TITLE: Evidence of Hydrothermal Alteration in Devonian Shales from the EGSP-2 Core of the Rome Trough, Appalachian Basin, USA

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ABSTRACT:

This study represents a comparative assessment of stacked shales within the Middle Devonian Marcellus through Upper Devonian Genesee formations in the EGSP-2 core (API No. 3700320980), Allegheny County, Pennsylvania. Mineralogy, petrography, total organic content (TOC) and geophysical logs were initially studied to gain insight regarding depositional controls

and structural impacts to shale reservoir integrity, but ultimately documented post-depositional processes in these shale reservoirs as well.

The core is located near a northwest-southeast trending cross-structural discontinuity and is situated within the Rome Trough, a northeast-southwest trending graben in the Appalachian Basin that initially formed during Cambrian rifting. Lithofacies descriptions were prepared using the core and geophysical logs. Bulk mineralogy, TOC, petrographic and scanning electron microscopy analyses were performed for samples taken at discrete depths throughout the stratigraphic interval.

Lithology ranges from carbonate-rich, organic-poor gray shale to quartz-rich, organic-rich black shale. Vein occurrence is not unique to specific facies, and vein mineralogy is of hydrothermal origin, consisting of calcium plagioclase, sulfides, quartz, gypsum~~,~~ and carbonates, as well as organic matter and thorium. ~~Platinum, silver and thorium were also detected within veins.~~ The hydrothermal mineralization eliminates fracture porosity, permeates into the shale matrix surrounding some veins, and suggests that fluids altered these Devonian shales, with reactivated faults facilitating fluid flow. Alteration has surely impacted reservoir quality, mechanical properties and/or thermal maturity. The cross-cutting nature of veins, replacement grains and complex vein mineralogy suggest that diagenetic alteration of the shale matrix occurred, followed by multiple hydrothermal fluid-flow events that delivered brines of varying chemistry through rock fractures.

TEXT:

INTRODUCTION

Domestic Shale Resources

Unconventional shale reservoirs are estimated to hold nearly half of the United States' recoverable gas resources (MIT Energy Institute, 2010). With the widespread use of horizontal drilling and hydraulic fracture stimulations in unconventional reservoirs, the energy industry has been revolutionized in the 21st ~~century~~Century. The recent depression of commodity prices and subsequent decrease in drilling activity offer the opportunity to conduct detailed studies to better understand the geology of these vast shale resources. Between 2011 and 2016, more than 28 trillion cubic feet (TCF) of natural gas and 102 million barrels (MMBbls) of oil/condensate had been produced from the almost 12,000 unconventional wells in the Appalachian Basin, and nearly 85 percent of these have been completed in the Middle Devonian Marcellus Shale Play (Kallanish Energy, 2017). By ~~the late 2000s~~2010, operators ~~began~~ were developing the Marcellus ~~Shale~~ shale extensively, and even the overlying Upper Devonian Geneseo Shale (also called the Burket ~~Formation~~ Shale in parts of central-eastern Pennsylvania and West Virginia; Carter, 2019) spurred interest amongst industry and researchers as well.

Within the past decade, various assessments have been prepared to estimate Marcellus ~~Shale~~ shale resource and reserve volumes. The ~~United States~~U.S. Geological Survey (USGS) publishes assessments of technically recoverable, undiscovered oil and gas resources for different basins and plays as deemed necessary by industry activity. In 2011 and 2019, the USGS assessed the Devonian Marcellus Shale ~~play~~ Play and reported mean undiscovered resources of 84.2 TCF and 96.5 TCF, respectively (Coleman et al., 2011; Higley et al., 2019). The Potential Gas Committee (PGC) prepares biennial assessments of technically recoverable, discovered *and* undiscovered gas resources for the United States. The PGC's most recent assessment of the nation's potential natural gas supply (for the period ending December 31, 2018) reported that

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organic-rich shales of the Appalachian Basin (a notable portion of which is contributed by the Marcellus ~~Shale~~shale) represent a "most likely" resource volume of 1,037.4 TCF gas, which represented a 21 percent increase over the PGC's previous 2016 assessment (Potential Gas Agency, 2019). Finally, with respect to proved reserves, the ~~United States~~U.S. Energy Information Administration (EIA) provides annual reports for oil and gas plays throughout the United States. For the Marcellus Shale ~~gas play~~Play, EIA reported proved gas reserves at 123.8 TCF and 135.1 TCF in 2017 and 2018, respectively (EIA, 2019).

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The Eastern Gas Shales Project

The rock core samples used in this study were collected as part of the Eastern Gas Shales Project (EGSP). The EGSP was an initiative of the U.S. Department of Energy (DOE), conducted from the late 1970s through 1992, where federal, state and academic research teams studied Mississippian and Devonian organic-rich shales in the Appalachian, Illinois and Michigan basins. This project sought to not only describe the geologic, stratigraphic and structural characteristics of these unconventional shale reservoirs but also to enhance production potential by developing new reservoir engineering technologies (Harper, 2008). An industry-led coring program completed numerous test wells throughout the EGSP region, collecting oriented shale cores from each. Five of these were drilled in Pennsylvania (Table 1), have been analyzed for various and sundry purposes over time, and are currently housed in the PAGS core library in Middletown, Pennsylvania. The reader is referred to Carter et al. (2011) for an expanded overview of the EGSP, and to the DOE's National Energy Technology Laboratory's (NETL) Natural Gas Program Archive (NETL, 2007) for a compilation of the many reports and findings produced by this important unconventional gas research program.

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Hydrothermal Alteration

Hydrothermal alteration features have been recorded in portions of the Appalachian and neighboring basins, and these observations are consistent with the supposition that hydrothermal fluids may significantly affect unconventional shale reservoir quality. The Middle-Upper Devonian New Albany Shale is a self-sourcing reservoir in the Illinois Basin with bitumen occurring in mineralized quartz and sulfide veins, suggesting the veins served as hydrocarbon migration pathways (Dumitrescu et al., 2004; Strapóc et al., 2010). Donoghue (2015) studied fluid inclusions, stable isotope chemistry and vein morphology to determine that fluid expulsion occurred over an extended period of geologic time during and after shale lithification. Although the fluid inclusions showed that quartz-filled veins have similar homogenization temperatures to those of Mississippi ~~Valley~~ Valley-Type (MVT) sulfide deposits of the Appalachian and Illinois basins, fluid salinities were not consistent with MVT deposits (Donoghue, 2015). Bradley and Leach (2003) attributed MVT deposits in the Illinois Basin ~~with~~ to fluid migration through flexure-related extensional domains or dilation zones associated with compression along strike-slip faults. Generally, two distinct MVT fluid-flow events in the United States have been identified: (1) Devonian/Mississippian; and (2) Permian. These coincide with the timing of the Acadian and Alleghenian/Ouchita orogenies, respectively (Pan et al., 1990; Leach et al., 2010).

Rose (1970) reported lead-zinc mineral localities, hosted in Paleozoic sedimentary rocks, in the western Pennsylvania counties of Allegheny, Armstrong, Butler, Indiana and Westmoreland. ~~As of 1970, however, only the Butler County locality was reported to have been mined.~~ The state's largest sulfide mining operations ~~are~~ were in eastern Pennsylvania, with some operations in the central portion of the state (Rose, 1970). The origin of sulfide deposits in

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Paleozoic strata of Pennsylvania's Ridge and Valley Province has historically been related to either an extension of a larger MVT system, in which sulfide mineralization occurred at relatively low temperatures during the Paleozoic (i.e., Howe, 1981; Heyl and West, 1982; Smith, 2003), or diagenesis by sulfidation of the host rock (Rose, 1999). ~~Mathur et al. (2008) analyzed rhenium-osmium (Re-Os) isotopes in sulfide-bearing veins and quartz fluid inclusions collected from veins and fault breccia in the western Ridge and Valley of Pennsylvania, concluding that an Eocene high-temperature mineralization event (related to Eocene intrusions in the Appalachian Basin) recorded in fault breccia pyrite overprinted older MVT mineralization in vein pyrite.~~

Globally, diagenesis and hydrothermal alteration have been documented to have varying effects on organic-rich shale reservoir/source rock quality. In the organic-rich shale of the Upper Ordovician Xinkailing Formation of South China, ~~hydrothermal activity is attributed to the origin of~~ siliceous minerals and organic matter enrichment have been associated with hydrothermal activity (Huang et al., 2018). Roberts (2017) interpreted mineralized veins in Woodford Shale core of the Anadarko Basin were altered by multiple hydrothermal fluid flow events, as recorded by veins filled with sulfides, feldspars, phosphates and carbonates. Shelton et al. (1986) reported Permian hydrothermal alteration in the Ordovician Womble Shale of the Ouachita Mountains and suggested faults accessed a reservoir of hydrothermal fluids. Still, evidence of hydrothermal alteration in Devonian shales of the Appalachian Basin, and more specifically, the Pennsylvania portion of the Rome Trough, have not been documented prior to the work reported herein.

STUDY PURPOSE AND RELEVANCE

Before the large-scale application of horizontal drilling and completion techniques to shale gas resource development, stratigraphic studies of Middle and Upper Devonian shale units

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in the Appalachian Basin generally relied on either outcrop observations (Grabau, 1917; Ettensohn, 1985; Lundegard et al., 1985; de Witt et al., 1993; Brett and Baird, 1996; Brett et al., 1996; ver Straeten, 1996; Brett et al., 2011) or the Devonian shale reports and datasets generated as part of the EGSP. Since the advent of the modern Marcellus Shale ~~play~~Play, however, subsurface data for Devonian shales are more readily available, facilitating the integration of outcrop descriptions with core, well log and geochemical analyses from various sources (Schmoker, 1981; Evans, 1980, 1994, 1995; Rickard, 1984; Arnold, 2010; Boyce, 2010; Lash and Engelder, 2011; VanMeter, 2012; Wang and Carr, 2013; Kohl et al., 2014; Schmid and Markowski, 2017). Despite the availability of legacy EGSP datasets and increase in data availability associated with development of these stacked shale reservoirs in parts of western Pennsylvania, a detailed comparative study of the Devonian Marcellus–Genesee interval, particularly one utilizing standard mineralogic and petrographic methods, has yet to be published.

The work reported in this paper began as a comparative study of the stacked, organic-rich Marcellus and Geneseo shales to better understand Devonian shale sequence stratigraphy and the potential influence of the Rome Trough on stratigraphy and depocenters in southwestern Pennsylvania (Beacom et al., ~~, Carter and Tamulonis,~~ 201~~8~~9; Freeland and Tamulonis, ~~2018~~2019). Indeed, Harper et al. (2017) and Schmid and Markowski (2017) described the influence of deep structure on Devonian lithostratigraphy and reservoir maturity, respectively, near cross-structural discontinuities (CSDs) throughout western Pennsylvania. Schmid and Markowski (2017) concluded that basement structures and lineaments likely played a role in hydrothermal fluid flow, total organic carbon (TOC) distribution and thermal maturity in Upper Devonian shales within the Rome Trough and recommended further ~~investigration~~investigation. ~~, and s~~Structure

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contour maps prepared by Carter (in ~~review~~press) for shallow oil and gas reservoir targets in eastern Washington and Greene counties, Pennsylvania, corroborate the influence of deep structure on Devonian units near areas of basement faulting in this corner of the state. Accordingly, the current study collected discrete samples from the Marcellus–Genesee interval (Figure 1) of the oriented EGSP-2 rock core extracted from API No. 3700320980, southeastern Allegheny County, Pennsylvania (Figure 2). This location is situated within the area of the Rome Trough and near the northwest-southeast-trending Pittsburgh-Washington CSD, both of which appear to have influenced the structure on top of the Marcellus ~~Shale~~shale. Both mineralogic and petrographic analyses were performed on core samples to delineate facies and facilitate interpretations regarding environments of deposition within and between the Marcellus and Geneseo shales. The results, however, provided unexpected insights into the character of these units, and have led us to broaden our study purpose to identify areas of potentially compromised shale reservoir integrity, and by association, areas less desirable for safe, responsible shale development, using standard laboratory techniques. In short, what began as a comparative stratigraphic study of the Marcellus–Genesee interval has become a mineralogic study of the hydrothermal alteration of organic-rich Devonian shales, with potential structural and reservoir maturity implications for future shale development.

DEVONIAN SHALE LITHOLOGY, STRATIGRAPHY AND PREVIOUS WORK

Middle Devonian Units

The Marcellus Formation was first named by Hall (1839) for the dark, thinly laminated shales exposed near the village of Marcellus in Onondaga County, New York. Carter et al. (2011) provided a summary of the evolution and usage of Appalachian Basin Marcellus lithostratigraphy since Hall's outcrop work, and~~, but since the preparation of that paper,~~ the Pennsylvania Geological Survey (PAGS) has since ~~-~~further refined~~ed~~ its terminology for the Marcellus Formation and overlying rock units in western and north-central Pennsylvania. Based on widespread subsurface geophysical log evaluation and correlation in these areas, PAGS has separated the formations of the Hamilton Group into members, formally adopting a modified version of western New York terminology for this interval. Regional geologic cross sections prepared by Harper et al. (2017) illustrate these lithostratigraphic correlations for Pennsylvania, as does the latest subsurface lithostratigraphic correlation diagram for the oil- and gas-producing regions of Pennsylvania (Carter, 2019).

The Middle Devonian Hamilton Group comprises the Marcellus, Skaneateles, Ludlowville and Moscow formations, in ascending order (Figure 1). The basal Marcellus Formation is thickest in northeastern Pennsylvania [>107 meters (m); >350 feet (ft)~~; >107 meters (m)~~] and thins to the west and north, eventually pinching out in Ohio and New York (Baranoski et al., 2007; Lash and Engelder, 2011; Wang and Carr, 2013). In southwestern Pennsylvania, the Marcellus Formation exhibits thicknesses of 30–61 m ~~100–200 ft~~ (100–200 ft~~30–61 m~~) and is juxtaposed between the underlying Onondaga Limestone and the overlying Stafford ~~Member of the Skaneateles Formation~~Limestone (Figure 1; Carter, 2019). Paleowater depths recorded by the organic-rich portions of the Marcellus Formation were at least 101 m ~~330 ft~~ (330 ft~~101 m~~) (Kohl et al., 2014).

Petrophysical studies of the Marcellus Formation have established a well-defined relationship between high gamma-ray values and an increase in ~~total organic content (~~TOC~~)~~, which ranges ~~between~~ from 5–20 percent and with relatively higher values correlating to high gamma "peaks" (Swanson, 1960; Schmoker, 1981; Boyce, 2010; Wang and Carr, 2013; Kohl et al.,

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2014). Wang and Carr (2013) reported that the most abundant minerals in the Marcellus Formation are quartz (35 percent by volume) and illite (25 percent by volume). Modeled clay mineralogy generally increases upward through the Marcellus Formation, from about 5 percent above the top of the Onondaga Limestone to nearly 50 percent at the top of the unit (Wang and Carr, 2013). Historically, Marcellus Formation provenance is interpreted to be from the Acadian Highlands located to the southeast and is divided into two, third-order transgressive-regressive sequences from subsurface data: (1) the Onondaga Limestone/Union Springs Member; and (2) the Cherry Valley Limestone/Oatka Creek member~~s~~ (Figure 3; Lash and Engelder, 2011; Kohl et al., 2014). The Union Springs Member is typically the horizontal drilling target due to its high TOC and low clay content.

Overlying the Marcellus Formation is the Skaneateles Formation, a siltstone/shale unit with the Stafford Limestone at its base. The lower portion of the Skaneateles contains some organic-rich black shale layers; these were previously included as part of the organic-rich "Marcellus facies" mapped by Piotrowski and Harper (1979). In fact, the discovery well for the modern Marcellus Shale ~~play~~Play, the Renz No. 1 Well (API No. 3712522074), was stimulated to produce from organic-rich shales of both the Skaneateles and the Marcellus (Carter et al., 2011).

The gray to dark gray shales of the Ludlowville and Moscow formations comprise the upper portion of the Hamilton Group. Basal limestones (the Centerfield and Tichenor members) divide the Ludlowville from the Skaneateles and the Moscow from the Ludlowville formations, respectively. The Tully Limestone overlies the Hamilton Group and marks the top of the Middle Devonian across the study area (Figure 1).

Upper Devonian Units

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The Upper Devonian clastic sequence of the Appalachian Basin is often interpreted to be a stacked series of upward coarsening turbidites interbedded with other sedimentary layers (Lundegard et al., 1985). Like the Marcellus Formation, the Genesee Formation was deposited as part of the larger Catskill delta complex formed in association with the Acadian Orogeny (Dennison, 1985; Harper, 1999).

The Genesee Formation overlies the Tully Limestone and is divided into the Geneseo and West River members in the subsurface of western Pennsylvania (Harper et al., 2017). The Geneseo member was first named by Chadwick (1920) for shale exposures in Geneseo, Livingston County, New York, and the Burket ~~Formation~~Shale, its lateral equivalent in parts of central-eastern Pennsylvania and West Virginia (Carter, 2019), was first described by Butts (1918~~)~~) for the black shale exposed at Burket, Blair County, Pennsylvania. The West River Member was first described by Clarke and Luther (1904) for shaly outcrops overlying the Genundewa limestone in West River Valley, a few miles east of Canandaigua Lake, Ontario County, New York.

The Geneseo Shale of New York State has been studied by many, including Grabau (1917), de Witt and Colton (1978), Ettensohn (1985) and VanMeter (2012), just to name a few, and is sometimes lumped into a generic “undifferentiated Upper Devonian shale” group that may also include the overlying Middlesex and Rhinestreet shales. Baird and Brett (1986, 1991) and Formolo and Lyons (2007) interpret the Geneseo of New York to be an anoxic black shale that was deposited in a shallow delta environment. Wilson and Schieber (2015) conducted a detailed facies correlation of surface and subsurface data from the shale, concluding that the shale facies record a complex interplay of eustatic-sea level rise and tectonically driven sediment supply, with an overall westward delta progradation in a storm-dominated, shallow epeiric sea.

Schmid and Markowski (2017) have prepared the most recent work on Upper Devonian organic-rich shales in Pennsylvania. This study used publicly available mineralogy, TOC and vitrinite reflectance data derived from rock cuttings samples housed at PAGS to characterize and map unconventional shale hydrocarbon production potential from the Geneseo Shale of the Genesee Formation, Burket ~~Member~~ Shale of the Harrell Formation and Rhinestreet Member of the West Falls Formation. Schmid and Markowski (2017) purported that through a combination of orogenic events, the Rome Trough and regional CSDs have impacted both the quality (i.e., vitrinite reflectance) and quantity (i.e., TOC) of organic matter in these unconventional reservoirs to varying degrees. Although these results are considered preliminary and warrant more evaluation, they offer a compelling argument regarding the potential influence of deep structure on shallow formations in the central Appalachian Basin.

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STRUCTURAL LANDSCAPE

Acadian Foreland Basin

Deformational loading created by the collision of the microplate Avalonia with Laurentia formed the northeast-southwest trending Acadian foreland basin (of the present-day Appalachian Basin), in which the Marcellus and Genesee formations were deposited. This basin was bounded to the southeast by the Acadian Mountains and to the northwest by the Findlay/Algonquin Arch (Castle, 2001; Ettensohn and Lierman, 2012). During this time, Laurentia was located within a subtropical climate (Edinger et al., 2002), which promoted the deposition of interbedded carbonates, organic-rich shales and clastic detritus shed northwestward from the Acadian highlands into the Rheic Ocean, which flooded the basin from the southwest (Mesolella, 1978; Brett and Baird, ~~1985~~1996; Ettehnson and Lierman, 2012). Throughout the Paleozoic,

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existing basement-rooted structures in the Appalachian Basin, most notably the Rome Trough, were reactivated in various manners due to changes in stress regime (Gao et al., 2000; Jacobi, 2002; Jacobi and Fountain, 2002; Tamulonis et al., 2014). The Precambrian basement map prepared for Pennsylvania by Gold et al. (2005) illustrates these basement-rooted structures relative to CSDs and shallower faults.

Rome Trough

The Rome Trough (Figure 2) is a northeast-southwest trending graben in the Appalachian Basin that initially formed during Early and Middle Cambrian rifting associated with the opening and spreading of the Iapetus Ocean and has been reactivated throughout the Paleozoic (Woodward, 1961; Harris, 1978; Drahovzal and Noger, 1995; Shumaker and Wilson, 1996; Gao et al., 2000). Over the past 50 years, geologists have studied the complex structural architecture of the trough to understand hydrocarbon generation and entrapment within the trough and the tectonic evolution of the Appalachian Basin (Woodward, 1961; Harper, 1989; Drahovzal and Noger, 1995; Dominic et al., 1996; Beardsley, 1997; Ryder et al., 1997; Patchen et al., 2006). Gao et al. (2000) examined along-axis segmentation and growth history of the Rome Trough in Cambrian to Pennsylvanian formations, and divided the trough into three segments based on subsurface and geophysical data: (1) an eastern Kentucky section; (2) a southern West Virginia section; and (3) a northern West Virginia/Pennsylvania section. Sub-segments within each of these sections have been observed to exhibit varying reactivation histories (Dominic et al., 1996). Subsurface evaluation and mapping suggest that faults of the Rome Trough were less active from the Late Ordovician to Pennsylvanian, and relatively low-relief inversion structures formed periodically as the Appalachian foreland basin developed (Gao et al., 2000). Lash and Engelder

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(2011) observed local variations in Marcellus Formation transgression/regression cycles in the western, more distal areas of the Appalachian Basin within the Rome Trough, which likely reflect reactivation of Rome Trough basement structures and northwest-striking CSDs that formed during and after Acadian plate convergence.

Fractures and Veins

Engelder et al. (2009; also see Engelder, 2004; Engelder and Whitaker, 2006; Engelder, 2008; Lash and Engelder, 2009) described two regional joint sets, J1 and J2, observed in Middle to Upper Devonian Appalachian Basin black shale outcrops and subsurface data. It is hypothesized that both joint sets formed near peak burial depths when natural fractures developed as the thermal maturation of organic matter induced high fluid pressures in the shales. The orientations of both joint sets vary slightly throughout the basin, with the J1 set approximately oriented in a west-to-east direction and the J2 set oriented in a northwest-to-southeast direction. Outcrop observations show that J1 and J2 joints are open at the surface, but EGSP cores analyzed by Engelder et al. (2009) show that relatively deep wells drilled through the Devonian shales in Pennsylvania and West Virginia have mineralized veins.

Specific to western Pennsylvania and West Virginia, Evans (1994, 1995) studied fractures and vein fluid inclusions in Appalachian Basin Devonian shale cores, including the EGSP-2 core. Evans (1994) divided subvertical veins into six sets based on joint clusters, vein orientation and mineralogy. Vein mineralogy was reported to contain calcite, dolomite, siderite, quartz and barite, and the orientations and mineral sequences suggested that vein formation was a continuous process (Evans, 1994). Fluid inclusion microthermometric analysis of numerous vein sets in Middle Devonian shales was interpreted to describe the evolution of fluids in the

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Appalachian Plateau during and since the Alleghenian orogeny (Evans, 1995). Two primary types of fluid inclusions were observed in the veins: (1) hydrocarbon inclusions and bitumen; and (2) two-phase aqueous inclusions with saline brines. The bitumen inclusions were found in the oldest vein set that formed during hydrocarbon generation, while the youngest vein set contained methane and two-phase aqueous inclusions that were initiated during maximum burial of the Middle Devonian shales. The veins that dated between these two age end members formed under lithostatic pore-fluid pressure conditions.

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METHODS

Core Samples and Geophysical Logs

The Combustion Engineering, Inc. No. 1 Well (API No. 3700320980) was completed in Forward Township, Allegheny County, Pennsylvania, to a depth of 2,290 m 7,512 ft (7,512 ft2,290 m) in March 1979 (EDWIN, 2020). The rock core extracted from this well (herein referred to as EGSP-2) was evaluated using various descriptive and analytical means in the late 1970s and early 1980s as part of the EGSP (NETL, 2007) and has also been the focus of numerous fracture and vein studies as described above. The EGSP-2 core is housed in the PAGS core library (Middletown, Pennsylvania), is 8.9 centimeters (cm)3.5 inches (in) [3.5 inches (in)8.9 centimeters (cm)] in diameter and includes a depth interval of 2,118–2,287 m 6,950–7,503 ft (6,950–7,503 ft2,118–2,287 m). Despite some gaps in the cored interval, nearly all of the 152 m 500 ft (500 ft152 m) interval evaluated for this study was available for inspection and sampling.

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The Combustion Engineering, Inc. No. 1 Well was logged using gamma-ray, neutron, density, resistivity and other geophysical tools at assorted depth intervals, and a sample description log was also prepared using borehole cuttings (Table 2). The gamma-ray, density,

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density porosity and resistivity logs were digitized for the Marcellus–Genesee interval to evaluate petrophysical observations relative to core descriptions, lithofacies determinations and laboratory analytical results (Figures 3 and 4). Geophysical and sample description logs were used to pick the tops of the Middle Devonian Onondaga, Marcellus and Skaneateles formations and the Upper Devonian Geneseo and West River members of the Genesee Formation in this well, as well as to inform an appropriate sampling strategy.

Having established a range of depths targeting the Marcellus–Genesee interval (2,134–2,286 m; 7,000–7,500 ft~~; 2,134–2,286 m~~), a macro-scale core description was prepared. Core lithofacies were defined based on grain size, bedding, color, sedimentary structures, macro-fossils and bulk mineralogy (Table 3), and the preliminary sampling plan was modified to collect samples in all described lithofacies, as well as the depths at which changes in lithofacies occurred. A total of 24 samples were collected by hand, with samples distributed throughout the Marcellus–Genesee interval as follows: Marcellus (7), Skaneateles (8), Geneseo (3) and West River (6) (Figures 3 and 4). Samples were split to accommodate the preparation of thin sections, bulk mineralogy testing and TOC analysis.

X-Ray Diffraction

The bulk mineral compositions of 24 dried, powdered samples taken from discrete depths within the Marcellus–Genesee interval were determined using X-ray powder diffraction (XRD). The samples were loaded in 16-millimeter (mm) (0.63-in) -diameter back-packed sample holders that were mounted in a sample spinner. The results were interpreted using PANalytical HighScore Plus software with a Malvern Panalytical Empyrean X-ray diffractometer, and minerals were identified using the International ~~Center~~ Centre for Diffraction Data PDF-4 Mineral file for 2018.

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Semi-quantitative results were developed using the Rietveld method, which uses the whole X-ray pattern, not just its most intense peaks, to find agreement between observed patterns and the published crystal structure data of the minerals through least-squares analyses. Quantities are then calculated based on these analyses. This method considers factors like preferred orientation and peak shape that can present problems in dealing with layered silicate minerals. The HighScore Plus software enabled the programming of an automated Rietveld procedure that took these factors into account, producing a level of precision sufficient for dividing the minerals into the major categories reported for this study. Mica group minerals are reported as muscovite, and chlorite group minerals are reported as clinochlore.

Total Organic Content

Samples were analyzed for ~~total organic content (~~TOC~~)~~ with a Costech elemental analyzer, and decarbonation procedures were based on the methodology of Hedges and Stern (1984). Sediments were weighed into silver capsules, wetted with pure water, and fumigated with hydrochloric acid in a glass ~~dessicator~~desiccator. The samples were then dried at 60 degrees Celsius (°C) overnight to drive off excess water. Organic carbon loss-on-ignition analysis was then conducted on all samples. Standards including acetanilide, caffeine, sorghum and low-organic content soil were analyzed after each batch of 10 samples to monitor for accuracy and precision.

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Optical Mineralogy, SEM Imaging and Chemical Analysis

Standard petrographic techniques were used to analyze polished thin sections prepared for this study. A Leica DM4500 petrographic microscope, accompanied by Leica Application Suite (LAS) V.4.12 software, was utilized with transmitted light microscopy up to 100x magnification to identify and characterize minerals, veins, fossils, bedding and alteration and replacement features. Cross-cutting relationships, replacement minerals and alteration features were key to describing the post-depositional processes evidenced in rock core samples.

A JEOL 6010LV scanning electron microscope (SEM) with an energy dispersive X-ray spectrometer (EDS) and tungsten filament source was used to image and quantify micron (µm)-scale sedimentologic and alteration features. The SEM was calibrated with a PELCO XCS-5 standard prior to the analysis of each sample, and slides were initially viewed under both secondary electron imaging (SEI) and backscattered electron imaging (BES). SEI was used for viewing topographic changes, and BES discerned compositional changes. SEM magnification ranged ~~between~~ from 30x to 5,000x, spot size ranged ~~between~~ from 10 to 60 µm and vacuum pressure ranged between 80 to 83 Pascal (Pa) to reduce sample charging. The EDS detector measured the number and energy of X-rays generated from the incident electron beam into an energy spectrum that determines element abundance. Features of interest initially observed under the petrographic microscope, such as veins, fossils, matrix and individual grains/crystals, were examined in detail with the SEM. EDS spot analysis was performed using BES imaging at low vacuum conditions (80 Pa) and 10-µm spot sizes.

RESULTS

Core Samples and Geophysical Logs

EGSP-2 formation tops were originally interpreted from the well's gamma-ray log, which used the Kelly Bushing as its reference elevation. This point is 3 m (10 ft ~~(3 m~~) higher than the well's ground level elevation, which is the reference elevation for rock core samples collected for this study. All measured depths and graphical representations of core and logs have been adjusted to represent measured depths relative to ground level.

The Marcellus Formation extends from 2,260 m ~~7,415 ft~~ (7,415 ft~~2,260 m~~) to the top of the Onondaga Limestone at 2,280 m ~~7,480 ft~~ (7,480 ft~~2,280 m~~) and is 20 m ~~65 ft~~ (65 ft~~20 m~~) thick. The top of the Union Springs Member occurs at 2,270 m ~~7,446 ft~~ (7,446 ft~~2,270 m~~), is 10 m ~~34 ft~~ (34 ft~~10 m~~) thick and contains the highest gamma-ray and resistivity measurements of the study interval (up to 844 API units and 100–~~-~~500 ohm-meters, respectively). The Cherry Valley Limestone (2,269–2,270 m; 7,444–7,446 ft~~; 2,269–2,270 m~~) directly overlies the Union Springs Member, is 0.6 m ~~2 ft~~ (2 ft~~0.6 m~~) thick and exhibits relatively low gamma-ray values. Some fractures (both healed and open) are found in the Cherry Valley, and an unconformity is located at the top of the member, as ~~indicated~~ illustrated by a wavy, erosive contact. Overlying the Cherry Valley Limestone is the Oatka Creek Member (~~7,415–7,444 ft;~~ 2,260–2,269 m; 7,415–7,444 ft), which is 9 m ~~29 ft~~ (~~9 m~~29 ft) thick and has less variable gamma-ray and resistivity log values. There is a thin zone in the middle of the Oatka Creek Member with relatively high porosity, low density and low resistivity values, though the gamma-ray curve exhibited no excursions here (Figure 3).

The Skaneateles Formation (~~7,321–7,415 ft;~~ 2,231–2,260 m; 7,321–7,415 ft) overlies the Marcellus Formation and is 27 m ~~94 ft~~ (~~27 m~~94 ft) thick. The Stafford ~~Member~~ Limestone (2,259–2,260 m; 7,410–7,415 ft~~; 2,259–2,260 m~~) is 2 m ~~5 ft~~ (5 ft~~2 m~~) thick and separates overlying ~~organic-rich~~ Skaneateles shales from the underlying Marcellus Formation. The organic-rich Skaneateles ~~interval~~ interval immediately overlies the Stafford ~~Member~~Limestone, is roughly 2–3 m ~~8 ft~~ (8 ft~~2–3 m~~) thick and has gamma-ray values comparable to those of the Oatka Creek Member.

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Approximately 76 m ~~250 ft~~ (250 ft~~76 m~~) of gray shale and limestone of the Moscow, Ludlowville and Tully formations separate the top of the Skaneateles Formation from the base of the Genesee Formation. The Geneseo ~~Member~~ Shale (2,149–2,156 m; 7,050–7,072 ft~~; 2,149–2,156 m~~) of the Genesee Formation is 7 m ~~22 ft~~ (22 ft~~7 m~~) thick and immediately overlies the Tully Limestone. It exhibits a range of log values, and the highest gamma-ray values occur near its base. A porosity log peak separates the Geneseo Shale from the overlying West River Member, the top of which occurs at 2,107 m ~~6,914 ft~~ (6,914 ft~~2,107 m~~). For the purposes of this work, however, the top of the study interval was set at 2,134 m ~~7,000 ft~~ (7,000 ft~~2,134 m~~) so that core description and sampling efforts could be focused on the lowermost 152 m ~~500 ft~~ (500 ft~~152 m~~) of the section above the Onondaga Limestone. In general, the studied portion of the West River Member (2,134–2,149 m; 7,000–7,050 ft~~; 2,134–2,149 m KB~~) has more uniform gamma-ray, porosity, density and resistivity log values compared to that of the underlying Geneseo Shale (Figure 4).

Core inspection found that the EGSP-2 Middle and Upper Devonian intervals of interest generally range from carbonate-rich, organic-poor gray mudstone to quartz-rich, organic-rich black shale. Sedimentary structures include planar laminations, parallel and non-parallel wavy laminations and planar beds (Table 4, Figures 3 and 4). Healed vertical to subvertical fractures occur in the Union Springs Member and Geneseo ~~members~~ Shale and range from less than 17 µm to nearly 1 mm (0.04 in) in diameter, and much of the core is broken along bedding planes due to natural and coring-induced fractures. Brachiopod and horn coral fossils were identified in the Stafford ~~Member~~ Limestone ~~of the Skaneateles Formation~~ and ~~the~~ Geneseo ~~Member~~ Shale~~of the Genesee Formation~~, and an ash layer is located at the base of the Union Springs Member,

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~~which is the youngest~~one of the higher beds of the Tioga Ash (Table 4, Figures 3 and 4). In general, the black shales of the Union Springs Member and Geneseo ~~members~~ Shale have higher gamma-ray and resistivity log values, while the lighter gray intervals (including the Cherry Valley Limestone and top of the West River Member) have higher density log values, and lower gamma-ray and resistivity values (Figures 3 and 4). An exception to this generalization is the top of the Cherry Valley Limestone, which exhibits both healed and open fractures.

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XRD and TOC

The bulk mineralogic composition of samples, as determined by semi-quantitative XRD analysis, included quartz, ~~calcite, dolomite~~carbonate, ~~muscovite, clinochlore~~clay, plagioclase, ~~dolomite, gypsum, pyrite, jarosite and magnesiocopiapite~~sulfate and sulfide minerals (Table 4). Quartz was found in all samples and ranged ~~between~~ from 17–70 percent. The lowest quartz content occurs at the base of the Union Springs Member (sample MS1), and the highest quartz was reported in the high gamma-ray section of the Union Springs Member (sample MS2). Mica group minerals (reported as muscovite) were also ubiquitous in these samples and ranged from 13–79 percent, with the highest values reported at the base of the Union Springs Member (sample MS1) and the lowest values in the high gamma-ray peak of the Union Springs Member (sample MS2). ~~Chlorite~~ The detection of chlorite group minerals (reported as clinochlore) ranged ~~between~~ from 7–16 percent, was highest in the West River Member (sample BS5) and ~~were~~ was not detected in the Union Springs Member of the Marcellus Formation. Plagioclase was reported in the Geneseo and West River members of the Genesee Formation. Here, detections ranged from 1–9 percent, with the highest value reported in the Geneseo ~~Member~~ Shale (sample BS2; Figures 3 and 4).

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Carbonate and sulfate minerals are less abundant in the Marcellus–Genesee interval. Calcite was found in 14 samples, ranging ~~between~~ from 7–31 percent, and was highest in the Stafford ~~Member~~ Limestone~~of the Skaneateles Formation~~. Where sampled, the Oatka Creek Member of the Marcellus Formation lacked calcite. Dolomite was found in only nine samples, ranging ~~between~~ from 2–12 percent, with the highest value found in the Skaneateles Formation (sample MS7). Dolomite was not detected in any of the Marcellus Formation samples. Gypsum ranged ~~between~~ from 1–8 percent in eight samples and was not detected in either the Union Springs or West River members. The greatest gypsum detections were found in the Oatka Creek Member (sample MS4).

Sulfide minerals were also found in samples collected for this study. Pyrite was ubiquitous throughout the Marcellus–Genesee interval, ranging from 1–7 percent, and the highest detection was found in the Skaneateles Formation (sample MS7). Magnesiocopiapite, typically formed by the oxidation of pyrite, was ~~also found~~ detected in one sample from the Oatka Creek Member of the Marcellus Formation at 14 percent (sample MS4). Jarosite, which can form from ~~the alteration of~~ pyrite oxidation or, in some cases, ~~–~~as a primary mineral in the presence of hydrothermal fluids, was also detected in one sample in the West River Member of the Genesee Formation at 10 percent (sample BS4; Figures 3 and 4). The occurrence of magnesiocopiapite and jarosite in the EGSP-2 core is attributed to the oxidation of pyrite post-coring (R. Smith II, 2020, personal communication).

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The TOC content of samples collected for this work was variable, ranging ~~between~~ from 0.03~~–~~ ~~and~~ to 8 percent (Figures 3 and 4). In the Skaneateles and Marcellus formations, higher TOC values correlated with relatively moderate to high quartz content. The highest TOC

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measurement in Middle Devonian shales occurred at the base of the Oatka Creek Member~~ which, coincidentally, also had the only magnesiocopiapite detection~~. In the Upper Devonian shales, the highest TOC was reported in the Geneseo Shale (sample BS2); this ~~same ~~sample also reported the highest plagioclase content of any samples collected for this work. Throughout the entire study interval, elevated TOC was coincident with relatively high gamma-ray and resistivity curve values (Figures 3 and 4).

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Lithofacies

Nine different lithofacies (Table 3) were defined for the study interval using core description and bulk mineralogy data. Six of these were found to repeat within the Marcellus–Genesee interval, and lithofacies are predominantly shale or mudstone. Lithofacies 1, a light gray, wavy laminated, low-quartz mudstone with muscovite, pyrite and ash layers, is only found at the base of the Union Springs Member. Lithofacies 2 is composed of white to gray, high-carbonate, low-TOC, thin-bedded shale with some wavy parallel and non-parallel beds/laminations, brachiopod and horn coral fossils and healed vertical fractures. Light gray to gray, moderate-quartz, moderate- to high-clay, low- to moderate-carbonate shale with thin, planar beds/laminations and some brachiopod fossils comprise ~~lithofacies ~~Lithofacies 3. Lithofacies 4 is gray to dark gray, moderate-quartz, low- to moderate-carbonate, low- to moderate-TOC, clay-rich, pyritic, thinly planar bedded shale. Lithofacies 5 is a black, moderate- to high-quartz, low-carbonate, high-TOC, thin, planar bedded shale with healed vertical fractures. Light gray to gray, planar-laminated, high-quartz and clay, low-carbonate, low-TOC mudstone composes Lithofacies 6, and gray to dark gray, planar-laminated, high-quartz, high-plagioclase, high-TOC shale

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comprises ~~lithofacies~~ Lithofacies 7. Lithofacies 8 and 9 are mudstones with varying amounts of clay and relatively low TOC, with ~~lithofacies~~ Lithofacies 9 having calcite-filled macro-veins.

Petrographic Analysis

Petrographic examination of thin sections from the EGSP-2 core documented numerous micro-fossils and alteration features in the Middle and Upper Devonian section that were not obvious when the core was described on a macro-scale (Tables 3 and 4; Figure 5). Individual quartz grains are categorized as being large and angular (20 to 100 µm ~~or less~~ in length/diameter), small (generally 20 µm or less in diameter) or microcrystalline. Angular, shard-like quartz was found only at the base of the Union Springs Member (sample MS1) where ~~the Tioga Ash Bed~~an ash bed was observed, and quartz grains in the Marcellus and Skaneateles formations were more disseminated throughout the rock matrix. Opaque minerals were found in 22 samples, and five samples exhibited euhedral pyrite crystals (samples MS1, MS10, MS13, MS14 and BS2). Laminations in thin section were observed only in the Skaneateles Formation (sample MS9). Fossils included crenulated shells, calcispheres, chambered foraminifera, textured foraminifera ~~(with and without tests)~~, ~~Styliolina~~ Styliolinids and unidentified fossils and shell fragments, as well as relict grains/clasts having traceable boundaries and comprised of differing colors and/or textures relative to the rock matrix (referred to herein as 'ghost clasts') (Table 4). Trace fossils included subvertical to subhorizontal burrows. The Union Springs Member (sample MS1) is the only one without fossils or trace fossils. Calcispheres and burrows were the most abundant features, and samples from the Skaneateles Formation (samples MS7, MS9 and MS10) and the West River Member (samples BS6C and BS7) of the Genesee Formation each had at least five observable fossil features (Table 4).

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Features attributed to diagenesis and hydrothermal alteration include partial –matrix alteration/replacement, red staining on grains or veins, quartz-filled fractures, fractures filled with a variety of other minerals, ~~crystal development within the rock matrix,~~ replacement minerals within fossils or pre-existing grains, cross-cutting veins~~,~~ and 'dusty'-tinted structures/minerals partially filled with organic matter. These features are ubiquitous throughout the Marcellus–Genesee interval, and 19 of the 24 samples have at least two alteration features.

Alteration Index

An alteration index (AI) was determined for each sample by summing the types of alteration features observed by petrographic analysis, with the intent of using AI values to look for similarities and potential trends within the larger sample set. AI values ranged ~~between~~ from 0 (sample MS13, Skaneateles Formation) ~~and~~ to 8 (sample BS2, Geneseo Shale) (Table 5). The AI for each sample was plotted against its bulk mineralogy content, TOC and geophysical log data. Unfortunately, no correlations were found between AI and these other parameters. Whether looking at data for individual geologic units or all 24 samples as a single dataset, R^2 values were less than 0.41.

SEM Analysis

Examining samples with an SEM provided detailed images for visual identification, as well as semi-quantitative insight regarding the chemistry of both macro- and micro-structures and fossils observed in thin section. Figures 6 through 10 visualize some of the alteration features observed throughout the Marcellus–Genesee interval, and EDS analysis was performed to identify mineral composition and organic matter in these features. In particular, SEM analysis was used to investigate areas of matrix replacement (samples MS10 and MS12; Figures 5A and

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5J), ~~larger crystals within the matrix (jarosite; Figure 6C)~~, plagioclase-filled veins (samples BS2 and BS6B; Figure 5E), veins with complex mineralogy (samples MS5, MS6 and BS2; Figure~~s~~ 5B~~ and 6C~~), structures and veins filled with or rimmed by organic matter (samples MS3, MS4, MS5 and BS6C; Figures 5H, 6A and 6B), and layers of euhedral pyrite (samples MS1 and BS2; Figure 5F), some of which are cross-cut by veins (sample BS2; Figure 7). Sphalerite surrounding quartz and pyrite was detected in the Union Springs Member (Figure 8).

Organic matter occurred within and along the rims of veins filled with gypsum, quartz, calcite and aluminum-rich minerals (Figure 6)~~. A cluster of jarosite crystals surrounded by a groundmass of quartz and clay minerals was identified in the West River Member (sample BS4; Figure 6C); a separate jarosite crystal cluster in this same sample was also found to contain up to 5 percent platinum (Figure 7)~~. Figure 7 shows an aluminum-rich ~~sillimanite~~ vein cutting through a layer of euhedral pyrite crystals in the Geneseo Shale (sample BS2). This vein is surrounded by a darker alteration halo within the surrounding matrix. An EDS transect across the pyrite crystals, halo and cross-cutting vein determined aluminum contents of <2 percent, 4 to >6 percent and >8 percent, respectively (Figure 7).

Macro-veins filled with calcium-rich plagioclase were observed in the West River Member (samples BS2, BS5 and BS6B). Figure 9 displays an anorthite macro-vein cross-cutting through quartz and clay mineral groundmass (sample BS6), with an angular groundmass fragment within the vein. EDS analysis determined approximate weight percentages of calcium, silica, oxygen and aluminum at 15, 16, 45~~,~~ and 20 percent, respectively; sodium was not detected at these EDS sample locations.

Sample MS6 contained the most complex chemistry observed with the SEM (Figure 10). The red-stained area observed under the petrographic microscope (Figure 5B) exhibits a sedimentary texture when viewed with the SEM, and the adjacent white vein has a rim of lighter-colored crystals with increased calcium content and an inner core with higher sulfur content. In some places, a relatively thin, darker layer with white spots is observed. The white spots contain up to 19 percent thorium~~, and the dark layers reported 4 to 8 percent silver~~.

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INTERPRETATION

Hydrothermal fluids have significantly altered the unconventional Devonian shale reservoirs in the EGSP-2 core, and it is probable that nearby deep, basement-rooted faults of the Rome Trough accessed hot reservoirs, providing fluid migration pathways to the overlying shales. Increased pressure and heat from the influx of hot fluids may have additionally fractured the reservoirs, created and destroyed porosity, and affected thermal maturity and geomechanical properties. This alteration likely exists beyond the Devonian stratigraphy examined in this study, and the lateral extent along and surrounding faults must be defined. These factors should be considered when developing unconventional fields within the Rome Trough, as production may be affected by hydrothermal alteration ~~around~~ in the vicinity of basement faults. What's more, potential environmental impacts associated with unconventional shale drilling in areas near these faults and associated fracture networks must be further studied.~~, as t~~ These structurally altered areas may affect the success of hydraulic fracturing operations and/or provide pathways for stimulation fluids to migrate from the reservoir to shallower formations, as well as ~~source~~add toxic metals to flow-back waters~~.~~

Hydrothermal Alteration

Hydrothermal alteration occurs when relatively hot fluids are introduced to cooler rock and happens at any temperature range, provided the fluids are hotter than the ambient rock temperature (White, 1957). The Middle and Upper Devonian shales of the EGSP-2 core have experienced diagenesis and hydrothermal alteration, as evidenced by the presence of ~~matrix replacement,~~ red staining of veins and grains, veins with complex mineralogy, replacement crystals, 'dusty'-tinted structures or veins filled with organic matter, alteration halos, sulfides and sulfates, as well as the detection of ~~platinum, silver and~~ crystals enriched with thorium, as indicated by SEM-EDS. This alteration complicates comparisons of sedimentary features among the shales, as it overprints much of the primary sedimentology. ~~Quartz~~ The disposition ~~content~~ of quartz in the Marcellus and Skaneateles formations is ~~more~~ disseminated, and grains tend to be small and more rounded when compared to ~~that~~ those of the Genesee Formation, ~~which exhibits~~where quartz occurs as angular ~~quartz~~ clasts. These observations suggest that the Upper Devonian shale quartz content is detrital in origin, although this hypothesis must be further explored in rock that has not been overprinted by hydrothermal alteration.

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The cross-cutting nature and complex mineralogy of some matrix and veins, quartz overgrowths and replacement grains in fossils suggest that hydrocarbon generation and diagenetic alteration of the shale matrix occurred, followed by sustained or multiple hydrothermal fluid-flow events that delivered brines of varying chemistry through fractures. Macro-veins filled with organic matter in this core have been extensively studied by Evans (1994, 1995) and are interpreted to have formed throughout hydrocarbon generation and maximum

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burial, and this study does not contradict that interpretation. However, numerous micro-veins and some macro-veins presented in this paper have ~~very~~ different mineralogies (e.g., anorthite, ~~sillimanite,~~ muscovite and gypsum) than those reported by Evans (1994, 1995), suggesting that additional events precipitated minerals in the fracture network. Organic matter may have migrated during diagenesis and/or exposure to hydrothermal fluids (Piane et al., 2018), further distributing it within veins and within and around other structures (e.g., fossils and detrital grains; Figures 5 and 6).

Silica and calcite replacement in microfossils and quartz overgrowths likely occurred in the early stages of diagenesis, as suggested by cross-cutting veins and textural relationships (Figure 5). Pyrite is found in multiple forms, which is an important finding that should be taken into consideration by future studies when utilizing XRD analyses. The framboidal pyrite is interpreted to be syndepositional or to have formed during early diagenesis (Blood and Lash, 2015). Euhedral/subhedral pyrite is concentrated as thin beds or surrounding veins and is interpreted to have a hydrothermal origin, as ~~are~~ is sphalerite~~, jarosite, magnesiocopiapite, silver and platinum~~ (Figures 5 and 7; e.g., Rockwell et al., 2000; Jamieson et al., 2005; ~~Mathur et al., 2008;~~ Leach et al., 2010; Roberts, 2017). ~~These sulfides, sulfates and metals may be associated with relatively low-temperature Paleozoic MVT mineralization events, where metals were primarily leached from surrounding sedimentary rock. However, petrographic~~ Petrographic and SEM data show that the hydrothermal fluids only locally altered the shale around the mineralized fractures (Figures 5 and 7). Euhedral/subhedral pyrite beds are cross-cut by veins with complex mineralogy ~~(e.g., sillimanite~~[CK1] ~~; Figure 8)~~, suggesting multiple flow events.

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The semi-quantitative XRD results do not corroborate the complex mineralogies observed in thin section. This is likely due to a combination of factors related to sample composition and instrumentation settings and/or limitations ~~limitations~~. The detection limit of the X-ray diffractometer used in this study has been estimated at ~1 to 3 percent, and can vary depending on the sample material (J. Barnes, 2020, personal communication~~, 2020~~). As much of the complex mineralogy documented by this study was found within and along micro-veins comprising only a small portion of the XRD sample size, it is unlikely that bulk XRD analyses could resolve or quantify these minerals (e.g., ~~silver,~~ sphalerite ~~and sillimanite~~). Furthermore, SEM analyses suggest that these ~~exotic~~ minerals only exist in ~~only~~ trace quantities.~~, likely less than the XRD detection limits.~~

Fluid Flow along Faults in the Rome Trough

Hydrothermal systems often occur in tectonic settings of crustal thinning and elevated heat flow, such as large-scale rifts and areas with flexural extension (Bradley and Kidd, 1991; Smith, 2008). The EGSP-2 Devonian shales suggest that higher pressure and temperature fluids (relative to the host rock) flowed through existing, reactivated faults, altering the unconventional reservoirs and likely the underlying and overlying stratigraphy as well. As previously stated, the EGSP-2 core is located within the Rome Trough portion of the Appalachian Basin near the junction of at least two basement-rooted faults (Figure 2), though it is currently unknown which fault(s) facilitated flow and the exact series of events. Mathur et al. (2008) ~~)~~ proposed that faults in central Pennsylvania provided conduits for hot, deep hydrothermal fluids that precipitated sulfides, and Evans (1994, 1995) recorded numerous mineralization events in the fractures of the

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EGSP-2 core. These interpretations corroborate the findings of Smith (1978) relative to the occurrence of lead and zinc in Pennsylvania.~~.~~

The Devonian shales in the EGSP-2 core may have experienced numerous hydrothermal events of varying sources and temperatures, and the series of events is currently being defined. Existing basement-rooted faults accessed one or more reservoirs of deep, hot fluids, resulting in their upward migration through a fault and fracture network. The fluids leached and mineralized the host rock along the regional, basement-rooted faults, as well as secondary faults/fractures as fluids moved away from the larger fault zone(s). Gao et al. (2000) noted that faults within and bounding the trough were reactivated in various ways throughout the Paleozoic, and it is possible that the faults have been active since. Hydrothermal fluids both enhanced and destroyed permeability and changed reservoir mineralogy. As the fluids flowed up from greater depths with higher pressures, additional fracturing and enlargement of existing fractures may have occurred (Smith, 2008). Fluid chemistry was altered during transport, and during either prolonged flow and/or numerous fluid pulses, precipitated a range of minerals within and near the fault/fracture network, including quartz, calcite, anorthite, pyrite~~, ~~ ~~jarosite, sillimanite, ~~and gypsum~~ and magnesiocopiapite~~, though the lateral and vertical extent of this alteration has yet to be defined.

Hydrothermal Effects on Reservoir Quality

Hydrothermal alteration of the EGSP-2 Devonian shales introduces hydrocarbon exploration and development uncertainty as it pertains to thermal maturity, migration of organic matter, creation of additional fractures, fracture and fault mineralization, geomechanics and the creation/destruction of porosity and permeability. Hydrothermal fluids may have locally

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increased the thermal maturity in the shales, resulting in hydrocarbon cracking and the formation of bitumen, which fills pores and fractures in the shale (e.g., Misch et al., 2016). Some hydrothermal mineralization also appears to have stratigraphic control, as anorthite was only found in the Upper Devonian study interval~~, magnesiocopiapite was detected in one sample in the Oatka Creek Member, and jarosite was only found in a single sample in the West River Member~~ (Figure~~s~~ 4~~ and 4~~). Euhedral pyrite is found in five samples in the Marcellus Formation, Skaneateles Formation and Geneseo Member, but was not observed in the overlying West River Member of the Genesee Formation.

It is likely that the brittler siliceous and carbonate facies contain more natural fractures and would be prone to additional fracturing due to pressures introduced by hydrothermal fluids, providing additional conduits for fluid flow and thus, alteration. Some of the diagenetic/hydrothermal minerals such as quartz, feldspar, dolomite and calcite promote additional brittle behavior (Jin et al., 2015). Intervals with numerous fractures where hydrothermal minerals have permeated into the matrix could influence the reservoir's geomechanical properties, though it is acknowledged that these properties are dependent on numerous factors in addition to mineralogy (Jin et al., 2015).

In the EGSP-2 core samples, AI was not correlated to geophysical log values, mineralogy or TOC, and an increased sample frequency would likely be necessary to document detailed alteration features and changes within the stratigraphy. Furthermore, a higher AI value may not necessarily indicate that the rock experienced more hydrothermal alteration, as the thin sections

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provide limited data at a given depth, and it is not likely that all alteration features formed under the same pressure and temperature conditions.

Environmental Implications

This study implies that the Devonian shales of the EGSP-2 core were part of a system open to external fluids. Though this study focused on hydrothermal alteration, it is important to consider how the Rome Trough's fault/fracture system is expressed in the stratigraphy underlying and overlying the study interval and within faulted areas. Porosity variations and hydrothermal minerals within the shale matrix and veins have likely impacted the geomechanical properties of these shale reservoirs and possibly the overlying strata. Regional faults also affect local stress regimes and are often associated with fracture networks, which could create or enhance hydraulic communication among Devonian shale reservoirs at different depths. The trough's basement-rooted faults and associated features may cause difficulties during completion operations, as they can form seals or provide fluid flow conduits to shallower strata. To better understand the potential environmental impact of drilling and completing unconventional wells around basement-rooted faults in the Rome Trough of the central Appalachian Basin, additional core must be examined for hydrothermal alteration features.

The combination of petrographic and mineralogic analyses used in this study may be helpful in identifying areas of compromised shale reservoir integrity, which could include structural impairment (the self-contained reservoir is no longer self-contained, making it less desirable for safe, responsible shale development), increased thermal maturation (making an area no longer prospective for wet gas development, for example),) or both. These standard analyses rely on routine, well-established methodologies that can be employed in academic or commercial laboratories, and can help assess the extent to which these shale reservoirs may have been impacted by basement-rooted faults, CSDs, fluid flow events or some combination of these.

CONCLUSIONS AND FUTURE WORK

This study began as an investigation of the stratigraphy of the Marcellus–Genesee interval using core descriptions and geophysical log data. Petrographic studies combined with mineralogical analyses (SEM with EDS and XRD) were then conducted to better delineate facies and environments of deposition within and between the Marcellus and Geneseo shales. The results of these combined analyses documented shale diagenesis and hydrothermal alteration of these rocks, indiscriminate of facies, member or formation throughout the study interval.

Although the findings presented herein provide preliminary insight into hydrothermal alteration of Devonian shales within the Rome Trough of southwestern Pennsylvania and support the findings of Schmid and Markowski (2017), additional work must be completed to enhance our understanding of the impact of basement-rooted faults in the study area on shale reservoir quality, geomechanics and fluid migration. Follow-on work could take many courses, but the following represent those focused efforts that may serve to enhance our understanding of the tectonic history of the Rome Trough area of the central Appalachian Basin and offer improved means of conducting environmentally responsible shale development:

1. *Higher resolution sampling of the EGSP-2 core* – The Marcellus–Genesee interval will be subjected to additional testing, which may include: whole rock geochemistry testing to better quantify trace minerals indicative of hydrothermal alteration; fluid inclusion

studies to assess fluid chemistry; and vitrinite reflectance or Rock-EVAL testing to assess potential variations in thermal maturity throughout the study interval. In addition, the orientation of the core will be considered to gain additional insight regarding fracture system geometry. These sampling efforts will provide insight regarding hydrothermal variation within the unconventional reservoirs and the vertical extent of the alteration.

2. *Investigating fluid flow events in the Rome Trough area* – Isotopic dating of veins and pyrite beds will be conducted on samples from the EGSP-2 Marcellus–Genesee interval. These results will be compared with other comparable studies (e.g., Mathur et al., 2008) to build on our understanding of the processes, timing and magnitude of hydrothermal mineralization in the central Appalachian Basin.

3. *Examining additional cores near CSDs and basement-rooted faults in the Rome Trough area* – Investigation of Middle and Upper Devonian shales in cores from other locations in western Pennsylvania and northern West Virginia may provide information regarding which faults (or areas along a fault) have experienced hydrothermal alteration, explain variations in petroleum hydrocarbon production in these areas and better delineate the extent of the Rome Trough in areas lacking robust subsurface data sets.

4. *Developing sampling workflows to assess potential adverse impacts to shale reservoir quality* – The multidisciplinary approach used in this study may offer a cost-effective alternative to other techniques (e.g., remote sensing, deep test well drilling and logging, etc.) used to identify areas impacted by deep structure and hydrothermal alteration. With additional studies, we intend to further develop a workflow that provides readily available, cost-efficient means to assess whether and/or to what extent self-sourcing

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Formatted: Space After: 12 pt, Outline numbered + Level: 1 + Numbering Style: 1, 2, 3, … + Start at: 1 + Alignment: Left + Aligned at: 0.25" + Indent at: 0.5" shale reservoirs may have been impacted by faulting, fracturing and/or episodic fluid flow events. This information can improve our understanding of the type and volume of petroleum hydrocarbons to be expected from these unconventional shale reservoirs near CSDs and overlying the deepest portions of the basin, and may influence where and how future shale development occurs in the Rome Trough area of the central Appalachian Basin.

5. *Developing a sequence stratigraphic framework and comparison of depocenters within the Rome Trough* – Although this objective was temporarily postponed to investigate the alteration featured observed in the EGSP-2 core, variations of the Devonian organic-rich shale stratigraphy, sequence/systems tract character, thicknesses, mineralogy and TOC within and adjacent to the reactivated, basement-rooted Rome Trough will be used to gain insight into the tectonic history of the trough and shale provenance during the Middle to Late Devonian.

A. 5. *Developing a sequence stratigraphic framework and comparison of depocenters within the Rome Trough – Though this objective was temporarily postponed to investigate the alteration featured observed in the EGSP-2 core, variations of the Devonian organic-rich shale stratigraphy, sequence/systems tract character, thicknesses, mineralogy, and total organic carbon (TOC) within and just outside the reactivated, basement-rooted Rome trough, will be used to gain insight into the tectonic history of the Rome Trough and shale provenance during the Middle to Late Devonian.*

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VITAE:

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Figure Captions

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Figure 1. Middle to Upper Devonian conceptual stratigraphic column of the southwestern Pennsylvania study area with nomenclature used in this study. Geologic age, generalized lithology, formation names and group names are displayed.

Figure 2. Map of the study area illustrating the location of the EGSP-2 core relative to regional lineaments, interpreted basements faults and the approximate location of the Rome Trough (Gold et al., 2005; Patchen and Carter, 2015). Structure contours represent the top of the Middle Devonian Marcellus Formation (ft MSL, 500-ft contour interval) (Harper et al., 2017).

Figure 3. Marcellus and Skaneateles geophysical logs, core description and facies, alteration index (Alt. Index), fossils, TOC and XRD data. Lithofacies descriptions can be found in Table 3 and Alteration Index is found in Table 4. Fossil abbreviations are as follows: Su = undifferentiated shell, Sc = crenulated shell, C = calcisphere, T = trace fossil, G = ghost clast, Ft = textured foram, Fc = chambered foram, St = Styliolina, U = unidentified. TOC = total organic content, MUSC = muscovite, $MgSO_4$ = magnesiocopiapite.

Figure 4. Genesee geophysical logs, core description and facies, alteration index (Alt. Index), fossils, TOC and XRD data. Lithofacies descriptions can be found in Table 3 and Alteration Index is found in Table 4. Fossil abbreviations are as follows: Su = undifferentiated shell, Sc = crenulated shell, C = calcisphere, T = trace fossil, G = ghost clast, Ft = textured foram, Fc = chambered foram, St = Styliolina, U = unidentified. TOC = total organic content, MUSC = muscovite.

Figure 5. Thin section photomicrographs under plane-polarized light unless noted otherwise. A) Skaneateles Formation (sample MS10) with quartz-filled vertical fracture (Q) surrounded by altered muscovite/illite groundmass enriched in aluminum with replacement quartz and calcite crystals; B) Skaneateles Formation (sample MS6) with quartz-filled micro-fractures (Q) and red layer; C) Skaneateles Formation (sample MS14) with smaller-diameter quartz-filled micro-fractures (Q) under cross-polarized light; D) Union Springs Member (sample MS2) with quartz crystal (Q) in shell fragment surrounded by calcite (C); E) West River Member (sample BS6B) with plagioclase (P) filled macro-fracture; F) opaque euhedral pyrite (Py), muscovite (M), and quartz (Q) in the Union Springs Member of the Marcellus Formation; G) Skaneateles Formation (sample MS9) quartz-filled vertical fracture cross-cutting quartz-filled subhorizontal fracture with calcite-filled shell fragment at bottom (C), H) West River Member (sample BS6C) multi-chambered foraminifer filled with organic matter (Fc); I) Geneseo Shale (sample BS2) quartz grain (Q) with quartz overgrowth cement; J) Geneseo Shale (sample BS3) irregular, relatively large area filled with sparry calcite and opaque minerals.

Figure 6. SEM images with acquisition specifications and scales at bottom of images. Scale = 200 µm, BES = backscattered electron: WD = working distance in millimeters; SS = spot size in microns, Pa = pressure in pascals. A) Quartz-filled shell fragments (Q) surrounded by black, organic matter (OM) in Union Springs Member (sample MS3). Circular features are pyrite framboids (F), and the groundmass is composed of quartz and clay; B) Micro-fractures filled with organic matter (OM) in Oatka Creek Member (sample MS5); C) Jarosite in West River Member (sample BS4). Darker gray fractures between crystals have similar elemental composition (K, Fe, S, O) as the larger jarosite crystals. Pyrite framboids (F) are off-white spheres in groundmass; D) calcium-rich plagioclase (P) vein in West River Member (sample BS6B); E) Horizontal fractures primarily filled with gypsum (G) and rimmed with darker organic matter (OM) in Union Springs Member (sample MS4). Vertical fracture is filled with quartz (Q); F) muscovite (M) and calcium-rich plagioclase (P) filled micro-fracture, quartz (Q), and pyrite framboid (F) in Geneseo Shale; G) alteration halo (H) around an aluminum-rich vein (Al) through

euhedral/subhedral pyrite matrix (Py) in in BS2; H) Red 'vein' (R) in sample MS5 with pyrite framboids and white vein (W).

Figure 7. SEM with EDS measurements (red letters) summarized in the chart in the upper right. Aluminum-rich vein (horizontal black layer, EDS location D, >8% Al) cross-cutting through euhedral pyrite (white layers, EDS locations A, B, F, and G; <2% Al) in the Geneseo Shale (sample BS2). XRD data are shown in weight percent in the bottom column. The dark gray layers contain intermediate Al content (4%< Al<7%). BES = backscattered electron: WD = working distance; SS = spot size; Pa = pascals.

Figure 8. SEM with EDS measurements (red letters A through D) summarized in the chart in the upper left. Sphalerite (location C) surrounding quartz (location B) and pyrite (location D) in a quartz/clay groundmass (location A) with some pyrite framboids in the Union Springs Member (sample MS3) . XRD data are shown in weight percent in the top column. SEI = secondary electron imaging; WD = working distance; SS = spot size; Pa = pascals.

Figure 9. SEM image of anorthite vein (light gray) cross-cutting through clay and quartz-rich groundmass (dark gray) in the West River Member (sample BS6B). The photomicrograph in the lower right corner shows SEM image location from Figure 5E. EDS analysis of the vein (red letters) are summarized in the chart on the left and show that Ca, Si, O and Al weight percent averages for the three locations are approximately 15%, 16%, 45% and 20%, respectively. XRD data are shown in weight percent in the top column. BES = backscattered electron: WD = working distance; SS = spot size; Pa = pascals.

Figure 10. SEM image of red layer in the Skaneateles Formation (sample MS6). The photomicrograph in the top left corner shows SEM image location from Figure 5B. This area shows the most complex chemistry observed under the SEM. Ag > 4% was detected at locations C, E, and G, and thorium was measured in excess of 19% at location A. The white area under plane-polarized light appears to have a lighter colored 'rim' enriched with calcium and an inner core with high sulfur content. XRD data are shown in weight percent in the top left column. BES = backscattered electron: WD = working distance; SS = spot size; Pa = pascals.

Table Captions

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Table 1. List of EGSP wells in Pennsylvania (EDWIN, 2020).

Table 2. Geophysical logs available for API No. 3700320980 (EDWIN, 2020)

Table 3. EGSP-2 lithofacies description.

Table 4. Sample ID, formation/member name, sample depth (feet MD), color, and features observed under petrographic microscope and SEM. A green box indicates the feature was observed in the respective sample and a white box indicates the feature was not observed.

Gray columns record various quartz occurrences, brown columns indicate opaque minerals and pyrite, laminations are represented in the light green column, and fossils are highlighted in orange.

Table 5. Sample ID (blue), sample depth (feet MD), and features attributed to diagenesis and hydrothermal alteration (light pink). If an alteration feature was observed for a particular sample, that box is colored pink and was assigned a value of “1”. An alteration index (dark pink) was calculated by summing all alteration features for a respective sample.