

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ABSTRACT

Two sets of experimental *in situ* fluid-rock interaction studies were implemented to understand the interactions between hydraulic fracturing fluid and rocks of the Marcellus shale gas play. Marcellus Shale and Huntersville Chert core samples were exposed to synthetically prepared fracturing fluid and recycled fracturing fluid from the field, respectively, and examined before and after *in situ* exposure using surface relocation techniques via high-resolution field-emission scanning electron microscopy (FE-SEM) to investigate chemical or physical alterations.

Results indicate that *in situ* pressure promoted fracture growth along the sedimentological (horizontal) bedding plane of the Marcellus Shale samples. Moreover, calcium carbonate (CaCO_3) dissolution was observed and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) appeared to precipitate both on the surface and in the numerous fractures. Barite (BaSO_4), strontianite (SrCO_3), celestine (SrSO_4), and apatite (CaPO_4) formed a unique pattern of precipitates on the surface of the Huntersville Chert samples. Additionally, Rhenium and rare earth element (REE) Europium were identified in minerals which precipitated on the Huntersville Chert surface identified by FE-SEM spectral analysis.

1.0 INTRODUCTION

The Appalachian Basin covers numerous states in eastern North America including New York, Pennsylvania, Ohio, Maryland, West Virginia, Kentucky, Tennessee, and Alabama. Overall, the Appalachian Basin as a whole covers an aerial extent of 185,500² miles, is 1,075 miles long, and ranges from 20 to 310 miles wide (Ryder, 1995). The hydrocarbon bearing Marcellus Shale Formation located within the Appalachian Basin spans 600 linear miles (Coleman et al., 2011). The less laterally extensive Huntersville Chert formation is located in west-central Pennsylvania within the Appalachian Basin and underlies the Marcellus Shale Formation (Harper, 1999). In order to access the hydrocarbons stored in the Marcellus Shale directional drilling and hydraulic fracturing is implemented.

Hydrocarbon exploration of the Marcellus Shale has resulted in over 12,000 permitted wells in Pennsylvania between 2005 and 2012 (Vidic et al., 2013). According to Vidic et al. (2013) these 12,000 wells produced between < 0.1 and > 20 million cubic ft/day of natural gas. Importantly, the Marcellus Shale can sustain the United States natural gas demand for approximately 15 years if usage remains the same at 23 trillion cubic ft/year (Soeder and Kappel, 2009). Due to the increase in drilled wells and high volumes of fluid utilized during hydraulic fracturing, experimental studies are required to determine whether chemical and physical alteration of Marcellus Shale and confining geologic formations occurs as residual fracturing fluid remains in the subsurface. Marcellus Shale well stimulation which utilizes a component of recycled flowback water can benefit from understanding the chemical and physical effects of fluid-rock interactions. For instance, determining alterations caused by the stimulation process with a recycled fluid component in Marcellus Shale production may improve fracturing fluid recipes based upon well-specific geochemistry to maximize hydrocarbon production.

Hydraulic fracturing of geologic formations has been utilized for the production of hydrocarbons across the United States since the 1940s (King, 2012). Modern hydraulic fracturing techniques are applied to both vertical and horizontal wells, with the majority being unconventional horizontal wells in tight organic-rich shale formations such as the Marcellus and Utica Shales of the Appalachian Basin in the northeastern United States. In order to successfully hydraulically fracture one horizontal Marcellus Shale well for hydrocarbon production, between 2 and 7 million gallons of water is required (Hayes, 2009).

Horizontal well stimulation of the hydrocarbon bearing Appalachian Basin Middle Devonian Marcellus Shale involves large volumes of hydraulic fracturing fluid that interacts with formation water and mineral surfaces within the subsurface (Pagels et al., 2013; Engelder et al., 2014). During stimulation, between 47 - 91% of the fracturing fluid remains in the subsurface

while 9 – 53 % returns out of the wellbore as flowback water (Energy Information Administration, 1993; Vidic et al., 2013). Fracturing fluid remaining in the subsurface can possibly alter petrophysical characteristics including surface area, porosity, and mineralogy of the host formation that may inhibit hydrocarbon permeability (Pagels et al., 2013). Captured flowback water is typically recycled into additional fracturing fluid for well stimulation (Rassenfoss, 2011; Boschee, 2014). Fracturing fluid is created by mixing high volumes of water with additives such as biocides, friction reducers, and proppants. The fluid is subsequently forced downhole under high pressure and into the target geologic formation. Once the target formation has been hydraulically stimulated, the fracturing fluid can return to the Earth's surface as flowback water for containment, but a portion of the fracturing fluid remains in the subsurface. On average 10 % of the fracturing fluid used to stimulate a horizontal Marcellus Shale well returns as flowback (Vidic et al., 2013), which means millions of gallons of fluid remain in the subsurface. The chemical and physical effects of the fracturing fluid remaining in the subsurface is uncertain, although shale absorption of the fluid through imbibition is one proposed hypothesis (Pagels et al., 2013; Engelder et al., 2014).

Flowback water from Marcellus Shale wells represents an environmental concern due to high salinity, total dissolved solids (TDS), and leachates from naturally occurring radioactive material (NORM) (Hayes, 2009; Dresel and Rose, 2010; Blauch et al., 2010; Chapman et al., 2012; Haluszczak et al., 2013; Capo et al., 2014; Soeder et al., 2014a). As a result of the complex chemistry and environmentally hazardous nature of flowback water, costly treatment was previously conducted via transportation to waste water facilities capable of handling high TDS fluids. Currently, service companies are recycling the flowback water for subsequent well stimulation (Rassenfoss 2011; Boschee, 2014). This process of utilizing recycled fluid for hydraulic fracturing requires additional research to understand the effect of elevated TDS fluids on the target formation.

The objective of this study was to identify chemical and physical alterations of solid core from the Marcellus Shale and Huntersville Chert (Onondaga Limestone) after interaction with fracturing fluid, as determined via feature relocation using field emission – scanning electron microscopy (FE-SEM). Both short-term (effects of fracturing fluid initially entering the subsurface) and long-term (effects of fracturing fluid remaining in the subsurface) scenarios were examined. Investigating fluid impact on Huntersville Chert in addition to the Marcellus was performed because Marcellus Shale wells in Pennsylvania are commonly drilled through a segment of the underlying chert/limestone in order to acquire “conservation well” status. Therefore, Huntersville Chert underlying the Marcellus Shale can be exposed to hydraulic fracturing fluid during well stimulation. Experiments were conducted to determine whether the rock structure changes upon interaction with fracturing fluid via mineral dissolution, precipitation, or chemical etching. This study also aimed to characterize chemical precipitates which formed during fluid contact.

2.0 MATERIALS AND METHODS

2.1 ROCK

Rock core utilized during this experiment was retrieved in September 2008 from a well site located in Greene County, Pennsylvania (Chan and Sharma, 2016). The main core sample was stored under atmospheric conditions until 2014. Subset samples of Marcellus Shale and Huntersville Chert were collected from the middle of the core in order to remove material directly in contact with the atmosphere. The samples were then immediately placed inside a nitrogen dessicator to prevent atmospheric alteration. Throughout the experiments utmost care was taken to limit atmospheric exposure of the rock samples.

2.1.1 *Marcellus Shale*

The Marcellus Shale sample was obtained from a depth of 7,801 ft (2378 m) and is classified as a grayish black shale. The shale was split into two pieces with a Buehler IsoMet low speed rock saw with a diamond blade. The samples were only exposed to the atmosphere long enough for cutting and analysis to take place. For storage between analyses the samples were placed in a nitrogen desiccator. One piece of the core was cut parallel to the sedimentary bedding plane denoted as “Marcellus Shale parallel cut” (Figure 1), and the second piece was cut transverse to the sedimentary bedding plane to expose an edge-on facies denoted as “Marcellus Shale transverse cut” (Figure 2). Cutting the core sample into two bedding planes allowed detailed electron microscopy studies to be conducted for both mineralogical surface orientations which encounter fracturing fluid during stimulation. Both Marcellus Shale samples had the internal rock face polished to allow for higher resolution FE-SEM images. For the parallel and transverse samples, 5 locations were captured per sample via FE-SEM (10 sites in total).

Figure 1: Marcellus Shale parallel cut core sample prior to FE-SEM initial characterization (3.40 grams).

Figure 2: Marcellus Shale transverse cut core sample prior to FE-SEM initial characterization (6.97 grams).

2.1.2 *Huntersville Chert (Onondaga Limestone)*

The Huntersville Chert sample (Figure 3) was obtained from a depth of 7,909.7 ft (2,410 m) and is classified as a dark gray calcareous/argillaceous chert. The chert was split into two pieces with a Buehler IsoMet low speed rock saw with a diamond blade. The samples were only exposed to the atmosphere long enough for cutting and analysis to take place. For storage between analyses the samples were placed in a nitrogen desiccator. One piece of the core was cut parallel to the sedimentary bedding plane and the second piece was cut transverse to the sedimentary bedding plane to expose an edge-on facies. Cutting the core sample into two bedding planes allowed detailed electron microscopy studies to be conducted for both mineralogical surface orientations. Both Huntersville Chert samples had the internal rock face polished to allow for higher resolution FE-SEM images and 5 locations per sample were captured via FE-SEM (10 sites in total).

Figure 3: Huntersville Chert parallel cut core sample (left) and transverse cut core sample (right). These images were taken after fluid-rock interaction with recycled fracturing fluid.

2.2 FRACTURING FLUIDS

Two fracturing fluids were used during this study (1) a synthetic fracturing fluid for the Marcellus Shale experiments and (2) a field collected recycled fracturing fluid for the Huntersville Chert experiments. The Huntersville Chert experiments were conducted first and resulted in a layer of sulphate precipitate the rock surface, which obscured FE-SEM re-analysis. As our study aimed to investigate physical changes to the rock surface before and after fluid contact, we created a synthetic fracturing fluid leaving out sulphate and barium in order to leave the Marcellus Shale's rock surface unobscured for FE-SEM analysis.

2.2.1 Synthetic Fracturing Fluid

Synthetic fracturing fluid was used for Marcellus Shale fluid-rock interaction. The recipe is detailed in Table 1. The chemical composition of the synthetic fracturing fluid was modeled by Liu (2013) after analyzing samples of fracturing fluids collected from a well site in Greene County, Pennsylvania (samples were collected by the U.S. Department of Energy) seen in Table 2. Three separate fracturing sites were sampled from the well-pad to provide average elemental concentrations for the synthetic fluid after inductively coupled plasma – optical emission spectroscopic (ICP-OES) and ion chromatographic (IC) analysis by Liu (2013).

Reagent grade salts and deionized water (Thermo Barnstead E-Pure system) were combined to generate 2 liters (L) of the synthetic fracturing fluid with a pH of 5.7. Salts used were calcium chloride dehydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), sodium chloride (NaCl), potassium chloride (KCl), strontium chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$), sodium bromide (NaBr), sodium bicarbonate (NaHCO_3), sodium sulfate (Na_2SO_4). Br^- is not an additive in hydraulic fracturing fluid, but was added in the form of NaBr as microgram quantities of Br^- have been observed in Marcellus Shale leaching experiments and can potentially be removed from the shale during fluid-rock interaction (Stewart et al., 2015). The synthetic fracturing fluid was stored in a Nalgene bottle and placed inside a nitrogen desiccator prior to use in order to prevent atmospheric alteration. Comparison of the Liu (2013) field collected fracturing fluid to this study's lab synthesized fluid can be seen in Table 2.

Component	Target conc. of comp., mg/L	Salt	Mass of salt added, g	Atomic Mass of comp., g/mol	Molecular wt. of salt, g/mol	Moles of Salt	Moles of comp. added	Mass of comp. added, g	Volume of solution, L	Comp. conc., mg/L
Ca ²⁺	2,100	CaCl ₂ *2H ₂ O	15.4028	40.08	147.02	0.1048	0.105	4.199	2	2,100
Mg ²⁺	200	MgCl ₂ *6H ₂ O	3.3468	24.31	203.27	0.0165	0.016	0.400	2	200
K ⁺	160	KCl	0.6114	39.10	74.55	0.0082	0.008	0.321	2	160
Na ⁺	7,260	NaCl	36.1755	22.90	58.44	0.6190	0.635	14.547	2	7,273
Sr ²⁺	200	SrCl ₂ *6H ₂ O	1.2184	87.62	266.65	0.0046	0.005	0.400	2	200
Br ⁻	140	NaBr	0.3613	79.90	102.89	0.0035	0.004	0.281	2	140
HCO ₃ ²⁻	260	NaHCO ₃	0.7166	61.02	84.01	0.0085	0.009	0.520	2	260
Cl ⁻	-	-	-	35.45	-	-	0.879	31.154	2	15,577
SO ₄ ²⁻	100	Na ₂ SO ₄	0.2965	96.06	142.04	0.0021	0.002	0.201	2	100
							Charge balance			TDS
							0.000			26,012
							pH	5.7		

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228 **Table 1:** The synthetic fracturing fluid (pH of 5.7) was created with the above salts mixed in 2 L of ultrapure water to replicate the

229 concentrations from recycled fracturing fluid collected in Greene County, PA. The final concentrations based on stoichiometric

230 calculations are reported in the far right column of this table.

Chemical Species	Fracturing Fluid from Greene Co., PA mg/L (used by Liu, 2013)	Synthetic Fracturing Fluid mg/L (this study)
Chloride (Cl ⁻)	15901	15577
Sodium (Na ⁺)	6607	7273
Sulfate (SO ₄ ²⁻)	811	100
Magnesium (Mg ²⁺)	219	200
Calcium (Ca ²⁺)	2207	2100
Potassium (K ⁺)	141	160
Bicarbonate(HCO ₃ ⁻)	-	260
Bromide (Br ⁻)	-	140
Strontium (Sr ²⁺)	441	200
pH	6.2	5.7

Table 2: Chemical species comparison between recycled fracturing fluid from Greene County, Pennsylvania determined by Liu (2013) via ICP-OES (left column) to synthetic fracturing fluid (right column, stoichiometric calculation) utilized during the Marcellus Shale experiment.

2.2.2 Recycled Fracturing Fluid

Recycled fracturing fluid¹, which contains formation water from previously stimulated Marcellus Shale wells was used directly for Huntersville Chert fluid-rock interaction. The fracturing fluid was stored in a Nalgene bottle inside a nitrogen desiccator to prevent atmospheric degradation. Elemental concentrations for recycled fracturing fluid collected from the same well as our fracturing fluid in Greene County, PA is seen in the left column of Table 2.

2.3 ROCK CHARACTERIZATION

2.3.1 Field emission – scanning electron microscopy (FE-SEM)

Characterization of the polished Marcellus Shale and Huntersville Chert samples was conducted on a FEI Quanta 600 FEG environmental – scanning electron microscope. The FE-SEM was equipped with energy dispersive X-ray spectroscopy (EDX). Although EDX does not identify mineral phases, relative abundance of elemental data was used to infer minerals present in shale and chert samples before and after fluid exposure. For each cut core of the Marcellus Shale and Huntersville Chert samples, 5 mineralogic sites were characterized (20 locations in total) via FE-SEM prior to fluid exposure. The 20 sites were then relocated after fluid-rock interaction and recharacterized. In order to relocate the initial image locations, detailed FE-SEM stage coordinates (X and Y positions) were noted in addition to capturing sequential wide field to high magnification images (e.g. magnification of 500x, 5,000x, and 10,000x) that aid in the relocation process (Kutchko et al., 2013). Both secondary electron and backscatter electron

¹ Recycled fracturing fluid was obtained by Rick Hammack of NETL from the blender on a well pad in Greene Co. Pennsylvania.

images were collected at a working distance of 10 mm and beam spot size of 4 with voltages of 10 kV and 20 kV to accommodate sample charging.

2.3.2 X-ray diffraction mineralogy

X-ray diffraction (XRD) characterization (Table 3) of the Marcellus Shale and Huntersville Chert core used in this study was performed to identify bulk rock mineralogy prior to fluid-rock interaction. XRD mineralogy of the Marcellus Shale identified quartz and illite as major minerals (> 25%); minor minerals were pyrite and chlorite (10-25%); and gypsum, calcite, and dolomite were trace minerals (< 10%). Huntersville Chert XRD contained quartz, calcite, and dolomite as major minerals (> 25%); minor mineral was illite (10-25%); and pyrite, microcline, and albite were trace minerals (< 10%).

Sample	Quartz	Muscovite/ Illite	Chlorite/ Clinocllore	Pyrite	Calcite	Dolomite	Gypsum	Microcline	Albite
Marcellus Shale	major	major	minor	minor	trace	trace	trace	-	-
Huntersville Chert	major	minor	-	trace	major	major	-	trace	trace

Major represents > 25 %
 Minor represents 10 to 25 %
 Trace represents < 10 %

Table 3: XRD mineralogy results of the Marcellus Shale and Huntersville Chert core samples utilized during this experiment represented as semi-quantitative weight percent. Major represents > 25%, minor represents 10 to 25%, and trace represents < 10%.

2.4 EXPERIMENTAL PROCEDURE

The two Marcellus Shale core samples were set inside separate 500 mL Teflon lined containers, submerged in 100 mL of synthetic fracturing fluid, and subjected to 4000 psi (27.6 MPa) and 77°C (based upon well logs) under an atmosphere of argon gas for 6 days (144 hours). Argon was selected as the autoclave atmosphere to reduce seal leaks and to serve as an inert environment. The experimental time of 6 days was chosen for the Marcellus Shale core samples to mimic short-term effects of fracturing fluid initially entering the subsurface. Temperature and pressure values were selected based upon *in situ* lithostatic pressure and temperature gradients from well completion reports for a Marcellus Shale well in Greene County, PA. After 6 days, the pressure in the vessels was slowly released over 2 days to prevent rapid gas release from damaging the structural integrity of the Marcellus Shale samples and were allowed to air dry for 15 minutes. Following the 15 minutes of drying the samples were placed inside a nitrogen dessicator. Both samples were characterized via FE-SEM after fluid contact to determine the extent of chemo-physical alteration.

The Huntersville Chert core samples were placed inside separate 500 mL Teflon lined containers, submerged with 85 mL of recycled (containing formation water) fracturing fluid, and subjected to 50°C at 1,500 psi (10.3 MPa) under an atmosphere of nitrogen for 89 days (2139 hours). Nitrogen was selected as the autoclave atmosphere to serve as an inert environment since argon was not available at the time of experiments. The experimental time of 89 days was selected for the Huntersville Chert to maximize potential reactions and mimic long-term effects

of fracturing fluid remaining in the subsurface. Temperature and pressure values were selected based upon *in situ* lithostatic pressure and temperature gradients from well completion reports, although autoclave seal issues prevented full pressure of 4,000 psi (27.6 MPa) from being reached to operate safely. After the 89 days of fluid exposure, the pressure in the vessel was slowly released over 2 days to prevent rapid gas release from damaging the structural integrity of the Huntersville Chert samples and were allowed to dry in a nitrogen desiccator for 1 day. Both samples were characterized via FE-SEM after fluid contact to determine the extent of chemo-physical alteration.

3.0 RESULTS

3.1 MARCELLUS SHALE

Mineral dissolution and etching was observed after synthetic fracturing fluid interaction for 6 days primarily on carbonate locations (light gray regions inside the black oval of Figure 4) compared to clay (dark gray outside the black oval of Figure 4) as determined by FE-SEM characterization. For example, Figure 4 from the Marcellus Shale transverse cut shows the morphological alteration of carbonate which was induced by the fracturing fluid. Foliated clay mineral grains dominate the background matrix and appear to be unaltered by fluid contact. The red outlined regions in both the before and after images shows the carbonate region underwent dissolution which altered carbonate surface morphology. Additionally, gypsum precipitation occurred due to fluid contact on the carbonate region circled in yellow, which might have precipitated after calcium was dissolved into solution. Pyrite seen as bright white circular framboids in Figure 4 appear to be unaltered by fluid contact. Comparing FE-SEM results of the transverse and parallel cut Marcellus Shale samples does not provide conclusive evidence that either grain orientation underwent higher or lower amounts of chemical and physical alteration.

The main fracture seen in the Marcellus Shale transverse cut outlined in red of Figure 5 prior to fluid-rock interaction increased in size after interaction, which was likely caused by experimental pressures of 4,000 psi (27.6 MPa). Pyrite is seen as bright white circular framboids in Figures 5 while foliated dark gray in color clay minerals dominate the background. There was no apparent chemical or physical alteration detected via FE-SEM to the clay matrix or pyrite after fluid contact. Fractures in the Marcellus Shale parallel cut trapped synthetic fracturing fluid and promoted gypsum mineral precipitation seen in Figures 6. Clay minerals dominate the background and appear unaltered after fluid contact. Pyrite seen as bright framboids in Figure 6 appear to be unaltered after fluid contact. Although not all fractures in the experimental Marcellus Shale samples had gypsum precipitates, there were multiple surface regions where gypsum formed.

Figure 4: Marcellus Shale transverse cut before (left) and after (right) synthetic fracturing fluid exposure FE-SEM backscatter images at 1,000x magnification. Gypsum precipitation occurred (outlined in yellow) on the surface of a carbonate region. Chemical dissolution of the carbonate region also occurred as the morphology changed between the before and after images (outlined in red).

Figure 5: Marcellus Shale transverse cut before (left) and after (right) Marcellus Shale synthetic fracturing fluid exposure FE-SEM backscatter images at 500x magnification. Magnified view of the fracture growth in the after image is outlined in red.

Figure 6: Marcellus Shale parallel cut before (left) and after (right) synthetic fracturing fluid exposure FE-SEM backscatter images at 5,000x magnification. Circled in yellow are gypsum crystals ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). This magnified view shows gypsum precipitation occurred in the Marcellus Shale fracture after fluid exposure.

3.2 HUNTERSVILLE CHERT

The FE-SEM EDX results of the Huntersville Chert transverse and parallel cut core samples results indicated mineral precipitates formed after the samples were exposed to recycled fracturing fluid for 89 days. EDX elemental abundances showed the likely minerals to precipitate included barite (BaSO_4), and a fine frained matrix precipitate including strontianite (SrCO_3), celestine (SrSO_4), and apatite (CaPO_4). Mineral precipitation occurred in large quantities and obscured the Huntersville Chert's surface (Figure 7). The mineral precipitation was also visible in the handsample core pieces (Figure 3), appearing as white coating covering the originally dark gray in color parallel cut and transverse cut core samples. Figure 7 shows pyrite framboids before and after fluid contact. The image on the right shows the strontianite, celestine, and apatite precipitation covering pyrite framboids. Mineral precipitation completely covered four out of ten initial characterization sites and allowed for only six to be re-characterized. Based on both morphology and elemental data, FE-SEM revealed that strontianite, celestine, and apatite formed as the crunchy and rice grained pattern precipitate across all samples such as that seen in Figure 8. Figure 8 shows a magnified view of a pyrite grain before and after fracturing fluid exposure. The strontianite, celestine, and apatite precipitation covered the pyrite grain after fluid interaction. Comparing FE-SEM results of the transverse and parallel cut Huntersville Chert samples did not provide conclusive evidence that either grain orientation underwent higher/lower amounts of chemical and physical alteration.

Barite was detected as large oval minerals seen in Figure 9 across all Huntersville Chert transverse and parallel samples after fluid contact. Figure 9 shows two after fluid contact images of the Huntersville Chert parallel cut showing mineral precipitation. The image on the left shows extensive barite precipitation as the white ovals and apatite, strontianite, and celestine as the gray background. The image on the right is a magnified view of barite crystals with the filamentous structure of the apatite, strontianite, and celestine visible throughout the background. Additionally, Rhenium and rare earth element (REE) Europium were detected via FE-SEM EDX on minerals which precipitated on all of the Huntersville Chert transverse and parallel cut samples. Prior to contacting the Huntersville Chert, the pH of the fracturing fluid was 4.3 with a conductivity of $60.3 \mu\text{S/cm}$ measured on a calibrated Mettler Toledo Seven Multi 8603. Post fluid-rock interaction, the pH of the fracturing fluid was 6.2 with a conductivity of $69.2 \mu\text{S/cm}$. The increase in pH and conductivity may be indicative of carbonate dissolution due to the acidic fracturing fluid.

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Figure 7: Huntersville Chert transverse cut before (left) and after (right) recycled fracturing fluid exposure FE-SEM secondary electron images at 30,000x magnification. This location shows pyrite framboids becoming encased in a precipitate believed to be apatite, strontianite, and celestine which was interpreted via EDX spectroscopy.

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Figure 8: Huntersville Chert parallel cut before (left) and after (right) recycled fracturing fluid exposure FE-SEM secondary electron images at 10,000x magnification. The before fluid exposure image on the left shows a large oval pyrite grain and surrounding carbonate (light gray). Following fluid exposure this pyrite and carbonate region was covered in a precipitate believed to be apatite, strontiate, and celestine, which was interpreted via EDX spectroscopy. Barite also precipitated and is seen as oval minerals in the middle and top right of the after fluid exposure image.

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Figure 9: Huntersville Chert parallel cut after recycled fracturing fluid exposure FE-SEM backscatter electron images at 2,410x (left) and 25,000x (right) magnification. Barite precipitated in the form of white ovals and spheres seen in both images. The filamentous background material is a precipitated layer believed to be apatite, strontiate, and celestine, which was interpreted via EDX spectroscopy.

4.0 DISCUSSION

4.1 EFFECTS OF FRACTURING FLUID ON THE MARCELLUS SHALE

This research builds upon the work of Pagels et al. (2013) by investigating the fluid-rock impact of fracturing fluid on the Marcellus Shale structure from a high resolution FE-SEM perspective under *in situ* conditions. Our analyses provided data on the physical (e.g. fractures) and mineralogical changes (e.g. dissolution or etching) that can occur as a result of synthetic fracturing fluid contact to mimic short-term effects of fracturing fluid initially entering the subsurface. According to Pagels et al. (2013), fracturing fluid remaining in the Marcellus Shale can degrade the performance of fracturing fluid proppants (i.e. sand grains), which can become imbedded into the shale due to the loss of rock strength from fluid imbibition. The region of shale which contacts the fracturing fluid undergoes sorption altering characteristics due to imbibition that can reduce fracture connections and negatively affect hydrocarbon transport (Pagels et al., 2013). Pagels et al. (2013) found that imbibition reduces hydrocarbon production in Marcellus Shale wells. Additionally, reduction of fracture connectivity might negatively affect reservoir storage potential during carbon dioxide (CO₂) sequestration in tight shale formations (Zhiyuan et al., 2014).

Dissolution and etching of carbonate minerals occurred in the Marcellus Shale core as seen in Figure 4, while clay minerals appeared unaltered in all FE-SEM images. Clay minerals remained visibly unaltered to FE-SEM characterization likely because illite and chlorite in the Marcellus Shale are not water sensitive (Houston et al., 2009). Carbonate has the potential to dissolve and become etched as the mineral structure is less stable compared to that of clay during interaction with acidic water based fracturing fluid. These short term effects are consistent with those reported by Kaszuba et al., (2013) where they noted that carbonates react and undergo dissolution quicker than silicates when in contact with acidic fluids.

FE-SEM results indicate that previous fractures in the Marcellus Shale samples widened and propagated post fluid contact possibly due to *in situ* pressure/temperature conditions in the autoclave (Figure 5). The alteration to the fractures in the transverse Marcellus Shale core may be due to the autoclave pressure (4,000 psi/27.6 MPa) overcoming the bedding plane strength. While this experiment aimed to replicate *in situ* conditions of the Marcellus Shale, additional research is needed to better understand if fracture widening would occur under confining lithostatic pressure and temperature found in subsurface conditions for fluid-rock interaction.

Our experiments provided evidence of mineral precipitation in the form of gypsum on the Marcellus Shale surface and in multiple fractures. Gypsum formed as a result of calcium interaction with water and sulphate (SO₄²⁻). The precipitation of gypsum in fractures observed in Figure 6 occurred under static laboratory conditions at temperature and pressure and requires further research in the form of core flow-through experiments at confining temperature and

pressures. Core flow-through experiments might identify if gypsum would precipitate during Marcellus Shale hydraulic fracturing under lithostatic forces. Importantly, the complex nature of Marcellus Shale reservoir mineralogy further complicates fluid-rock geochemical reactions inside fractures. Potential reactions include dissolution and precipitation of fluids trapped in fractures as fluid chemistry alters by contacting the rock (Kaszuba et al., 2013). Kaszuba et al. (2013) described that reservoir locations with high fluid flow were likely to experience dissolution while regions with low fluid flow were likely to experience precipitation. Whether or not these dissolution and precipitation reactions alter hydrocarbon flow through a reservoir like the Marcellus Shale requires further investigation.

4.2 EFFECTS OF FRACTURING FLUID ON THE HUNTERSVILLE CHERT

Our analyses provided data on the physical (e.g. fractures) and mineralogical changes (e.g. dissolution or etching) that can occur as a result of exposure to recycled fracturing fluid to maximize potential reactions of the Huntersville Chert and mimic long-term effects of fracturing fluid remaining in the subsurface. Precipitation of barite (BaSO_4) after fluid-rock interaction determined via FE-SEM EDX characterization occurred on both Huntersville Chert transverse and parallel cut samples. Barite precipitation was due to the fact that drilling mud commonly contains barium and sulphate as additives and combined into solution with the fracturing fluid. Strontianite (SrCO_3), celestine (SrSO_4), and apatite (CaPO_4) also precipitated seen in Figures 7-9. Marcellus Shale recycled fracturing fluid commonly contains strontium, barium, and sulphate, which explains the precipitation of minerals bearing these elements on the Huntersville Chert surface (Blauch et al., 2009; Hayes, 2009; Dresel and Rose, 2010; Chapman et al., 2012; Haluszczak et al., 2013; Capo et al., 2014; Soeder et al., 2014b). Mineral precipitation occurred in high quantities and limited the relocation of six out of ten initial features to be identified via FE-SEM. The sample coverage in mineral precipitation is likely the result of high TDS fluid-rock interaction over the long-term 89 days of exposure. Due to barite being a non-water soluble mineral the precipitate coating was unable to be removed from the Huntersville Chert surface by simple rinsing before recharacterization. Removal of the precipitate, which was not achieved, would have allowed for investigation of surface alteration to the chert including possible chemical etching and dissolution features.

Rhenium and rare earth element (REE) Europium were likely observed with EDX elemental FE-SEM analyses and are believed to have either (1) leached out of minerals in the Huntersville Chert core sample, or (2) dissolved out of subsurface formations and into the recycled fracturing fluid. Middle Devonian aged dolomites have been found to contain REEs (Qing and Mountjoy, 1994). REEs have the potential to substitute in for Ca^{2+} and Mg^{2+} in carbonate minerals and are present in higher concentration compared to freshwater sources (Qing and Mountjoy, 1994). Additionally, REEs can be found in minerals such as quartz, feldspar, and clay minerals. The Huntersville Chert sample utilized during this study contained quantities of quartz, carbonate, illite, pyrite, and feldspar, which possibly contain Rhenium and Europium.

Qing and Mountjoy (1994) observed Middle Devonian limestone, dolomite, and calcite contained the REE Europium, although their study did not report Rhenium. During this study, Rhenium and Europium were potentially leached from the cherts mineral structure during laboratory fluid-rock interaction and recrystallized on the chert surface; or were dissolved into the fracturing fluid during subsurface fluid-rock interaction. Due to the fact that recycled fracturing fluid contains formation water which underwent fluid-rock interactions in the subsurface, the source of REE might be from the recycled component of the fracturing fluid and not the Huntersville Chert core sample mineral structure. Additional research investigating the Huntersville Chert elemental composition (total rock dissolution) and REE geochemistry of the recycled fracturing fluid might help provide an origin of REE detected in the precipitate's mineral structure.

5.0 CONCLUSION

The preliminary results of this study show physical and chemical changes to Marcellus Shale and Huntersville Chert after exposure to fracturing fluid. Both short-term (effects of fracturing fluid initially entering the subsurface) and long-term (effects of fracturing fluid remaining in the subsurface) scenarios were examined. Chemical and physical alteration of the Marcellus Shale and Huntersville Chert occurred after fluid-rock interaction at *in situ* conditions with fracturing fluid. After Marcellus Shale interaction with synthetic fracturing fluid the dissolution of carbonate, fracture propagation, and gypsum precipitation was observed based upon FE-SEM pre and post-fluid contact imaging. Huntersville Chert samples interacted with recycled (containing a component of formation water) fracturing fluid and the precipitation of barite, strontianite, celestine, and apatite occurred as inferred from FE-SEM x-ray dispersive spectroscopy. Carbonate dissolution was also believe to have occurred as pH changed from an initial pre-fluid rock interaction value of 4.3 to 6.2 after fluid-rock exposure. Rhenium and rare earth element Europium was identified in FE-SEM energy dispersive x-ray spectroscopy of the Huntersville Chert samples, which possibly leached from the Huntersville Chert structure or was present in the initial recycled fracturing fluid and mineralized on the chert's surface.

This *in situ* temperature and pressure experiment investigated the chemical and physical effects of fracturing fluid, but there are numerous limitations to consider. This study was not a core flow-through experiment, i.e. the samples were unconfined, (Pagels et al., 2013; Laio et al., 2014), which might closely replicate fluid-rock interaction in subsurface geologic formations. The Marcellus Shale experiment did not utilize fracturing fluid with additives (biocides, proppants, friction reducers, etc). Once removed from the fluid Marcellus Shale and Huntersville Chert samples were not immediately rinsed with water, or another solution to remove excess fracturing fluid. Moreover, XRD analysis was not performed post fluid-rock interaction due to time constraints. We recommend that future studies be conducted under strictly controlled conditions with FE-SEM and XRD to further investigate and quantify these changes.

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