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**EFFECT OF MATURITY AND MINERALOGY ON FLUID-ROCK REACTIONS IN
THE MARCELLUS SHALE**

John Pilewski

Thesis Submitted to:
The Eberly College of Arts and Sciences
West Virginia University

In partial fulfillment of the requirements for the degree of

Masters of Science
in
Geology

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ABSTRACT

EFFECT OF MATURITY AND MINERALOGY ON FLUID-ROCK REACTIONS IN THE MARCELLUS SHALE

John Pilewski

The advancement in drilling technology and discoveries of large quantities of natural gas in the United States has led to a substantial increase in hydraulic fracturing (HF) operations in the past two decades. The Marcellus Shale is a world-renowned source rock that has been extensively exploited via HF, and this study aims to analyze the complex chemical reactions that take place during this process of hydrocarbon extraction. Fluid-shale reactions were conducted using a mixture of synthetic brine, and synthetic hydraulic fracturing fluid reacted with three shale samples of varying maturity and mineralogy. Static autoclave reactors were used to mimic in situ reservoir reaction parameters, roughly 2,500 psi and 100°C respectively. Reactions were carried out for 14 days in accordance with the shut-in time when fluid remains in the reservoir during the HF process. The chemical analysis focused on observing major changes in ionic species concentrations and the proliferation of low molecular weight organic compounds with respect to maturity and mineralogy. Shale samples LM-2 and MIP-3H containing relatively greater amounts of carbonate minerals reacted as buffering agents during the reaction increasing the effluent pH to near neutral. Ion Chromatography results indicate an increase in sulfate and phosphate ions and decrease in barium ions in all fluid-shale effluents. These results suggest that the relative abundance of minerals, particularly calcite and pyrite, affect mineral dissolution and precipitation during HF operations. Results also show organic acids are generated in the control fluid, HPT-PF, by placing it under high pressure/temperature conditions without any shale interaction. Overall dissolved organic carbon concentrations decrease in all effluent samples compared to the control fluid. The GC-MS analysis focused on the observation of benzene, toluene, ethylene, and xylene (BTEX) analytes. Results indicate toluene and xylene were generated in the control fluid, HPT-PF, without any shale interaction. The least mature LM-2 sample generated effluent containing the highest concentrations of target VOC analytes, and the most mature MIP-3H sample generated no observable analytes. These results suggest that HFF additives are being transformed at reservoir pressure/temperature conditions, low mature shale is releasing geogenic, labile organic compounds, and high mature shale is adsorbing any VOCs generated from HF processes.

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1.0 Introduction

The discovery of large domestic shale reservoirs and advancements in hydraulic fracturing (HF) technology have shifted energy production in the United States toward unconventional natural gas extraction (U.S. EIA, 2017). HF is process by which an engineered fluid known as hydraulic fracturing fluid (HFF) is pumped into a “tight” reservoir at high hydrostatic pressure, effectively fracturing the rock and releasing hydrocarbons to the surface. Typically, the tight reservoir is an organic-rich, low permeability shale containing trapped hydrocarbons in a multitude of unconnected nanoscale pores. The newly formed fractures increase permeability in the shale and are held open by a proppant from the fluid, which facilitates the flow of the hydrocarbons to the wellbore (PA DEP, 2010). The fluid used for this process is made of mainly freshwater, proppant and a relatively small quantity of chemical additives that increase the efficacy of the fracturing process. An average well requires upwards of 5 million gallons of HFF in order to complete hydrocarbon extraction (PA DEP, 2010). On average roughly 40% of this fluid returns to the surface upon completion and is then considered produced fluid. Produced fluid has a chemical signature distinctly different from the initially injected HFF (Strong et al., 2014, Hoelzer, et al., 2016, Marcon, et al., 2017) and the copious amounts of fluid generated from thousands of wells drilled within the Marcellus Shale necessitate a better understanding of reactions occurring between HFF and the shale reservoir. Recycling and remediation efforts of produced fluid are of great concern to industry, environmental scientists, and the general public. Understanding changes in HFF chemistry throughout different stages of unconventional well production is vital to determining potential environmental impacts, HFF recycling techniques, and methods that increase the efficacy of HF.

Marcellus Shale

The Marcellus Shale is one of the major natural gas reservoirs in the United States that has been extensively exploited via HF over the past decade. The reservoir consists of Devonian-age black shale that covers roughly 95,000 sq. miles in the ancient sedimentary system known as the Appalachian basin. The organic-rich shale contains a relatively large weight percent of total organic carbon (TOC), and it is estimated to contain nearly 400 tcf of recoverable natural gas, making it a world-renowned source rock (U.S. EIA, 2017). It is composed of varying percentages of mixed-layer clays, quartz, feldspar, pyrite, calcite, dolomite, and gypsum. The depth and thickness vary longitudinally across the reservoir with the thickest and the deepest portion lying on the eastern edge below northeastern and central Pennsylvania, extending down into eastern West Virginia. The variation in depth corresponds to varying thermal maturity that ranges from the oil/wet gas in the east to dry gas window in the west (U.S. EIA, 2017). Each of these maturity zones contains the different type and amount of hydrocarbons and have different economical potential. The maturity zones or windows of the reservoir are separated into two main categories wet gas and dry gas. Natural gas liquids (NGLs), such as ethane, propane, and butane, produced from the less mature, wet gas window of the reservoir have become increasingly targeted due to their relatively high value compared to methane produced from the deeper, dry gas window (DOE 2017).

Organic matter in the Marcellus Shale was sourced from a mixture of marine and terrestrial sources and shows a mixture of Type II/III kerogen (Chen et al., 2015, Agrawal and Sharma, 2018a, b). Diagenetic and catagenic reactions, including the removal of heteroatoms and cracking of bonds, transformed the organic matter over millions of years into the hydrocarbons extracted today. Kerogen, the macromolecule leftover from thermal degradation, has been

analyzed from different maturity zones of the Marcellus to determine how its chemical structure is altered during these processes and how it varies with depth (Agrawal and Sharma, 2018b). These studies have indicated that samples from less mature Marcellus Shale have a more aliphatic kerogen structure and a higher percentage of labile functional groups. The kerogen from more mature dry gas window of the Marcellus Shale has a more aromatic structure. The higher aromaticity results in an increase in pore size and higher surface area for adsorption (Chalmers et al., 2008, 2012; Zhang et al., 2012; Zargari et al., 2015.)

Hydraulic Fracturing Fluid (HFF)

Hydraulic fracturing fluid (HFF) is one of the most important components of HF operations. It is designed to perform particular functions throughout hydrocarbon extraction, such as over pressuring and fracturing the source rock, placing proppant within fractures, and conveying gas and fluid flow to the well bore. As mentioned previously, different zones of the reservoir exhibit varying mineralogy and organic matter maturity. These variations are taken into account when designing and implementing a unique HFF mixture at each well. Amounts of freshwater, proppant, and additives must be properly proportioned to address the geologic properties of each targeted reservoir zone. The additives utilized in HFF are of great significance as they play important roles in how the fluid reacts with the shale and facilitate effective hydrocarbon extraction. Main additives used include an acid to prevent mineral scaling, gelling agents to carry and place proppant, surfactants to reduce surface tension and convey fluid flow, and breakers which control the fluid's viscosity after proppant placement (PA DEP, 2010).

HFF is used to fracture the reservoir in stages along a lateral wellbore which can be thousands of feet long. Each stage is typically 100-200 feet long placement (PA DEP, 2010) and they are plugged in succession until they are drilled out after they have all been successfully

fractured. This method implies that HFF is left in contact with the freshly fractured shale for days or weeks until well completion and production begins. During this shut-in phase, HFF reacts with the shale rock in reservoir at a relatively high temperature and pressure conditions. In situ conditions and residence time in the subsurface alter the fluid significantly and provide a distinct chemical signature to the flowback and produced fluid that is very different from the initial injection fluid (Vankeuren et al., 2017).

Compounds Observed in Produced Fluid from Marcellus Shale

Studies aimed at analyzing produced water from HF operations in the Marcellus Shale mainly focus on sampling and analyzing fluid from various well sites and from laboratory fluid-shale experiments. Significant variations in mineralogy and maturity throughout the basin and the utilization of unique mixtures of HFF make it difficult to comprehensively assess chemical signatures of produced fluid from different parts of the reservoir. Many studies provide evidence of mineral dissolution, and precipitation (He and Vidic, 2016, Marcon et al., 2016, Vankeuren et al., 2017) and elevated levels of dissolved organic carbon (DOC) observed in fluids returning to the surface (Abualfaraj et al., 2014).

Mineral precipitation and dissolution are of great concern during HF operations and can ultimately affect production. Dissolution of carbonate minerals can significantly alter the fluid pH, affecting any anti-scaling efforts (He and Vidic, 2016). Some HF wells have been observed to show a large decline in production after completion, and it is postulated this decrease may be due to the precipitation of minerals that clog fractures and inhibit gas flow and decrease the efficacy of a well.

There are multiple contentions regarding the source of DOC observed in HFF returning to the surface post-fracturing: anthropogenic (from HFF) or geogenic (from the formation)

(Marcon et al., 2016). Potential sources of LMWOCs include the mobilization of compounds from shale and the transformation of organic additives in HFF. Research also shows flowback and produced waters from Marcellus Shale production contain elevated levels of low molecular weight organic compounds (LMWOCs) compared to the high molecular weight organic compounds found in injection fluid (Maguire-Boyle & Barron, 2014). Specifically, benzene has been detected at elevated levels 40 days after well completion (Ziemkiewicz et al., 2015). The presence of these organic compounds in produced fluid presents one of the biggest complications in effectively recycling and reusing produced fluid. Methods used to remediate the fluid include reverse osmosis and filtration, both of which are costly. Better understanding of the controls on the amount and type of inorganic and organic compounds in the produced fluid and how it varies in different parts of the basin could potentially help in designing better HFF fluids and developing better targeted produced water reuse-recycle technologies. This would not only reduce risk of contamination but also ultimately reduce the amount of freshwater needed per well.

Fluid-Shale Experiments

Attempts at studying fluid-shale reactions via high pressure and temperature reaction vessels in a laboratory setting have shed light on expected products from the complex chemical reaction occurring at in situ reservoir conditions. Inorganic species in produced fluid have been extensively studied. Analysis of fluid-shale reactions show the amount of calcite within a shale sample can affect fluid pH upon reaction and subsequently dictate mineral reactions. Carbonate material acts as a buffer, increasing effluent pH. Pyrite is another important mineral in the shale as its oxidation may lead to the generation of sulfate ions in solution. Studies have shown the

oversaturation of sulfate ions may lead to scaling minerals, due to the affinity of Ba^{2+} in solution to react with the SO_4^{2-} to form barite.

Recently published data regarding aqueous organic compounds derived from fluid-rock reactions reveal an increase in low molecular weight organic compounds (LMWOCs) and an overall decrease in DOC concentrations (Vieth-Hillebrand et al., 2016, Zhu et al., 2015).

The fluid used in many of these studies do not always emulate the complex mixture of injection fluid observed at HF operations, and shale maturity is not always taken into consideration when determining the source and fate of dissolved organic compounds. Shale maturity must be taken into account when considering the evolution of organic compounds observed in produced fluid. Low maturity zones contain labile compounds that have the potential to become solubilized into HFF once the reservoir is fractured and saturated with the injection fluid. Overmature dry gas zones contain more aromatic organic material with bigger pore size that presents potential adsorption sites for DOC and may contribute to the loss of organic additives in HFF upon reservoir fracturing and saturation.

Performing laboratory-scale fluid-shale reactions using the complex mixture of additives that accurately represent HFF used in operations throughout the Marcellus Shale, with consideration of the shale maturity and mineralogy, provides an accurate insight into the proliferation of inorganic and organic compounds during hydraulic fracturing.

1.1 Format of Thesis

Chapter 1 of this paper contains the background information review done in preparation of this study and manuscript. Chapter 2 is a manuscript of this thesis for potential submissions to a scientific journal. Chapter 3 is a summary of the final conclusions of this thesis.

2.0 Effect of Maturity and Mineralogy on Fluid-Rock Reactions in the Marcellus Shale

Abstract

Natural gas exploitation from the Appalachian Basin has significantly increased in the past decade. The push to properly dispose, reuse/recycle the large amounts of produced fluid associated with hydraulic fracturing operations and designing better fracfluids has necessitated a better understanding of the subsurface chemical reactions taking place during hydrocarbon extraction. Using autoclave reactors, this study mimics conditions of deep subsurface shale reservoirs to observe the chemical evolution of fluids during the shut-in phase of hydraulic fracturing (HF), a period when hydraulic fracturing fluid (HFF) remains closed in the reservoir. The experiment was conducted by combining synthetic hydraulic fracturing fluid and powdered shale core samples in high temperature/pressure static autoclave reactors for 14 days. Shale samples of varying maturity and mineralogy were used to assess the effect of these variations on the proliferation of inorganic ions and low molecular weight organic compounds, mainly benzene, toluene, ethylene and xylene (BTEX) and monosubstituted carboxylic acids. Ion chromatography results indicate the relative abundance of ions present were similar to those of produced water from HF operations in the Marcellus Shale. Main observations showed the increase of SO_4^{2-} and PO_4^{3-} ions and the decrease in Ba^{2+} ions upon fluid-shale reaction. Major ionic shifts indicate calcite dissolution in two fluid-shale reactions and barite precipitation in all fluid-shale reactions. GC-MS analysis of reacted fluids in the shale-free control experiment showed toluene and xylene analytes were produced by thermal breakdown of fracturing fluid additives. However, the most significant increase in BTEX analytes was observed in reactions with low maturity shale and the high maturity shale reaction produced no measurable BTEX compounds, due possibly to their adsorption onto the high maturity organic matter matrix. Ion

chromatography results indicate that the production of carboxylic acids took place without any shale reaction in the control reaction. A slight decrease was observed in overall dissolved organic carbon content in all fracturing fluid-shale reactor set-ups, suggesting adsorption onto the organic matter matrix. The results from this study highlight that the nature of organic matter and mineralogy play a key role in determining the fate of inorganic and organic compounds during fluid-shale interactions in the subsurface shale host rock. Overall this study aims to contribute to the growing understanding of complex chemical interactions that occur in the shale reservoirs during HF, which is vital for determining potential environmental impacts of HF and designing more efficient HFF and produced water recycling techniques for environmentally conscious natural gas production.

2.1 Introduction

The Marcellus Shale is the largest natural gas producing reservoir in the United States and has been extensively exploited in the past decade. The amount of natural gas extracted from the reservoir has almost tripled due to advancements in horizontal drilling technologies (U.S. EIA, 2017). As a result, thousands of wells have been drilled in areas of Pennsylvania, Ohio and West Virginia where the majority of the reservoir is underlain. Each well requires millions of gallons of fluid to hydraulically fracture the shale reservoir (PA DEP, 2010), which releases natural gas to the surface (Maguire-Boyle & Barron, 2014). This injection fluid is also known as hydraulic fracturing fluid (HFF) and is comprised of water, sand, and chemical additives. It is pumped into the subsurface formation at high pressure, inducing fractures, creating pathways for the gas to escape. The reservoir rock is fractured in stages along the lateral portion of the well. These stages are typically 100-200 feet in length, and a lateral leg can run for thousands of feet (PA DEP, 2010). Once all stages of the lateral have been fractured and proppant placed into fractures, HFF

from all stages is returned to the surface. Depending on the timing of events, HFF may remain in the reservoir for several days up to an entire month while all of the stages are fractured. This interval of time during the HF process is known as the shut-in phase; when the fluid and shale are in contact under relatively high pressure and temperatures (Vankeuren et al., 2017). Once returned to the surface, the fluid is considered produced water, and to efficiently recycle or dispose of this fluid, it is critical that we understand the reactions taking place between the organic-rich shale reservoir and HFF under in situ reservoir conditions. Better knowledge of these reactions leads to the optimization of HFF mixtures, which ultimately provide more efficient and environmentally conscious natural gas extraction.

Hydraulic fracturing fluid (HFF) is comprised of three main ingredients: 95% fresh water, 4% proppant or silica sand, and 1% chemical additives (FracFocus Chemical Disclosure Registry). Even though the additives make up only 1% of the overall mixture, they are the most significant portion as they control the fluid reactions with the shale formation and how the induced fractures effectively transport gas to the surface. Chemical additives are utilized at specific times during HF to facilitate effective fracturing of the shale formation and initiate gas migration to the well bore. In the initial stages fracturing the formation, the fluids' friction must be lowered via friction reducing organic additives such as WFR-61LA (PA DEP, 2010). This additive contains petroleum distillates and ethoxylated alcohols, which enhances the fracturing process. Next, the fluid must become viscous enough to transport proppant into the induced fractures, holding open the pathway for gas to escape. Gelling agents are used to increase the fluid's viscosity, creating an effective transporter. The proprietary gelling agent WGA-15L was used in this study to simulate gelling agents used in HF operations. Another common organic additive used to increase the viscosity down hole is guar gum. Gelling additives create a linked

3D polymer structure with the addition of cross linkers such as boric acid and ethanolamine. Once the viscosity has increased and proppant is placed, the viscosity must subsequently be decreased to allow the fluid to flow back to the surface. The crosslinked 3D polymer structure is broken down via breakers such as ammonium persulfate. The breaker creates SO_4^{2-} free radical ions at elevated temperatures (Tasker et al., 2016), which react with the linkages of the polymer structure, breaking up the compounds and allowing the fluid to flow back to the surface. Both experimental and field samples have proven that the chemical signature of produced fluid can be significantly different from the initial injection fluid (Strong et al., 2014, Hoelzer, et al., 2016, Marcon, et al., 2017). Produced water is typically characterized by its relatively high TDS, varying concentrations of dissolved organic carbon (DOC), and sometimes an abundance of radioactive elements (Vankeuren et al., 2017). All of these chemical components create complexities when trying to reuse and recycle produced fluid. Solubilized organic compounds play a key role in assessing potential environmental contamination and designing HFF recycling strategies. Monocyclic aromatic hydrocarbons such as BTEX and low molecular weight organic acids represent the most common solubilized organic compounds observed in produced water (Lee & Neff, 2011). Determining the source of these compounds is particularly difficult due to variations in organic additives used from well to well and the difference in organic matter throughout different maturity zones of the Marcellus Shale (Abualfaraj et al., 2014). Inferring sources of organic carbon and its evolution throughout the HF process is crucial for predicting which additives to use in HFF and how it must be handled at the surface after it has interacted with the organic-rich shale in the reservoir.

Marcellus Shale is characterized by its low permeability and high concentrations of total organic carbon (TOC) (U.S. EIA, 2017). The reservoir varies in depth longitudinally, increasing

from 3,000 ft in the northwest to 8,000 ft in the southeastern portion of the reservoir. This variation in depth results in different maturity windows throughout the reservoir ranging from 0.5% R_o at shallower depths up to 3.5% R_o at the deepest zones of the reservoir (U.S. EIA, 2017). These windows contain altered organic matter (kerogen) of different maturation stages and subsequently generate different amounts and types hydrocarbons. Recent economic evaluation of the wet gas window of the Marcellus reservoir indicates that this low maturity window may be an economically viable resource that has been relatively untapped (DOE 2017). Gas-rich, over mature zones of the Marcellus contain type II-III kerogen that has been thermally altered, providing a predominantly aromatic chemical signature (Agrawal and Sharma, 2018a, b). Less mature zones have similar type II-III kerogen, but it has not been thermally degraded or altered to the same extent, resulting in a relatively more aliphatic chemical signature (Craddock et al., 2015, Agrawal and Sharma, 2018b). The decrease in aliphatic to aromatic carbon ratio of the kerogen in Marcellus Shale has been observed in a study by Agrawal and Sharma, 2018b in which the chemical structure of low and high maturity kerogen was analyzed via ^{13}C NMR. Once fractured and saturated with HFF, there is a potential for leaching of different organic contaminants into the produced water from these shallow, less mature formation depths where the aliphatic chemical structure provides the potential for labile compounds to be solubilized into HFF during the shut-in reaction time.

Along with the variable maturity, varying mineralogy plays an important role in which additives are utilized in HFF and how the HF operation proceeds. The Marcellus Shale is comprised of mostly mixed-layer clays, quartz, feldspar, calcite, and pyrite (U.S. EIA, 2017). Relative abundances of these minerals can vary from zone to zone, and mineralogical variances can result in pH fluctuations of HFF that can impact mineral dissolution or precipitation during

HFF. Therefore, controlling pH becomes vital to completing a productive fracturing job. In some cases, the shale acts as a buffering agent with increasing amounts of carbonate material and calcite dissolution. Previous fluid-rock reaction studies, conducted at ambient pressures, have shown that the dissolution or precipitation of iron bearing minerals is dependent upon dissolved organic compounds, carbonate content of the shale during (buffering capacity) and the overall pH of the system (Harrison et al., 2017, Jew et al., 2017).

The objective of this study is to use laboratory experiments to effectively simulate chemical reactions taking place at in situ reservoir conditions, to elucidate the fate of inorganic and organic reactants and products from these operations. Having the ability to simulate these fluid-shale reactions in a laboratory setting, with shale of varying maturity and mineralogy, will help in elucidating the chemical reactions taking place between HFF and shale. It will also shed light on the inorganic and organic products expected in produced water from different zones within the reservoir. Determining the chemical evolution of the fluid used to fracture the Marcellus is critical for protecting surrounding watersheds, making HFF recycling an attainable goal, and improving hydrocarbon recovery from tight shales.

2.2 Materials and Method

Fluid-shale reactions were conducted using Parr 6600 static autoclaves to mimic and analyze the in situ fluid-shale reactions that take place during the shut-in phase of hydraulic fracturing. The specific analysis focused on the major changes of inorganic ions and the proliferation of low molecular weight organic compounds within the fluid.

2.2.1 Sampling and Preparation

The fluid used in the reaction vessels was a mixture of synthetic formation brine and synthetic HFF provided by collaborators at the National Energy Technology Laboratory (NETL) Morgantown. The synthetic brine was created using a mixture of spring water and salts that are typically found in produced water from the HF operations in the Marcellus Shale reservoir. Synthetic HFF was created in accordance with typical chemical additives found in HFF from HF operations within the Marcellus Shale and per additives found in FracFocus Chemical Disclosure Registry. Most of the components of the synthetic HFF and brine were mixed at NETL of Morgantown. The three shale samples of varying maturity were collected from Marcellus Shale cores from different depths and geographical zones of the reservoir (Table 1). All samples have relatively high TOC values and organic matter sourced from mixed marine and terrestrial sources, representing type II-III kerogen (Chen et al., 2015, Agrawal and Sharma, 2018a, b). The maturity of the samples is represented as a %R_o value which is calculated directly from T_{max} values (Jarvie and Lundell., 1991). Mineralogy was analyzed as part of this study and described in the results section. To prepare shale samples for HPT reactions, core samples were first washed using deionized water to avoid contamination from drill mud, then crushed using SPEX mixer mill to 100 mesh powder to maximize reaction potential.

2.2.2 Experimental Set-up

To emulate reservoir conditions during the shut-in phase, reactions were conducted using two 4660 Parr Instrument Company 600 ml high-temperature/pressure vessels set to ~2,500 psi and 100°C respectively. These values were used to best mimic in situ reservoir conditions of the Marcellus Shale while remaining within the limitations of the vessels. Inside each 600 ml pressure vessel, a small Teflon cup was placed containing a fixed HFF-shale ratio (20:1)

following research done by similar studies conducted at NETL Pittsburgh (Marcon et al., 2017). Fluids were at steady state with the lab atmosphere with regards to dissolved O₂ prior to adding them to the reactor. The remaining volume of each vessel was then filled with pressurized, inert N₂. Four reactions were conducted, each for 14 days in order to mimic the shut in phase of an HF operation. One reaction with solely fluid and no shale, and three fluid-shale reactions with each of the shale samples.

Due to the inability to add fluids to the static autoclaves during fluid-shale reactions without returning the experimental conditions to atmospheric, all of the aforementioned additives are combined at the same time.

2.2.3 Analytical Methods

Samples were collected and analyzed from the five fluids in this study: NR-PF (Non-reacted produced fluid) that served as control, HPT-PF (High pressure/temperature produced fluid) without any shale interaction, and LM-2, WV-7, and MIP-3H effluents from the fluid-shale reactions.

In accordance with average shut in time of typical HF wells, samples were taken at the conclusion of the 14-day reaction using an HDPE Luer syringe and filtered via a 0.45u filter attachment. Samples for ion chromatography (IC) were collected with minimal headspace in pre-cleaned 10 mL glass vials. IC and NPOC/DIC analysis were conducted at NETL Pittsburgh (Dionex 5000+, Thermo Scientific and Shimadzu TOC Analyzer) and focused on observing low molecular weight mono substituted carboxylic acids and dissolved inorganic species such as Ba²⁺, SO₄²⁻, and PO₄³⁻. VOC analytes were sampled in accordance with methods described in Chapter 4 of EPA SW-486 Compendium: Organic Analytes. Samples for VOC analysis were placed in pre-cleaned 60 mL volatile organic analysis (VOA) vials and acidified with minimal

headspace to preserve target analytes. Samples were taken to REIC Labs in Morgantown, WV for gas chromatography-mass spectrometry (GC-MS) analysis within one day of sampling and kept at 4°C until analyzed. The GC-MS analysis was focused on BTEX compounds as they are commonly observed low molecular weight organic compounds in produced fluid from the Marcellus Shale (Abualfaraj et al., 2014), and they also pose the greatest contamination risk to water and air.

For mineralogy analysis, the three shale samples were powdered using SPEX mixer mill and prepared for loading into the diffractometer. XRD analysis was performed using the PANalytical X'Pert Pro X-ray Diffractometer at West Virginia University Shared Research Facilities. The spectra were interpreted using the X'pert HighScore Plus Program to evaluate the percentage of various mineral phases present.

2.3 Results

2.3.1 Mineralogy and Aqueous Inorganic Chemistry

The shale's mineralogy is mainly made up of mixed layer clays with smaller fractions of carbonate, quartz, pyrite, and feldspar (Figure 1, Table 2). An exception involved the WV-7 shale sample, which contained little to no carbonate. The abundance of calcite in LM-2 is 21% and in MIP-3H is 16%. WV-7 sample contains no observable calcite contributing to its overall mineralogy (Table 3). All samples contain similar amounts of dolomite, LM-2 5%, WV-7 4% and MIP-3H 5%. LM-2 and MIP-3H each contain 5% pyrite, and WV-7 contains 2% pyrite. Mixed clay and quartz content varies amongst all samples. A more detailed description of the shale mineralogy is provided in Table 2.

Fluids without shale contained 9.6 mg/L SO_4^{2-} in (NR-PF) and 10.6 mg/L SO_4^{2-} in (HPT-PF), as measured by IC (Figure 2a, Table 4). All effluent samples show an increase in SO_4^{2-} concentration upon shale reaction. LM-2 effluent had 189.8 mg/L SO_4^{2-} , WV-7 effluent had

271.5 mg/L SO_4^{2-} , and MIP-3H effluent had 66.1 SO_4^{2-} (Figure 2a, Table 4). Results show a Ba^{2+} concentration of 96.2 mg/L in NR-PF and 39.1 mg/L in HPT-PF, and all effluent samples showed a decrease in Ba^{2+} concentration upon reaction with shale (Figure 2b, Table 4). LM-2 effluent had 3.8 mg/L Ba^{2+} , WV-7 contained no measurable Ba^{2+} and MIP-3H effluent had 10.6 mg/L Ba^{2+} (Figure 2b). No measurable PO_4^{3-} was present in NR-PF or HPT-PF. LM-2 effluent contained 6.9 mg/L PO_4^{3-} , WV-7 effluent had 29.8 mg/L PO_4^{3-} , and MIP-3H effluent had 9.6 mg/L PO_4^{3-} (Figure 2c, Table 4).

The pH of NR-PF was measured to be 1.3, and HPT-PF pH measured 1.9. WV-7 effluent had a relatively low pH of 2.3 compared to LM-2 effluent with a pH of 6.07 and MIP-3H effluent with a pH of 5.73 (Table 4). Dissolved inorganic carbon was detected in only two samples, LM-2 and MIP-3H. LM-2 contained 35.18 C mg/L DIC and MIP-3H contained 15.8 mg/L DIC. WV-7 effluent had no observable inorganic carbon. The most significant changes observed in IC-analyzed inorganic species for shale-reacted effluents, where both SO_4^{2-} and PO_4^{3-} increased and the decrease in Ba^{2+} .

2.3.2 Aqueous Organic Chemistry

Significant observations attributed to organic compounds are the presence of solubilized target VOCs within HPT-PF, relatively higher concentrations of VOCs in the effluent from the reaction with low maturity shale, and the absence of these compounds in the effluent from the reaction with high maturity shale and NR-PF. Dissolved organic carbon (DOC) concentrations are expressed as non-purgeable organic carbon. NPOC was measured at 316.8 mg/L in HPT-PF, 271.5 mg/L in WV-7 effluent, 189.8 mg/L in LM-2 effluent, and 66.1 mg/L in MIP-3H effluent (Figure 2). Fluid samples contained four observable low molecular weight organic acids: acetate,

formate, butyrate, and succinate. HPT-PF contained the highest organic acids concentrations of 19.34 ± 0.61 mg/L acetate and 13.85 ± 0.54 mg/L formate. HPT-PF contained 1.52 ± 0.45 mg/L butyrate and 0.99 ± 0.19 mg/L succinate. LM-2 effluent contained 12.49 ± 0.47 mg/L acetate, 10.20 ± 0.11 mg/L formate, 2.98 ± 0.20 mg/L butyrate, and 0.94 ± 0.02 mg/L succinate. WV-7 effluent contained 16.34 ± 0.43 mg/L acetate, 6.89 ± 0.15 mg/L formate, 1.68 ± 0.06 mg/L butyrate, and 2.97 ± 0.22 mg/L succinate. MIP-3H effluent contained 12.70 ± 0.33 mg/L acetate, 9.38 ± 0.41 mg/L formate, 2.31 ± 0.35 mg/L butyrate, and 1.13 ± 0.07 mg/L succinate (Figure 4).

Target VOC analytes, BTEX compounds, were observed in HPT-PF at relatively low concentrations. HPT-PF fluid contained toluene concentrations of 2.7 $\mu\text{g/L}$ and xylene concentrations of 9.7 $\mu\text{g/L}$. Effluent from the LM-2 reaction was the only effluent which contained benzene, at a concentration of 2.5 $\mu\text{g/L}$. LM-2 effluent produced concentrations of toluene of 14.8 $\mu\text{g/L}$ and xylene of 15.8 $\mu\text{g/L}$. WV-7 effluent produced toluene concentration of 1.3 $\mu\text{g/L}$ and xylene concentration of 7.1 $\mu\text{g/L}$. Effluent from MIP-3H reaction produced no observable BTEX compounds. It is also important to note that NR-PF had no measurable BTEX compounds (Figure 5, Table 5).

2.4 Discussion

2.4.1 Aqueous Inorganic Chemistry

The low pH of NR-PF and HPT-PF is a common observation amongst HFF used in the Marcellus Shale region (Jew et al., 2017). HCl is a common additive used to prevent scaling of secondary minerals and was also used in creating the synthetic HFF used in this study. The pH rose to nearly 6 in samples LM-2 and MIP-3H (Table 3) indicating that carbonate minerals in these shale samples acted as effective buffers during the reaction similar to prior observations (Vankeuren et al., 2017). The shale-reacted effluent from WV-7 had a pH similar to the HPT-PF

indicating its poor buffering capacity or low amounts of carbonate material. The XRD analysis of WV-7 sample shows no observable calcite. Further evidence of the buffering capacity of the shale samples is apparent in the amount of DIC within the effluent samples (Harrison et al., 2017), LM-2 and MIP-3H and their calcite content of 21% and 16% respectively. These observations suggest that fluid chemistry was primarily controlled by shale buffering capacity.

The ionic composition of the fluids used in this study shows a strong similarity to the chemical signature of produced water sampled from the Marcellus Shale. The piper diagram in Figure 6 shows fluid samples from the Marcellus Shale reservoir analyzed by the USGS, overlain by the effluent samples from this study. Relatively high amounts of chlorine and overall high TDS are typical of produced fluids (PA DEP, 2010) and are similar to the effluents produced in our experiments. The similarity indicates that this study emulates the in-situ reactions taking place during hydraulic fracturing in the reservoir.

Noticeable shifts observed upon closer inspection of specific ionic species show the increase in SO_4^{2-} and PO_4^{3-} and a decrease in Ba^{2+} concentrations in LM-2, WV-7 and MIP-3H effluents (Figure 2 a,b,c). An increase in SO_4^{2-} concentration in the fluid-shale effluent can be attributed to the ammonium persulfate breakers in HFF and the dissolution and subsequent oxidation of sulfur-containing minerals, such as pyrite, within the shale. Ammonium persulfate breakers are ubiquitous ingredients associated with HF, used to break down linked guar gum that carries proppant into reservoir fractures. The breaking down of the guar gum restores the fluid to the desired viscosity to remove it from the reservoir. Previous studies show the persulfate compounds form free radical SO_4^{2-} anions once it reaches a temperature above 50°C (Vankeuren et al., 2017). The low SO_4^{2-} concentration in the HPT-PF suggest that the persulfate breakers in the synthetic HFF minimally contributed to the SO_4^{2-} observed in the effluent from fluid-shale

reactions (Figure 2a), indicating that sulfur-bearing minerals in the shale significantly control the effluent's sulfate concentration. The highest concentrations of SO_4^{2-} in WV-7 effluent suggests that oxidative dissolution of the primary sulfur-bearing mineral, pyrite, likely occurred to a greater extent relative to the other shale samples. This is supported by the relatively low pH of the fluid, caused by the lack of carbonate material and low buffering capacity of the shale sample. The oxidation reaction of pyrite further decreases the fluids pH resulting in the higher concentrations of SO_4^{2-} ions in the WV-7 effluent. On the other hand, shale samples that had higher abundances of calcite (Table 3), LM-2 21% and MIP-3H 16%, acted as effective buffers and increased pH of effluent closer to neutral, thereby limiting the amount of pyrite dissolution that could occur.

The amount of SO_4^{2-} generated from the dissolution reactions has a direct impact on the precipitation of the mineral barite (Vankeuren et al., 2017). Ba^{2+} is observed within NR-PF and HPT-PF at relatively high concentrations and is shown to decrease in all effluent samples upon reaction with the powdered shale (Figure 2b). This is an indication that reaction between ions generated from the shale is causing the precipitation of barite $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4$ (Figure 7). Our results are similar to previous studies that were able to conclusively show the precipitation of barite occurs in high pressure and temperature fluid-shale reactions using SEM imaging (Vankeuren et al., 2017). They also show that barite precipitation can be predicted based on calculated saturation indices and that additives used to prevent secondary mineral precipitation are less effective at higher temperatures. Our results also clearly suggest that barite precipitation occurs in these shales, but precipitation can be significantly affected by the buffering capacity or mineralogy of the shale. Therefore, additives designed for scaling must take into account the variations in the mineralogy of shale being targeted.

The absence of PO_4^{3-} in the NR-PF and HPT-PF and increase in concentrations in all effluent samples is evidence that the PO_4^{3-} is leaching from the powdered shale (Figure 2c), presumably from the dissolution of the PO_4^{3-} -containing mineral apatite. In all effluent samples, there is also an increase in fluoride and calcium ion concentrations, the other ions, which make up the mineral. The increase in pH for both LM-2 and MIP-3H effluent samples may be a further indication of apatite dissolution. WV-7 effluent, which remained at a low pH around 2, created a solution that is under saturated in apatite. Even though apatite was not directly detected via XRD analysis, further dissolution of minerals and pH increases are attributed to trace amounts present in the shale and therefore should be considered when analyzing overall mineral dissolution upon fluid-shale reactions.

2.4.2 Aqueous Organic Chemistry

DOC concentrations in all effluent samples are lower compared to the HPT-PF. Due to the high TOC concentration, the shale organic matter matrix (kerogen) may act as a sight for adsorption of these compounds onto the surface. More mature shale contains more aromatic compounds within its organic matter, resulting in higher organic porosity and the relatively high surface area within this matrix (Zargari et al., 2015, Zhang et al., 2012). This organic porosity creates an effective adsorbent trap for organic molecules used or generated in the hydraulic fracturing process (Zhang et al., 2012). Other laboratory fluid-shale studies observed a similar decrease in DOC in the effluent from autoclave reactions, while also observing an increase in TOC in the solid sample (Tasker et al., 2016, Marcon, et al., 2017). This supports the hypothesis that a portion of the organic compounds observed in HPT-PF is being adsorbed to the shale surface, hence decreasing the overall DOC concentrations of the effluent from fluid-shale reactions. The physical characteristics of the shale organic matter at the molecular level is a

major contributing factor in DOC concentrations in fluids produced from these reactions and should be taken into consideration when assessing environmental impact and recycling strategies associated with flowback and produced water.

This may result in some discrepancies in the data regarding the DOC evolution during laboratory experiments, which attempt to emulate the chemical reactions occurring during hydraulic fracturing. For example, the increase in non-purgeable organic carbon observed in the HPT-PF compared to the NR-PF (Figure 3) may be due to the gelling agent effectively linking purgeable compounds without being affected by the SO_4^{2-} breakers. Due to the SO_4^{2-} ions affinity to react with the Ba^{2+} in solution at higher temperature and pressure, precipitation of barite persists and leaves the linked polymers intact. Hence the increase in NPOC observed in the HPT-PF.

Our results indicate that subjecting solely synthetic fluid to high temperature and pressure conditions results in the proliferation of organic acids. In particular, acetate is observed at a relatively high concentration in all experimental fluid samples (Figure 4). This relatively high concentration of organic acids generated from the synthetic mixture suggests that the transformation or degradation of organic additives is the main source of organic acids. Research suggests organic acids are a cause of increased SO_4^{2-} and Ba^{2+} concentrations in produced fluid (Hakala et al., 2017). Saturation indices of SO_4^{2-} minerals are shown to decrease with an increase in organic acid concentration, which form complexes with cations such as Ba^{2+} (Hakala et al., 2017).

Low molecular weight carboxylic acids, in particular, acetate and formate, have been observed in both produced water and effluent from similar fluid-shale experiments (Lee & Neff, 2011, Zhu, et al., 2015, Hoelzer, et al., 2016). The proliferation of these compounds is believed

to be related to the labile ester linked carboxyl functional groups attached to the organic matter within the shale formation. These labile functional groups are formed from throughout the process of diagenesis and are thought to be extracted from the shale reservoir upon hydraulic fracturing and fluid saturation (Zhu et al., 2015). Other theories regarding the proliferation of these compounds suggest that the degradation of linked polymers used to increase viscosity for proppant placement are the main source of the carboxylic acids. Tasker, et al., 2016 was able to show the degradation and transformation of gelling agents used in HF operations.

Our results show that subjecting the synthetic HFF to high pressure and temperature near reservoir conditions without any shale rock interaction, results in the formation of target VOCs toluene and xylene (Figure 5). A portion of the observed VOCs from fluid-shale reactions can, therefore, be attributed to the transformation of compounds within the synthetic HFF when exposed to reservoir pressure and temperature conditions. Specific compounds undergoing such transformations have yet to be determined as the proprietary additives consisting of petroleum distillates is not completely characterized. It is believed that a portion of the proprietary organic chemicals may be undergoing high-temperature transformations, which produce target analytes without any shale interaction. Tasker, et al., 2016 were able to determine that some organic additives such as gelling and friction agents degraded under these conditions and were able to produce lower weight organic compounds after subjecting particular gelling agents to reservoir conditions.

Highest VOC concentrations were observed in effluent produced from low maturity shale LM-2 reactions with HFF. The LM-2 sample contains a larger portion of labile hydrocarbons, as the organic matter within the shale has not been thermally degraded or altered to the same extent as the high maturity rocks. Similar to the degradation of gelling agents, the labile portion of these

larger macromolecules are subsequently transformed and solubilized into the fluid under high pressure and temperatures. It has been shown the persulfate breakers have been utilized to dissolve or breakdown the kerogen within subterranean formations (US Patent 2017/066959A1). Breakers used to target the linked polymers have been observed in produced water after the fluid has degraded. These residual breakers might react with organic matter (kerogen), and may potentially release these labile compounds over the life of the well.

VOCs are commonly observed in both gaseous and solubilized forms around hydraulic fracturing operations and fluid-shale experiments (Maguire-Boyle & Barron, 2014, Orem, et al., 2014, Marcon, et al., 2017). They tend to readily dissolve or solubilize into produced water at the high pressures within the shale formation and must be taken into consideration once that fluid returns to the surface (Butkovskiy et al., 2017). Separators are implemented at the wellhead to control the release of VOCs over the life of the well (US Patent 2013/0087511A1). Separators are effective for reducing some of the VOCs in produced fluid, but some compounds remain solubilized, further proving the necessity of knowing the source of these compounds over the life of the well. In particular, BTEX compounds, which have relatively high solubility and toxicity compared to other potential compounds are of greatest concern (Shores et al., 2017, Benko and Drewes 2008; Todd et al. 1999)

The absence of target VOCs in effluent produced from synthetic HFF and high maturity MIP-3H shale reactions is believed to be a result of nanopores present in the kerogen matrix which is highly aromatic in nature. These nanopores created by thermal maturation of kerogen increases the surface area of adsorption for VOCs. Research suggests that the relatively high salinity of produced fluid caused by the mixing of injection and formation fluid may increase the sorption of organic compounds onto activated carbon (Butkovskiy et al., 2017), which may be a

proxy for the highly mature kerogen of MIP-3H. As mentioned earlier, DOC and BTEX concentrations are observed to decrease in effluent produced from the HFF-high maturity shale reaction. Future studies in our laboratory will focus on better understanding the mechanisms related to changes in adsorption behavior of shales of different maturity.

2.5 Conclusions

The similarity in chemical composition of shale interacted experimental fluids analyzed in this study with the published produced water chemistry data clearly indicate the efficacy of static autoclave experiments to simulate the in-situ chemical reactions taking place during HF. Analyzing and comparing the chemical composition of non-reacted HFF (NR-PF) with fluid reacted at high pressure and temperature (HPT-PF) and effluent produced from HPT fluid-shale reactions allowed us to clearly evaluate the effect of thermal degradation of HFF and its interaction with shale on the inorganic/organic geochemistry of produced fluids. Utilizing shale samples from three different maturity windows and varying mineralogy provided insight into which inorganic reactions and VOCs can potentially occur in different maturity windows within the Marcellus. The variations in chemical signatures of produced fluids clearly suggest that contaminants released may vary significantly in different parts of the basin and therefore disposal and recycling strategies need to be designed accordingly. Our research group is further investigating the processes by which compounds are adsorbed and what particular mechanisms govern the fate of low molecular weight organic compounds. Our results also indicate that mineralogy of the shale can have a significant effect on release and precipitation of inorganics hence chemical composition of HFF's should be modified to better target the varying mineralogical compositions encountered in different parts of the basin.

2.6 Acknowledgements

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3.0 Conclusion

This study conducted high pressure temperature reactions with mixture of HFF and brine coupled with shale samples from varying maturity zones within the Marcellus Shale to understand the variations in chemical constituents of produced fluid. As expected the produced fluid pH was shown to be affected by the shales mineralogy, specifically the amount of carbonate material it contained. The persistence of sulfate in solution was impacted not only by the persulfate breakers used as an HFF additive but also from the oxidation of pyrite within the shale. Inorganic species only present in effluent from fluid-shale reactions suggest ion leaching from the shale is a mechanism, which controls overall TDS and secondary mineral precipitation. When considering dominant inorganic species in solution, barium, sulfate, and phosphate shows the largest degree of change and suggest that these compounds are being consumed by precipitation or released due to dissolution. Organic acids were shown to proliferate in all fluids that were subject to high heat and pressure. The formation of organic acids in the control solution suggests that thermal breakdown of the brine and HFF mix can produce organic acids and hence the shale is not the main contributor of these compounds in the produced fluid. Organic acids also have the potential to react with some of the inorganic species such as barium ions in solution and get removed from the solution as well. The VOCs investigated in this study were observed in all fluids that were subject to high temperatures and pressure, including the control. This suggests that VOCs such as toluene and xylene can be produced both by the thermal breakdown of HFF and brine and its reaction with shale. The relatively high concentrations toluene and

xylene produced from the low mature LM-2 sample is plausibly due to solubilization of the labile compounds attached to the organic matter into solution upon reservoir saturation. The trend towards no visible VOCs in effluent produced from high maturity shale MIP-3H effluent suggests that there are no labile compounds present to be solubilized and any VOCs created by the transformation of additives is adsorbed onto the organic matter matrix due to the higher adsorption capacity of mature OM or kerogen in these shales. Further investigation is required to determine which particular minerals may be precipitating upon shale reaction and how this can be mitigated. Other further studies may be done to conclude how VOCs or low molecular weight organic compounds adsorb to the shale surface and how long they stay trapped within the organic matter.

4.0 Tables

Sample ID	Depth (ft.)	%Ro	T _{max} (°C)	TOC (wt%)
LM-2	5825.7	0.8	443	15.4
WV-7	6615.8	1.4	475	12.9
MIP-3H	7511.8	2.9	561	9.0

Table 1. Three shale samples from Marcellus Shale cores, collected from three different depths and geographical areas. Note the high amounts TOC for each sample and the varying maturity represented by %Ro values.

Sample ID	Mineral Composition (wt%)				
	Quartz	Calcite	Dolomite	Pyrite	Mixed Clays
LM-2	28	21	5	5	42
WV-7	23	0	4	2	71
MIP-3H	46	16	5	11	22

Table 2. Mineral composition of the three shale samples used in this study. Semi-quantitative XRD data from previously conducted studies are used for WV-7, and MIP-3H samples and XRD analysis was completed for LM-2 for this study.

Sample ID	Calcite (wt%)
LM-2	21
WV-7	0
MIP-3H	16

Table 3. Relative amounts of calcite within each shale sample. Note WV-7 sample has no detectable amounts, resulting in effluent with the same pH as the control fluid.

Sample ID	pH	F ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ⁻²	PO ₄ ⁻³	Cl ⁻	Li ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Mg ⁺²	Ca ⁺²	Sr ⁺²	Ba ⁺²	TDS
NR-PF	1.3	0.6	107	4.5	9.6	0	16729	0	6583	89	393	213	2015	464	96	26704
HPT-PF	1.9	0.5	60	2.3	10.6	0	7809	0	3277	52	165	104	967	224	39	12709
LM-2	6.1	3.2	68	1.7	189.8	6.8	9060	0.1	3727	51	205	132	1606	211	4	15266
WV-7	2.3	9.9	110	5.1	271.5	29.8	16867	0.2	6663	92	427	418	2576	367	0	27836
MIP-3H	5.7	3.6	65	1.6	66.1	9.6	8894	0.2	3673	50	202	165	1418	228	11	14788

Table 4. All cation and anion concentrations in mg/L measured via ion chromatography. Also included is pH for each fluid sample and overall TDS.

Sample ID	DOC concentrations in mg/L					VOC concentrations in µg/L			
	NPOC	Acetate	Formate	Butyrate	Succinate	Benzene	Toluene	m,p-Xylene	o-Xylene
NR-PF	243	0.0	6.1	0.0	1.9	0.0	0.0	0.0	0.0
HPT-PF	317	19.3	13.9	1.6	1.0	0.0	2.7	5.9	3.8
LM-2	264	12.5	10.2	3.0	0.9	2.5	14.8	10.2	5.6
WV-7	197	16.3	6.9	1.7	3.0	0.0	1.3	4.7	2.4
MIP-3H	235	12.7	9.4	2.3	1.1	0.0	0.0	0.0	0.0

Table 5. DOC concentrations in mg/L and VOC concentrations in µg/L for each fluid sample.

5.0 Figures

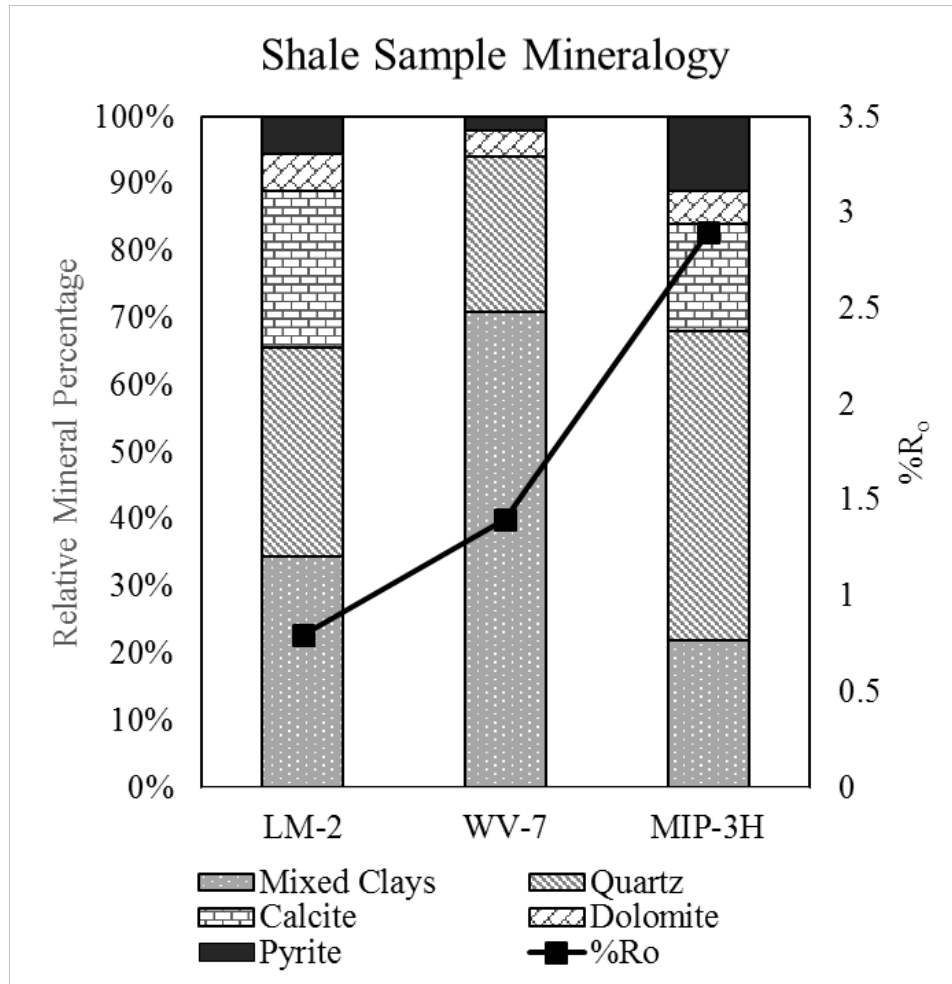


Figure 1. Relative percentages of minerals in three shale samples overlain by their %R_o (maturity) values.

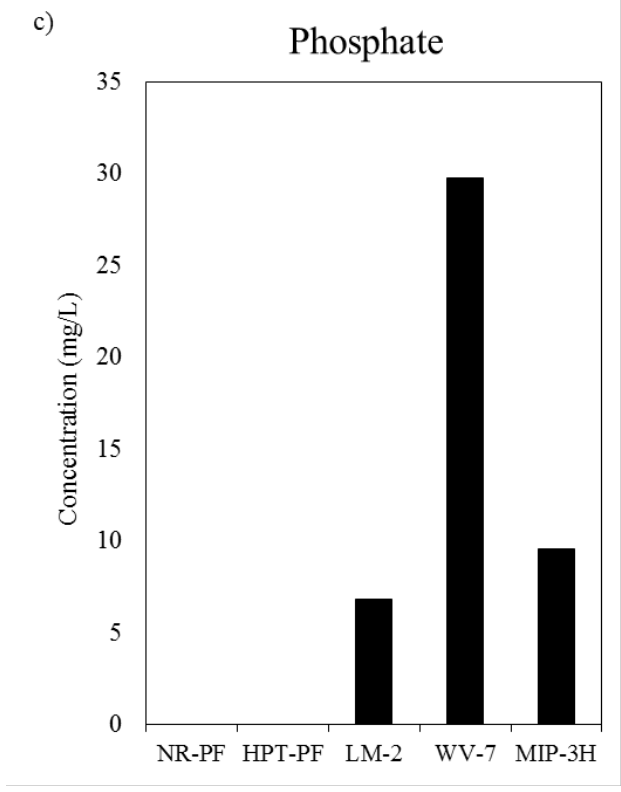
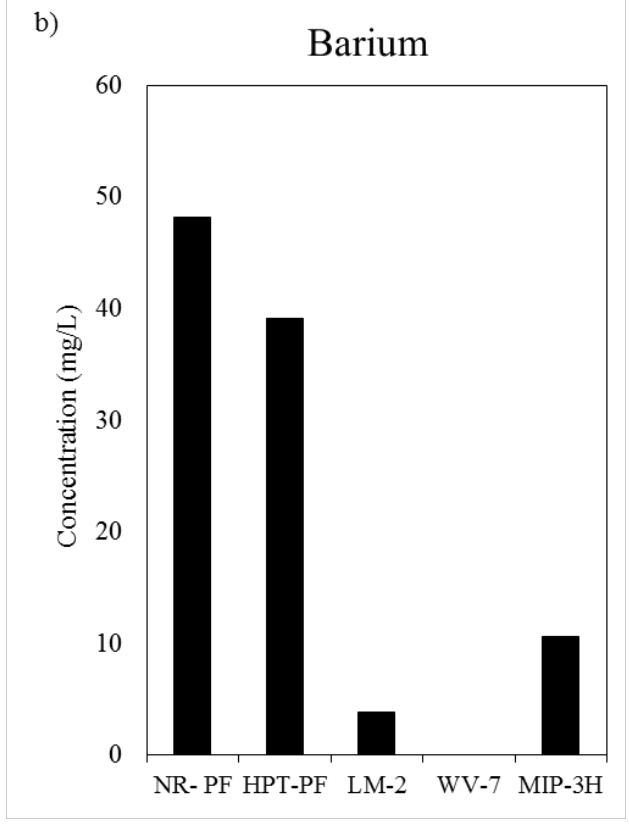
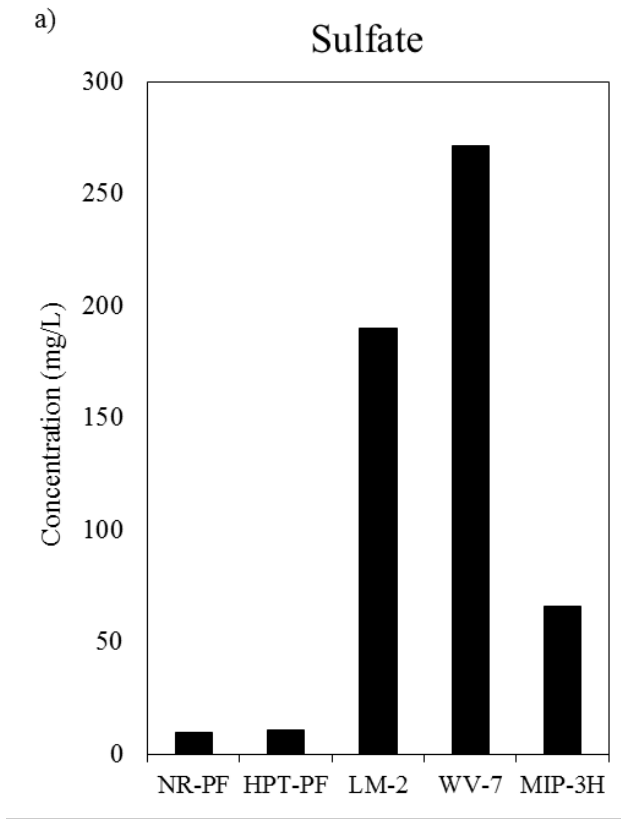


Figure 2. a) Sulfate concentrations in all fluid samples with a notable increase in all effluents. b) Barium concentrations in all fluid samples with a notable decrease in all effluents. c) Phosphate concentrations in all fluid samples. Only observed in effluent samples and presumably leached from mineral dissolution in the shales.

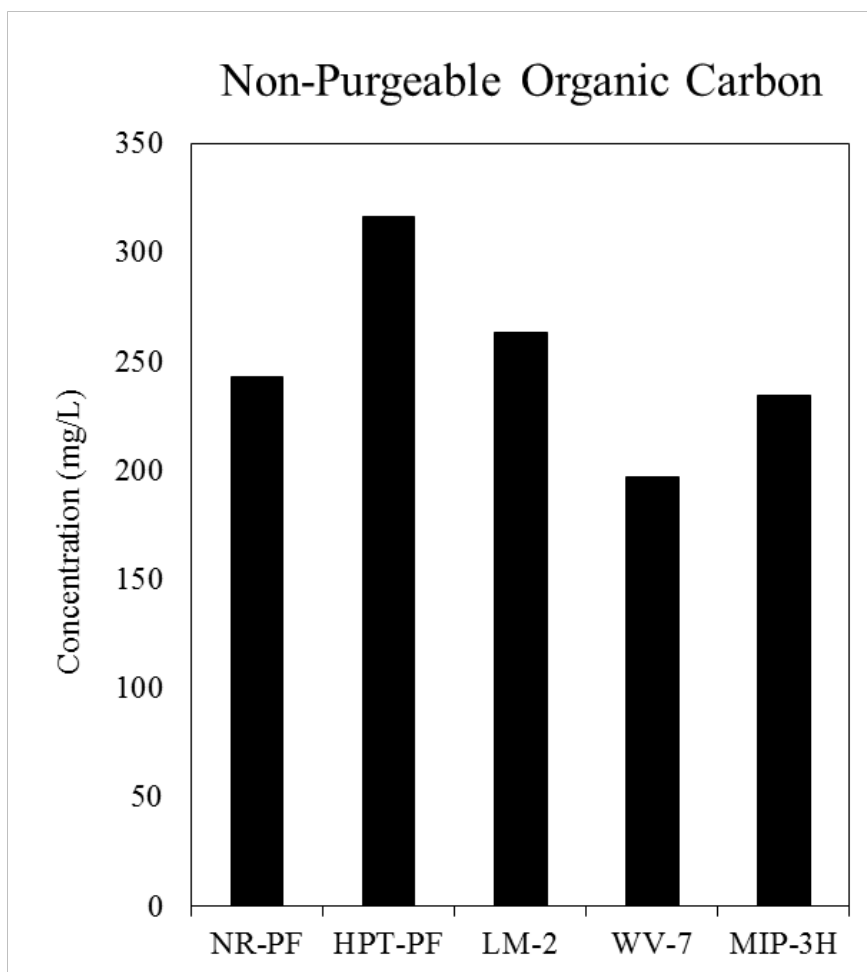


Figure 3. Non-purgeable organic carbon or DOC results from all fluid samples. Note the increase in HPT-PF due to the gelling agents linking potential purgeable compounds.

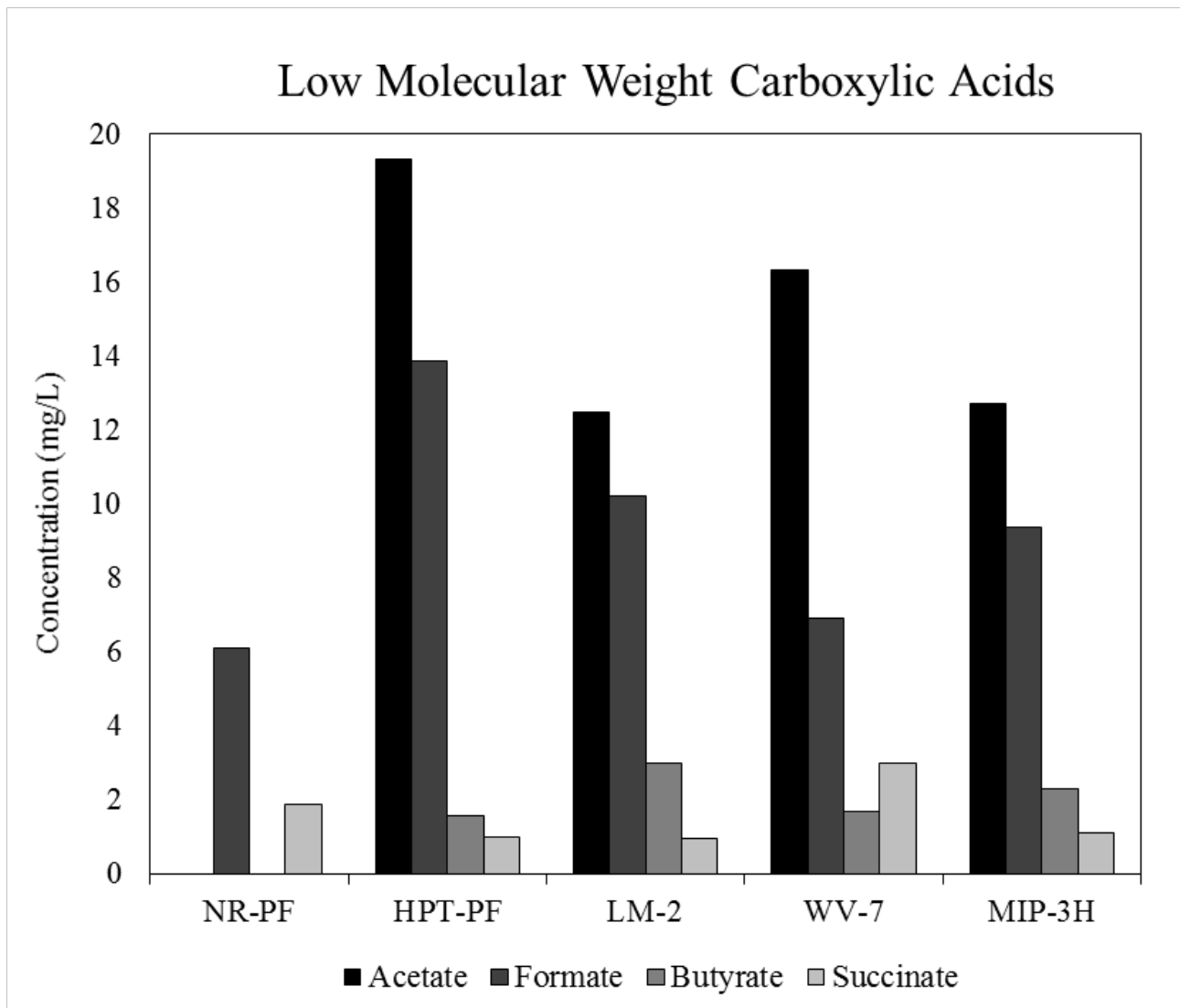


Figure 4. Organic acid concentrations of all fluid samples. Note the relatively low concentrations in NR-PF and a distinct increase in HPT-PF without any shale interaction. This increase is an indication that low molecular weight organic acid proliferation during HF is a result of subjecting HFF additives to reservoir pressure-temperature conditions. Organic acid concentrations also affect the complexes generated with cations such as Ba^{2+} and lead to an increase in sulfate concentrations due to scaling inhibition.

Volatile Organic Compounds

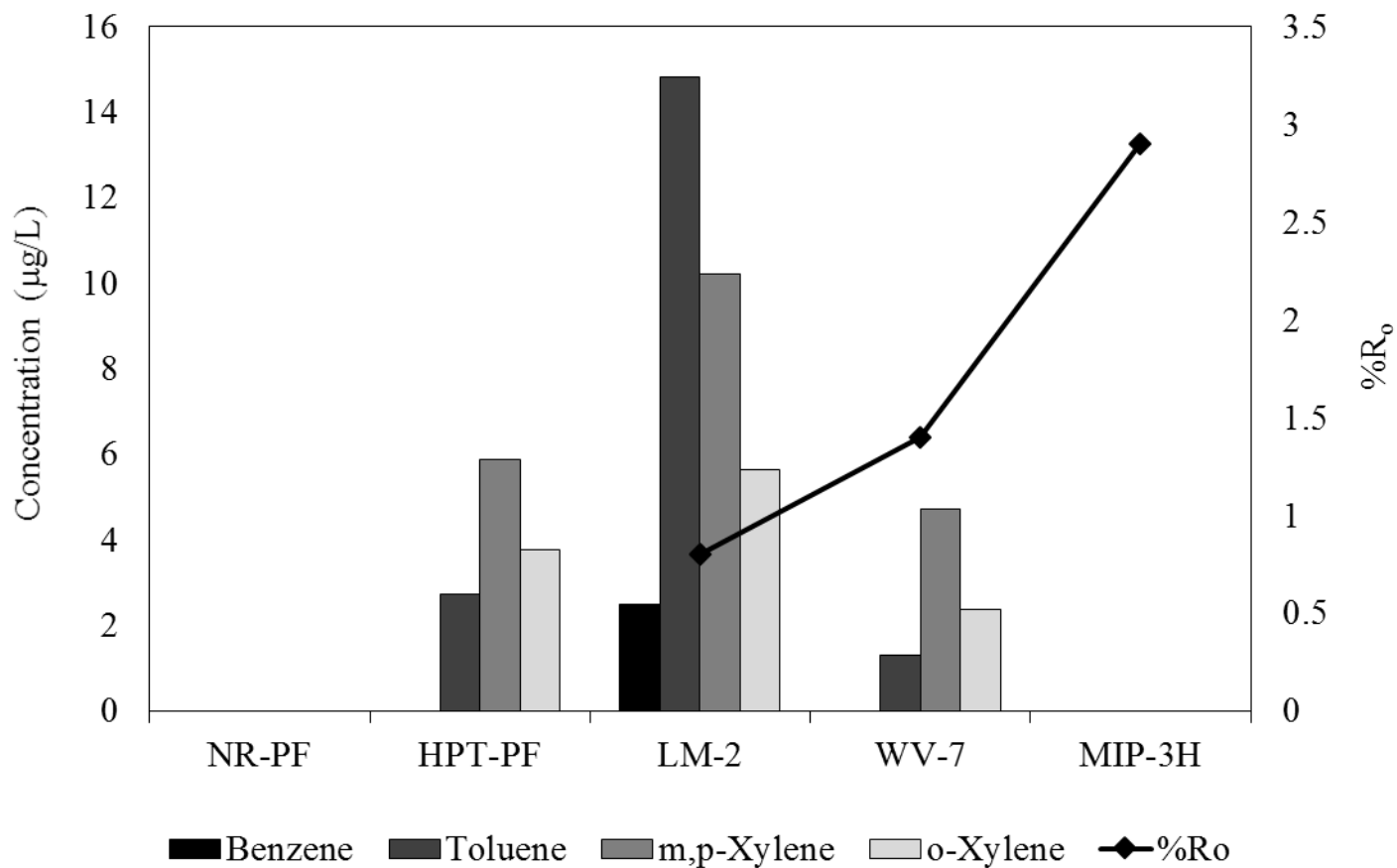


Figure 5. Volatile organic compound concentrations in all fluid samples. Note presence of benzene in the LM-2 effluent, the least mature sample and the absence of VOCs in both NR-PF and MIP-3H effluent.

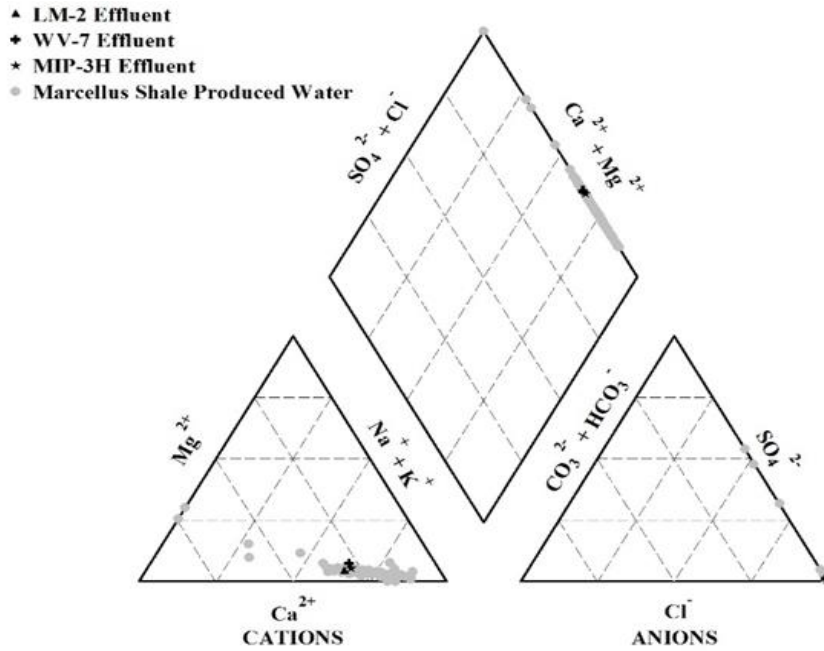


Figure 6. Piper diagram showing the relative amounts of the most abundant ions in solution. Grey dots represent produced water from hydraulic fracturing operations in the Marcellus Shale basin collected by the USGS and the black markers overlain, represent the three effluents produced from fluid-shale reactions in this study.

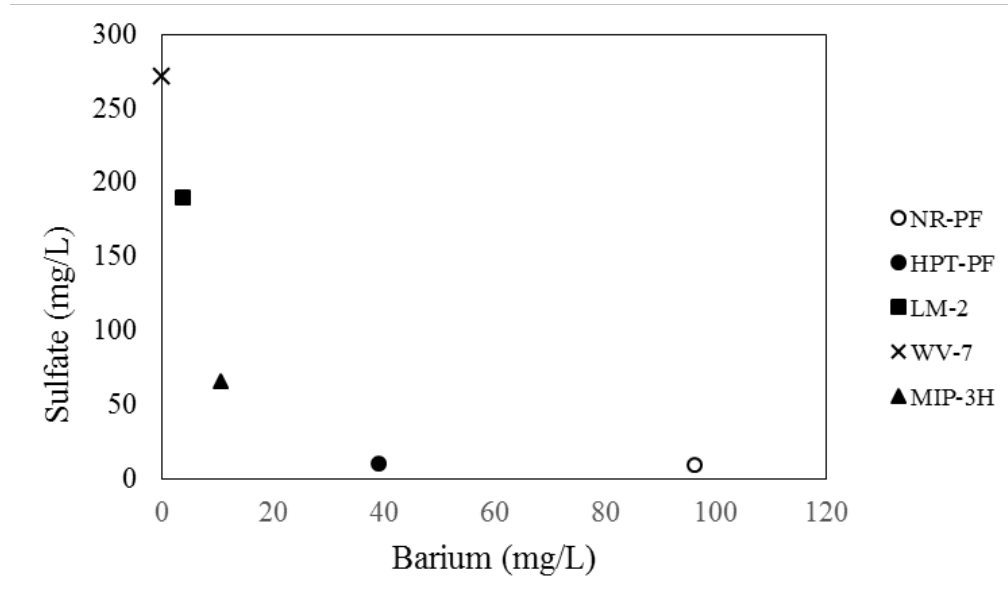


Figure 7. Relative amounts of sulfate and barium in each fluid sample. A high concentration of sulfate corresponds to a low barium concentration. An indication of breaker free radical formation and barite precipitation during high pressure/temperature reactions.

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