

**PHYSICOCHEMICAL EFFECTS OF SYNTHETIC HYDRAULIC FRACTURING
FLUID ON CORE SAMPLES OF THE MIDDLE DEVONIAN MARCELLUS SHALE
AND UNDERLYING HUNTERSVILLE CHERT, GREENE COUNTY,
PENNSYLVANIA, USA**

by

Matthew Frederick Dieterich

B.S. Environmental Science, Robert Morris University, 2013

Submitted to the Graduate Faculty of the
Kenneth P. Dietrich School of Arts and Sciences in partial fulfillment
of the requirements for the degree of
Master of Science

University of Pittsburgh

2015

UNIVERSITY OF PITTSBURGH
KENNETH P. DIETRICH SCHOOL OF ARTS AND SCIENCES

This thesis was presented

by

Matthew Frederick Dieterich

It was defended on

April 14th, 2015

and approved by

Dr. Rosemary Capo, Ph.D., Associate Professor, Department of Geology

Dr. Brian Stewart, Ph.D., Associate Professor, Department of Geology

Dr. Nadine McQuarrie, Ph.D., Assistant Professor, Department of Geology

Copyright © by Matthew Frederick Dieterich

2015

**PHYSICOCHEMICAL EFFECTS OF SYNTHETIC HYDRAULIC FRACTURING
FLUID ON CORE SAMPLES OF THE MIDDLE DEVONIAN MARCELLUS SHALE
AND UNDERLYING HUNTERSVILLE CHERT, GREENE COUNTY,
PENNSYLVANIA, USA**

Matthew Frederick Dieterich, M.S.

University of Pittsburgh, 2015

Hydraulic fracturing from directional drilling involves the injection of large quantities of fluid into the target formation, and creates a significant volume of rock with a high surface area in contact with injection fluid and associated brines. Over time, fluid-rock interactions between the saline injection fluids, formation waters released by fracturing, and the fractured rock results in physical and chemical alteration that can lead to changes in rock strength and fracture connectivity. Factors affecting alteration processes include temperature, rock mineralogy, and the composition and ionic strength of the fluids. Experiments conducted at surface (23°C) and borehole temperatures (70°C) assessed the effect of high ionic strength fluids on the mineralogical, textural and chemical characteristics of high surface area core samples of organic rich Marcellus Shale and underlying Huntersville Chert. Comparison of pre- and post-experiment fluid composition and rock mineralogy, surface area, and textures indicate that some reactions were temperature- and/or lithology-dependent. The results also suggest that fluid-rock interaction, including cation exchange reactions, sorption, mineral alteration, and dissolution and mobilization of some trace metals (e.g., nickel, boron, manganese and lithium) can be observed over short (days) time scales.

TABLE OF CONTENTS

PREFACE.....	X
1.0 INTRODUCTION.....	1
1.1 HYDRAULIC FRACTURING AND DIRECTIONAL DRILLING OF UNCONVENTIONAL HYDROCARBON RESERVOIRS.....	1
1.2 COMPOSITION OF HYDRAULIC FRACTURING FLUID	5
1.3 CHEMO-PETROPHYSICAL CHANGES RELATED TO FLUID-ROCK INTERACTION	5
1.4 APPALACHIAN BASIN MARCELLUS SHALE FLUID-ROCK INTERACTIONS	7
1.5 RESEARCH OBJECTIVES AND RATIONALE	8
2.0 EXPERIMENTAL APPROACH	10
2.1 CORE LOCATION AND SAMPLE DESCRIPTIONS.....	10
2.1.1 Marcellus Shale core sample (GC-MS 7801)	11
2.1.2 Huntersville Chert core sample (GC-HC 7909.7).....	13
2.2 ROCK SAMPLE PREPARATION.....	15
2.3 PREPARATION OF THE SYNTHETIC FRACTURING FLUID	16
2.4 EXPERIMENTAL PROTOCOL.....	17
2.5 ANALYTICAL METHODS	18

3.0 RESULTS	20
3.1 CHANGES IN CHEMICAL COMPOSITION	20
3.2 BET SURFACE AREA CHANGES	24
3.3 MINERALOGICAL AND TEXTURAL CHANGES	26
4.0 DISCUSSION	28
4.1 DISSOLUTION – PRECIPITATION REACTIONS.....	29
4.2 CATION EXCHANGE PROCESSES	30
4.3 TRACE METAL MOBILIZATION.....	31
5.0 CONCLUSIONS	33
BIBLIOGRAPHY	34

LIST OF TABLES

Table 1: Mineralogy of samples determined by XRD.....	13
Table 2: Composition of the synthetic fracturing fluid used for the experiments and hydraulic fracturing fluids used in Marcellus Shale wells.....	16
Table 3: Composition of synthetic fracturing fluid used in experiments.....	17
Table 4: The major cation, anion and trace element composition of the starting synthetic fracturing fluid and the leachates from GC-MS 7801 (Marcellus Shale) and GC-HC 7909.7 (Huntersville Chert) for the 23°C and 70°C experiments.....	21
Table 5: Surface area of samples pre-experiment and post-experiment changes.	25

LIST OF FIGURES

Figure 1: Shale gas plays located in the United States (Lower 48 States shale plays, 2015).	2
Figure 2: Illustration of the process of hydraulic fracturing from Zusman (2010).....	3
Figure 3: Map view showing location of horizontally drilled Marcellus Shale wells from a well pad in Greene County (top). Cross section view showing hydraulically fractured laterals extending into the Marcellus Shale (bottom) from Hammack et al. (2014).	4
Figure 4: Relationship between TDS in flowback and volume of discharge with time (Hays, 2009).	6
Figure 5: Map of the extent of the northeastern portion of the Marcellus Shale within the Appalachian Basin. Study samples are from a drill core in Greene County, Pennsylvania (green).	11
Figure 6: Marcellus shale from the section of the Greene County core that sample GC-MS-7801 was taken.....	12
Figure 7: (a) E-SEM backscatter electron image (100x magnification) of a slab from the core that GC-MS 7801 was taken from. (b) E-SEM backscatter electron image of the square inset shown in (a) at 500x magnification.....	13
Figure 8: Huntersville Chert from the section of the Greene County core that sample GC-HC-7909.7 was taken from.....	14

Figure 9: (a) E-SEM backscatter electron image from the core that GC-HC 7909 was taken from.	
(b) E-SEM backscatter electron image of the square inset shown in (a).	15
Figure 10: Flowchart of experimental procedure.....	18
Figure 11: Change in sodium, potassium and calcium content in leaches after fluid-rock interaction at 23°C and 70°C.	22
Figure 12: Change in barium content in leaches after fluid-rock interaction at 23°C and 70°C..	22
Figure 13: Change in post-experiment sulfate content.	23
Figure 14: Change in nickel content in leaches after fluid-rock interaction at 23°C and 70°C....	24
Figure 15: BET adsorption isotherms for samples pre- and post-experiment at 70°C.	25
Figure 16: XRD plot for Marcellus Shale sample GC-MS-7801 showing gypsum loss after the 70° experiment.	26
Figure 17: E-SEM backscatter images showing possible aluminosilicate mineral rounding in the GC-MS 7801 sample after 23°C and 70°C synthetic fracturing fluid interaction.	27

PREFACE

I would like to thank my family for all their support and encouragement while completing this thesis. I also would like to thank Tracy Bank, William Garber, and Brian Kail of the NETL-Pittsburgh Analytical Laboratory for chemical analyses, Bret Howard (NETL) for XRD analysis, and Sittichai Natesakhawat (NETL) for BET analysis.

1.0 INTRODUCTION

1.1 HYDRAULIC FRACTURING AND DIRECTIONAL DRILLING OF UNCONVENTIONAL HYDROCARBON RESERVOIRS

Unconventional oil and gas resources such as low (millidarcy) permeability shale units are increasingly being exploited for energy production (Arthur and Cole, 2014). In the United States, organic-rich shale formations represent a major unconventional hydrocarbon resource (Fig. 1). Extraction of economic quantities of oil and gas from these rocks requires methods such as hydraulic fracturing that increase permeability, and directional drilling that increases the volume of accessible fractured rock (Fig. 2; Soeder et al., 2014a).

Hydraulic fracturing involves the injection of large quantities of fluid (typically 2-7 million gallons; Soeder and Kappel, 2009) into the target formation (King, 2012). Directional drilling creates lateral sections (horizontal legs) that can extend as much as 2000 m from the vertical segment of the well (Husain et al., 2011). Multiple laterals are often drilled from the same well pad (Fig. 3) and can extend below shallower producing units (Hammack et al., 2014). Following completion of the lateral legs, hydraulic fracturing shatters the target formation; proppant such as sand is co-injected to keep the fractures open (Harper, 2008).

The implementation of hydraulic fracturing and horizontal drilling techniques has allowed the Appalachian Basin Marcellus Shale to become one of the largest unconventional

natural gas plays in the United States (Engelder and Lash, 2008; Coleman et al., 2011; Zagorski et al., 2012). Based on hydrocarbon production data from 117 counties in the Appalachian Basin, Engelder (2009) estimated that it contains at least 489 trillion cubic feet (TCF) of natural gas. More than 6,000 producing wells have been directionally drilled and fractured between 2008 and 2015 (Whitacre and Slyder, 2015).

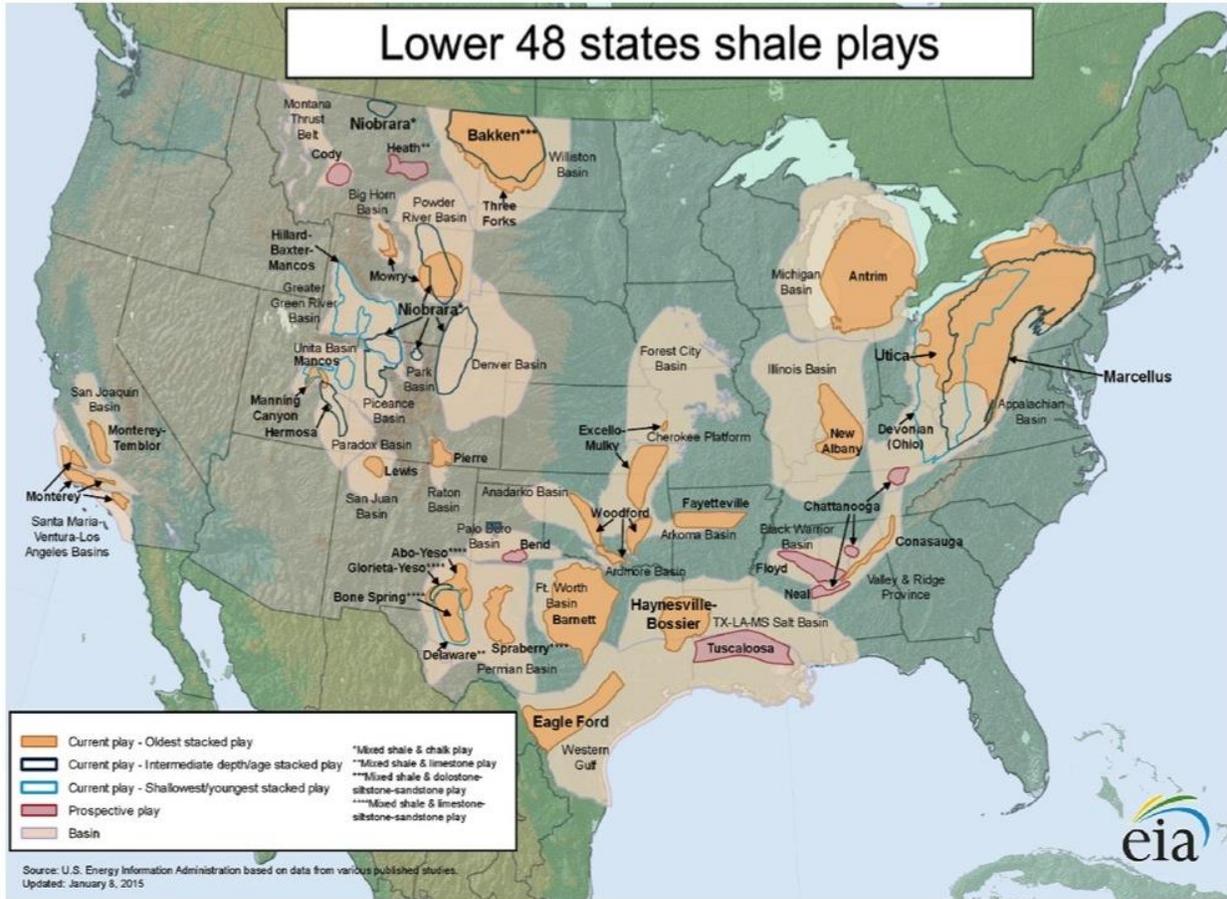


Figure 1: Shale gas plays located in the United States (Lower 48 States shale plays, 2015).

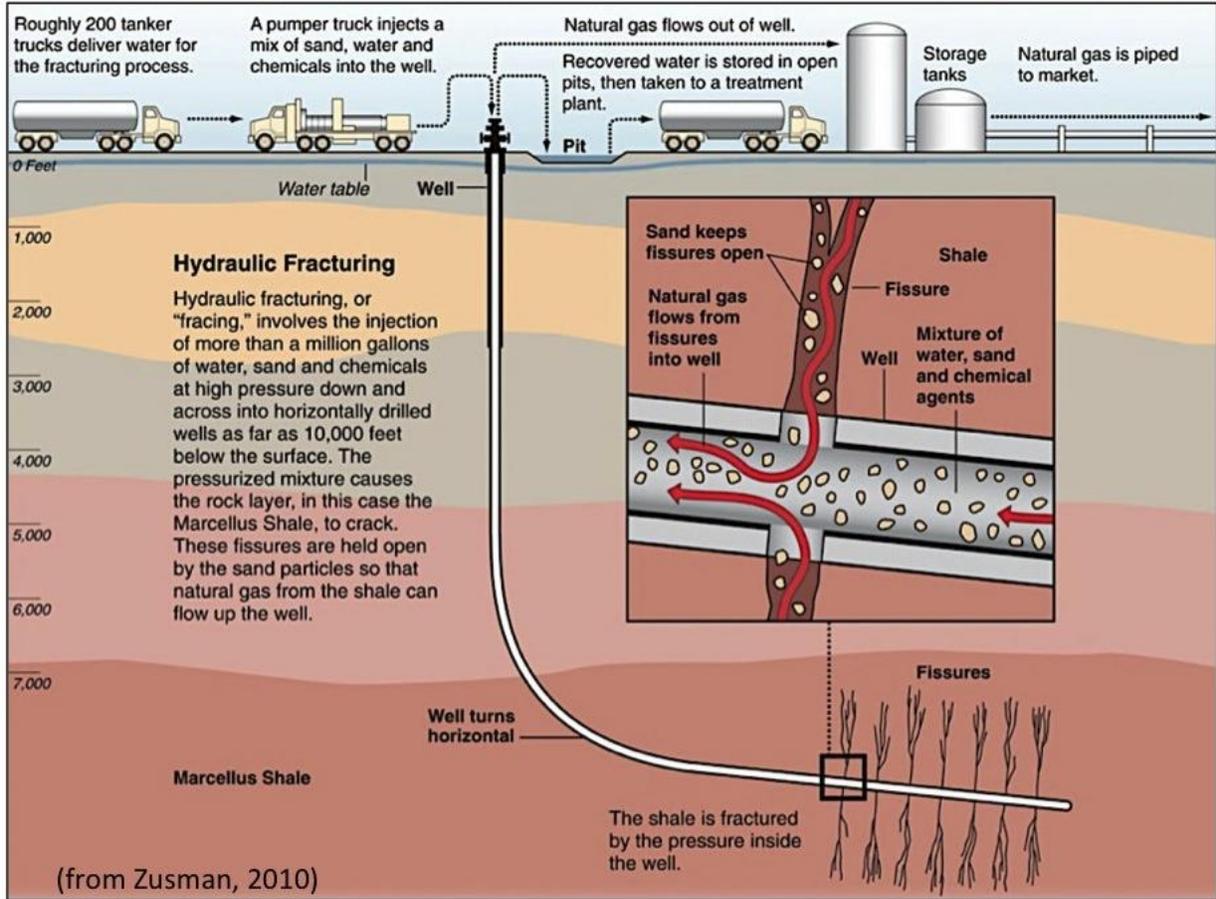


Figure 2: Illustration of the process of hydraulic fracturing from Zusman (2010).

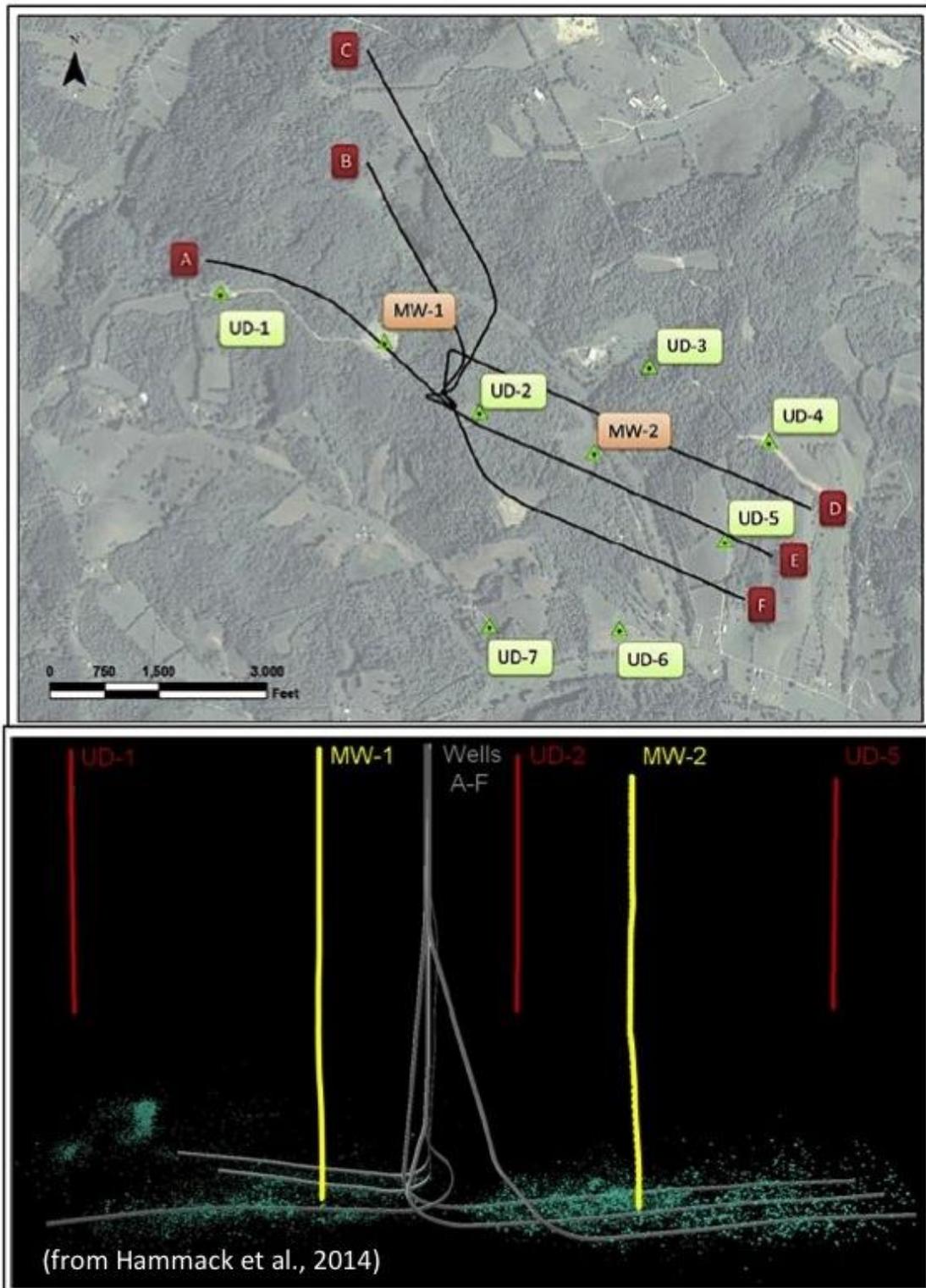


Figure 3: Map view showing location of horizontally drilled Marcellus Shale wells from a well pad in Greene County (top). Cross section view showing hydraulically fractured laterals extending into the Marcellus Shale (bottom) from Hammack et al. (2014).

1.2 COMPOSITION OF HYDRAULIC FRACTURING FLUID

Hydraulic fracturing fluid is composed of approximately 99% water (by volume) with ~1% of additives such as biocides, friction reducers and anti-scaling agents (Hayes, 2009; Soeder and Kappel, 2009; Gregory et al., 2011; Soeder et al., 2014b). The water component of fracturing fluid can contain up to 100% freshwater, but currently many service companies are recycling produced water from other wells to fracture subsequent wells (Vidic et al., 2013). Although injection fluid composed entirely of recycled produced water has been used successfully (Papso et al., 2011), the addition of recycled saline produced waters to fresh water for hydraulic fracturing can potentially result in precipitation in the wellbore and on drilling equipment due to the interaction of calcium (Ca), barium (Ba), and strontium (Sr) with sulfates and other ions (Blauch et al., 2009; Rassenfoss, 2011; He et al., 2013; Boschee, 2014). Therefore, depending on salinity and chemical composition, the produced water component undergoes on-site geochemical treatment prior to injection to mitigate precipitation of barite and other salts (Bryant et al., 2010; Papso et al., 2011).

1.3 CHEMO-PETROPHYSICAL CHANGES RELATED TO FLUID-ROCK INTERACTION

Following well stimulation, between 5 and 50% by volume of the initial injected volume returns from the well as flowback water (Pagels et al., 2013; Vidic et al., 2013). The remaining fluid is retained in the shale primarily by imbibition, which is a function of rock characteristics including mineralogical composition and texture (Engelder et al. 2014). Hydraulic fracturing greatly

increases the surface area of rock exposed to *in situ* formation water and injected fluids. The volume of flowback water generally decreases rapidly over the first few days and weeks as imbibition of the fluid into the shale progresses; the salinity of the returned fluid (produced water) increases concurrently (Fig. 4). Thus the chemical composition of produced waters reflects a mixture of the injection water and formation fluids released by fracturing, and fluid-rock interactions such as sorption, dissolution and ion exchange between reactive minerals in the formation (Capo et al., 2014; Stewart et al., 2015).

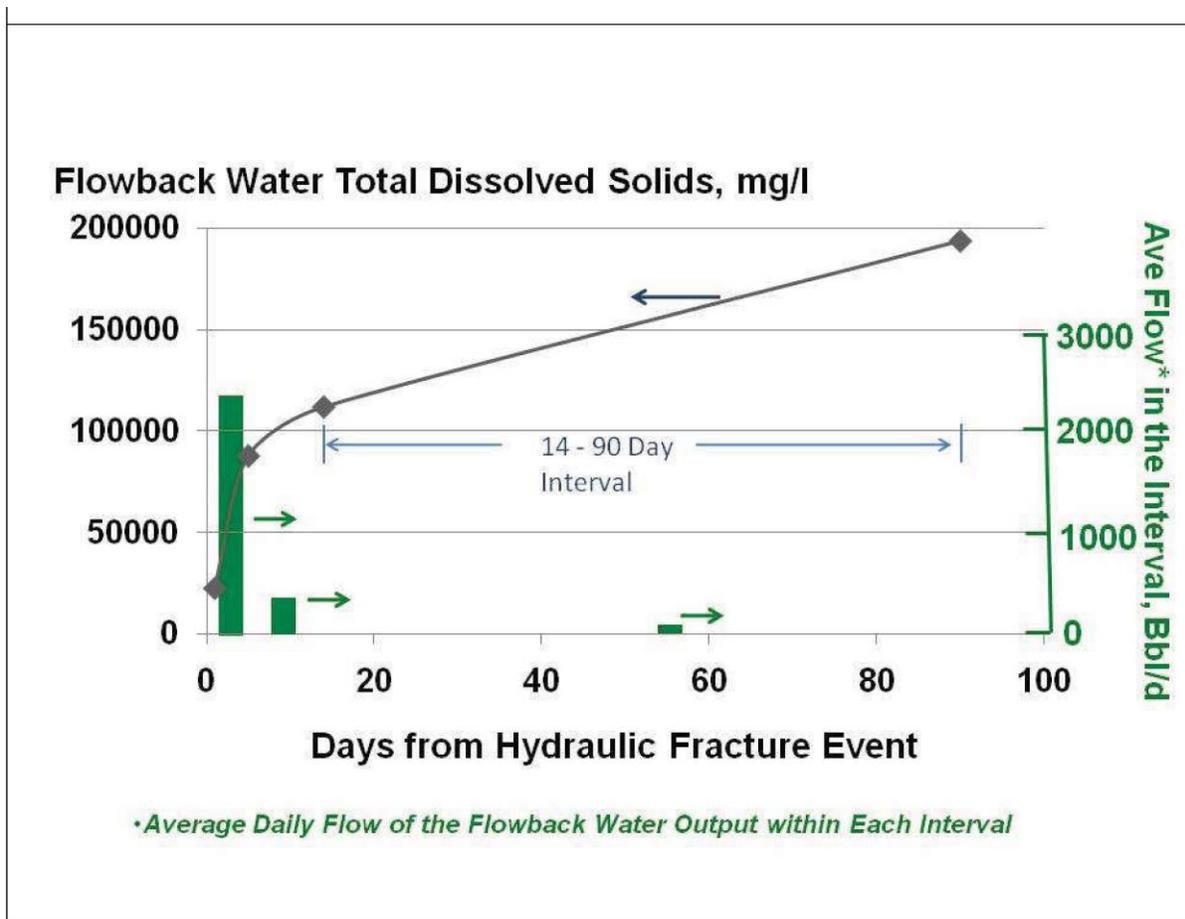


Figure 4: Relationship between TDS in flowback and volume of discharge with time (Hays, 2009).

Previous work indicates that the interaction of hydraulically fractured units with water-based fluids, such as brines, that are used for drilling or well completion results in physical and chemical changes in these rocks. The nature and magnitude of these changes are a function of factors such as mineralogy, the composition and ionic strength of the fluid, temperature, exposure time, and fluid saturation (van Oort, 2003). This alteration can affect rock strength and conductivity and has implications for both wellbore stability and hydrocarbon production. For example, shale weakening has been attributed to the interaction of clay minerals with saline drilling fluid (Pagels et al., 2013). Ewy et al., (2008) found an inverse correlation between initial porosity and confined compressive strength of shale following brine interaction.

1.4 APPALACHIAN BASIN MARCELLUS SHALE FLUID-ROCK INTERACTIONS

Produced waters from unconventional wells in the Marcellus Shale are typically sodium-calcium brines, with total dissolved solids (TDS) averaging 218,000 mg/L and reaching as high as 300,000 mg/L (Rowan et al., 2011; Chapman et al., 2012; Staub, 2014; Rowan et al., 2015). Marcellus Shale produced water contains higher concentrations ($\geq 10^3$ mg/L) of barium (Ba) and strontium (Sr) than seen in typical oil and gas brines (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). Based on the analysis of over 150 drill hole cores, Hosterman and Whitlow (1982) reported that the Marcellus Shale contains approximately 50% clay minerals and chlorite, 25% calcite, and 20% quartz silt, and 5% pyrite. The clay-sized fraction is predominantly illite (~70%), with chlorite and smectite/illite mixed layer clays making up ~15% each; illite-chlorite mixed layer clay was also present in trace amounts. Time series analysis of the geochemical and

isotopic composition of produced waters from hydraulically fractured Marcellus Shale wells indicates that as the temporal changes following well stimulation stabilize, there is a gradual transition to formation water chemistry (Rowan et al., 2011; Chapman et al., 2012; Capo et al., 2014).

Understanding the fluid-rock processes involved in the alteration of hydraulically fractured rocks, as well as the source(s) of the chemical species found in produced waters, is an area of active research (see Zagorski et al., 2012; Pagels et al., 2013). Long and Angino (1982) found that high salinity fluids can leach metals from shale formations. Based on mineralogical and chemical analyses of core and outcrop samples of Appalachian Basin black shale, Staub (2014) concluded that cation exchange processes in lateral sections of hydraulically fractured Marcellus Shale wells could contribute significantly to changes in the chemical composition of flowback and produced waters. More work is needed to better understand the physicochemical effects of saline fluids (both injection waters and formation waters liberated by fracturing) on hydrocarbon-bearing shales and seal rocks.

1.5 RESEARCH OBJECTIVES AND RATIONALE

Fluid-rock experiments were carried out to assess the physical and chemical alteration of the Marcellus Shale and underlying Huntersville Chert upon interaction with hydraulic fracturing fluids, and to characterize the resulting changes in fluid composition. The experiments were designed to provide information regarding the nature of subsurface processes that affect fluid-rock properties, and to address the following questions:

(1) How are petrophysical characteristics (reactive surface area, mineralogy and mineralogical texture) of the Marcellus Shale and Huntersville Chert affected by interaction with water and fracturing fluid?

(2) How does interaction of injected fluid with the rock change the chemical composition of the fluid released?

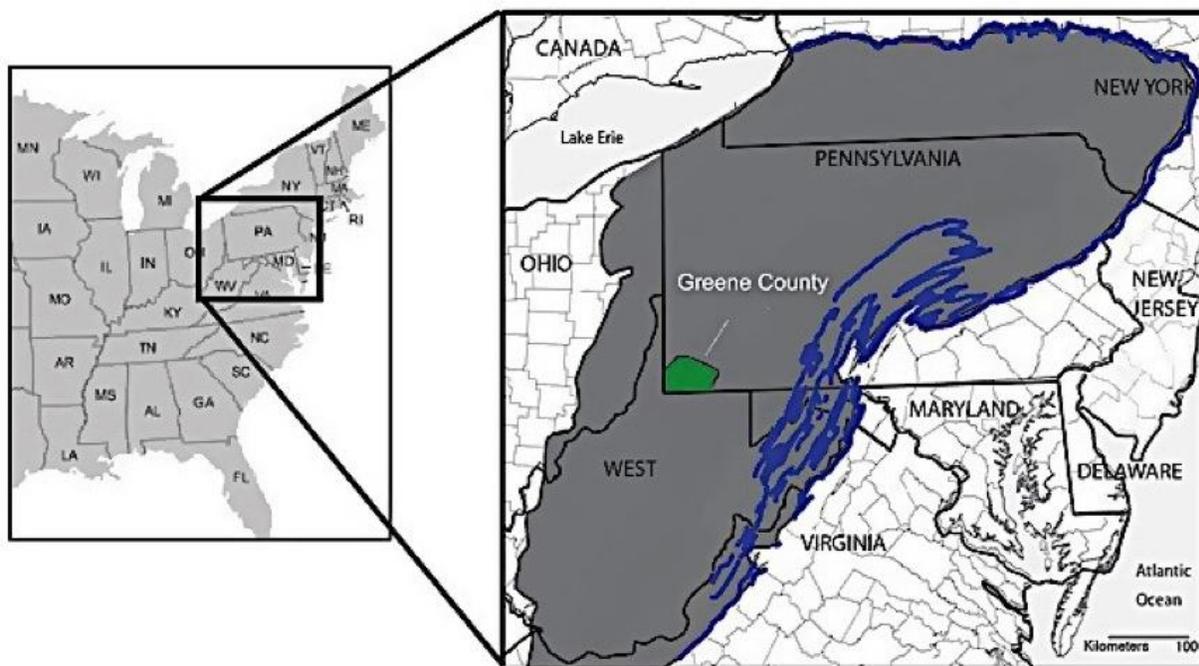
Previous experiments carried out at borehole temperatures indicated that temperature and ionic strength are the dominant factors influencing metal mobility (Long and Angino, 1982; Hakala et al., 2015 in prep.). In addition to providing information about mineralogical and textural alteration of low permeability clay-rich and clay-poor rocks related to contact with high ionic strength fluids, the results of these experiments will increase our understanding of the relationship between these physical changes and the chemical composition of post-fracturing produced waters.

This could allow better use of the temporal variations in the chemical composition of produced water to assess fracturing fluid-induced alteration of both source rocks and confining rocks. Furthermore, information regarding changes in injection water chemistry related to its interaction with the Marcellus Shale could aid in identifying the source of, and processes responsible for, the high concentrations of Ba (>10,000 mg/L) and Sr (>5,000 mg/L) in Marcellus Shale produced waters relative to other Appalachian Basin formation waters (Chapman et al., 2012).

2.0 EXPERIMENTAL APPROACH

2.1 CORE LOCATION AND SAMPLE DESCRIPTIONS

Outcrop samples of Marcellus Shale have undergone mineralogical and chemical changes due to subaerial weathering (Jin et al., 2013). To more accurately assess changes related to subsurface processes, core samples from a drill hole in Greene County, Pennsylvania (Fig. 5) were used for this study. The Marcellus Shale occurs at 7,785 ft (2,373 m) depth in the core. The Marcellus is underlain by the calcareous Huntersville Chert, which begins at ~7,885 ft (2,403 m). A well completion report indicates that borehole temperatures in the region are between 65°C and 70°C (Wrightstone, 2008).



(Modified from Kolesar Kohl et al., 2013).

Figure 5: Map of the extent of the northeastern portion of the Marcellus Shale within the Appalachian Basin. Study samples are from a drill core in Greene County, Pennsylvania (green).

2.1.1 Marcellus Shale core sample (GC-MS 7801)

Sample GC-MS 7801, from the organic-rich lower portion of the Marcellus Shale, is from a depth of 7,801 ft (2,378 m) in the core. It is a grayish black shale with planar cleavage and sub-millimeter scale pyrite grains visible in hand sample (Fig. 6) and environmental-scanning electron microscopy (E-SEM; Fig. 7). Minerals identified by XRD for sample GC-MS 7801 are presented in Table 1. Major minerals (>25%) are quartz and illite; minor minerals (10-25%) are chlorite (clinochlore) and pyrite; and trace minerals (<10%) are calcite, dolomite, and gypsum. The clay mineral component includes illite, chlorite, and mixed layer illite/chlorite. These mineral distributions are similar to those found in other analyses of Marcellus Shale (Hosterman and Whitlow, 1983; Benelli, 2012). The surface area of the Marcellus Shale GC-MS 7801

sample before fluid-rock interaction was $18.2 \text{ m}^2/\text{g}$ determined by Brunauer–Emmett–Teller (BET) analysis.



Figure 6: Marcellus shale from the section of the Greene County core that sample GC-MS-7801 was taken.

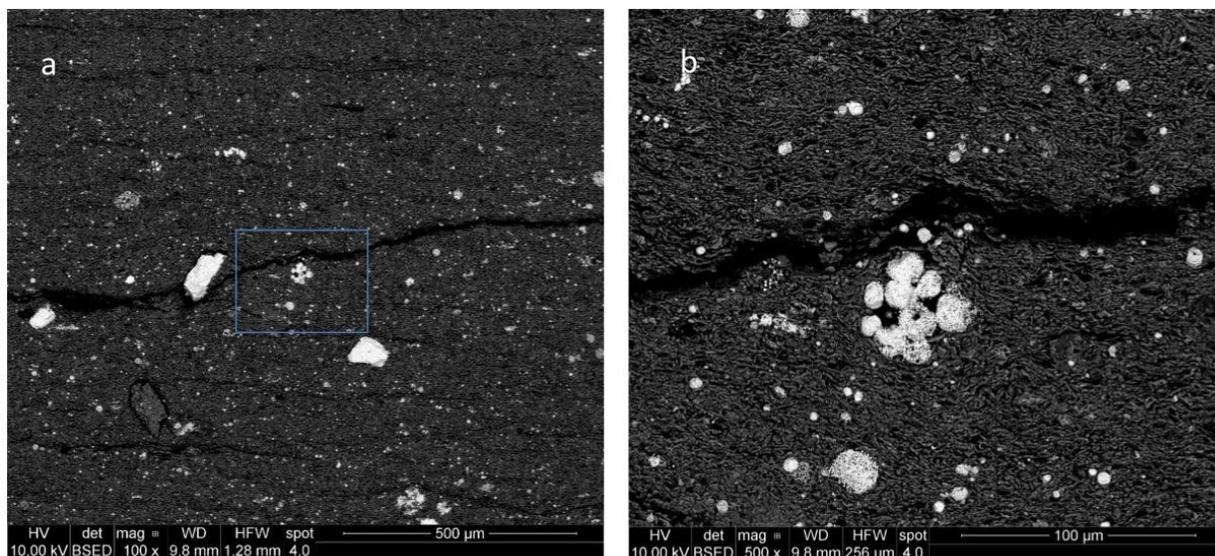


Figure 7: (a) E-SEM backscatter electron image (100x magnification) of a slab from the core that GC-MS 7801 was taken from. (b) E-SEM backscatter electron image of the square inset shown in (a) at 500x magnification.

Table 1: Mineralogy of samples determined by XRD.

Sample	Quartz	Muscovite/ Illite	Chlorite/ Clinocllore	Pyrite	Calcite	Dolomite	Gypsum	Microcline	Albite
GC-MS 7801 (Marcellus Shale)	major	major	minor	minor	trace	trace	trace	-	-
GC-HC 7909.7 (Huntersville Chert)	major	minor	-	trace	major	major	-	trace	trace

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

2.1.2 Huntersville Chert core sample (GC-HC 7909.7)

The Huntersville Chert sample (GC-HC 7909.7) is from a depth of 7,909.7 ft (2,411 m) in the core. It is a calcareous dark gray chert (Fig. 8). E-SEM images of GC-HC 7909.7 before crushing show macro-morphologic features such as pyrite and clay minerals (Fig. 9). Major minerals identified by XRD (>25%) are quartz, calcite, and dolomite; a minor mineral (10-25%) is illite; trace minerals (<10%) include pyrite, microcline, and albite. The surface area of the Huntersville Chert GC-HC 7909.7 sample before fluid-rock interaction was 2.3 m²/g as determined by BET analysis.



Figure 8: Huntersville Chert from the section of the Greene County core that sample GC-HC-7909.7 was taken from.

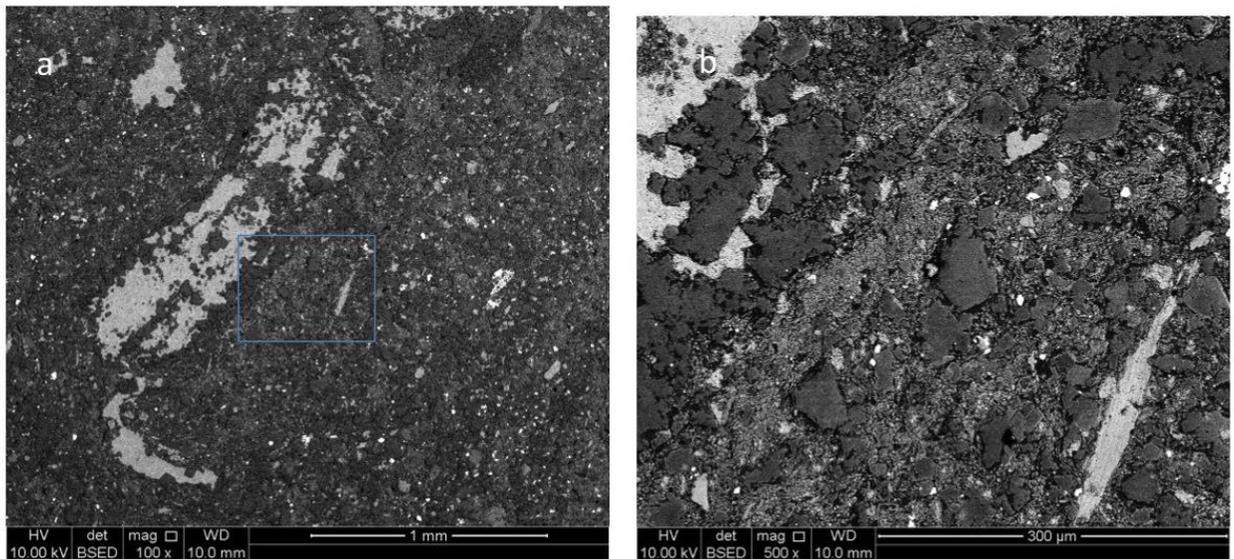


Figure 9: (a) E-SEM backscatter electron image from the core that GC-HC 7909 was taken from. (b) E-SEM backscatter electron image of the square inset shown in (a).

2.2 ROCK SAMPLE PREPARATION

Samples were removed from the core using a rock saw; the outermost surface of the core was avoided, and cut samples were stored in a nitrogen desiccator to minimize alteration from subaerial exposure. Samples were crushed with a corundum mortar and pestle and passed through a pre-cleaned 850 μm sieve to simulate the increased surface area and reactive surfaces following fracturing. The starting mass of Marcellus Shale sample GC-MS 7801 was 23.7 grams and that of Huntersville Chert (GC-HC 7909.7) was 17.8 grams. Samples were divided into approximately 2 g homogeneous portions using a splitter, transferred to glass vials and stored in a desiccator prior to use.

2.3 PREPARATION OF THE SYNTHETIC FRACTURING FLUID

The composition of the synthetic fracturing fluid used for the experiments was based on published data for hydraulic fracturing fluids used in Marcellus Shale wells (Table 2). For Marcellus Shale wells, a mixture of 15-30% produced water and 70-85% freshwater is most commonly used (S. Fragale, personal communication). This study focused on interaction of rock with high ionic strength solutions, and the synthetic fracturing fluid did not contain additives such as biocides or proppants.

Reagent grade salts were added to approximately 2 L of deionized water, in the proportions used by Hakala et al. (2015, in prep.) (Table 3). Salts used were calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), 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 bicarbonate (NaHCO_3), sodium sulfate (Na_2SO_4) and sodium bromide (NaBr). The initial pH of the fluid was 5.70; ionic strength was 0.5 M.

Table 2: Composition of the synthetic fracturing fluid used for the experiments and hydraulic fracturing fluids used in Marcellus Shale wells.

	Temp. °C	pH	Na	Ca	Mg	K	Ba	Ni	Mn	B	Li	Br ⁻	Cl ⁻	SO ₄ ²⁻ mgL ⁻¹	NO ₂ ⁻	HCO ₃ ⁻
			mgL ⁻¹				µgL ⁻¹					mgL ⁻¹				
<i>Synthetic Fracturing Fluid</i>	-	5.7	6,762	2,033	229	175	38	44	nd	<71	<3	75	17,082	14	26	54
GC-MS 7801 Marcellus Shale	23 °	5.7	7,187	2,035	185	169	1,025	78	46	73	24	<6.6	14,883	131	<3.4	43
	70 °	5.4	7,120	2,076	192	179	1,472	72	181	129	36	<6.6	15,033	216	<3.4	22
GC-HC 7909.7 Huntersville Chert	23 °	5.8	7,257	2,056	189	179	154	64	19	128	BDL	<6.6	13,595	74	<3.4	24
	70 °	5.5	7,394	2,067	203	174	185	67	54	202	46	<6.6	14,926	74	<3.4	17

Table 3: Composition of synthetic fracturing fluid used in experiments.

Component	Salt	Molecular weight	Atomic mass	Target concentration	Mass of salt added	Mass of component added	Moles of component added	Concentration
		gmol ⁻¹	gmol ⁻¹	mgL ⁻¹	g	g	mol	mgL ⁻¹
Ca ²⁺	CaCl ₂ *2H ₂ O	147.02	40.08	2100	15.40	4.20	0.10	2100
Mg ²⁺	MgCl ₂ *6H ₂ O	203.27	24.31	200	3.35	0.40	0.02	200
K ⁺	KCl	74.55	39.10	160	0.61	0.32	0.01	160
Na ⁺	NaCl	58.44	22.90	7260	36.18	14.55	0.62	7273
Sr ²⁺	SrCl ₂ *6H ₂ O	266.65	87.62	200	1.22	0.40	0.00	200
Br ⁻	NaBr	102.89	79.90	140	0.36	0.28	0.00	140
HCO ₃ ²⁻	NaHCO ₃	84.01	61.02	260	0.72	0.52	0.01	260
Cl ⁻	-	-	35.45	-	-	31.15	-	15577
SO ₄ ²⁻	Na ₂ SO ₄	142.04	96.06	100	0.30	0.20	0.00	100

2.4 EXPERIMENTAL PROTOCOL

Leaching experiments (Fig. 10) were carried out at the University of Pittsburgh Department of Geology and Planetary Science. Experiments were conducted using a fluid-rock ratio of 100:1 to maximize fluid contact with the rock (after Spivak-Birndorf et al. 2012; Stewart et al., 2015). Approximately 2 g splits of crushed rock and 200 mL of synthetic fracturing fluid were reacted in acid-washed 500 mL Teflon vessels at ambient temperature (23°C) and at approximate borehole temperature (70°C). Experiments were conducted at 1 atm pressure; previous experiments indicate that temperature and ionic strength are the dominant factors influencing metal mobility (Long and Angino, 1982; Hakala et al., 2015, in prep.)

The fluid-rock mixtures were continuously stirred for four days, and then decanted, centrifuged, and the leachate transferred into acid-washed high-density polyethylene (HDPE) bottles. Aliquots for anion determination were preserved by refrigeration. Samples for elemental analysis were preserved by acidification with ultrapure nitric acid to pH 2. Samples of the rock residue were dried for post-experiment mineralogical and textural characterization.

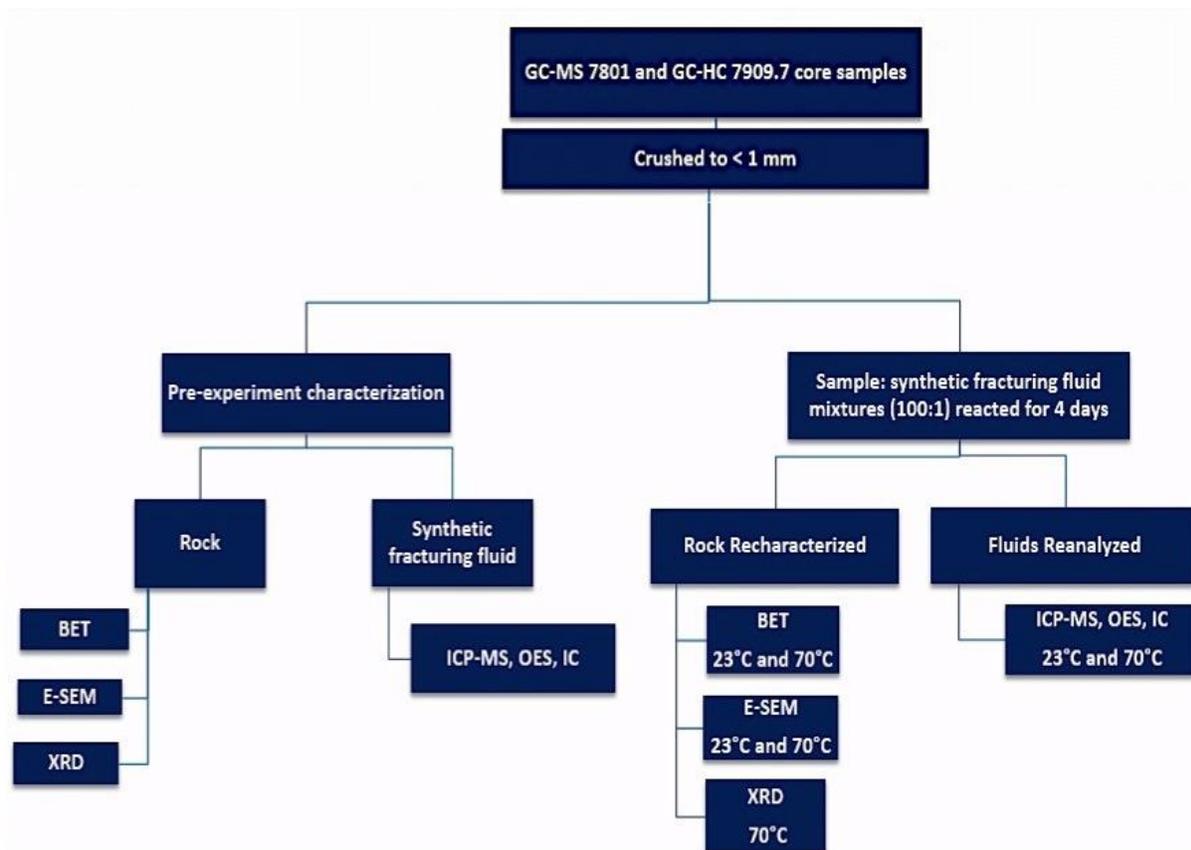


Figure 10: Flowchart of experimental procedure.

2.5 ANALYTICAL METHODS

E-SEM was carried out at the Department of Energy-National Energy Technology Laboratory (NETL) in Pittsburgh, in backscatter mode on a FEI Quanta 600 FEG environmental scanning electron microscope and using energy dispersive x-ray spectroscopy (EDX) for *in situ* chemical compositions. Leachate chemistry data was provided by the NETL Pittsburgh Analytical Laboratory. Surface area was determined by BET analysis on approximately 0.5 g crushed

samples by Sittichai Natesakhawat (NETL) on a Quantachrome Autosorb 1-C using nitrogen gas. Prior to BET analysis, the sample was degassed at 110°C under vacuum to drive off moisture. Bret Howard (NETL) carried out x-ray diffraction (XRD) analyses on a PANalytical X'pert Pro powder diffractometer with a Cu source. Geochemical modeling was done using The Geochemist's Workbench.

3.0 RESULTS

3.1 CHANGES IN CHEMICAL COMPOSITION

The major cation, anion and trace element composition of the starting synthetic fracturing fluid and the leachates from GC-MS 7801 (Marcellus Shale) and GC-HC 7909.7 (Huntersville Chert) for the 23°C and 70°C experiments are shown in Table 4. Sodium (Na), potassium (K) and calcium content did not change significantly in leaches of either lithology after fluid-rock interaction at surface (23°C) or borehole temperature (70°C) (Fig. 11). Barium content increased in the shale and chert low temperature leachates by ~2,600% and ~300% respectively, and in the borehole temperature leachates ~3,800% and 390% respectively (Fig. 12). Among anions, chloride (Cl⁻) in the shale and chert low temperature leachate decreased 13% and 20%, respectively, and in the 70°C experiment by ~10% for both lithologies (Fig. 11). Sulfate (SO₄²⁻) increased in both shale and chert leachates at low temperature (840% and 430%, respectively) and 70°C experiments (1440% and 430% respectively; Fig. 13).

Among trace elements, boron (B), manganese (Mn), lithium (Li), and nickel (Ni) concentrations increased in both shale and chert leachates. The concentrations of B in the 70°C leachates were nearly double those at 23°C in both samples; boron in shale at 23°C was 73 µg/L, compared to 129 µg/L at 70°C; the chert shifted from 128 µg/L (23°C) to 202 µg/L (70°C). Shale leachate Mn concentrations were 46 µg/L and 181 µg/L in the 23°C and 70°C leachates respectively, while chert leachate Mn concentrations were 19 µg/L and 54 µg/L in the 23°C and 70°C leachates respectively. Lithium concentrations in the shale leachate increased from 24 µg/L to 36 µg/L in the 23°C and 70°C leachates respectively. Ni in the shale and chert low temperature leachate increased by 77% and 45%, respectively and by similar amounts at 70°C (Fig. 14).

Table 4: The major cation, anion and trace element composition of the starting synthetic fracturing fluid and the leachates from GC-MS 7801 (Marcellus Shale) and GC-HC 7909.7 (Huntersville Chert) for the 23°C and 70°C experiments.

	Temp. °C	pH	Na	Ca	Mg	K	Ba	Ni	Mn	B	Li	Br ⁻	Cl ⁻	SO ₄ ²⁻	NO ₂ ⁻	HCO ₃ ⁻
			mgL ⁻¹				µgL ⁻¹					mgL ⁻¹				
<i>Synthetic Fracturing Fluid</i>	-	5.7	6,762	2,033	229	175	38	44	nd	<71	<3	75	17,082	14	26	54
GC-MS 7801 Marcellus Shale	23 °	5.7	7,187	2,035	185	169	1,025	78	46	73	24	<6.6	14,883	131	<3.4	43
	70 °	5.4	7,120	2,076	192	179	1,472	72	181	129	36	<6.6	15,033	216	<3.4	22
GC-HC 7909.7 Huntersville Chert	23 °	5.8	7,257	2,056	189	179	154	64	19	128	BDL	<6.6	13,595	74	<3.4	24
	70 °	5.5	7,394	2,067	203	174	185	67	54	202	46	<6.6	14,926	74	<3.4	17

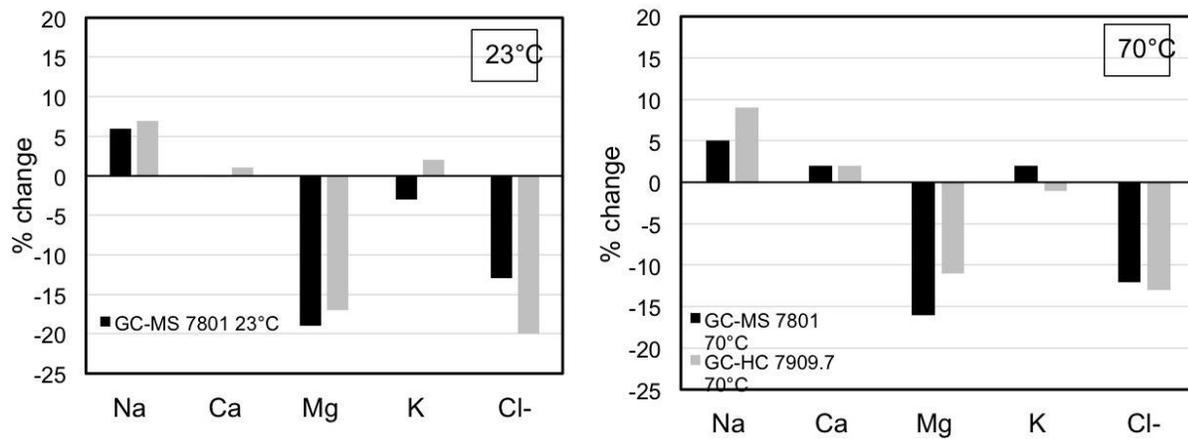


Figure 11: Change in sodium, potassium and calcium content in leaches after fluid-rock interaction at 23°C and 70°C.

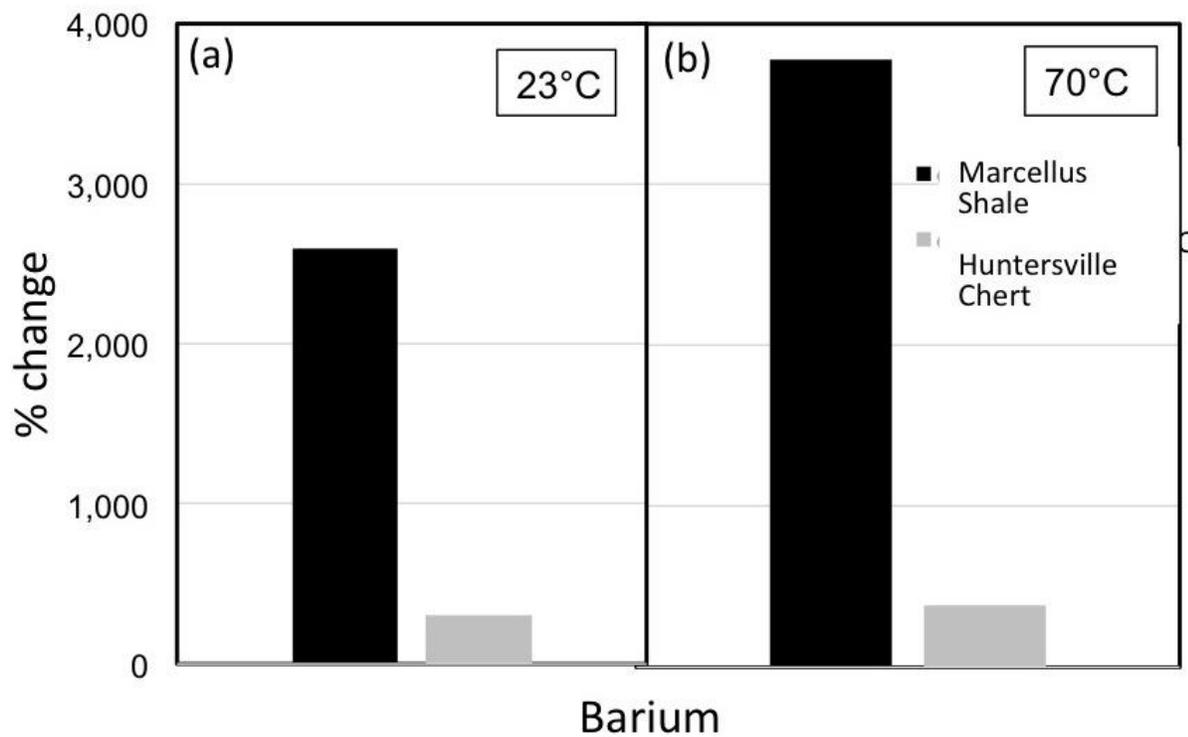


Figure 12: Change in barium content in leaches after fluid-rock interaction at 23°C and 70°C.

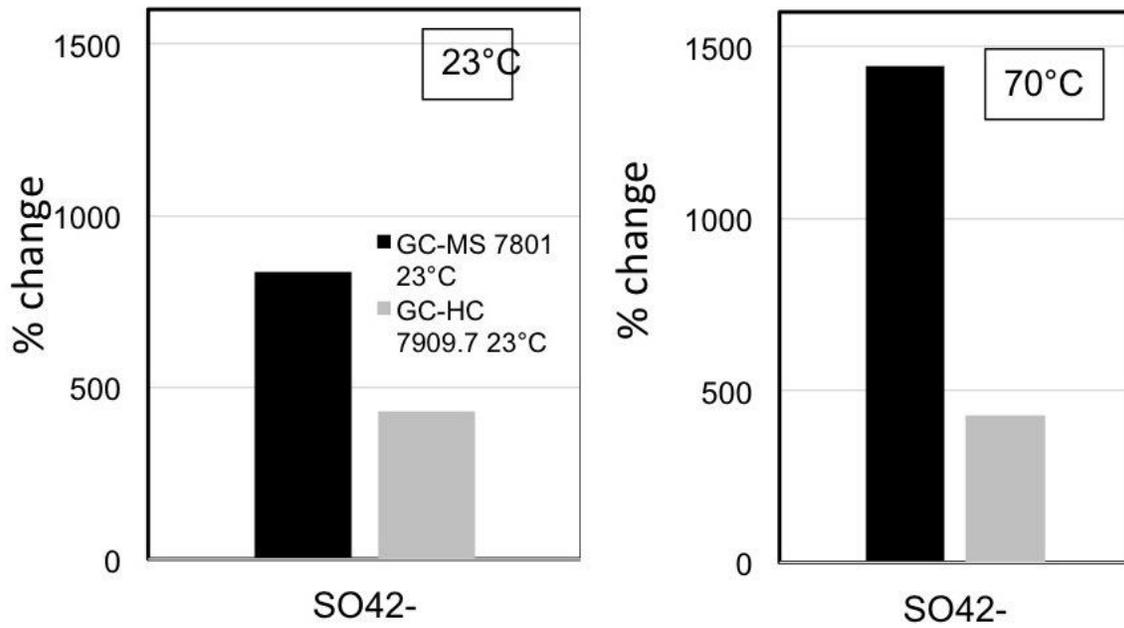


Figure 13: Change in post-experiment sulfate content.

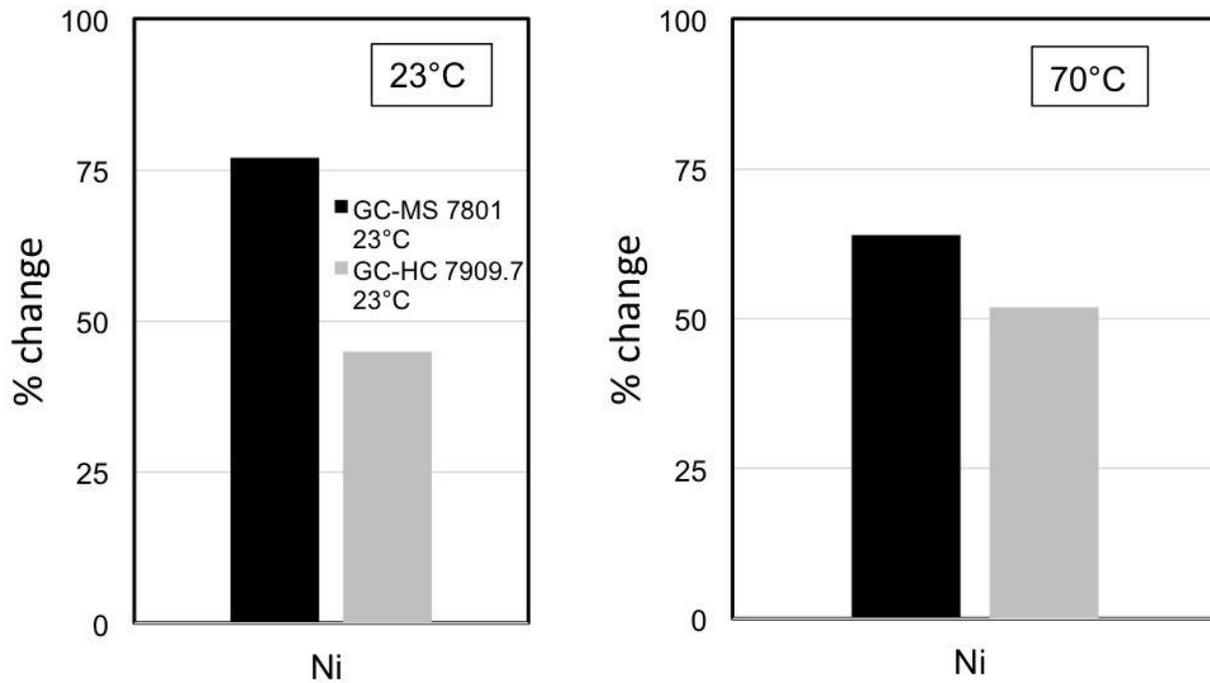


Figure 14: Change in nickel content in leaches after fluid-rock interaction at 23°C and 70°C.

3.2 BET SURFACE AREA CHANGES

Pre-experiment surface area on the <1mm Marcellus Shale sample (GC-MS 7801) was 18.2 m²/g (Table 5). The Huntersville Chert sample (GC-HC 7909.7) had a much lower starting surface area of 2.3 m²/g. Following interaction with the synthetic fracturing fluid the shale showed a slight decrease in surface area at 70°C (Fig. 15a). The chert surface area showed significant increase after both 23°C (+ 26%) and 70°C (+35%) experiments (Figure 15b).

Table 5: Surface area of samples pre-experiment and post-experiment changes.

Sample	Temp. °C	Surface area m^2g^{-1}	Total pore volume cm^3g^{-1}	Average pore diameter nm	Change in surface area	Change in pore volume %	Change in average pore diameter
Marcellus Shale (GC-MS 7801) post-experiment	-	18.2	0.029	6.4			
	23 °	18.1	0.048	10.5	-1	+64	+64
	70 °	17.2	0.030	7.0	-5	+2	-52
Huntersville Chert (GC-HC 7909.7) post-experiment	-	2.3	0.008	14.6			
	23 °	2.9	0.014	19.7	+26	+42	+35
	70 °	3.1	0.009	12.0	+35	+10	-18

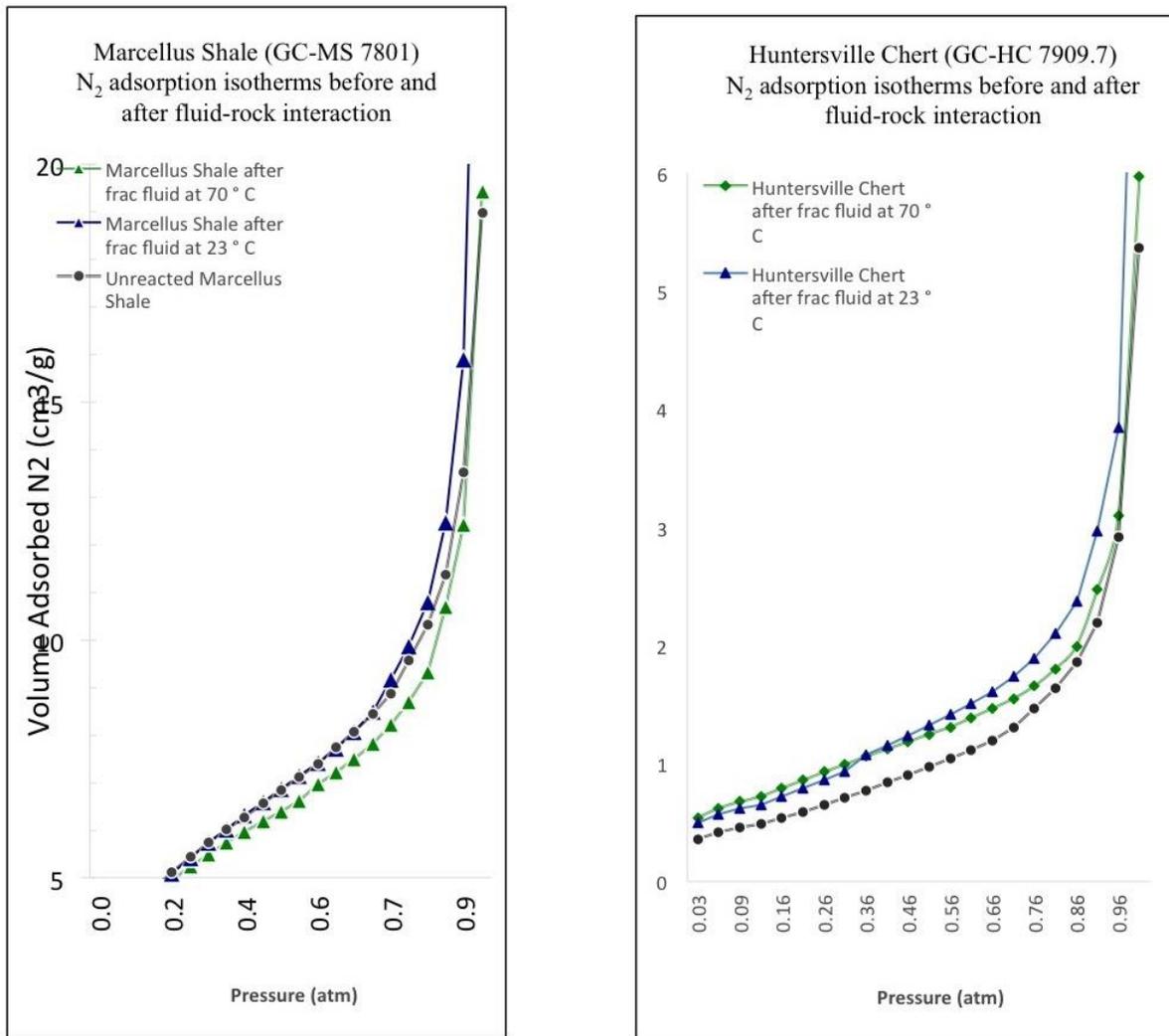


Figure 15: BET adsorption isotherms for samples pre- and post-experiment at 70°C.

3.3 MINERALOGICAL AND TEXTURAL CHANGES

Clay minerals (<3.9 μm) (illite and/or chlorite group) and fine-grained framboidal pyrite were observed in backscatter E-SEM of the Marcellus Shale sample (GC-MS 7801) before crushing (Fig. 7), and in the post-experiment crushed shale residue.

XRD results for rock residues from Marcellus Shale sample GC-MS 7801 post-70°C experiments indicate that some gypsum dissolution occurred (Fig. 16). E-SEM analysis of the post-70°C shale residue showed a decrease in grain angularity and evidence of dissolution along the edges of clay-sized illite/chlorite (Fig. 17; Table 5). Pyrite was observed in pre-and post-shale residues.

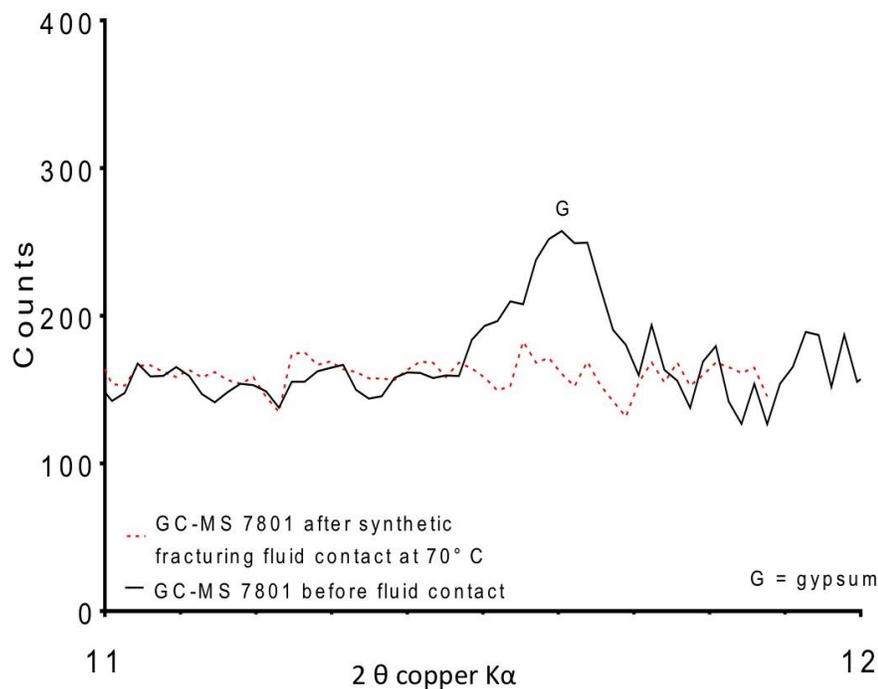


Figure 16: XRD plot for Marcellus Shale sample GC-MS-7801 showing gypsum loss after the 70° experiment.

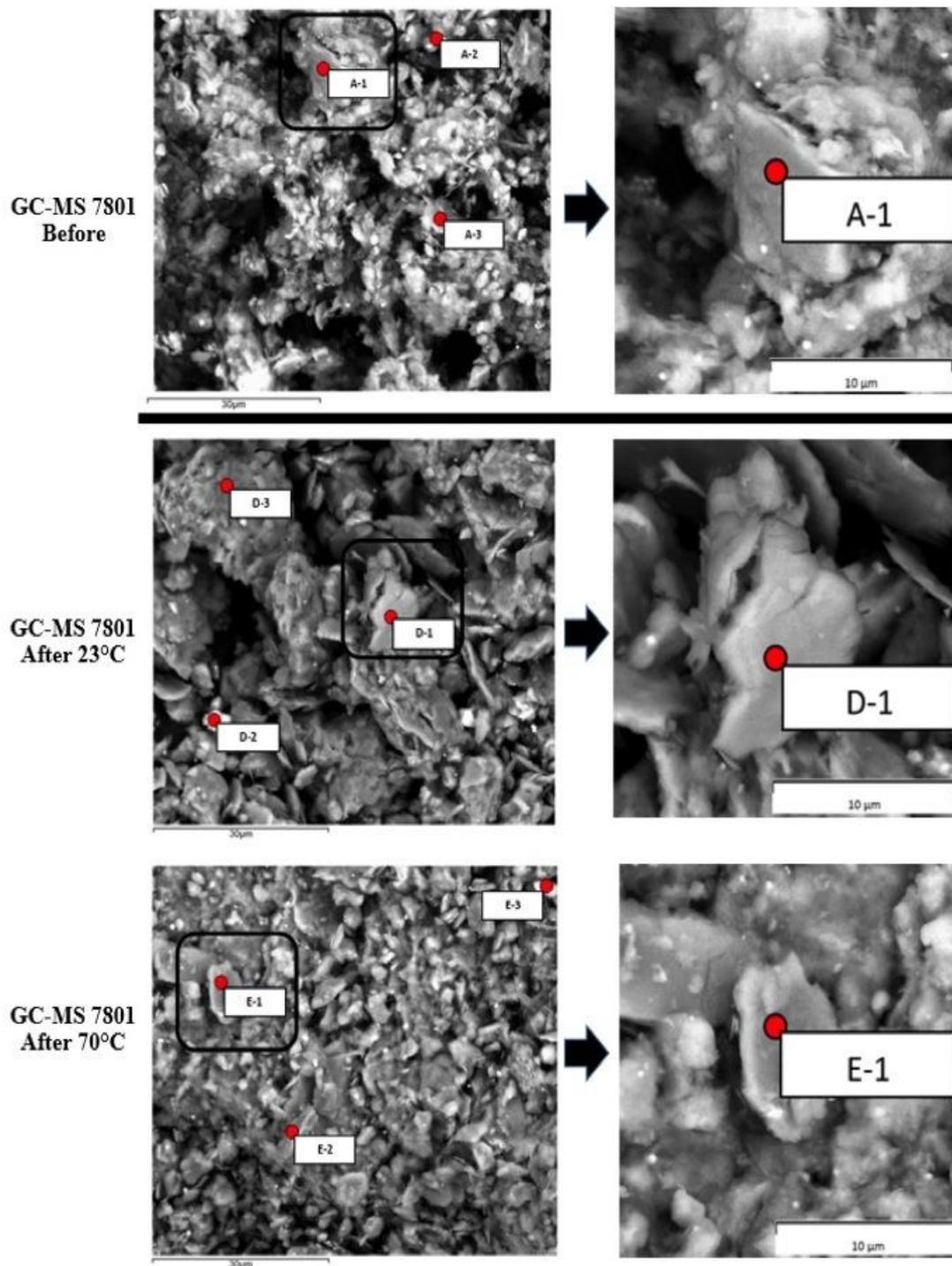


Figure 17: E-SEM backscatter images showing possible aluminosilicate mineral rounding in the GC-MS 7801 sample after 23°C and 70°C synthetic fracturing fluid interaction.

4.0 DISCUSSION

The experimental results indicate that temperature-dependent and lithology-dependent changes in the chemical composition of the saline fluid and the mineralogy and texture of the rock samples occurred as a result of water-rock interaction. Decreased concentrations of some chemical constituents such as chloride could be related to fluid imbibition (Engelder et al., 2014). Other changes are likely the result of several processes, including mineral dissolution and precipitation reactions, cation exchange on clay surfaces, and mobilization of trace metals related to elevated temperature and reaction with high ionic strength fluids. Although the absolute mass of the elements released as a result of fluid-rock interaction in these experiments was significantly lower than the concentrations observed in Marcellus produced waters (e.g. Hayes, 2009; Chapman, 2012, Haluszczak, 2013), the changes in mineralogical composition and elemental concentrations in the leachates provide information about mineral dissolution and exchange reactions occurring as a result of interaction of Marcellus Shale and Huntersville Chert with saline fluids.

4.1 DISSOLUTION – PRECIPITATION REACTIONS

Silicate dissolution can occur during shale-brine interaction (Credoz et al., 2009). Alteration of clay-sized minerals in the Marcellus Shale (chlorite or illite, based on E-SEM-EDX and XRD) was observed along grain edges, which were rounded in comparison to the pre-leaching samples. Saturation indices calculated from the experimental fluid composition indicate that illite, chlorite, microcline and albite identified in the experimental shale sample could dissolve in the synthetic fracturing fluid ($Q/K < 1$). Liu et al. (2012) reported feldspar dissolution following interaction of shale with synthetic brine under high temperatures and pressures (200°C and 300 bars). Illite dissolution increases with temperature, and as pH moves towards basic conditions (Kaszuba et al., 2013). The experiments by Kaszuba et al. (2013) were conducted at 1 atm and lower temperatures; thus silicate dissolution likely involves clay minerals.

Autochthonous salts such as halite (NaCl) and anhydrite (CaSO₄) can be present in the Marcellus Shale (Blauch et al., 2009; Laughrey et al., 2011). Gypsum but not anhydrite was identified in the Marcellus Shale sample in this experiment. Gypsum (CaSO₄•2H₂O) is present in Marcellus Shale exposed to subaerial weathering, likely a result of pyrite and calcite dissolution or hydration of anhydrite (Allin, 2014). In our experiments, gypsum is undersaturated in the starting fluid; XRD analysis confirms that gypsum dissolution occurred in the Marcellus Shale sample after brine exposure. Because the experimental fluid is saturated with respect to pyrite ($Q/K > 1$), the presence of gypsum in the shale before leaching could be related to hydration of anhydrite during the sample preparation process.

4.2 CATION EXCHANGE PROCESSES

Cation exchange processes in shales are a function of mineralogy and the ionic strength and chemical composition of fluids interacting with the minerals (Long and Angino, 1982; Van Oort, 2003). Addition of cations into interlayer exchange sites on expandable clays such as smectite can result in volume expansion and a reduction in permeability (Mohan et al., 1999). Exchange of divalent cations such as Mg, Ca and Ba and release of sodium can enhance dissolution/precipitation reactions and can change fluid composition.

Diagenetic barite (BaSO_4) has been identified in black shales and cherts of Cambrian age (Wang and Li, 1991), and is found in nodular form within the Marcellus Shale (Nuelle et al., 1986). Barite is undersaturated in the fluid and concurrent release of sulfate and barium in the post-experiment leachates could suggest barite dissolution. However, nodular barite was not present in the Marcellus Shale sample analyzed in this study, and Hosterman and Whitlow (1983) found no evidence for disseminated barite in Devonian Appalachian Basin shales. Although barite is relatively insoluble, microbial sulfate reduction could have solubilized Ba and allowed it to migrate through pore fluids (Arthur and Sageman, 1994), where Ba has an affinity for exchange sites on clay minerals.

Analysis of whole rock and sequential extraction leachates of Marcellus Shale and associated calcareous rocks indicates that although much of the barium remains in the silicate residue, the majority of extractable barium is held on exchange sites, rather than in soluble salts or carbonate minerals (Phan et al., 2015; Stewart et al., 2015). The results of this study are consistent with release of Ba from both the shale and chert by cation exchange processes, as Ba release was more significant in the clay-rich shale than in the chert. The increase in sulfate

concentration in the shale leachates is considered to be primarily the result of gypsum dissolution, as discussed above.

4.3 TRACE METAL MOBILIZATION

Manganese and nickel are redox-sensitive elements associated with organic carbon deposition in sedimentary rocks such as marine shales (Piper and Calvert, 2009). Although the increases in Ni concentrations in leachates from both samples were not measurably affected by temperature, manganese release increased with temperature. Sequential extraction experiments indicate that extractable nickel in the Marcellus Shale is likely held on exchange sites or in carbonate minerals, while manganese is primarily held in carbonate minerals (Stewart et al., 2015). The observed mobilization of nickel and manganese from the shale and chert as a result of interaction with high ionic strength fluids is consistent with experimental work on other metals (Cu, Pb, and Zn) released from shales. For example, Long and Angino (1982) found that mobilization of metals from shale in contact with saline fluids increased with temperature and ionic strength of the fluid, and that the fluid composition also affected the suite of trace metals released.

Boron and lithium concentrations increased in the synthetic fracturing fluid leachates of both shale and chert, and measurably increased with temperature. This was most apparent in the 70°C leachate of the calcareous Huntersville chert. Lithium is associated with weathering reactions and high cation exchange capacity (CEC) clay minerals, where it replaces Na on silicate surfaces or substitutes for Mg in secondary clays (Huh et al., 2004; Millot et al., 2010; Liu et al., 2013). Boron in sedimentary rocks is present in water-soluble borate minerals associated with evaporites, sorbed onto marine sediments, and incorporated into biogenic marine

carbonates (Vengosh, 1991). It can also occur in potassium feldspar such as microcline, which is present in trace amounts (<10%) in the Huntersville Chert sample. As there is no evidence for feldspar dissolution, it is likely boron and lithium were released from carbonate minerals and/or by cation exchange on clays.

5.0 CONCLUSIONS

Interactions between clay-rich shale and calcareous or clay-containing seal rocks with saline formation waters or water-based hydraulic fracturing fluids are reflected in the geochemical composition of the returning fluid. This research project involved experiments that were designed to simulate fluid-rock interactions at borehole temperatures (70°C) between saline hydraulic fracturing fluids and fractured Marcellus Shale and the underlying Huntersville Chert.

Post-experiment changes in both the rock and the fluid suggest that barium release from both lithologies is primarily by cation exchange processes on clay surfaces. Dissolution of gypsum in the shale could be related to hydration of anhydrite related to subaerial exposure or during subsurface exposure to fluids after hydraulic fracturing. Textural evidence indicated possible incipient dissolution of illite/chlorite. Boron and lithium were released from both shale and chert, most likely from clay surfaces and from carbonate mineral dissolution. Mobilization of nickel and manganese was consistent with exchange reactions associated with high ionic strength fluids. These changes occurred over a time span of four days, and could be indicative of processes operating soon after fracturing and fluid-rock contact. The results have relevance to the interaction of both saline injection fluids and *in situ* formation waters with the Marcellus Shale and related confining rocks; the increased reactive surface area resulting from hydraulic fracturing could enhance these reactions.

BIBLIOGRAPHY

- Allin, N. C. (2014) Secondary minerals and constituents of the Marcellus Shale Formation. *The Juniata Journal of Geology*, 1, 1-5.
- Arthur, M. A., & Sageman, B. B. (1994) Marine black shales; depositional mechanisms and environments of ancient deposits. *Annual Review of Earth and Planetary Sciences*, 22, 499-551.
- Arthur, M. A., & Cole, D. R. (2014) Unconventional hydrocarbon resources; prospects and problems. *Elements*, 10(4), 257-264.
- Benelli, P. (2012) Comparison between whole rock lithochemistry and fine lithochemistry of marcellus shale (Order No. 1519899). Available from ProQuest Dissertations & Theses Full Text: Science & Technology; ProQuest Dissertations & Theses Global: Science & Technology. (1114137845).
- Blauch, M. E., Myers, R. R., Moore, T. R., & Lipinski, B. A. (2009) Marcellus Shale post-frac flowback waters – where is all the salt coming from and what are the implications? *Society of Petroleum Engineers, SPE 125740*, 1-20.
- Boschee, P. (2014) Produced and flowback water recycling and reuse economics, limitations, and technology. *Oil and Gas Facilities*, 17-22.
- Bryant, J., Welton, T., & Haggstrom, J. (2010) Will flowback or produced water do? *Energy & Production*.
- Capo, R. C., Stewart, B. W., Rowan, E. L., Kolesar Kohl, C., A., Wall, A. J., Chapman, E. C., Schroeder, K. T. (2014) The strontium isotopic evolution of Marcellus formation produced waters, southwestern Pennsylvania. *International Journal of Coal Geology*, 126, 57-63.
- Chapman, E.C., Capo, R.C., Stewart, B.W., Hammack, R., Schroeder, K., and Edenborn, H.M. (2012) Geochemical and strontium isotope characterization of produced waters from Marcellus Shale natural gas extraction. *Environmental Science and Technology* v.46: 3545-3553

- Coleman, J.L., Milici, R.C., Cook, T.A., Charpentier, R.R., Kirschbaum, Mark, Klett, T.R., Pollastro, R.M., and Schenk, C.J. (2011) Assessment of undiscovered oil and gas resources of the Devonian Marcellus Shale of the Appalachian Basin Province: U.S. Geological Survey Fact Sheet 2011-3092, 2 p.
- Creodoz, A., Bildstein, O., Jullien, M., Raynal, J., Petronin, J.-C., Lillon, M., Pozo, C., Geniaut, G. (2009) Experimental and modeling study of geochemical reactivity between clayey caprocks and CO₂ in geological storage conditions. *Energy Procedia* 1, 2445-3452.
- Dresel, P.E., and Rose, A.W. (2010) Chemistry and origin of oil and gas well brines in western Pennsylvania: Pennsylvania Geological Survey, 4th ser., Open-File Report OFOG 10-01.0 48 p.
- Engelder, T., & Lash, G. G. (2008, May) Marcellus Shale Play's Vast Resource Potential Creating Stir in Appalachia. *The American Oil and Gas Reporter*.
- Engelder, T. (2009) Marcellus 2008: Report card on the breakout year for gas production in the Appalachian Basin. *Basin Oil and Gas*, (20), 18-22.
- Engelder, T., Cathles, L. M., & Bryndzia, L. T. (2014) The fate of residual treatment water in gas shale. *Journal of Unconventional Oil and Gas Resources*, (7), 33-48.
- Ewy, R. T., Bovberg, C. A., & Stankovich, R. J. (2008) Shale Triaxial Strength Alteration due to Brine Exposure. In ARMA-08-304: The 42nd U.S. Rock Mechanics Symposium (USRMS), 29 June-2 July, San Francisco, California (pp. 1-9). American Rock Mechanics Association.
- Gregory, K. B., Vidic, R. D., & Dzombak, D. A., (2011) Water management challenges associated with the production of shale gas by hydraulic fracturing. *Elements*, 7(3), 181-186.
- Hakala, A. J., Marcon, V., Joseph, C., Hedges, S., Carter, K., Garber, W., Disenhof, C., Howard, B., Mouser, P. (2015 in preparation) Geochemical Reactions between Marcellus Shale and Hydraulic Fracturing Fluids, Part 1: Evaluating Metal Release from Shale through Laboratory Experimentation. NETL-TRS EPAAct Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Pittsburgh, PA.
- Haluszczak, L. O., Rose, A. W., & Kump, L. R. (2013). Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Applied Geochemistry*, 28, 55-61.
- Harper, J. A. (2008) The Marcellus Shale—An old “new” gas reservoir in Pennsylvania. *Pennsylvania Geology*, 38, 2-13.

- Hammack, R., Harbert, W., Sharma, S., Stewart, B., Capo, R., Wall, A., Wells, A., Diehl, R., Blaushild, D., Sams, J., Veloski, G. (2014) An Evaluation of Fracture Growth and Gas/Fluid Migration as Horizontal Marcellus Shale Gas Wells are Hydraulically Fractured in Greene County, Pennsylvania; NETL-TRS-3-2014; EPAAct Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Pittsburgh, PA; p 76.
- Hayes, T. (2009) Sampling and analysis of water streams associated with the development of Marcellus shale gas. Report by Gas Technology Institute, Des Plaines, IL, for the Marcellus Shale Coalition.
- Hosterman, J. W., and Withlow, S. I., 1983, Clay Mineralogy of Devonian Shales in the Appalachian Basin, *in* USGS, ed., Volume Geological Survey Professional Paper 1298.
- Husain, T. M., Yeong, L. C., Saxena, A., Cengiz, U., Ketineni, S., Khanzhode, A., & Muhamad, H. (2011) EME 580: Integrative Design of Energy & Mineral Engineering Systems: Economic Comparison of Multi-Lateral Drilling over Horizontal Drilling for Marcellus Shale Field Development. State College, PA: The Penn State University.
- He, C., Li, M., Liu, W., Barbot, E., Vidic, R. D. (2013) Kinetics and equilibrium of barium and strontium sulfate formation in Marcellus Shale flowback water. *Journal of Environmental Engineering* B4014001, 1-9.
- Huh, Y., Chan, L. and Chadwick, O. (2004) Behavior of lithium and its isotopes during weathering of Hawaiian basalt, 2004, *Geochemistry, Geophysics, Geosystems* 5; 1-22.
- Jin, L., Mathur, R., Rother, G., Cole, D., Bazilevskaya, E., Williams, J., Carone, A., Brantley, S. (2013) Evolution of porosity and geochemistry in Marcellus Formation black shale during weathering. *Chemical Geology* 356, 50-63.
- Kaszuba, J.P., Yardley, B., and Andreani, M. (2013) Experimental perspectives of mineral dissolution and precipitation due to carbon dioxide-water-rock interactions: *Reviews in Mineralogy & Geochemistry*, v. 77, p. 153-188.
- King, G.E. (2012) Hydraulic Fracturing 101: What Every Representative, Environmentalist, Regulator, Reporter, Investor, University Researcher, Neighbor and Engineer Should Know About Estimating Frac Risk and Improving Frac Performance in Unconventional Gas and Oil Wells. Society of Petroleum Engineers, SPE 152596, 1-80.
- Laughrey, C. D., Ruble, T. E., Lemmens, H., Kostelnik, J., Butcher, A. R., Walker, G., & Knowles, W. (2011) Black Shale Diagenesis: Insights from Integrated High-Definition Analyses of Post-Mature Marcellus Formation Rocks, Northeastern Pennsylvania. Search and Discovery Article #110150. AAPG Annual Convention and Exhibition, Houston, Texas, USA.

- Liu, F., Lu, P., Griffith, C., Hedges, S.W., Soong, W., Hellevang, H., Zhu, C. (2012) CO₂-Brine-Caprock Interaction: Reactivity Experiments on Eau Claire Shale and a Review of Relevant Literature. *International Journal of Greenhouse Gas Control*, (7), 153-167.
- Liu, S. (2013) Laboratory Investigations on the Geochemical Response of Groundwater-sediment Environment to Hydraulic Fracturing Fluids (Master's thesis). The Ohio State University, Columbus, OH.
- Liu, X.M., Rudnick, R.L, McDonough, W.F., Cummings, M.L (2013) Influence of chemical weathering on the composition of the continental crust: Insights from Li and Nd isotopes in bauxite profiles developed on Columbia River Basalts, *Geochimica et Cosmochimica Acta*, 115, 73-91.
- Long, D. T., & Angino, E. E. (1982) The mobilization of selected trace metals from shales by aqueous solutions; effects of temperature and ionic strength. *Economic Geology and the Bulletin of the Society of Economic Geologists*, 77(3), 646-652.
- Lower 48 States shale plays. (2015) U.S. Energy Information Administration. Retrieved from http://www.eia.gov/oil_gas/rpd/shale_gas.pdf
- Millot, R., Vigier, N., Gaillardet, J. (2010) Behaviour of lithium and its isotopes during weathering in the Mackenzie Basin, Canada, *Geochimica et Cosmochimica Acta*, 74, 3897-3912.
- Mohan, K.K., Reed, M.G., Fogler, S.H. (1999) Formation damage in smectitic sandstones by high ionic strength brines, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 154, 249-257.
- Nuelle, L. M., & Shelton, K. L. (1986) Geologic and geochemical evidence of possible bedded barite deposits in devonian rocks of the valley and ridge province, appalachian mountains. *Economic Geology and the Bulletin of the Society of Economic Geologists*, 81, 1408-1430.
- Pagels, M., Willberg, D.M., Edelman, E., Zagorski, W., Frantz, J. (2013) Quantifying Fracturing Fluid Damage on Reservoir Rock to Optimize Production. Proceedings of the Unconventional Resources Technology Conference, URTeC 1578948.
- Papso, J., Blauch, M., & Grottenthaler, D. (2011) Cabot Gas Well Treated with 100% Reused Frac Fluid. Nabors Completion & Production Services Co. Houston, TX: Nabors Completion & Production Services Co.
- Phan, T.T. Capo, R.C., Stewart, B.W., Graney, J.R. Johnson, J.D., Sharma, S., Toro, J. (2015) Trace metal distribution and mobility in drill cuttings and produced waters from Marcellus Shale gas extraction: Uranium, arsenic, barium, *Applied Geochemistry*, <http://dx.doi.org/10.1016/j.apgeochem.2015.01.013>.

- Piper, D. Z., & Calvert, S. E. (2009) A marine biogeochemical perspective on black shale deposition. *Earth-Science Reviews*, 95, 63-96.
- Rassenfoss, S. (2011) From Flowback to Fracturing: Water Recycling Grows in the Marcellus Shale. *Journal of Petroleum Technology*, 49-52.
- Rowan, E.L., Engle, M.A., Kirby, C.S., and Kraemer, T.F. (2011) Radium content of oil- and gas-field produced waters in the northern Appalachian Basin (USA)—Summary and discussion of data: U.S. Geological Survey Scientific Investigations Report 2011–5135, 31p.
- Rowan, E. L., Engle, M. A., Kraemer, T. F., Schroeder, K. T., Hammack, R. W., & Doughten, M. W. (2015) Geochemical and isotopic evolution of water produced from Middle Devonian Marcellus shale gas wells, Appalachian basin, Pennsylvania. *AAPG Bulletin*, 99, 181-206.
- Soeder, D. J., & Kappel, W. M. (2009) *Water Resources and Natural Gas Production from the Marcellus Shale*. Baltimore, MD: U.S. Geological Survey.
- Soeder, D. J., Enomoto, C. B., & Chermak, J. A. (2014a) The Devonian Marcellus Shale and Millboro Shale. *GSA Field Guide*, 35, 129-160.
- Soeder, D., Sharma, S., Pekney, N., Hopkinson, L., Dilmore, R., Kutchko, B., Stewart, B.W., Hakala, J.A., Carter, K., Capo, R.C. (2014b) U.S. DOE methods for assessing the environmental risks of shale gas development, *International Journal of Coal Geology* 126, 4-19.
- Spivak-Birndorf, L., Stewart, B. W., Capo, R. C., Chapman, E. C., Schroeder, K. T., & Brubaker, T. M. (2012) Strontium isotope study of coal utilization by-products interacting with environmental waters. *Journal of Environmental Quality*, 41, 144-154.
- Staub, P. (2014) *Clay mineralogy of the Marcellus and Utica Shales: Implications for fluid development via cation exchange*. MS Thesis, University of Buffalo.
- Stewart, B.W., Chapman, E.C., Capo, R.C., Johnson, J.D., Graney, J.R., Kirby, C.S., Schroeder, K.T., (2015). Origin of brines, salts and carbonate from shales of the Marcellus Formation: Evidence from geochemical and Sr isotope study of sequentially extracted fluids, *Applied Geochemistry*, <http://dx.doi.org/10.1016/j.apgeochem.2015.01.004>.
- Van Oort, E. (2003) On the physical and chemical stability of shales, *Journal of Petroleum Science and Engineering*, 38, 213-235.
- Vengosh, A., Kolodny, Y., Starinsky, A., Chivas, A., and McCulloch, M. (1991) Coprecipitation and isotopic fractionation of boron in modern biogenic carbonates, *Geochimica et Cosmochimica Acta*, 55, 2901-2910.

- Vidic, R.D.; Brantley, S.L.; Vandenbossche, J. M.; Yoxtheimer, D.; Abad, J.D. (2013) Impact of shale gas development on regional water quality. *Science*, 340, online 1235009-1-9, DOI: 10.1126/science.1235009
- Wang, Z., & Li, G. (1991) Barite and witherite deposits in lower cambrian shales of south china; stratigraphic distribution and geochemical characterization. *Economic Geology and the Bulletin of the Society of Economic Geologists*, 86, 354-363.
- Whitacre, J. V, and Slyder, J. B. (2015) Carnegie Museum of Natural History Pennsylvania Unconventional Natural Gas Wells Geodatabase (v.2014-Q4) [computer file]. Pittsburgh, PA: Carnegie Museum of Natural History. Available download: URL: <http://maps.carnegiemnh.org/index.php/projects/unconventional-wells/>. Accessed: April 8, 2015.
- Wrightstone, G. (2008) Marcellus Shale – Geologic Controls on Production. Presentation at the Eastern Section Meeting of the American Association of Petroleum Geologists.
- Zagorski, W. A., Wrightstone, G. R., & Bowman, D. C. (2012) The Appalachian basin Marcellus gas play; its history of development, geologic controls on production, and future potential as a world-class reservoir. *AAPG Memoir*, 97, 15-18.
- Zusman, N. (2010) Fracking: Gas Drilling and the Marcellus Shale. Retrieved October 21, 2014, from Fracking Resource Guide website: <http://frack.mixplex.com/fracking>.