A COMPARISON OF SEQUENCE STRATIGRAPHY AND MINERALOGICAL VARIATIONS ASSOCIATED WITH TOTAL ORGANIC CARBON IN THE MARCELLUS FORMATION: WASHINGTON COUNTY, PENNSYLVANIA

A Thesis

Presented to

the Faculty of the Department of Earth and Atmospheric Sciences

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In Partial Fulfillment

of the Requirements for the Degree

Master of Science

By

Austin Taylor Luker

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A COMPARISON OF SEQUENCE STRATIGRAPHY AND MINERALOGICAL VARIATIONS ASSOCIATED WITH TOTAL ORGANIC CARBON IN THE MARCELLUS FORMATION: WASHINGTON COUNTY, PENNSYLVANIA

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ABSTRACT

A recent surge of interest has arisen concerning the Devonian organic-rich black shales native to the Appalachian Basin of the east coast of the United States and their potential as gas producers The Marcellus Shale Formation is part of the middle Devonian Hamilton Group (380 Ma) and is one of ten extensive black shale units in the Appalachian Basin deposited as part of a cyclic repetitive progression of three distinct rock types consisting of organic-rich shales, coarser clastics (silty shales, siltstones, and sandstones), and carbonates (Roen, 1984; Lash and Engelder, 2009). Gas production from these shales is widespread; with high versus low production rates not only controlled by the gas content in the shale, but also largely by the mineral content of the rock that makes the rock more conducive to fractures remaining open.

It is hypothesized that the ability of shale to fracture is controlled by the amount of silica and/or calcite in the rock, and that the variability in the occurrence of those minerals can be predicted by sequence stratigraphy. The construction of a sequence stratigraphic model on a basinwide scale over the state of Pennsylvania began with a correlation of 821 wireline well logs. Then, to tie the working sequence stratigraphic model to mineralogy within individual zones of rock, analysis of 24 rotary sidewall cores was conducted using qualitative x-ray diffraction to determine the mineralogy of each sample.

This study determined that the mineralogy of the organic-rich shales within the Marcellus Formation can be predicted by sequence stratigraphy, and also found there to be a relationship between mineralogy and total organic carbon (TOC). Now that a

relationship is found between mineralogy, TOC, and its location within a sequence stratigraphic framework specific zones may be identified in a predicable manner within certain sequences that are likely more productive than others.

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1 INTRODUCTION

1.1 INTRODUCTION

A recent surge of interest has arisen concerning the Devonian organic-rich black shales native to the Appalachian Basin of the east coast of the United States and their potential as gas producers; and at the forefront of this newfound attention are the organic-rich shales of the Marcellus Formation.

The Marcellus Formation is part of the middle Devonian Hamilton Group (380 Ma) and is one of ten extensive black shale units in the Appalachian Basin deposited as part of a cyclic repetitive progression of three distinct rock types consisting of organic rich shales, coarser clastics (silty shales, siltstones, and sandstones), and carbonates (Roen, 1984; 2009). Originally, the Marcellus Formation was referred to as the Marcellus Shale by researchers. The first to coin the name “Marcellus Shale” to an organic-rich black and gray shale that outcropped near the town of Marcellus, Onondaga County, New York was James Hall (1839). Eight decades later the Marcellus Shale became known as the Marcellus Formation and was subdivided into the Union Springs Member and the overlying Oatka Creek Member by Cooper (1930). There have been numerous estimates of the extent of the shales within the Marcellus Formation in recent years. The Marcellus Formation encompasses 34,000,000 acres of the Appalachian Basin (Engelder and Lash, 2008) and is currently estimated by the U.S. Department of Energy to have 4 trillion m^3 (141 trillion cubic feet) of recoverable natural gas reserves (U.S.EIA, 2012). It is this economic value as a major energy resource that has recently elevated interest in the Devonian black shales, including the Marcellus Shale, and subsequently aided in the further geologic understanding and interpretation of the stratigraphy of the Devonian system of the northeastern United States (Roen, 1993).

For assessment purposes, petroleum resources have commonly been divided into two distinct types, conventional and unconventional resources (Milici and Swezey, 2006). Conventional resources are characterized by discrete trapping configurations that allow for the accumulation of hydrocarbons and water that separate into their gaseous and liquid phases depending on their immiscibilities and relative buoyancies. These conventional resources are dependent on many separate elements (source rock, overburden, reservoir rock, migration routes, seal rocks, and traps) that must occur in a critical timing sequence. Unconventional resources differ from conventional resources in that they are regional stratigraphic accumulations of hydrocarbons which commonly occur as laterally extensive blanket-like sedimentary deposits (Milici and Swezey, 2006). Unlike conventional resources, these unconventional resources are not broken into discrete fields dependant on the trapping configurations needed to accumulate hydrocarbons. Instead, unconventional resources are regionally continuous accumulations of organic matter that generate hydrocarbons. In short, a continuous (unconventional) resource acts as its own source rock, reservoir, and trap. The Marcellus Formation is one example of a classic unconventional resource.

Devonian black shales have long been known to produce significant quantities of hydrocarbons. The first American gas wells produced out of shale beds overlying the Dunkirk Shale were drilled in Fredonia, New York in 1821 (de Witt et al., 1993). In the past 20 years, technological advances and improvements in horizontal drilling and hydraulic fracturing have allowed for economical extractions of hydrocarbons in shale transforming these shales from source rock to reservoir.

The inherent extremely low permeabilities of the Marcellus Shale poses challenges in getting the hydrocarbons generated within the shale out of the rock in economical quantities. The current method for extracting natural gas from the Marcellus Shale is by injecting massive quantities of water mixed with proppant into the zone of interest, stimulating the formation to fracture artificially, thereby allowing the rock to release its hydrocarbons. In this well completion method, large amounts of water mixed with proppant is injected into the formation at high pressures that exceed the lithostatic pressure of the overburden initiating hydraulic fractures to propagate through the rock (Daniel and White, 1980). Proppant typically consists of sand-sized particles, engineered to a specific diameter,that is mixed in with fracturing fluid that is being injected into wells. Once injection pressure from the surface is terminated, the lithostatic pressure from the overburden causes the newly formed fissures at depth to instantaneously close. The purpose of the proppant is to hold open the newly created fissures after injection pressure from the surface ceases. In order to successfully extract natural gas from the rock formation, the rock must be hard enough to support itself once pressure is released from the surface. Shales inherently have a high clay content, which may cause the rock to lack the structural integrity necessary for the proppant to hold fractures open.

There are compositional qualities in unconventional reservoirs that influence critical reservoir characteristics, such as porosity, permeability, and brittleness. Some minerals of otherwise malleable organic-rich shales that act to enhance reservoir quality are quartz, pyrite, calcite, and dolomite; whereas, other assemblages of clays such as illite, smectite, and organic carbon (Kerogen) act to reduce reservoir quality. Kerogen is the term applied to deposited organic matter in sediments that is insoluble in normal petroleum solvents, such as carbon disulfide. Consisting of carbon, hydrogen, and oxygen, with minor amounts of nitrogen and sulfur, kerogen is the fundamental chemical component from which all hydrocarbons originate. The Marcellus Formation's organic-rich shale members are inherently rich in kerogen and, unfortunately, rich in clay content as well. High kerogen content coupled with high clay content makes for a malleable reservoir rock that creates difficulties in the completion process of hydraulically fracturing the rock. Sequence stratigraphic analysis of the Marcellus Formation shows that the enrichment of malleable reservoir rock due to organic material and clay content is greatest in the transgressive system tract through the transition to the early highstand systems track of each Marcellus sequence (Lash and Engelder, 2011). Fortunately, these systems tracts also were deposited in a manner that favored the deposition of an increased quartz and carbonate content, which enhance the reservoir quality of the shale. In addition, the depositional environment of the organic-rich members also favored the precipitation of pyrite, likely due to the reducing environment present on the sea floor (Werne et al., 2002). The enrichment of quartz, carbonates, and pyrite enhances reservoir quality significantly in the malleable organic-rich shales. If mineralogy follows a predictable pattern with respect to sequence stratigraphy, more accurate targeting of horizontal well placement may be possible. Two key questions addressed in this study were 1) can mineralogy be predicted within specific zones of the Marcellus Shale, and, 2) is there a relationship between mineralogy and total organic carbon?

Sequence stratigraphic analysis utilizing wireline well logs has been demonstrated by many researchers (Van Wagoner et al., 1990; Embry and Johannessen, 1992; Embry, 1993; Partington et al., 1993; Emery and Meyers, 1996; Brown et al., 2005; Singh et al., 2008; Lash and Engelder, 2011) . Once constructed, sequence stratigraphic models have been used in a wide variety of conventional resource plays to reduce risk in the exploration of hydrocarbons, especially in basinal areas where well control is sparse or nonexistent. This study focuses on an unconventional resource and the construction of a sequence stratigraphic model of the Marcellus Formation of Pennsylvania that will be used to test whether mineralogical differences within shale can be predicted by sequence stratigraphy. In addition, this study will perhaps reveal if a relationship exists between mineralogy and total organic carbon (TOC). If mineralogy and TOC do behave in a predictable manner with respect to sequence stratigraphy, then this relationship may allow for a more accurate placement of horizontal wells in zones of rock that are more conducive to fracturing.

1.2 SEQUENCE STRATIGRAPHY

Sequence stratigraphy provides an exceptionally useful methodology for the analysis of time – rock relationships in sedimentary strata. Utilization of sequence stratigraphic concepts allows for a fundamental hierarchy of related sedimentary stratal units to be created and thus a regional model of deposition on a basinwide scale. The following definitions are taken from the work of Van Wagoner et al., (1990). The sequence is the elemental unit for sequence stratigraphic analysis (Mitchum, 1977).

Sequences are relatively conformable, genetically related successions of strata that are bounded by sequence boundaries in the form of unconformities or their correlative conformities (Vail et al., 1977; Van Wagoner, 1985; Van Wagoner et al., 1988). A sequence boundary (SB) is a chronostratigraphic surface that separates the rock below it from the rock above it and form in marine environments from the rise and fall of base-level through time (Van Wagoner et al., 1990). Making up each sequence are parasequences and systems tracts. Parasequences are composed of genetically related beds and bedsets that are bounded by flooding surfaces. Parasequences can be stacked into genetically related parasequence packages called parasequence sets when accommodation and time allows for multiple depositional cycles before a major erosional event forming a sequence boundary can occur. Each sequence can be subdivided into systems tracts that are named depending on its relative position within the sequence. There are three systems tracts that can be identified in an ideal clastic sequence. The lowstand systems tract (LST) is bounded below by the sequence boundary and above by the first regionally pervasive flooding surface. It is commonly interpreted to represent a period of time from relative sea-level fall to initial sea-level rise and is characterized by subaerial exposure in proximal basinal areas coupled with high sedimentation rates in distal area of the basin. In foreland basins it is not uncommon to have subaerial exposure in the distal basin along the uplifting forebulge. The transgressive systems tract (TST) is bounded below by the first regional persistent flooding surface, the transgressive surface (TS), and bounded above by a maximum flooding surface (MFS). The MFS marks the change from a backstepping transgressive pattern of parasequences to a progradational pattern associated with a rapid relative sea-level rise. The TST is characterized by lower sedimentation rates as seen in the LST and the beginning of condensation resulting from the increasing starvation of sediments lost to more proximal deposition. The third systems tract is the highstand systems tract (HST) which is bounded below by the maximum flooding surface and above by a sequence boundary (SB) that marks the sharp transition back to lowstand conditions. The highstand systems tract is commonly interpreted to have been deposited during periods of decelerating relative sea-level rise or stillstand where accumulation of sediments exceeds accommodation resulting in aggradation of sediment deposits. During the early stages of the highstand the top bounding surface of the TST is coincident with the lower bounding surface of the HST along which the clinoform toes of the HST can merge with the TST and become very thin. This period of transition between the transgressive systems tract and highstand systems tract is when a condensed section is deposited. A condensed section is a facies of thin hemipelagic or pelagic deposits laid down as parasequences migrate landward, starving the shelf of terrigenous sediments (Van Wagoner et al., 1990). Condensed sections experience continuous deposition but accumulate extremely slow, resulting in anomalously thin deposits that encompass large amounts of time.

The Marcellus Formation is largely an alternating cycle of deep water shales and shallow water carbonates deposited in a generalized carbonate ramp setting (Ver Straeten, 2008); therefore, it is important to recognize that the development of systems tracts in a clastic system, explained above, varies greatly from the development of sequences and systems tract in carbonate systems (Sarg et al., 1988; Emery and Meyers, 1996; Bosence and Wilson, 2003; Ver Straeten, 2008). During the development of a LST in biologically produced carbonate platforms, the carbonate mineral production process is decreased or possibly ceased altogether due to the reduction in shallow water environments where skeletal material forms. The development of a TST in a carbonate platform that is experiencing elevated sedimentation rates as the carbonates try to catch up with sea-level rise will not be characterized by condensation but rather will be characterized by the aggradation of deposits. Conversely, if sea-level rise out paces carbonate production causing the system to drown then indeed a TST of this sort will have similar characteristic of a clastic TST. The development of a HST in carbonate platforms is commonly characterized by carbonate bypass and highstand shedding during the latter stages of sea-level stabilization where carbonate production can outpace accommodation space. Just as carbonate platforms differ in their systems tract characterization as compared to clastic systems, carbonate ramps also can differ from carbonate platforms. In a carbonate ramp, deep water facies progressively migrate over shallow water facies during the TST. During the TST, sediment starvation may occur in the deeper parts of the ramp and organic-rich deposits may be accumulated (Emery and Meyers, 1996). Then, as sea-level rise begins to reach its maximum and starts to slow, carbonate sediments tend to aggrade and prograde basinward during the early highstand. During the latter stages of the HST and the beginning of the LST sedimentation bypass and erosion of exposed areas leads to offlap and the appearance of missing section.

1.3 TECTONIC HISTORY

The Appalachian Basin, as preserved today, is approximately 2,050 km long claiming an area of almost 536,000 km^2 trending southwest to northeast from northern

Alabama in the United States extending to southern Quebec, Canada (Ettensohn, 2008) (Figure 1). The black shales of Devonian age rocks in the present day Appalachian Basin are a part of a unique series of rock sequences and share a complex tectonic history.

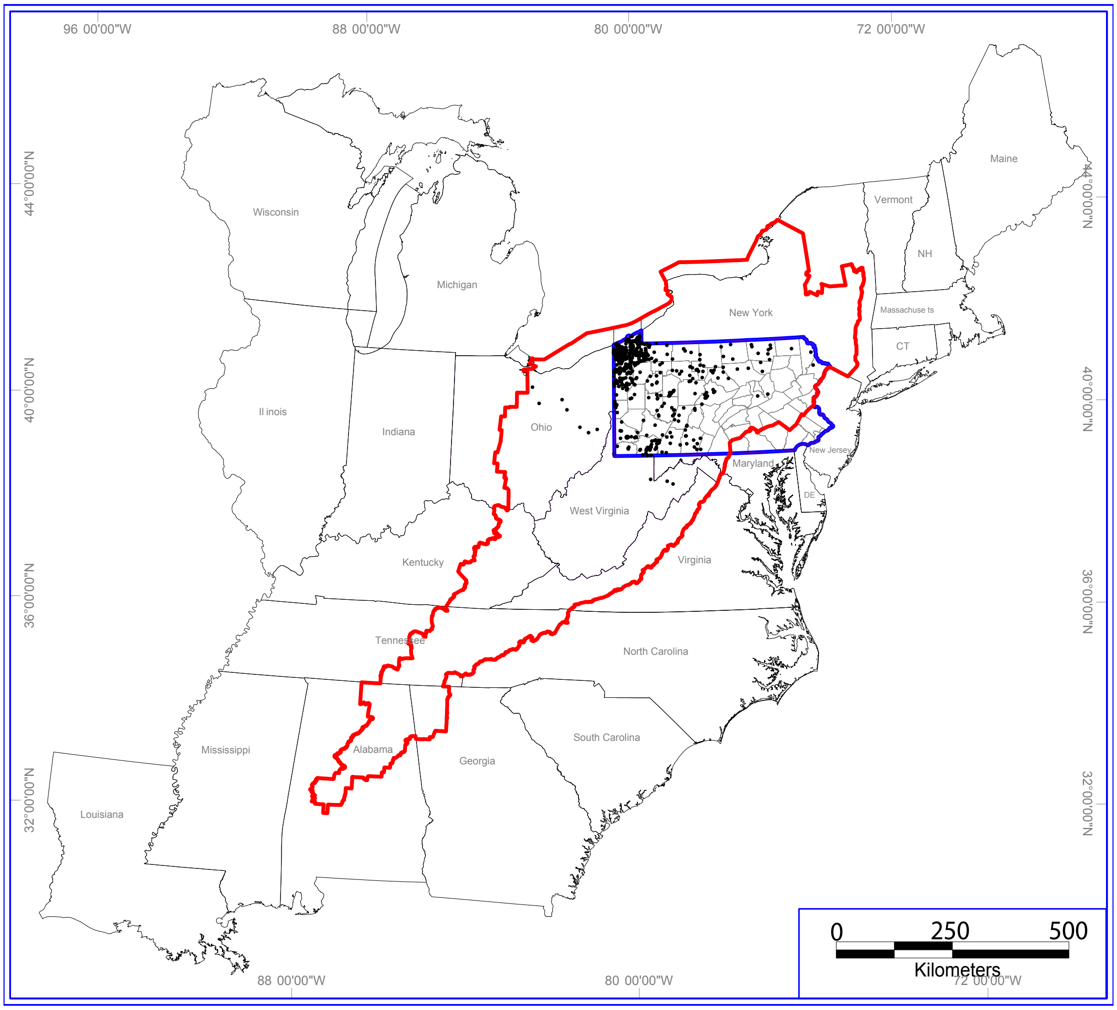

Figure 1: Map of the Appalachian Basin Province of the eastern United States, outlined in red, as defined by the USGS Open-File Report 2011-1298. The state of Pennsylvania, outlined here in blue, is the focus of the study and contains within it well locations marked by black dots.

During the initial stages of an orogeny, surface and subsurface loads accumulate along a cratonic margin and cause severe loading of the lithosphere. The response to such loading is isostatic compensation of the lithosphere resulting in the adjacent craton downwarping into a retroarc foreland basin, immediately cratonward of the collision zone, and an uplifted peripheral bulge on the distal margin of the basin. It is at this stage of basin development that accommodation is created and sediments can be deposited. As long as crustal collision continues and the thrust sheets continue to move cratonward, the foreland basin and peripheral bulge will also move cratonward through time (e.g., Beaumont, 1981; Tankard, 1986).

The Appalachian Basin is a classic foreland basin that began its development with the initiation of the Taconic Orogeny around the time of the Early – Middle Ordovician transition ~472 Ma (Ettensohn, 2008). Growth of the Appalachian Basin persisted for another 200 Ma spanning a nearly continuous series of four orogenies that echo with the closing of the Iapetus and Rheic paleo-oceans as the super continent of Pangea was being formed. The Taconic Orogeny is responsible for the formation of the Taconic highlands that act as an eastern barrier for the maturing Appalachian Basin (Faill, 1997). Following the Taconic Orogeny is the Middle Devonian Acadian Orogeny. The Acadian Orogeny resulted in oblique convergence along a strike-slip fault zone that once separated the Laurasian terrain , which was by then the majority of the North American craton, from a microcontinent know as the Avalon Terrane (Williams and Hatcher, 1982). It is thought that the Avalon Terrane was most likely part of the larger Armorican plate that originated on the western margin of Africa before it collided with the North American craton

(Laurasia) in the Devonian (Van Der Voo, 1983; Perroud et al., 1984). The Avalon Terrane moved in a northeasterly direction along a major strike-slip fault zone when it collided obliquely with the southeastern portion of the North American craton. Movement along a strike-slip fault is mostly horizontal but can have a vertical dip-slip component (Reading, 1980) and the resulting convergent nature of the strike-slip fault may lead to folding, thrusting, and vertical uplift of topography. This is the case of the Acadian Orogeny resulting in the formation of the Appalachian Basin.

Four major tectonic phases have been recognized along the length of the Acadian Orogeny (Boucot et al., 1964; Johnson, 1971) and have been described in detail by Ettensohn (1985) (Figure 2). Phase I occurred during the Early-Middle Devonian in present day Maine and the Canadian Maritime provinces. Phase II occurred during the Middle Devonian in present day New York and eastern Pennsylvania. Phase III occurred during the Late Devonian and into the earliest Mississippian and was concentrated in present day southern Pennsylvania and the Virginias. Each tectonic phase is represented by a cyclic pattern of four stages, as seen in the sedimentary record of the filling sediments, as provided by the Catskill Delta Complex (Ettensohn, 1985). Stage 1 begins as the onset of tectonism and the formation of a peripheral basin via rapid subsidence. Here transgression dominates and is reflected by the deposition of basinal black shales. Stage 2 is the impending collision and the southward migration of deformation though time. Because movement along the collision zone was episodic, this stage often is characterized by minor transgressive-regressive cycles. Stage 3 is represented by collision, usually accompanied with a period of regional uplift of the peripheral bulge, and subsequent erosion forming a regional unconformity. Stage 4 is a time of tectonic quiescence and is represented by widespread carbonate deposition in slowly transgressing seas or periods of stable sea-level (Ettensohn, 1985).

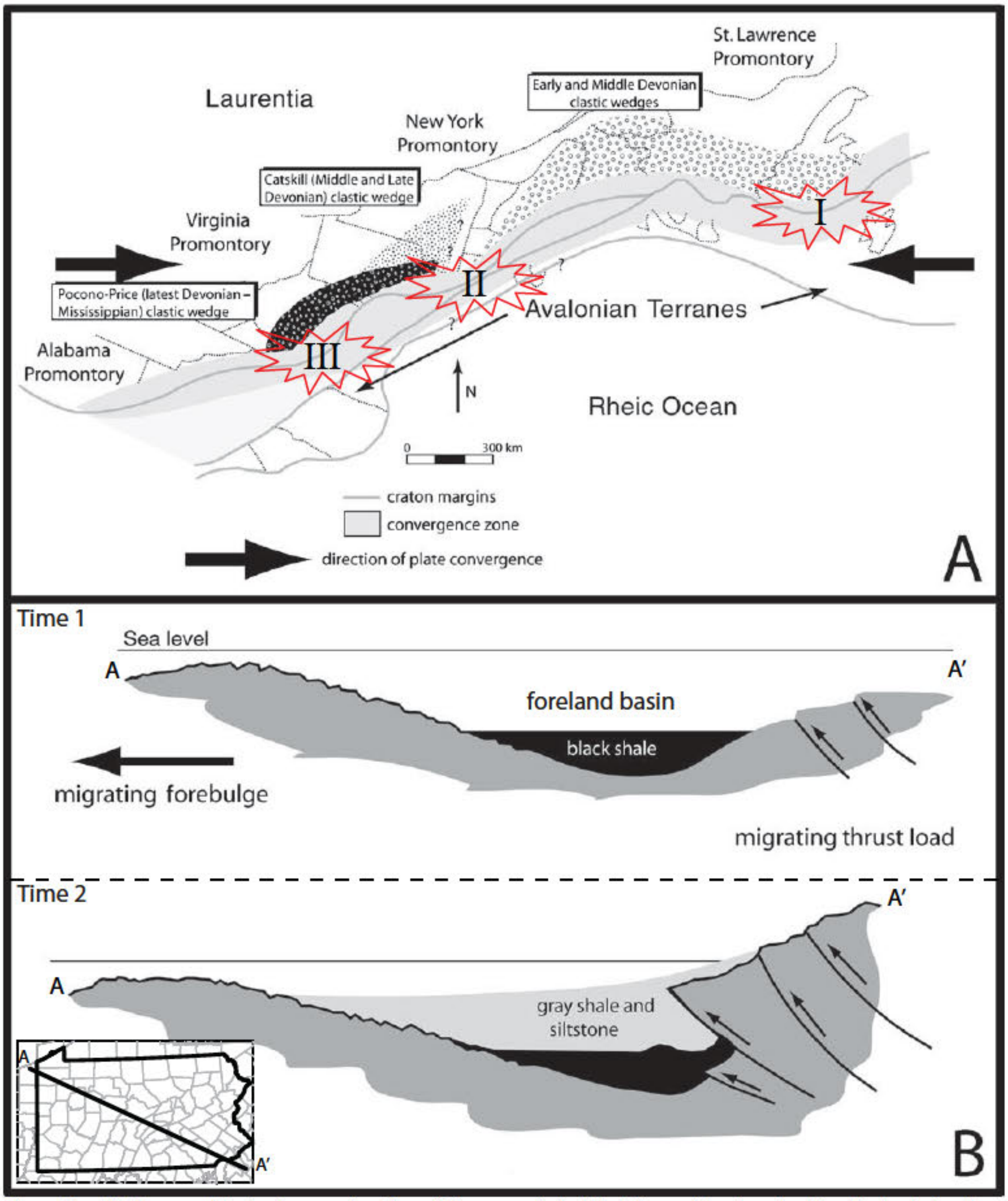

Figure 2: A) A general tectonic reconstruction of the orogenic belt that formed the Appalachian Basin during the Acadian Orogeny and the approximate locations of the resulting synorogenic sediment deposits. Red stars represent the approximate locations of tectonic phases I - III as discussed in text. Modified from Ferrill & Thomas (1988); Ettensohn (1992); and Lash & Engelder (2011). B) Illustration depicting the relationship, through time, among thrust loading, foreland basin increase of accomodation space, black shale deposition, and forebulge migration caused by regional orogenic collision. Modified from Ettensohn (1994).

1.4 PALEOGEOGRAPHY

Paleomagnetic data suggest that at the time of the Acadian Orogeny the Appalachian margin was located in the subtropics as far as 40^{o} south of the equator (Miller and Kent, 1988; Witzke and Heckel, 1988; Scotese and McKerrow, 1990). At this latitude the Acadian margin was located in the path of early trade winds laden with moisture from the Iapetus and Rheic Oceans (Woodrow, 1985). The paleoclimate over the Devonian Appalachian Basin is thought to be semi-arid to arid and highly seasonally variable due to the Acadian Orogen casting a major rainshadow over the basin (Woodrow, 1985). The Acadian Orogeny was likely subjected to strong, seasonal monsoonal rains (Woodrow et al., 1973; Heckel and Witzke, 1979; Scotese et al., 1985; Woodrow, 1985; Witzke and Heckel, 1988; Witzke, 1990). This postulation of climatic conditions is backed by deposits of the Hamilton Group, home to the Marcellus Shale, showing abundant indication of major storm events in nearshore (Woodrow, 1985; Slingerland and Loule, 1988; Prave et al., 1996; Werne et al., 2002) and offshore facies (Brett and Baird, 1986; McCollum, 1988). The semi-arid to arid climatic conditions along with the surrounding paleogeographic features (Figure 3) likely created a restricted basin with conditions favorable, at least at certain times of the year, to preserve organic matter (Blakey, 2010).

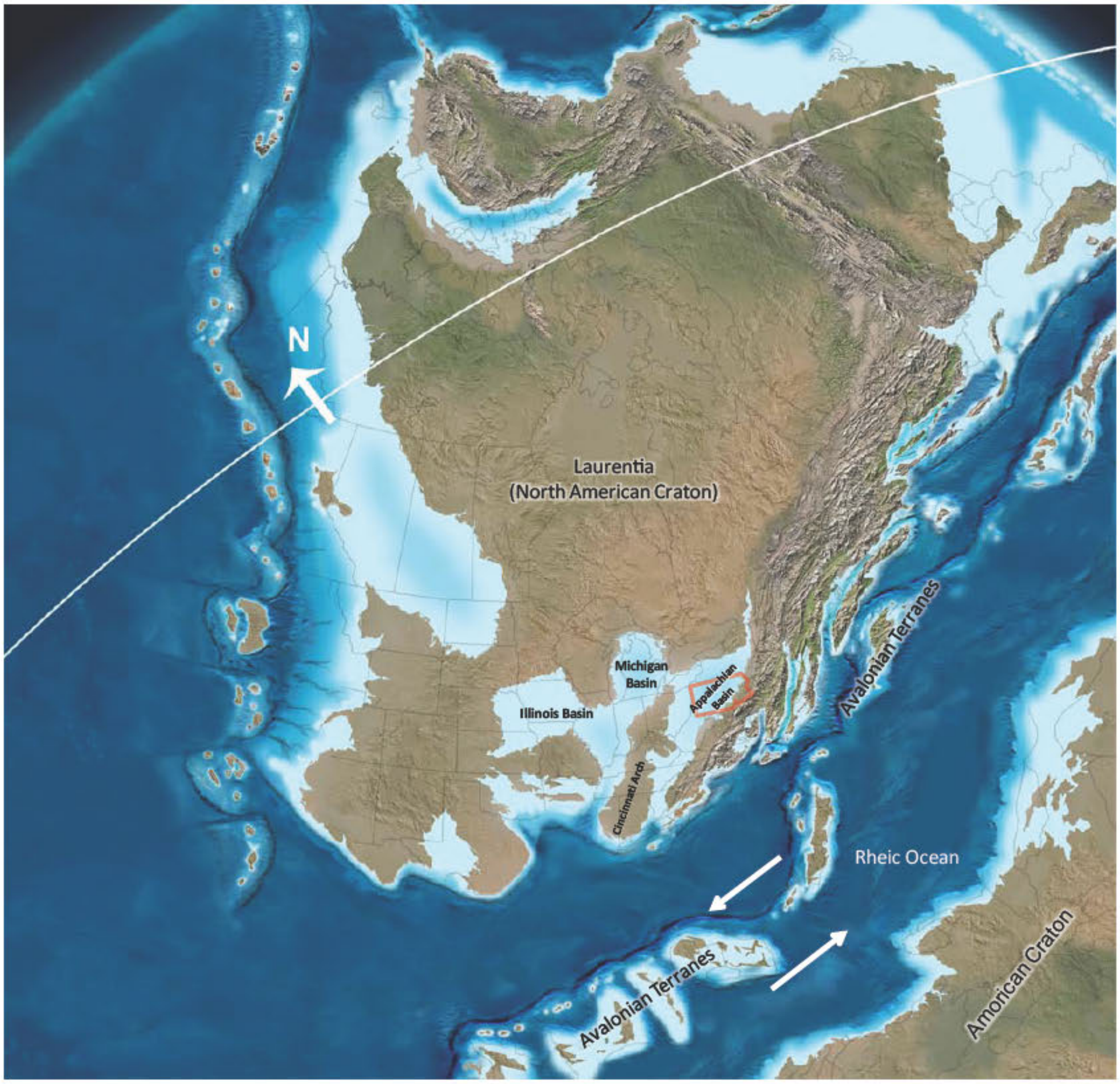

Figure 3: Paleo-reconstruction of the study area, oulined in red, as it may have appeared during Middle Devonian time (~385 Ma). Modified from Blakey, (2010).

In the marine environment, the source of organic matter is both autochthonous and allochthonous, being derived from various phytoplankton species in the photic zone of open marine expanses as well as terrestrial sources transporting allochthonous material from continents. Only a minute fraction of all the organic matter ever produced reaches the seafloor, where it is further degraded by aerobic and anaerobic processes (Zonneveld et al., 2010). Currently, the accumulation of organic matter in marine environments is believed to be the result of biologic productivity and preservation. In the past, there has been much debate concerning the factors that influence the accumulation and preservation of the high amounts of organic matter present in the Marcellus Shale and similar black shales through geologic time. The classic assumption for the deposition of black, organic-rich shales in marine sediments has long been associated with deposition in deep, stagnant, anoxic (0.0 ml/L O_2) water columns The main controls affecting the accumulation of organic carbon in marine sediments has been shown to include bulk sediment accumulation rate, water column oxygen content, and the flux of organic matter to the sea floor (e.g., Demaison and Moore, 1980; Pratt, 1984; Arthur et al., 1987; Zonneveld et al., 2010). Although the main factors controlling preservation of organic matter have been identified, the many mechanisms by which they operate are only partly understood. Until recently there existed two schools of thought that placed different emphasis on the mechanisms that can lead to high organic matter concentrations in sediments, high organic matter supply, and enhanced organic matter preservation (Calvert et al., 1996). The two end members have been categorized by Werne et al. (2002) into what they call the “preservation” model and the “productivity” model. Those who support the preservation model suggest that long-term preservation of organic carbon in sediments is the result of permanent water column stratification with bottom-water anoxia or low oxygen concentrations (e.g., Demaison and Moore, 1980; Canfield, 1989; Demaison, 1991; Canfield, 1994). The opposing groups, in support of the productivity model, propose that surface plankton productivity is the main driver for the supply of organic matter and the main factor controlling the carbon content of oceanic sediments. In the productivity model, primary production is thought to create conditions which promote an increase in the biological oxygen demand to the point where productivity can no longer keep pace with O_2 demand (e.g., Pedersen and Calvert, 1990; Calvert and Pedersen, 1992). The result is a shortage of dissolved oxygen in the water column and anoxic conditions. A key difference between these two end members is that in the productivity model, anoxic conditions are a consequence, not the cause, of organic enrichment of sediments. Furthermore, a study done by Tyson and Pearson, (1991) supports a seasonal dysoxia-anoxia cycle (2.0-0.2 ml/L O_2) as the best model to account for the characteristics of many ancient epeiric sea black shales. Their work suggests that as summer water temperatures increased, rates of oxygen consumption in shallower shelf areas would also increase while oxygen solubility would decrease, and thermocline stability would have strengthened. This combination of a thin bottom water layer with lower mixing and high biological oxygen demand would have lead to widespread dysoxic or anoxic conditions throughout all offshore areas of the epeiric sea. Over the last few decades it has become evident that though the factors controlling accumulation of organic matter is understood, the preservation of organic matter is highly selective, and the amount and composition of the organic matter that gets preserved varies heavily among different regions and depositional environments (Zonneveld et al., 2010). Understanding the manner in which organic matter is preserved is important because this knowledge also gives way to the appreciation of the depositional environment in which organic-rich shales were deposited. The same environments favorable to organic matter preservation also favors the precipitation of pyrite which enhances reservoir quality.

1.5 DEPOSITIONAL ENVIRONMENT AND STRATIGRAPHY

In the first Pennsylvania Geological Survey, formed in 1836, Henry Darwin Rogers referred to what is known now to be Marcellus equivalent strata as the “Cadent Lower Black and Ash-Colored Slate” in his report to the state (Millbrooke, 1981). However, the first to coin the name “Marcellus Shale” to an organic-rich black and gray shale that outcropped near the town of Marcellus, Onondaga County, New York was James Hall (1839). Eight decades later the Marcellus Formation was subdivided into the Union Springs Member and the overlying Oatka Creek Member by Cooper (1930). This nomenclature has largely been adopted by researchers specializing in Lower Hamilton Group studies in outcrop as well as in the subsurface below the states of Pennsylvania, New York, and Ohio (Oliver Jr. et al., 1969; Van Tyne, 1983; Rickard, 1984; Rickard, 1989). Over 150 years of study in the Hamilton Group and related strata, the names pertaining to the various stratigraphic intervals studied grew complex and often times confusing. In a series of articles written over a span of the last 15 years (Ver Straeten et al., 1994; Ver Straeten and Brett, 1995; Ver Straeten and Brett, 2006; Ver Straeten, 2007) have proposed a revised Marcellus stratigraphy targeted at reducing the accumulated and confusing verbiage (Lash and Engelder, 2011) . The revised stratigraphy links the distal, generally fine-grained, Marcellus succession with the proximal eastern side of the basin where the Marcellus Formation is a less complex, generally shallowing upward trend of basinal black shales to nearshore sandstone and fluvial deltaic deposits. It was Ver Straeten and Brett (2006) that raised the Marcellus Formation to the subgroup level within the Hamilton Group, and upgraded the Union Springs and Oatka Creek members to the formation level, thus keeping the nomenclature consistent with the other overlying units of the Hamilton Group (Lash and Engelder, 2011). Ver Straeten's (2006) detailed subdivision of units with seemingly indistinguishable defining characteristics is not applicable with a basinwide correlation of well logs of varying quality made available to the public. Of course as time continues and the newer modern well logs are made available to the public, such a detailed interpretation of the Hamilton Group will indeed be possible on a regional scale. Therefore, this study will adopt a hybrid lithostratigraphy that lends itself to a subsurface correlation of the available array of wireline logs. This study will follow Lash and Engelder (2011) in designating the Union Springs Member as the basal member of the Marcellus Formation. Separating the Union Springs Member from the overlying Oatka Creek Member is the Cherry Valley Member. The Cherry Valley Member correlates with the Stoney Hall Member of the Union Springs Formation and the Hurley and Cherry Valley Members of the Oatka Creek Formation used by Ver Straeten and Brett (2006). The upper member of the Marcellus Formation which directly underlies the Stafford and Mottville members of the Skaneateles Formation in this study, will also be designated as the Oatka Creek Member.

2 METHODS

2.1 OVERVIEW

To construct a sequence stratigraphic model on a basinwide scale over the state of Pennsylvania, this study began with a correlation of wireline well logs. Then, to tie the working sequence stratigraphic model to mineralogy within individual zones of rock, analysis of 24 rotary sidewall cores was conducted using qualitative x-ray diffraction to determine the mineralogy of each sample. In addition, a statewide correlation and analysis of 821 wireline and geophysical logs was completed in order to construct a sequence stratigraphic model of the Marcellus Formation with a concentration on, but not limited to, the southwestern Pennsylvanian counties of Washington, Greene, Fayette, and Somerset. Other available data include a previously completed total TOC analysis of the same 24 rotary side wall cores.

2.2 DATA SET

2.2.1 Well Log Data

The data used in this study include 821 geophysical logs and were made available in both digital log ASCII Standard (.las) and raster (.tiff) formats (Figure 4). Older electric logs, hence forth referred to as "e-logs" were initially available only as rasters; however, the Pennsylvania Internet Record Imaging System (PA*IRIS) is currently in the process of digitally archiving all available oil and gas well records in the Commonwealth and the availability of .las files is growing daily. To supplement the areas where digital log coverage was sparse or nonexistent, 192 raster logs were selectively picked and manually digitized using IHS Petra software. The logs used in this study are: gamma ray (GR), neutron porosity, bulk density, resistivity, conductivity, photo electric (PE), caliper, and spontaneous potential logs (SP). In addition, Rice Energy provided a full gas analysis suite as well as a Compensated Neutron/Density (CND) logging suite from a vertical pilot hole located in Washington County, Pennsylvania.

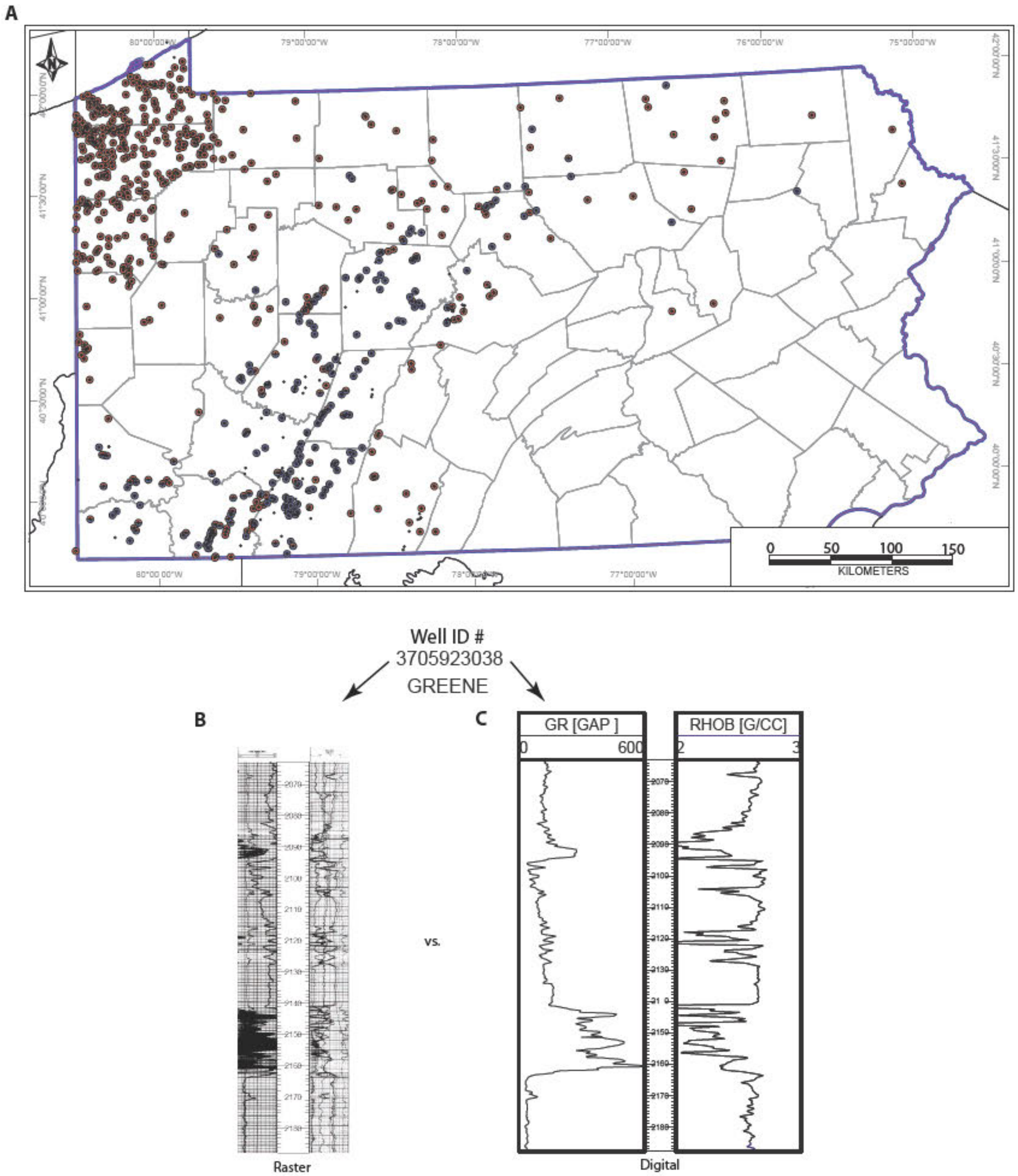

Figure 4: A) Distribution of well log data used in this study. Blue dots represent well logs available as raster files. Red dots represent well logs available in Log ASCII Standard format. Raster logs used in this study were manually digitized and converted to .las format using IHS Petra® software. An example of the differences between a raster image well log (B) and a digital well log (C) taken from the same well on the same scale. See text for discussion.

2.2.2 Sidewall Core

X-ray diffraction analysis of 24 rotary sidewall cores taken at key depths throughout the full section of Hamilton Group was carried out to determine mineralogy. To make a comparison between mineralogy and TOC this study used TOC calculations previously completed on this same group of sidewall cores. Total organic carbon work was completed by Weatherford Laboratories.

2.2.3 Core Location

The set of sidewall cores used in this study were taken from a Rice Energy well located in central Washington County (Figure 5A). The specific depth points were determined by the onsite geologist present during logging operations and are shown by (Figure 5B and 5C). The core depths were chosen in an effort to accurately represent mineralogical changes through the full section of Lower Hamilton Group strata.

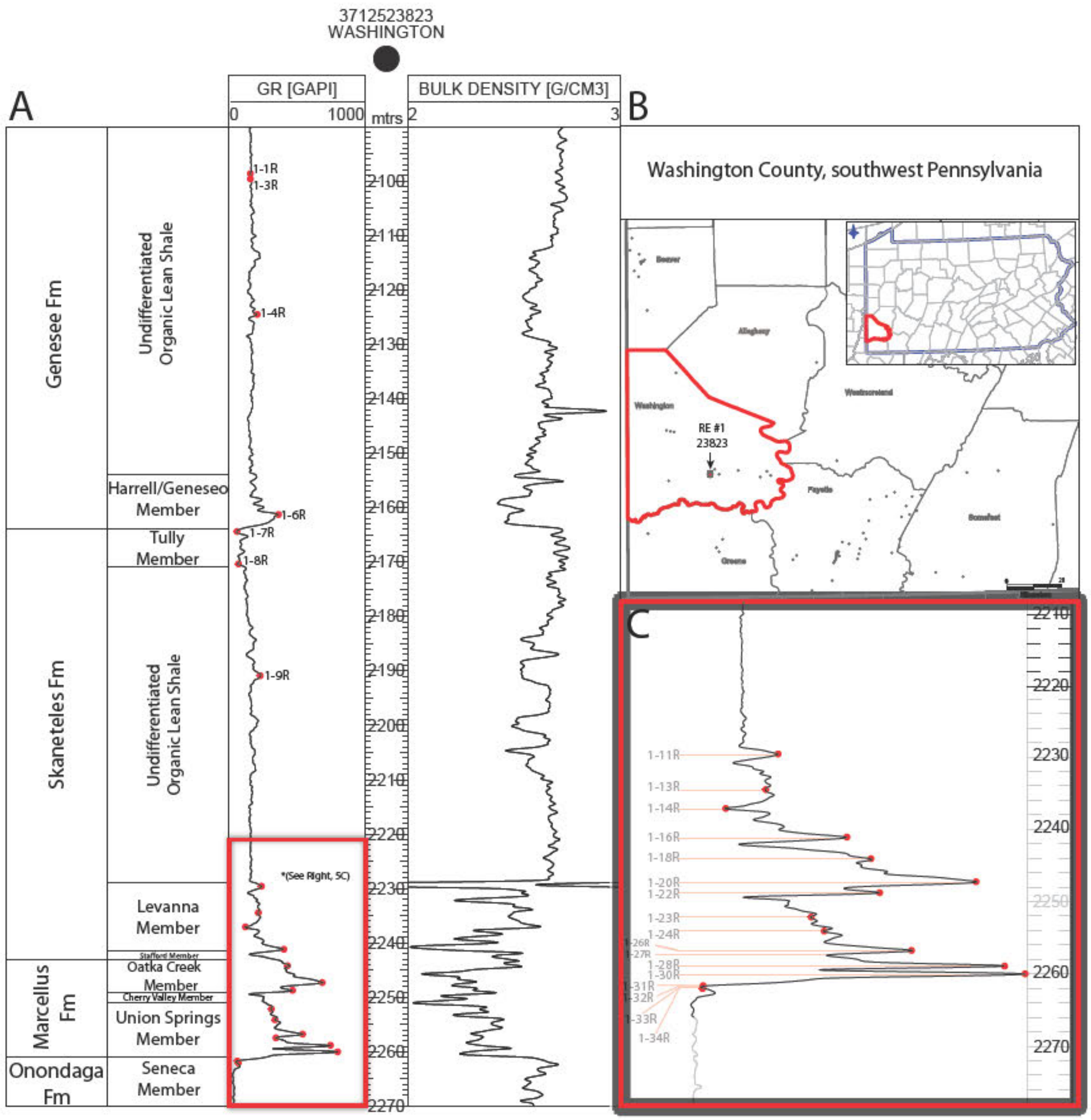

Figure 5: A) Wireline type log of the RE #1 showing the depth at which each sidewall core was taken and its position relative to the stratigraphic section. Each red dot, on the gamma-ray curve (GR), corresponds to an x-ray diffraction data point as well as a measured TOC (weight %) value. **B)** Location of the RE #1, Washington County, Pennsylvania. **C)** Gamma-ray curve zoomed-in to the Marcellus Formation.

2.3 MINERALOGICAL ANALYSIS

2.3.1 X-ray Diffraction Sample Preparation

In an effort to minimize contamination of the samples and to ensure the most accurate and repeatable results possible, each sample was prepared in strict accordance to the USGS x-ray diffraction laboratory manual for powder mineral identification (Poppe et al., 2001). Samples were crushed using a standard ceramic mortar and sieved to a grain size of 3µm. XRD analysis of all samples was performed on a Siemens D5000 powder diffractometer in house at the Texas Center for Superconductivity at the University of Houston (TcSUH) and interpreted using PANalytical's X'Pert HighScore software.

2.4 LOG ANALYSIS

The application of a wireline logs to perform sequence-stratigraphic analysis on a basin-wide scale has been successfully demonstrated by several workers to reduce risk in unexplored fringes of basins or areas within a basin that for one reason of another has sparse well control (Embry and Johannessen, 1992; Embry, 1993; Partington et al., 1993; Emery and Meyers, 1996; Embry, 2002; Brown et al., 2005; Singh et al., 2008; Lash and Engelder, 2011). Using a sequence-stratigraphic approach enables one to subdivide basin fill into a hierarchy of bounding and internal flooding surfaces based on depositional models based by observation of facies trends, well log trends, and facies dislocations that violate Walther's Law (Lash and Engelder, 2011). In order to begin the process of identifying and correlating the Middle Devonian Lower Hamilton Group, a type log representative of the whole section being mapped was established in Washington County (Figure 6). If available, a combination of gamma ray, photoelectric index (PE), bulk density, and resistivity curves were used to ascertain formation boundaries, though the vast majority of the well log data used in the study is limited to just gamma ray, and bulk density curves.

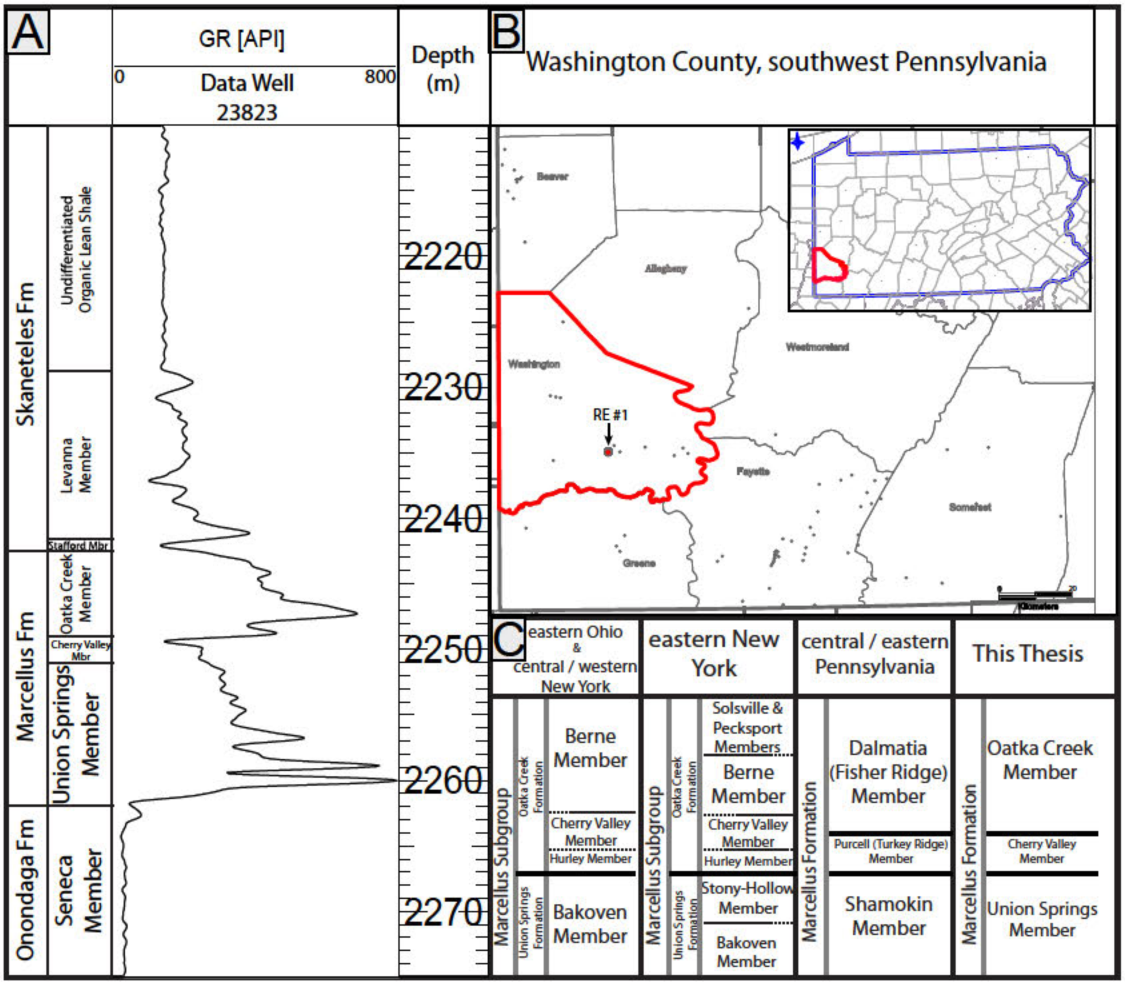

Figure 6: A) Wireline gamma-ray log with a typical stratigraphic section taken from the RE #1 located in Washington County. The gamma-ray log signatures shown are characteristic of the Union Springs, Cherry Valley, and Oatka Creek Members of the Marcellus Formation of southwestern Pennsylvania. See text for discussion of the variability of the overlying Stafford Member, which here marks the base of the Skaneateles Formation. B) Location of the primary data well in Washington County from which sidewall core analysis was performed for this study. C) A comparison of the Marcellus Formation Stratigraphic nomenclature used in this study with the newly revised stratigraphic nomenclature from Ver Straeten & Brett (2006) (From Lash & Engelder, 2011).

2.5 SUBSURFACE STRATIGRAPHY

The Marcellus Formation is part of the middle Devonian Hamilton Group (380 Ma) and is one of ten extensive basal black shale units in the Appalachian Basin deposited as part of a cyclic repetitive progression of three distinct rock types consisting of organic rich shales, coarser clastics (silty shales, siltstones, and sandstones), and carbonates (Roen, 1984; Lash and Engelder, 2009).

Within the scope of this study focus was placed upon the rock units that fall between the middle Devonian and upper Devonian age rocks; specifically, the study covers the Onondaga Formation, the Marcellus Formation (made up of the Union Springs Member, the Cherry Valley Member, and Oatka Creek Member), the Mahantango Formation, and the upper Devonian Genesee Formation (Figure 7).

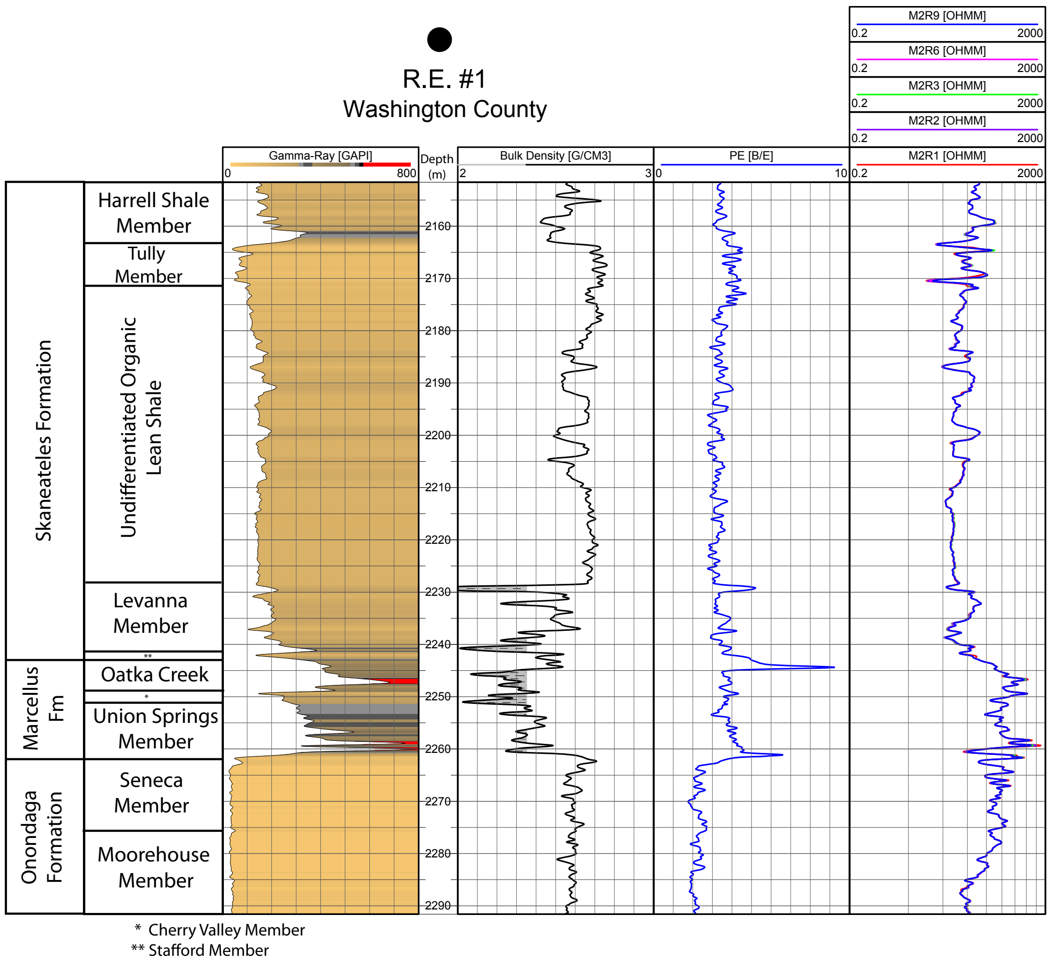

Figure 7: Wireline log suite from RE #1 used to construct a sequence stratigraphic model of the Marcellus Formation throughout Pennsylvania. From left to right: The gamma-ray curve in Track 1 ranges from 0 - 1000 API Units. Typically gamma-ray curves are plotted on a 0 - 200 API scale and when values exceed 200 API the curve wraps around track. Here the scale is expanded to eliminate curve overlap which greatly enhances interpretation. The bulk density curve is shown in Track 2 and is filled in grey for values less than 2.55 g/cm3. Because shales are inherently less dense than limestones and sandstones, it is common that areas trending with an increase in gamma-ray and decrease in bulk density are likely shale. The PE or photo-electric curve is plotted in Track 3 and ranges from 0 - 10 barns / electron. The resistivity curve is plotted in Track 4 and is scaled on a logarithmic scale from .2 - 2000 Ohmms (Ohm-meters). The resistivity curve is used to help identify formation fluids at depth. See text for full discussion of open hole logging.

2.5.1 Onondaga Formation

The Onondaga Formation is composed of limestones and dolostones that were deposited during the Middle Devonian before the deposition of the Marcellus Formation. The Onondaga Formation has been described as a very fine grained to crystalline, light to dark brownish gray, somewhat argillaceous and cherty limestone (Fettke, 1961). The Onondaga has, at its base, the Moorehouse Member that is overlain by the Seneca Member. Separating these two members is the Tioga B Ash Bed, a K-bentonite, which is actually comprised of a cluster of multiple separate ash falls (Ver Straeten, 2004). The Moorehouse Member, an olive-gray, fine-grained, massive bedded limestone with abundant chert nodules is the basal member of the Onondaga (Staubitz and Miller, 1987). Directly overlying the Moorehouse Member is the Seneca Member, which is characterized also as a light to dark olive-gray, massive bedded, dark nodular cherty limestone. The Onondaga Formation can be readily identified in the subsurface by having a gamma-ray value of 30-110 API, a photoelectric (PE) value of 5 barns/electron and a bulk density value of 2.71 g/cc (Boyce and Carr, 2009) (Figure 7).

2.5.1.2 Tioga Ash

The correlation of the Upper-Middle Devonian Onondaga Formation has largely been made possible by the incorporation of four different ash beds that occur commonly in four different positions within the Onondaga strata (Rickard, 1984) (Figure 8). The ash layers were originally observed near the base of the Middle Devonian black shales in the Tioga gas field of northern Pennsylvania by Fettke (1931) but was proposed as the "Tioga Bentonite" in 1949 (Ebright et al., 1949). The ash beds are frequently seen in well logs at points A, B, C, and D; however, it is not unusual for any one or more not to be present in a given well bore (Rickard, 1984). These ash beds are not always continuous and do not just occur within the Onondaga Formation. Depending on the location, the Union Springs Member has been known to contain up to four ash bed clusters that can be distinguished from organic rich deposits that share similar increases in gamma-ray signatures by their bulk density signature which remains close the grey organic lean shales (Ver Straeten, 2004; Lash and Engelder, 2011). The Tioga Ash is well defined paleontologically and was defined to be the base of the Seneca member in central New York (Oliver, W.A., 1954). Ash falls, such as the Tioga Ash beds represent altered volcanic ash layers generated during eruptive events in which the ash was transported to, deposited, and preserved in sedimentary environments making them prime correlation markers that also can give precise geochronological ages.

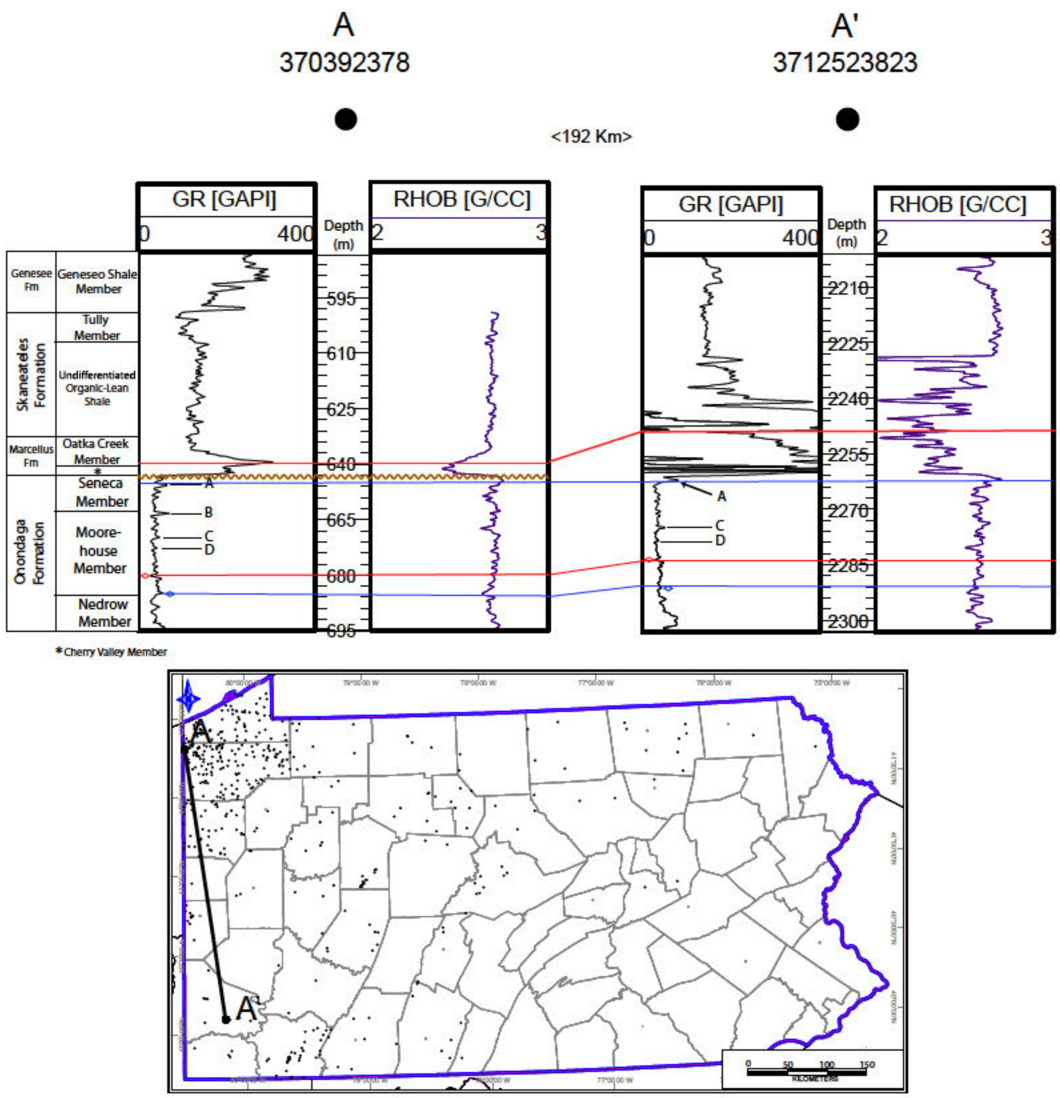

Figure 8: Typical gamma-ray logs of the Onondaga Formation. Marked on the gamma-ray curves are points A, B, C, and D that represent ash bed gamma-ray signatures. The Tioga Ash sequence, specifically Tioga Ash Layer B, can be an excellent datum marker when present (see text for discussion). Here the two wells have been flattened on the Tioga Ash A. Also shown are correlation points (red diamond with line / blue diamond with line). By using the Tioga Ash beds as a datum the identification of an erosional surface from A to A' is poss ble. This erosional surface or period of nondeposition of the Union Springs Member would be difficult to pick without a reliable datum.

2.5.2 Marcellus Formation

Directly overlying the Onondaga Formation is the Marcellus Formation. The Marcellus Formation is divided into two distinct organic-rich black shales separated by a transgressive limestone.

2.5.2.1 Union Springs Member

The Union Springs Member in southwestern Pennsylvania is characterized as the basal member of the Marcellus Formation identified in wireline logs as being extremely radioactive having a gamma-ray log signature of >600 API and a low density of 2.35 g/ml (Lash and Engelder, 2011). Common to the lower part of the Union Springs Member are intermittent thin carbonate intervals and pyrite-rich layers. The upper section of the Union Springs Member consists of a generally shallowing up progression seen in logs as a diminishing gamma-ray response and gradual increase in bulk density (Lash and Engelder, 2011) (Figure7).The Union Springs Member sharply contacts the underlying Onondaga Formation in southwestern Pennsylvania (Figure 7). Lash and Engelder (2011) correctly points out that many researchers have interpreted the contact of the Onondaga Formation with the Union Springs Member to be a regional unconformity (e.g. Potter et al., 1982; Rickard, 1984; Rickard, 1989). In contrast, Ver Straeten (2007) maintains that the contact between the Onondaga Formation and the Union Springs Member is actually conformable across the majority of Pennsylvania, western New York, West Virginia, Ohio, and Maryland – with the exception of central New York and eastern Pennsylvania. However, this study found the Union Springs Member to be absent altogether in northwestern Pennsylvania and western New York. Obviously in areas of the basin where the contact with the Onondaga Formation is non-existent because of erosion of the Union Springs Member the contact surface is unconformable (Lash and Engelder, 2011). Elsewhere it has been observed that the contact between the Onondaga Formation and Union Springs Member progressively cuts deeper into the Onondaga Formation from central New York to the Hudson Valley (Rickard, 1989). This observation may indicate an actual deepening of the erosional surface or just a gradational contact with a transition zone of interbedded shale and limestone (Oliver, 1954; Oliver, 1956).

2.5.2.2 Cherry Valley / Purcell Member

The Union Springs Member of Southwestern Pennsylvania is overlain, locally, by the Purcell Limestone but is correlative to the Cherry Valley Member of northwest Pennsylvania and western New York (Lash and Engelder, 2011). In well logs, the Purcell Limestone is marked by a sharp decrease in gamma-ray units with respect to the high gamma-ray values of the Union Springs. The Purcell Limestone typically has a gamma-ray signature of <200 API units, a PE value of approximately 5, and a bulk density of 2.71 g/cc (Boyce and Carr, 2009) (Figure 7). The Purcell Limestone is made up of an interval alternating siltstone, shale, and limestones both bedded and nodular (Cate, 1963). As previously mentioned, the Purcell and Cherry Valley equivalents are present throughout much of the study area with the exception of northwestern Pennsylvania where it suddenly disappears from either lack of deposition or erosion in the same areas that the Union Springs Member seems to be missing. There are areas in northwestern Pennsylvania where the absent Union Springs Member causes the

Purcell/Cherry Valley Limestone to appear as a plateau in gamma-ray signature just below the radioactive, organic-rich, basal Oatka Creek Member (Figure 9).

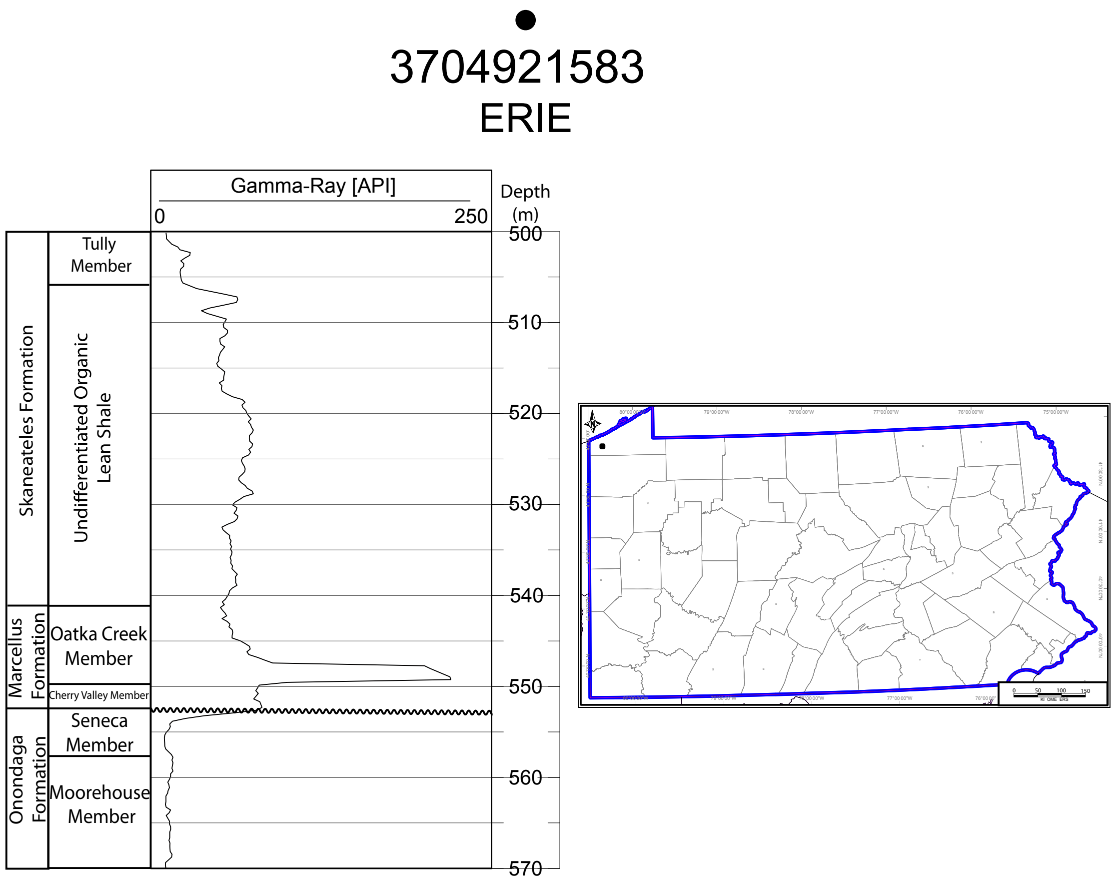

Figure 9 A: Well log showing the Cherry Valley Member resting disconformably on the Onondaga Formation in Eerie County, PA. The Union Springs Member is absent altogether in this example for northwestern Pennsylvania.

2.5.2.3 Oatka Creek Member

The Oatka Creek Member overlies the Purcell/Cherry Valley Limestone Member and is readily recognizable by the sudden increase of gamma-ray units, locally < 500 API, similar to the basal Union Springs Member caused by the radioactive, organic-rich black shales and a bulk density of < 2.55 g/cc (Boyce and Carr, 2009). The upward progression of radioactive black shales into more organic lean, gray shales with decreased radioactivity and increasing bulk density is better observed in the more proximal areas of the basin where the upper organic lean section thickens considerably to the east. The Oatka Creek Member of northwestern Pennsylvania rests disconformably on the Onondaga Formation in the absence of the Purcell/Cherry (Figure 9). In most cases, the Oatka Creek Member shows a sharp contact with Onondaga Formation in contrast to the sometimes gradational contact shared between the Union Springs Member and Onondaga Formation (Figure10).

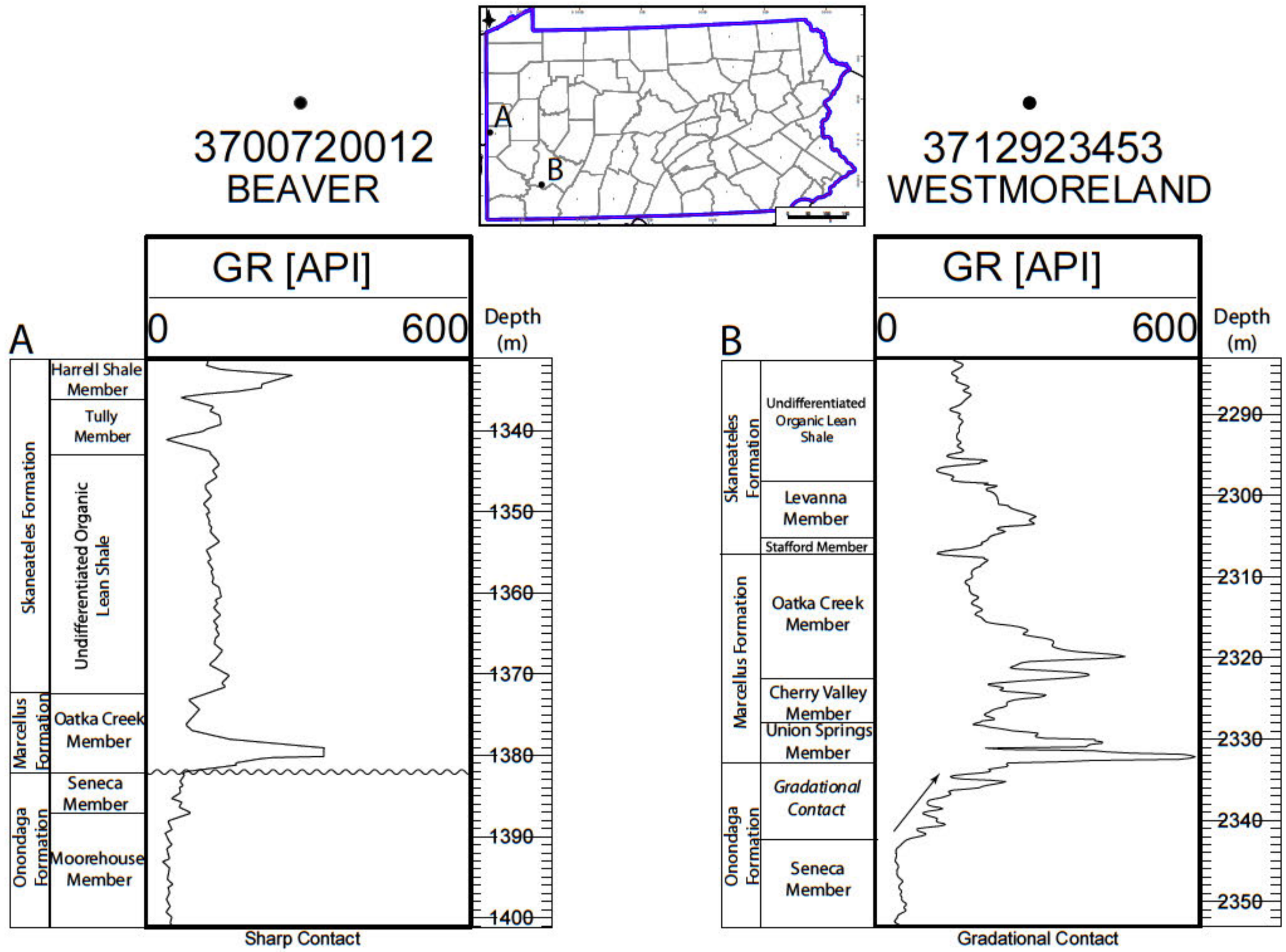

Figure 10: A) Example of a sharp contact between the Onondaga Formation and the overlying Oatka Creek Member of the Marcellus Formation. Here the Union Springs Member is completely missing. B) Well log showing a more gradational contact of the Union Springs Member with the underlying Onondaga Formation.

2.5.3 Skaneateles Formation

2.5.3.1 Stafford and Levanna Members

Marking the top limit of the Oatka Creek Member is the Stafford (Mottville) Member, the basal member of the Skaneateles Formation. The Stafford Member is predominately a limestone that lends itself as relatively evident markers in well logs wherever present (de Witt et al. 1993). In areas with no Stafford Member present, picking the Oatka Creek Member-Skaneateles Formation contact is up to interpretation. This study used a density maximum or a gamma-ray minimum, depending on log availability, that could be correlated laterally with surrounding wells to pick the Oatka Creek Member-Skaneateles Formation contact. Overlying the Stafford Member is the Levanna Member of the Skaneateles Formation. There has not been a great deal published on the Levanna Member, likely because it is a relatively geographically restricted organic-rich carbonaceous shale (Lash and Engelder, 2011). The Levanna Member differs from the radioactive Union Springs and Oatka Creek Members in well log signatures by a gradual increase in gamma-ray with decreasing depth, in contrast with the highest gamma-ray readings directly above the flooding surface in the Marcellus Formation (Lash and Engelder, 2011). The Stafford Member provides a convenient correlation marker for the Marcellus – Skaneateles Formation contact. However, in areas lacking the organic-rich Levanna Member, picking the upper cutoff can sometime be difficult. When the Levanna Member is absent, the Oatka Creek Member transitions laterally from organic-rich black shales to undifferentiated organic-lean gray shales of the Skaneateles Formation. To designate a top to the Marcellus Formation in areas absent of the Stafford Member the contact is picked on a gamma-ray minimum and/or density maximum. If reliable curve data is not available, then a cutoff placed at a subtle gray-shale baseline shift (~15-20 API) can be used to designate a top (Figure 11). This method in picking the top of the Levanna Member is used by Lash and Engelder (2011) and is similar to what was used by de Witt et al. (1993) for the Eastern Gas Shales Project.

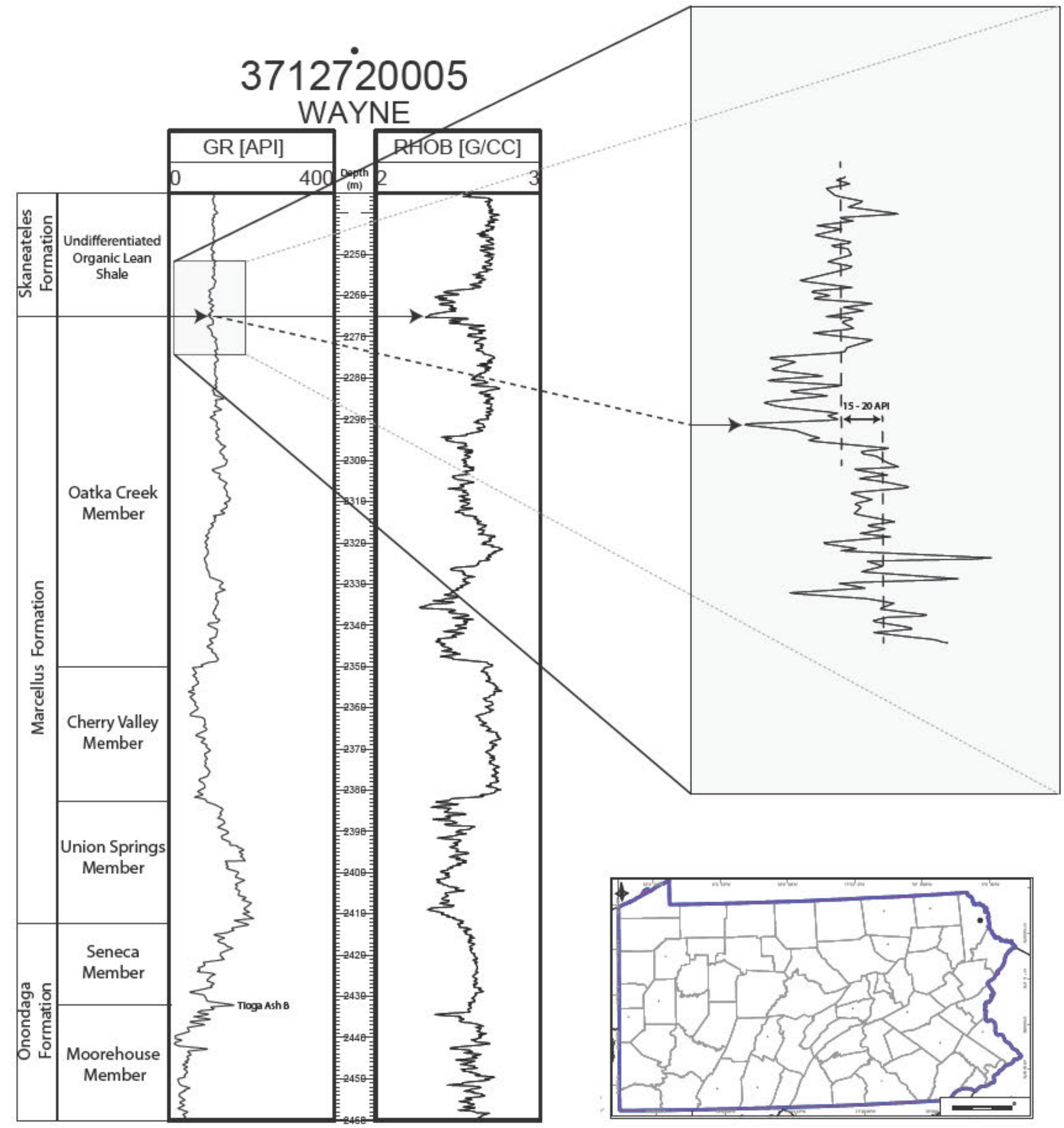

Figure 11: Well log demonstrating how the top of the Oatka Creek Member of the Marcellus Formation is picked in distal parts of the basin where the Stafford Member is absent and organic lean gray shales dominate eliminating an obvious contact. The top of the Marcellus Formation can either be picked using a gamma-ray maximum in conjunction with a bulk density minimum (shown by arrows in tracks 1 & 2) or by placing a cut-off at the slight gamma-ray baseline shift marking the lateral transition to gray shales. (Modified from Lash and Engelder, 2011).

3 RESULTS

A series of structure and isopach maps were created as a part of this study, based on the lithostratigraphic correlation of subsurface data from 821 available well logs throughout Pennsylvania. A structure map of the top of the base of the Marcellus Formation (Top of the Onondaga Formation) shows the general structural trend of southwestern Pennsylvania to be northeast to southwest, matching the regional subsurface structural trend of the state (Figure 12). In addition, a sequence stratigraphic model was constructed for the Onondaga Formation though the Geneseo Member of the Genesee Formation using a framework of significant surfaces as defined in Van Wagoner et al. (1990). According to these results, the Hamilton Group is made up of four sequences that were deposited during the Middle Devonian.

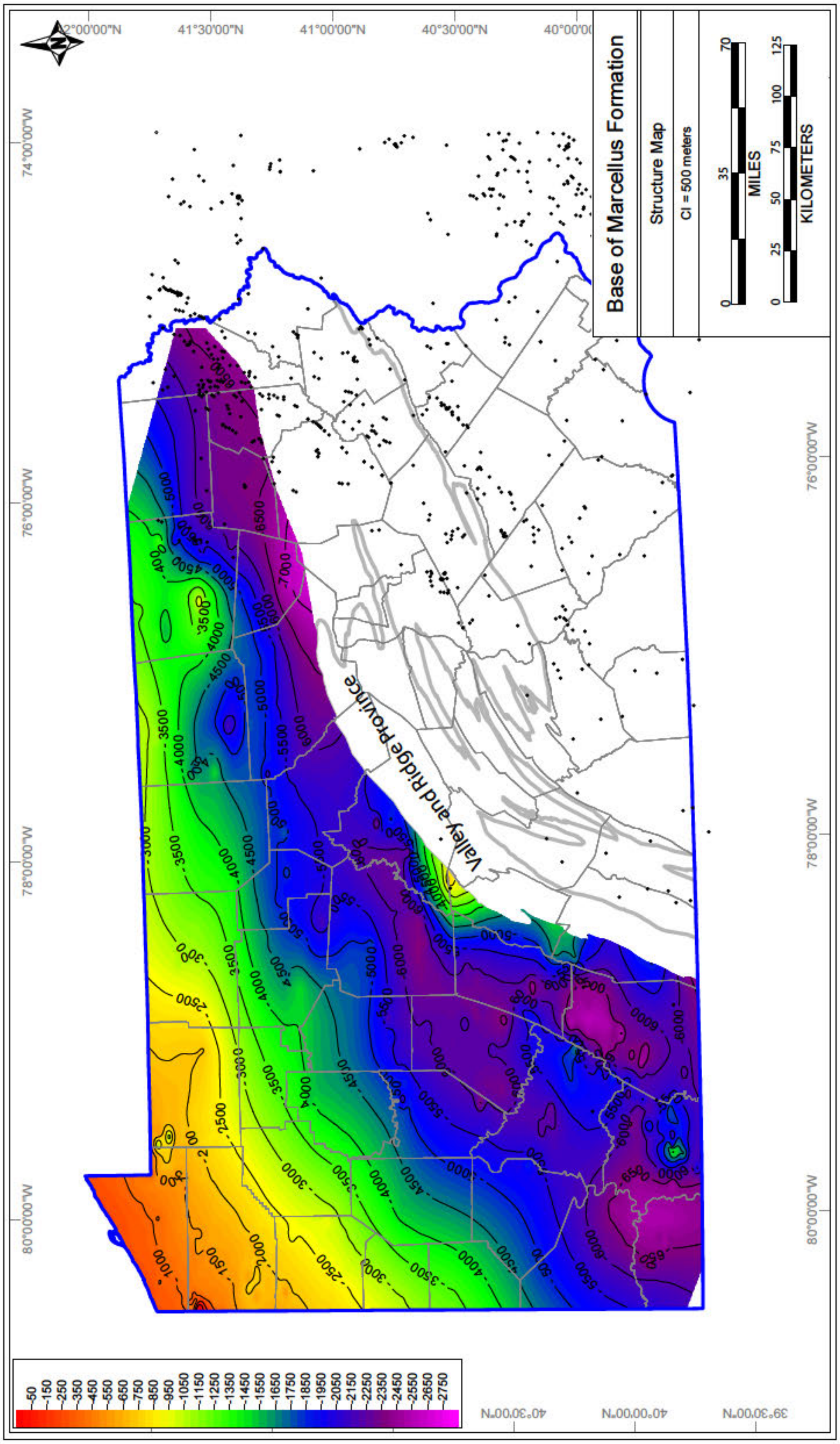

Figure 12: Structure map of the base of the Marcellus Formation of Pennsylvania.

3.1 LITHOSTRATIGRAPHIC RESULTS

3.1.2 Onondaga Formation

The Onondaga Formation is the oldest rock unit that was mapped and analyzed in this study. The Onondaga Formation also serves as a useful marker bed because it is widespread throughout the basin and is easily recognizable due to the sharp contrast in gamma-ray log signatures with the overlying Union Springs Member. The depths of the Onondaga Formation vary from 214 meters below modern sea-level to 2279 meters. The Onondaga Member is shallowest in Eerie County, northwest Pennsylvania and progressively deepens basinward to the south and east into central Pennsylvania (Figure 12).

3.1.3 Marcellus Formation

The Union Springs Member of the Marcellus Formation, sometimes referred to as the "lower Marcellus" among drillers, overlies the Onondaga Formation. The base of Union Springs shares the structure map with the top of the Onondaga Formation. The isopach map of the Union Springs Member shows a range of thickness of 63 meters, thickening eastward towards the Allegheny Structure Front from a maximum thickness of 63.4 meters to just 0.4 meters in northwest Pennsylvania (Figure 13). The Union Springs is absent in parts of northwest Pennsylvania and will be discussed further in the Discussion Section.

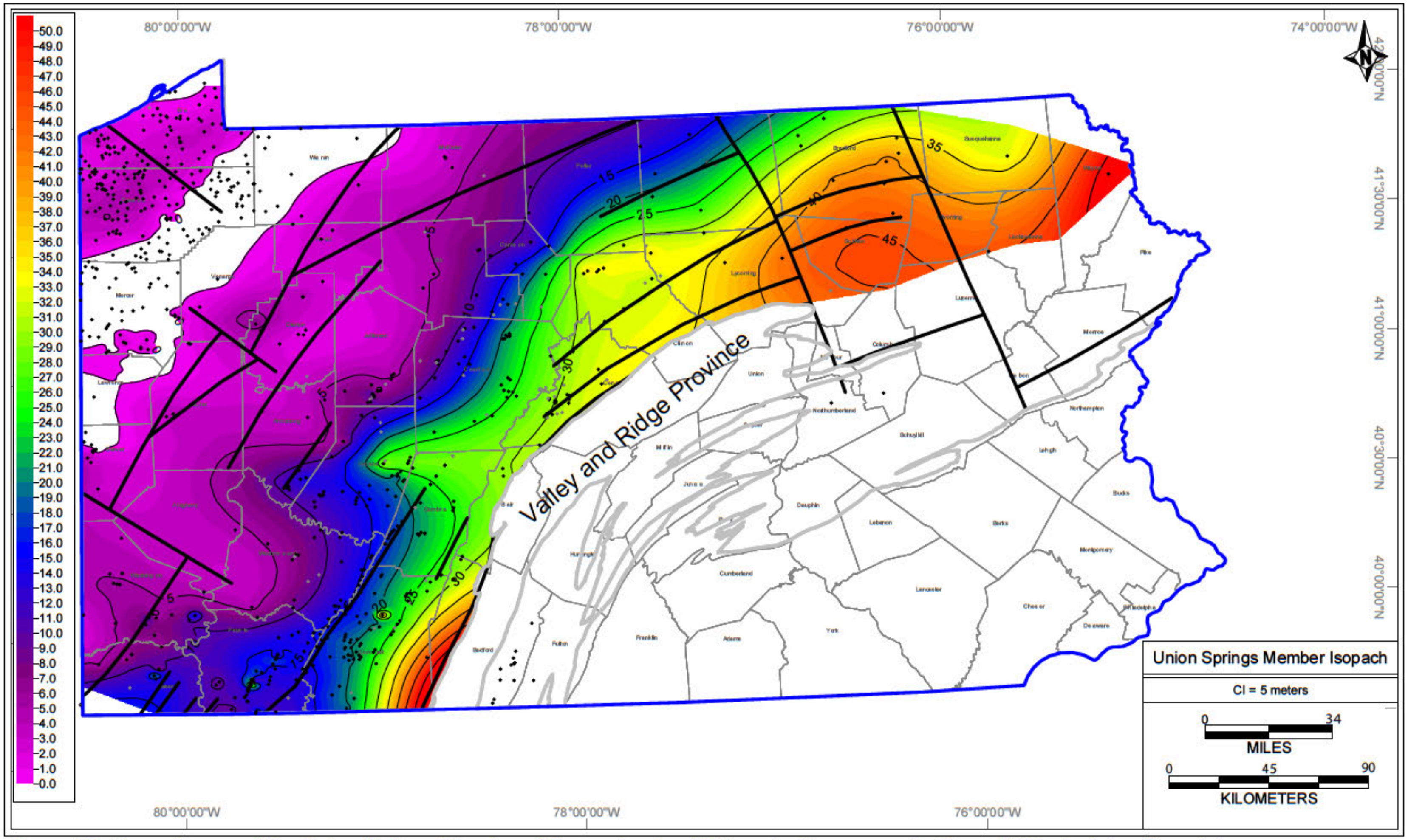

Figure 13: Isopach map of the Union Springs Member of Pennsylvania. Well control is represented by solid black dots. Grey dots represent wells that did not penetrate and/or were not logged through the Union Springs Member. Black lines represent underlying regional basement faults (See text for discussion).

Above the Union Springs Member is the Cherry Valley / Purcell Limestone Member of the Marcellus Formation. The Cherry Valley has thickness range of 35 meters. The isopach map of the Cherry Valley / Purcell Limestone Member shows a minimum thickness of less than a meter in northwestern Pennsylvania to 35 meters in eastern Pennsylvania (Wayne County) (Figure 14). The Cherry Valley / Purcell Limestone Member is absent in an area of northwest Pennsylvania similar to the area of missing Union Springs.

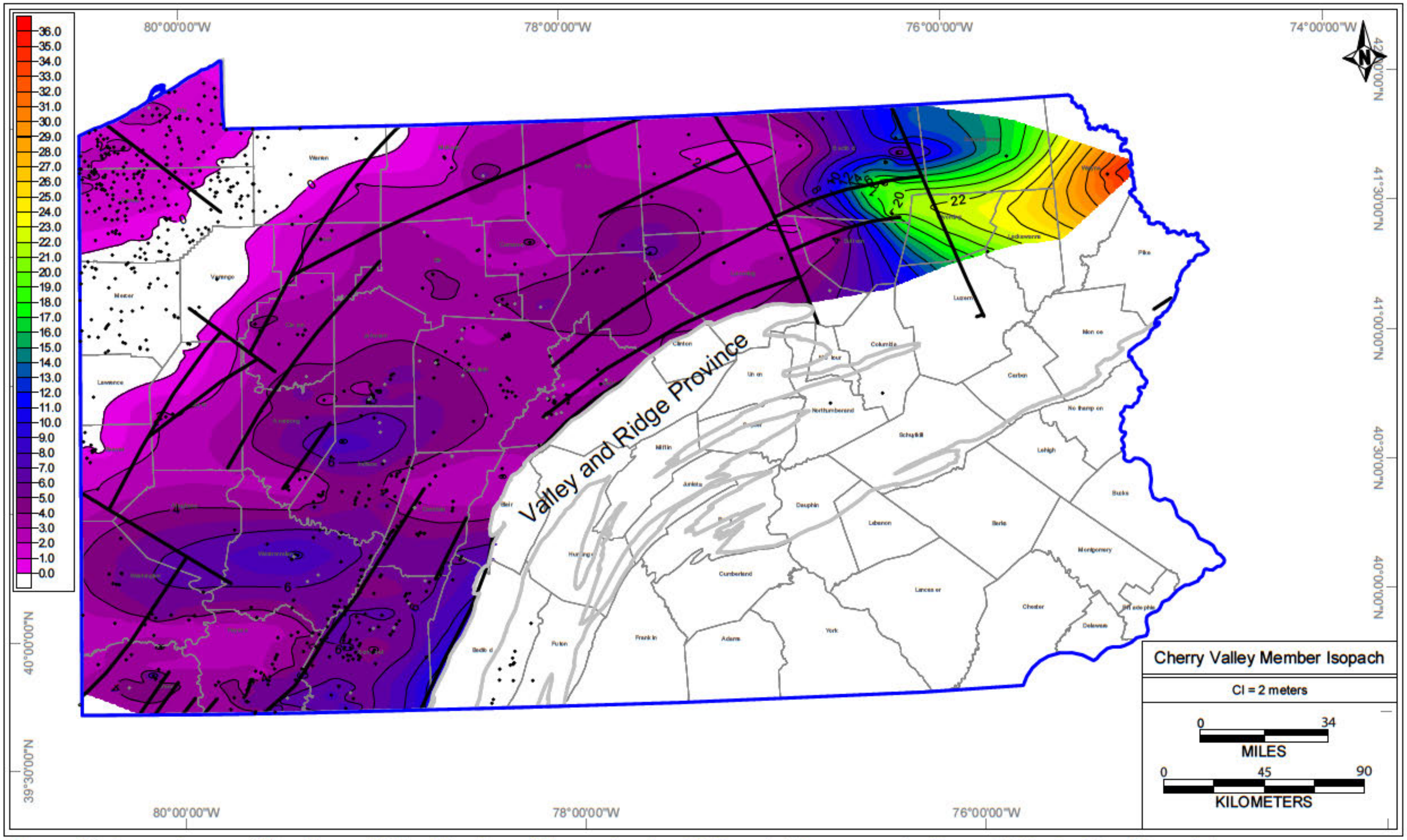

Figure 14: Isopach map of the Cherry Valley Member of Pennsylvania. Well control is represented by solid black dots. Grey dots represent wells that did not penetrate and/or were not logged through the Cherry Valley Member. Black lines represent underlying regional basement faults (See text for discussion).

Overlying the Cherry Valley / Purcell Limestone Member is the Oatka Creek Member of the Marcellus Formation. The Oatka Creek Member has a maximum thickness of 98 meters. The isopach map of the Oatka Creek shows the thickness increasing from 2 meters in southwestern Pennsylvania to 100 meters in Wayne County (Figure 15). This thickness trend follows the deepest part of the basin thickening as it moves to more distal settings to the east. The Oatka Creek is present in all logs used in this study, excluding where it is truncated along and east of the Allegheny Structure Front.

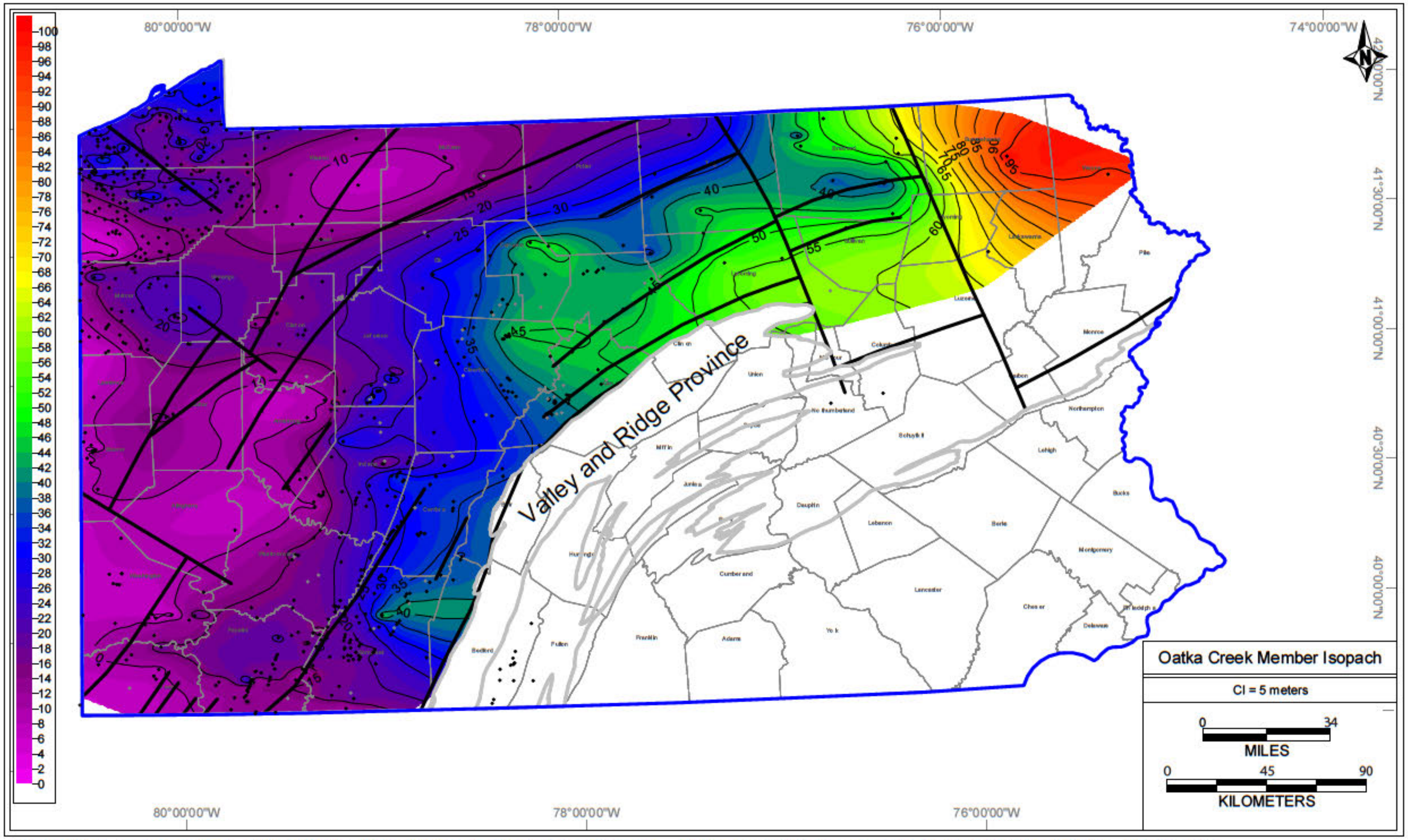

Figure 15: Isopach map of the Oatka Creek Member of Pennsylvania. Well control is represented by solid black dots. Grey dots represent wells that did not penetrate and/or were not logged through the Oatka Creek Member. Black lines represent underlying regional basement faults (See text for discussion).

3.1.4 Skaneateles Formation

In southwestern Pennsylvania, specifically Washington County, the Stafford Limestone Member marks a clear top to the Marcellus Formation. The Stafford Member is, at its thickest, only 4 meters thick and thins down to 0.5 meters around the fringes of the north-south trending limestone (Figure 16) before passing laterally into shale.

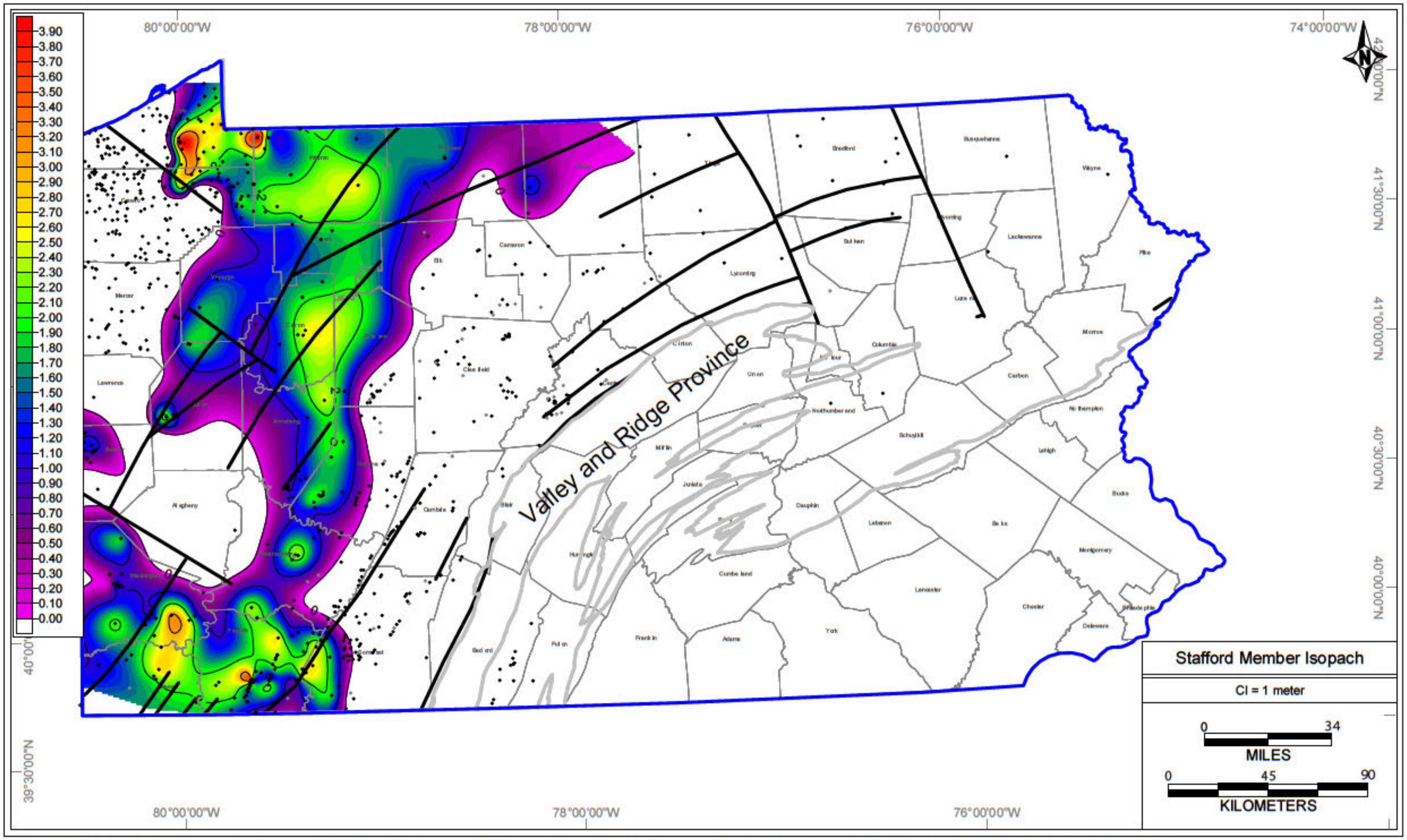

Figure 16: Isopach map of the Stafford Member of Pennsylvania. Well control is represented by solid black dots. Grey dots represent wells that did not penetrate and/or were not logged through the Stafford Member. Black lines represent underlying regional basement faults (See text for discussion).

The Stafford Member is overlain by an organic-rich shale know as the Levanna Member. This relatively geographically restricted carbonaceous shale is sometimes mistaken for the Marcellus Formation (de Witt et al., 1993) but can be differentiated from the older Oatka Creek and Union Springs Members by its tendency to have increasing gamma-ray signature response progressing up section. The bulk of the Levanna Member trends from southwest Pennsylvania to western New York and has a maximum thickness of approximately 10 meters (Figure 17). The Levanna Member tends to pass laterally into the undifferentiated gray shales of the Skaneateles (sidewall core sample 1-9R).

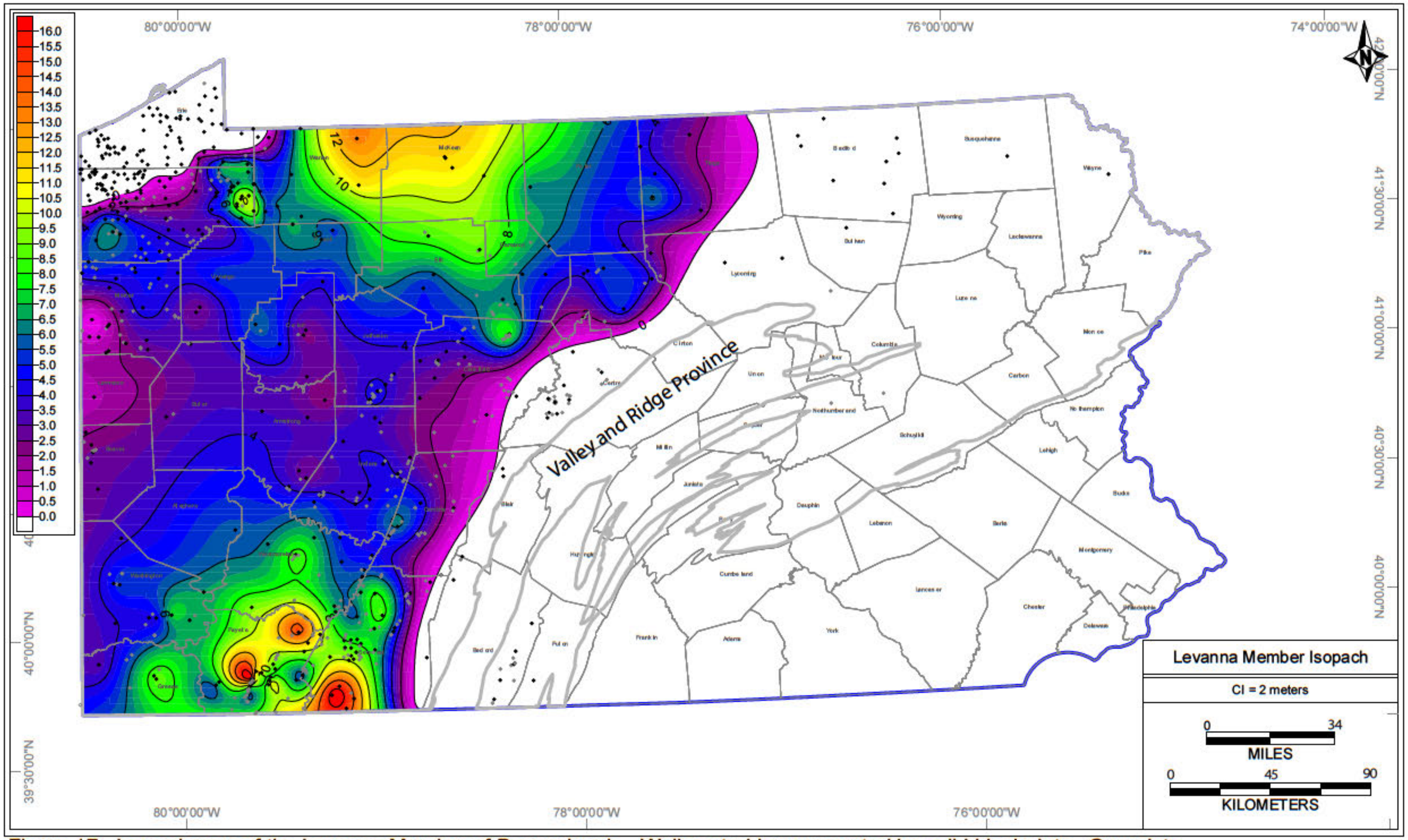

Figure 17: Isopach map of the Levanna Member of Pennsylvania. Well control is represented by solid black dots. Grey dots represent wells that did not penetrate and/or were not logged through the Levanna Member. Black lines represent underlying regional basement faults (See text for discussion).

The Tully Member of the Skaneateles Formation is the upper most member of the Hamilton Group before passing into the Genosee Formation. An isopach map of the Tully Limestone shows a maximum thickness of 58.5 meters (Figure 18). The thicker areas (< 30m) trend from southwest Pennsylvania to northeast Pennsylvania.

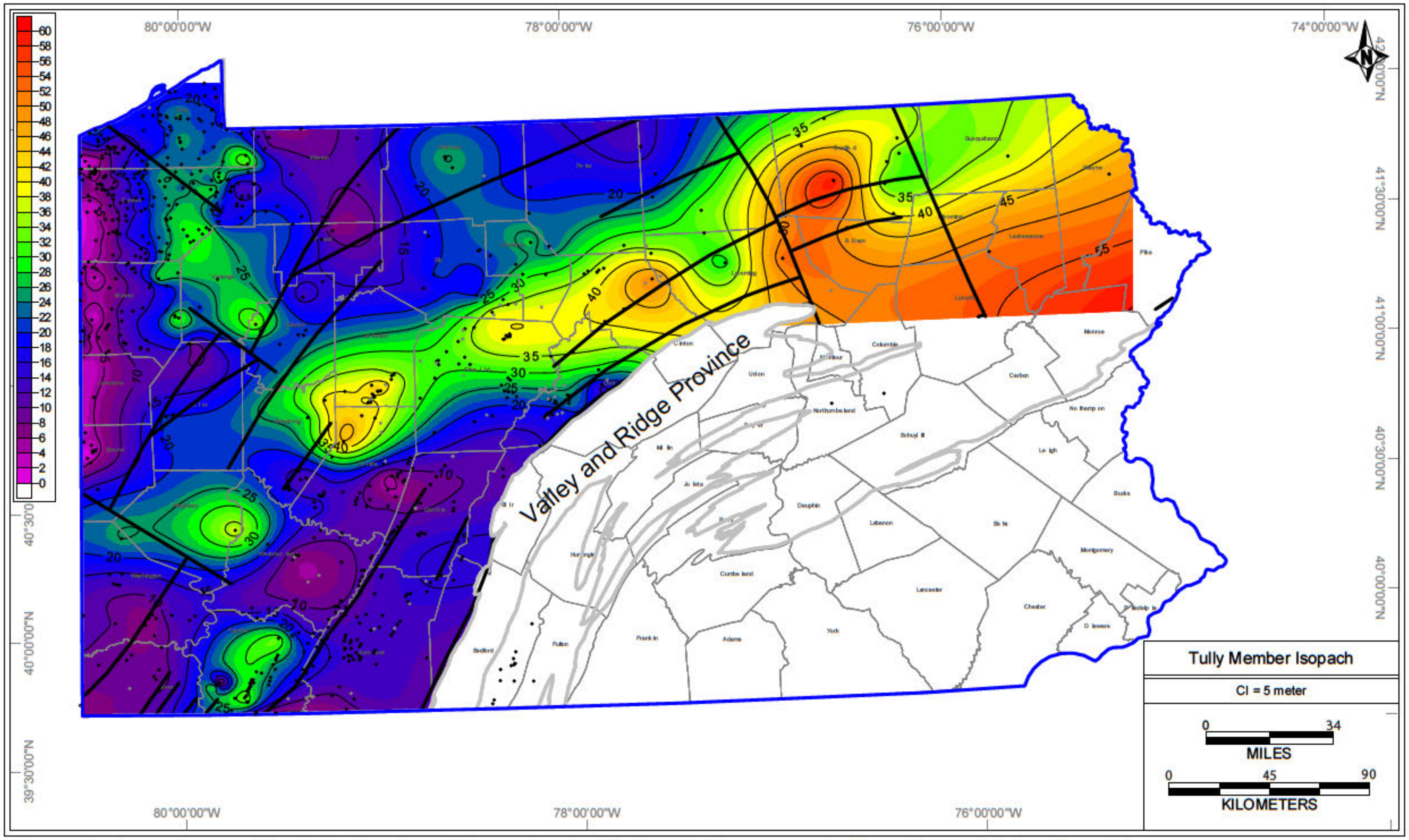

Figure 18: Isopach map of the Tully Member of Pennsylvania. Well control is represented by solid black dots. Grey dots represent wells that did not penetrate and/or were not logged through the Tully Member. Black lines represent underlying regional basement faults (See text for discussion).

Directly overlying the Tully Member of the Skaneateles Formation is the Harrell/Geneseo Member at the base of the Genesee Formation (Figure 5).

3.2 SIDEWALL CORE ANALYSIS

3.2.1 Total Organic Carbon

In an effort to link mineralogy and deposition of the Marcellus Formation, a total of 24 rotary sidewall cores were analyzed during the course of this study (Figure 5). These sidewall cores are a part of a proprietary data set owned by Rice Energy, LLC. Prior to the start of this project TOC analysis on the same set of sidewall cores had already been concluded by Weatherford Laboratories. Total organic carbon measurements were performed on the sidewall core samples, which were taken from the Geneseo Shale of the Skaneateles Formation through the Onondaga Formation (1-6R – 1-33R) (Table 1). The TOC values span a range from 0.07 % to 15.76 %.

Sample #	Depth Meters	Depth Feet	Systems Tract	TOC (% wt)	Calcite	Dolomite	Illite	Muscovite	Pyrite	Smectite	Quartz
1-1R	2096.72	6879	HST	no sample	x		x				x
1-3R	2097.02	6880	HST	no sample			x	x		x	x
1-4R	2124.46	6970	HST	no sample			x	x	x	x	x
1-6R	2161.03	7090	TST	6.84			x	x	x	x	x
1-7R	2164.69	7102	LST	0.16	x	x	x				x
1-8R	2170.18	7120	LST	0.07	x	x	x				x
1-9R	2190.9	7188	HST	4.22			x	x	x	x	x
1-11R	2229.61	7315	HST	0.64			x	x	x	x	x
1-13R	2234.18	7330	HST	4.23			x	x	x	x	x
1-14R	2236.93	7339	HST	0.8	x	x	x				x
1-16R	2241.19	7353	TST	3.49			x	x	x		x
1-18R	2242.11	7356	HST	12.75	x		x	x	x		x
1-20R	2247.29	7373	TST	14.36			x	x	x	x	x
1-22R	2248.81	7378	TST	6.49	x		x	x			x
1-23R	2252.17	7389	LST	7.42	x		x	x	x		x
1-24R	2254.3	7396	LST	8.55	x		x	x	x		x
1-26R	2256.74	7404	LST	12.92			x	x	x		x
1-27R	2257.35	7406	LST	1.62	x						x
1-28R	2258.87	7411	LST	15.76	x		x	x	x		x
1-30R	2260.09	7415	TST	13.78	x		x	x	x		x
1-31R	2261.62	7420	LST	0.3	x						x
1-32R	2261.62	7420	LST	0.3	x						x
1-33R	2261.92	7421	LST	0.09	x						x
1-34R	2261.92	7421	LST	0.09	x						x

Table 1: X-ray diffraction and total organic carbon analysis summary done on a suite of sidewall cores from R.E. #1. Samples are arranged from shallowest to deepest. Red TOC values denote percentages in excess of 1%. The presence of each mineral is represented by an “x” in its corresponding cell. Refer to Appendix 1 for specific XRD curves.

3.2.2 X-Ray Diffraction

A mineralogical analysis of 24 rotary sidewall cores was conducted using qualitative x-ray diffraction to determine the mineralogy of each sample. The set of sidewall cores used in this study were taken from a Rice Energy well located in central Washington County (Figure 5). The specific depth points were determined by the onsite geologist present during logging operations and are shown by (Figure 5). The sidewall core depths were chosen in an effort to accurately represent mineralogical changes through the full section of Lower Hamilton Group strata. Minerals present in the samples are quartz, calcite, dolomite, muscovite, pyrite, illite, and smectite (Table 1) (Appendix 1).

3.3 SEQUENCE STRATIGRAPHIC RESULTS

While mapping lithostratigraphic units in the subsurface has long been utilized for basin analysis in an explorationist mindset, the application of sequence stratigraphy to basin analysis is a powerful tool in minimizing risk when drilling along the fringes of basins where well data is commonly sparse or nonexistent. A sequence stratigraphic approach allows subdivision of complex basin fill into a framework of systems tracts made up of internal and bounding surfaces that are based on depositional models governed by geologic principles. For this study, the construction of a sequence stratigraphic model for the Marcellus Formation initiated with a wireline type log placing the Marcellus Formation within a geologic framework that can be later be applied to a regional correlation of related surfaces. The type well chosen for this study resides in Washington County, southwestern Pennsylvania (Figure 5).

The Hamilton Group of Pennsylvania is composed of a total of four sequences (S1, S2, S3, and S4) and encapsulates parts of the Onondaga Formation as well as the entirety of the overlying Marcellus and Skaneateles Formations (Figure 19). Above this succession of Hamilton Group strata lies a fifth sequence (S5) that represents the base of the Genesee Formation (Figure 5). Because S5 lies outside of the focus of this study no maps will be provided.

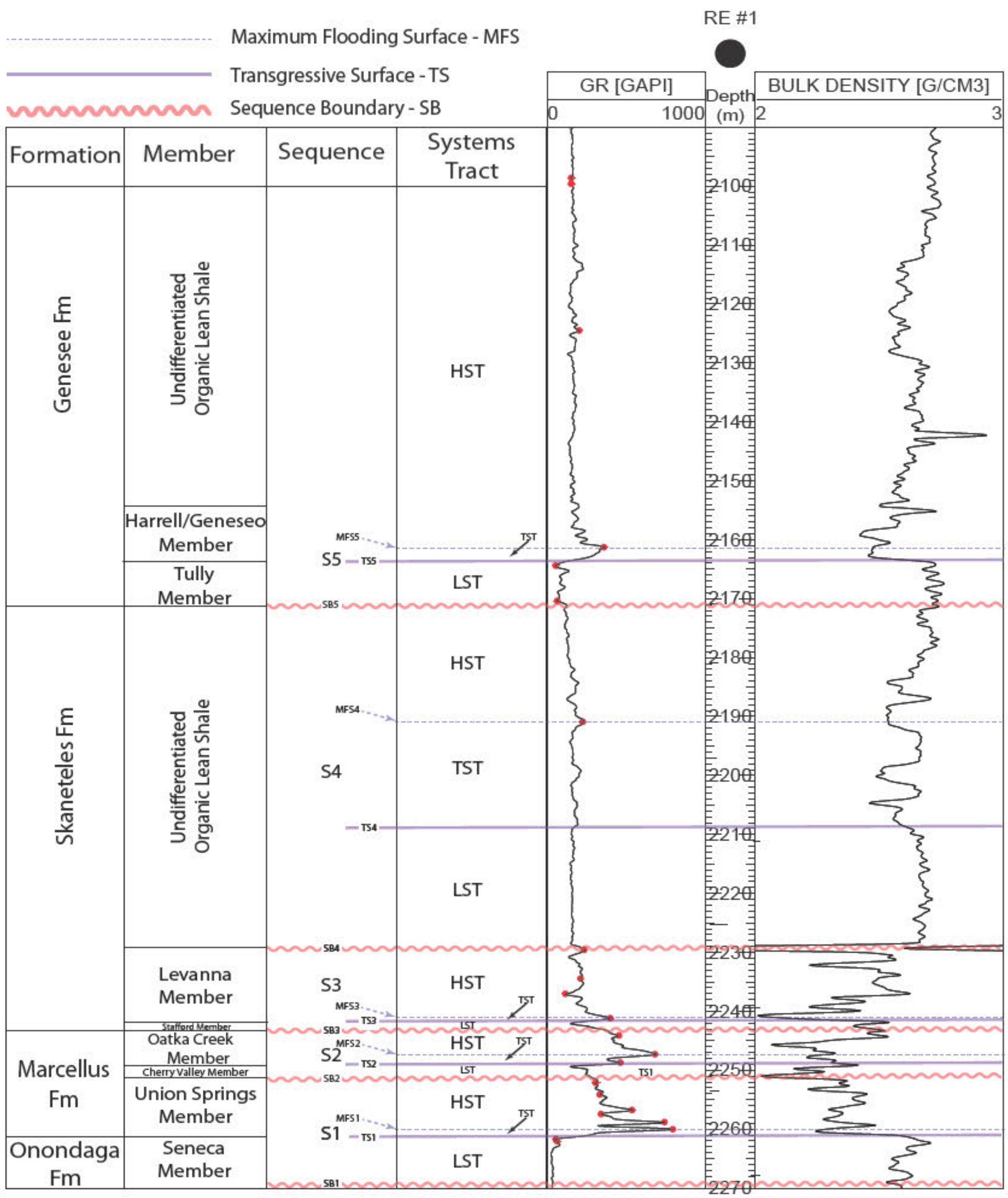

Figure 19: Sequence stratigraphic type section of the Marcellus Formation as well as the rest of the strata ecompassed in the Lower Hamilton Group. S1- S5 = Sequences 1 - 5; LST = Lowstand systems tract; TST = Transgressive systems tract; HST = Highstand systems tract. Red dots (•) represent sidewall core locations (See Figure 5).

Each mapped sequence can be broken down into a cyclic occurrence of lowstand, transgressive, and highstand sequence tracts (Figure 19). The overlap of lithostratigraphic tops and sequence stratigraphic bounding surfaces illustrates the fundamental differences between the two schools of thought. The nomenclature for each formation used in this thesis is lithostratigraphic in origin and is being used to illustrate how each lithostratigraphic top relates to its respective position in sequence stratigraphic space.

3.3.1 Sequence 1

Sequence 1 contains the Seneca Member of the Onondaga Formation and the Union Springs Member of the Marcellus Formation (Figure 19). S1 is represented in well logs as a complete succession of a LST, a TST, and a HST. Bounding the LST of S1 is a sequence boundary (SB1) below and a transgressive flooding surface (TS1) above. The TST is bounded by TS1 below and a maximum flooding surface referred to as MFS1 above. The HST is then bounded by MFS1 below and the sequence boundary above (SB2). With the exception of a northeast – southwest trending axis in northwest Pennsylvania where erosion has caused one and/or all of the systems tracts to be absent, S1 is distributed across the state as a full sequence (Figure 20).

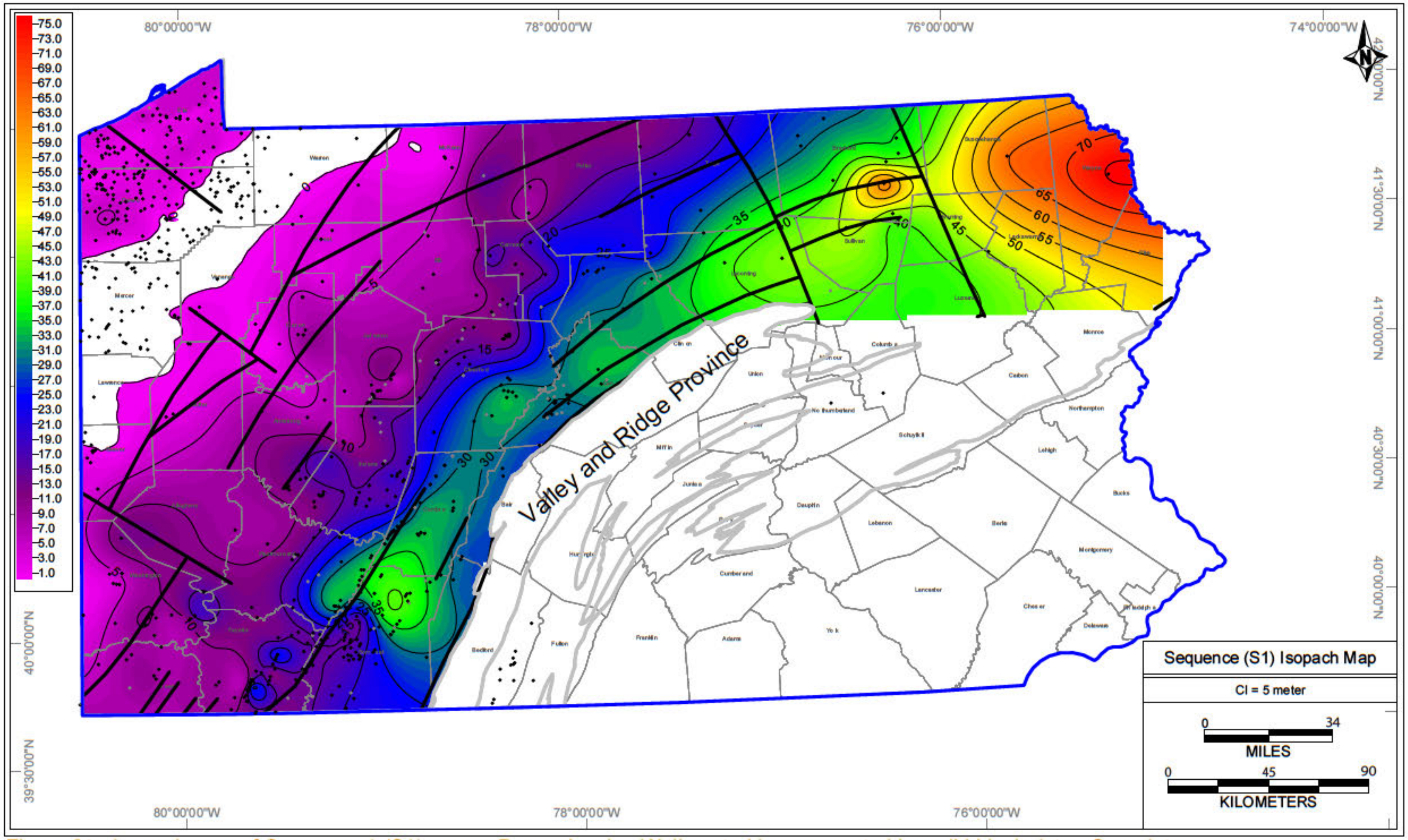

Figure 20: Isopach map of Sequence 1 (S1) across Pennsylvania. Well control is represented by solid black dots. Grey dots represent wells that did not penetrate and/or were not logged through the S1. Black lines represent underlying regional basement faults (See text for discussion).

3.3.2 Sequence 2

Sequence 2 contains the Cherry Valley and Oatka Creek Members of the Marcellus Formation (Figure 19). S2 is represented in well logs as a complete succession of a LST, a TST, and a HST. Bounding the LST of S2 is a sequence boundary (SB2) below and a transgressive flooding surface (TS2) above. The TST is bounded by TS2 below and a maximum flooding surface referred to as MFS2 above. The HST is then bounded by MFS2 below and the sequence boundary above (SB3). S2 is distributed in a similar manner as the underlying S1 and also seems to thin in a northeast – southwest direction in northwest Pennsylvania that locally places Oatka Creek shales directly on top of Onondaga limestones (Figure 10A) (Figure 21).

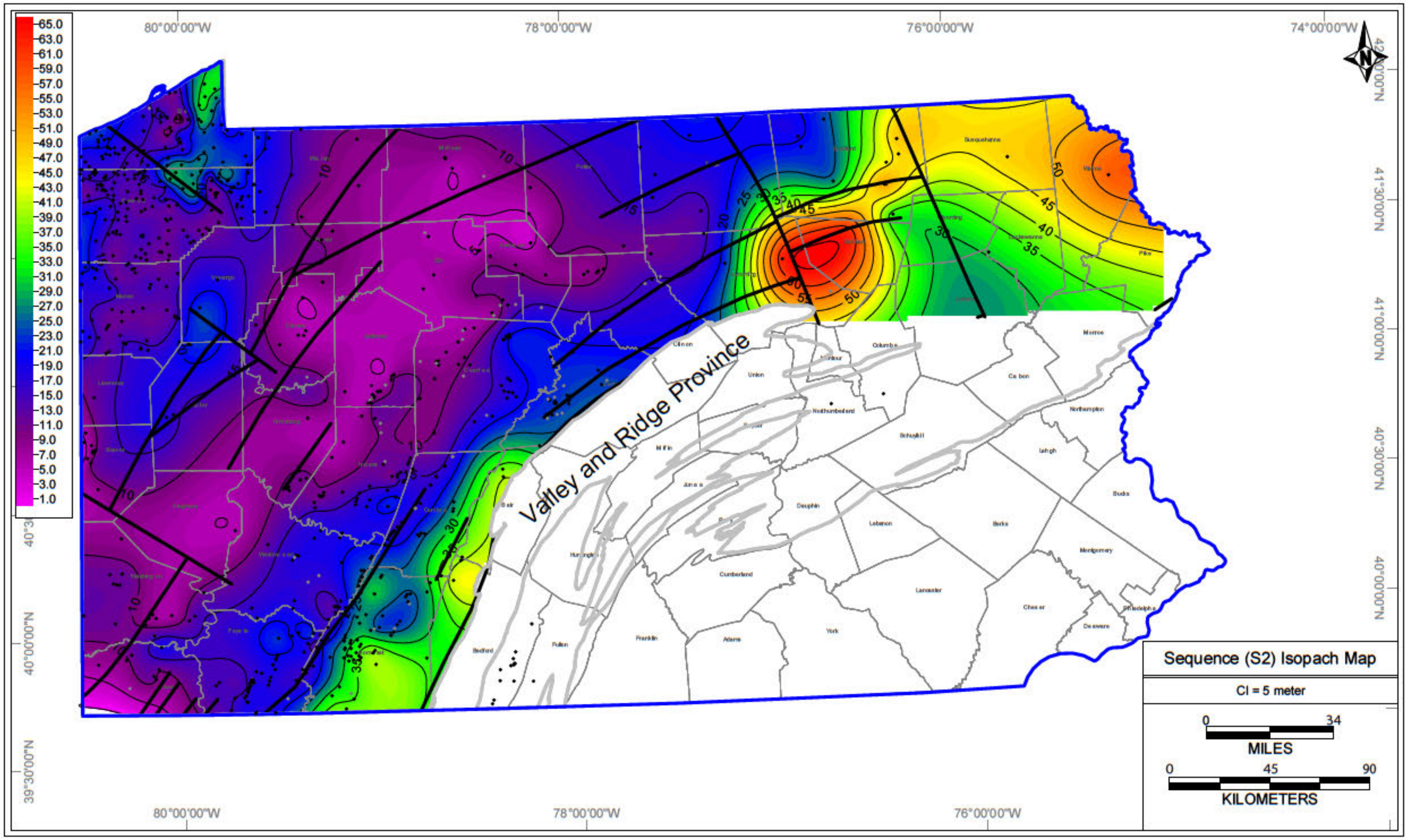

Figure 21: Isopach map of the Sequence 2 (S2) across Pennsylvania. Well control is represented by solid black dots. Grey dots represent wells that did not penetrate and/or were not logged through S2. Black lines represent underlying regional basement faults (See text for discussion).

3.3.3 Sequence 3

Sequence 3 contains the Stafford and Levanna Members of the Skaneateles Formation and is represented in well logs as a full succession of systems tracts (Figure 19) (Figure 22). S3 is represented in well logs as a complete succession of a LST, a TST, and a HST. Bounding the LST of S3 is a sequence boundary (SB3) below and a transgressive flooding surface (TS3) above. The TST is bounded by TS3 below and a maximum flooding surface referred to as MFS3 above. The HST is then bounded by MFS3 below and the sequence boundary above (SB3). S3 is distributed across Pennsylvania much like S1 and S2 only it is preserved as a full sequence across the mapped basin. Although S3 is not a component of the Marcellus Formation it was mapped nonetheless to add to the sequence model of the lower Hamilton Group strata.

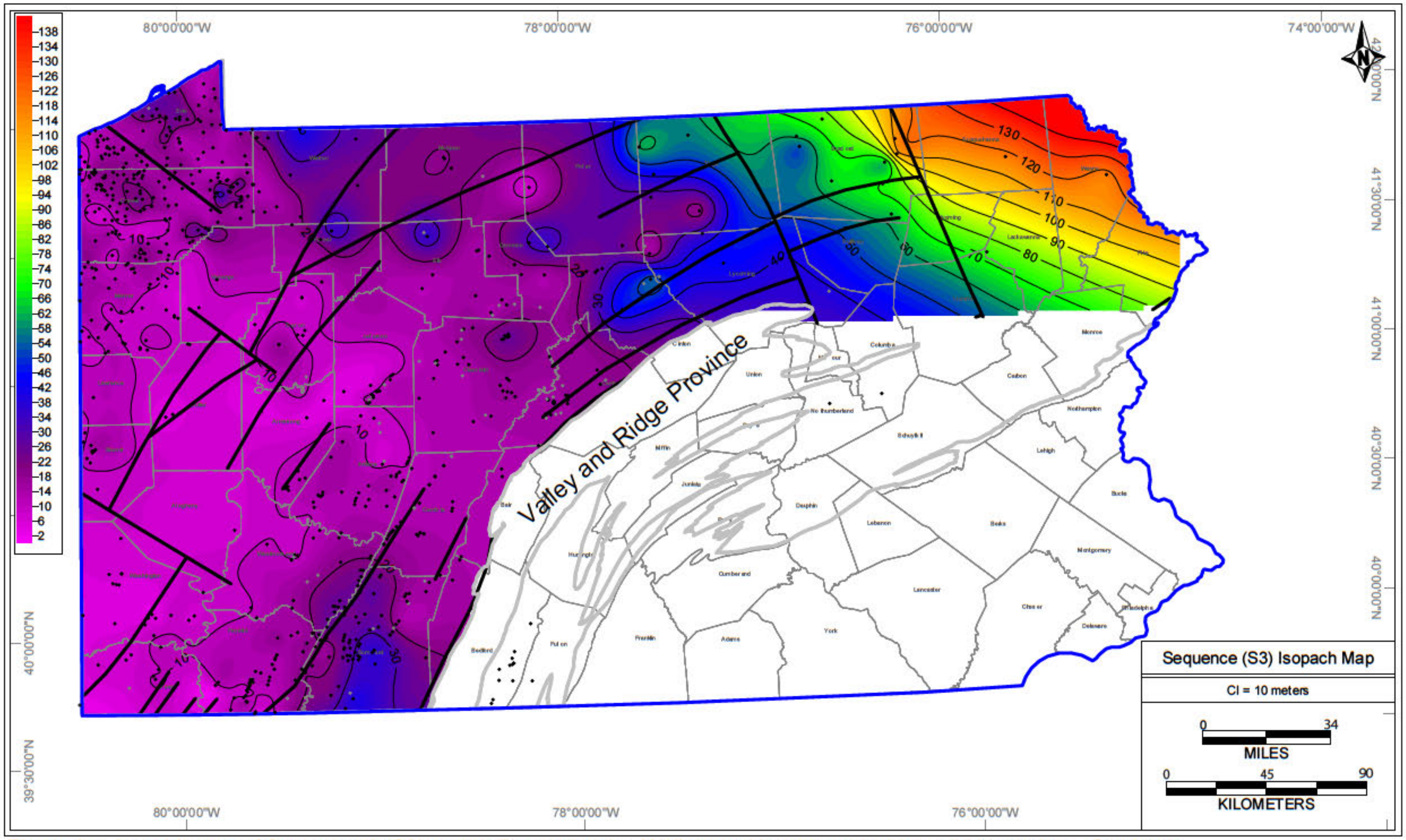

Figure 22: Isopach map of Sequence 3 (S3) across Pennsylvania. Well control is represented by solid black dots. Grey dots represent wells that did not penetrate and/or were not logged through S3. Black lines represent underlying regional basement faults (See text for discussion).

3.3.4 Sequence 4

Sequence 4 is the uppermost sequence of the Skaneateles Formation before passing into the Genesee Formation (Figure 19). S4 is a complete succession of systems tracts deposited throughout Pennsylvania (Figure 23). S4 is represented in well logs as a complete succession of an LST, a TST, and an HST. Bounding the LST of S4 is a sequence boundary (SB4) below and a transgressive flooding surface (TS4) above. The TST is bounded by TS4 below and a maximum flooding surface referred to as MFS4 above. The HST is then bounded by MFS4 below and the sequence boundary above (SB4). S4 is at its thinnest in Eerie and Crawford Counties but thickens eastward into the proximal basin.

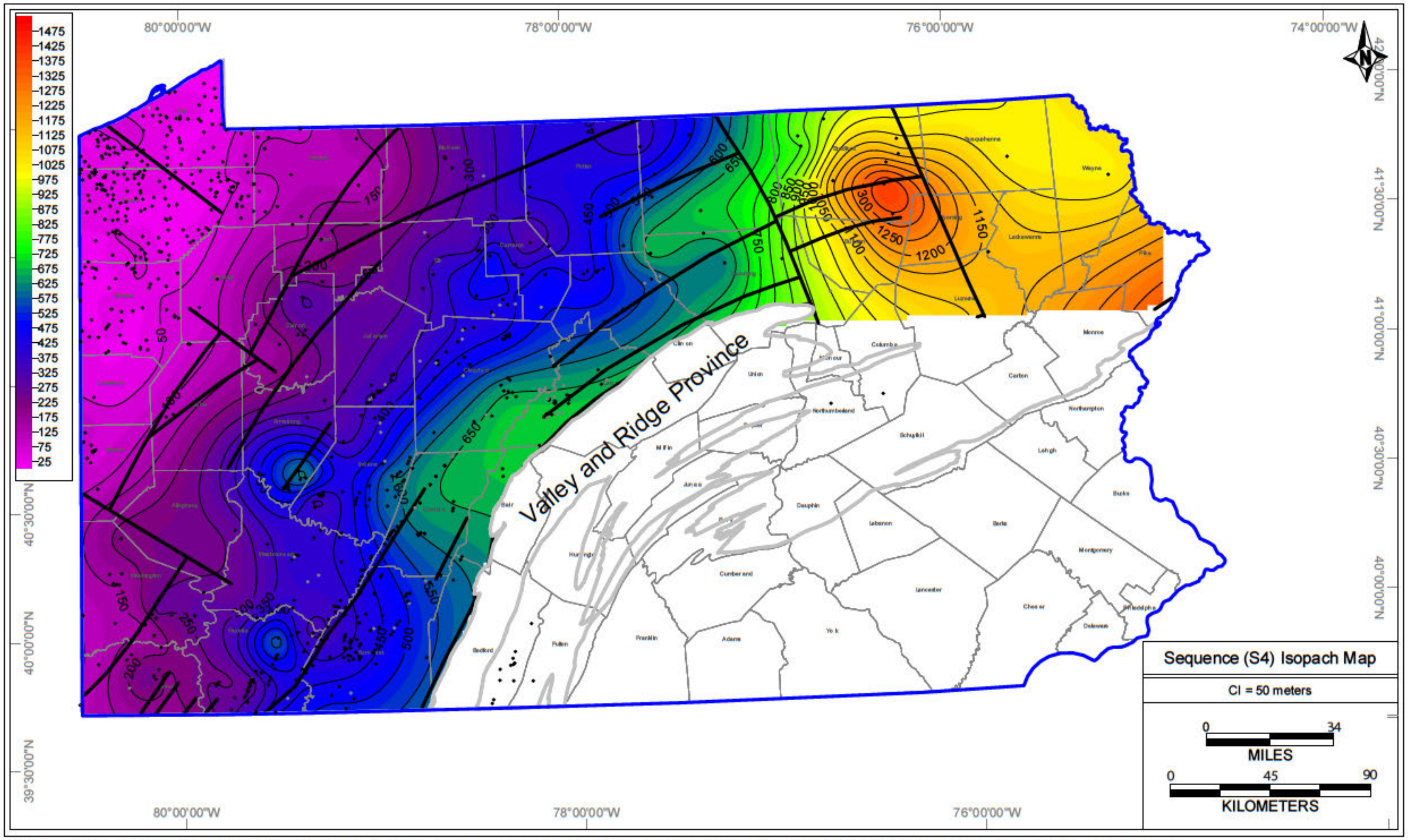

Figure 23: Isopach map of Sequence 4 (S4) across Pennsylvania. Well control is represented by solid black dots. Grey dots represent wells that did not penetrate and/or were not logged through S4. Black lines represent underlying regional basement faults (See text for discussion).

4 DISCUSSION

The Marcellus Formation, as previously defined, is actually comprised of two type-1 sequences (S1, S2) bounded by sequence boundaries SB1, and SB2 (Figure 20) (Van Wagoner, 1990). These surfaces are similar and somewhat equivalent to Johnson et al. (1985)'s transgressive–regressive cycles (T-R Cycles) Id and Ie, Ver Straeten's (2007) Eif-2 and Eif-3 sequences, and Lash and Engelder's (2011) MSS1, and MSS2 T-R Sequences.

4.1 SEQUENCE 1

S1 is the oldest of the three sequences present in the Lower Hamilton strata and bounded below by the sequence boundary SB1. This surface, which is placed at the base of the Seneca Member, is identified in well logs as a sharp increase in gamma-ray values marking an erosional surface separating the Onondaga Formation from the underlying Moorehouse Formation (Figure 20). The lowstand systems tract (LST) of S1 happens to coincide with the Seneca Member of the Onondaga Formation but is the rock bounded below by SB1 and above by the first regionally transgressive surface. This transgressive surface (TS1) defines the base of the Marcellus Formation and is placed at the gamma-ray minimum / bulk density maximum at the top of the Seneca Member of the Onondaga Formation (Figure 19). The contact between the Onondaga Formation with the overlying Union Springs Member has been interpreted in the past to be a regional unconformity (Potter et al., 1982; Rickard, 1982, 1989). However, data from this study finds that the Union Springs Member / Onondaga Formation contact to be relatively conformable across the bulk of Pennsylvania. The exception to this can be found in northwestern Pennsylvania, where the correlation of tightly spaced wireline well logs indicates, quite obviously, that the Union Springs Member is absent along a northeast – southwest trend in that part of the basin. However, methodical and consistent correlation of well logs also reveals the Union Springs to be present in parts of Eerie and Crawford Counties (Figure 13). There is no structural high apparent in Figure 12 that would indicate a period of nondeposition leaving one inclined to interpret the culprit of the absent Union Springs Member to be erosion. This interpretation would be in agreement with Lash and Engelder (2011). The basal Union Springs Member is a highly radioactive (>600 API units) organic rich shale with a low bulk density (<2.35 g/mL). The TST of S1 starts at TS1 and extends to the maximum flooding surface MFS1. Inspection of the TST of S1 shows a general upward-increasing of gamma-ray readings and an upward-decreasing in densities. This log curve relationship is responding to an overall increase in TOC with a decrease of overall grain size that could be reflecting the increase in base level inherent with transgressive systems tracts. In areas of the basin that were more proximal to sediment supply, the contact between the TST and its bounding MFS1 tends to be more gradational than in more distal parts of the basin where the TST deposits are very thin or absent altogether showing a sharp contact (Figure 5C) (Figure 10B). A sharp contact distally possibly indicates that base level rise far exceeded clastic sediment flux. The top of the TST, just below MFS1, is associated with a condensed section deposited as the shoreline progressively marches cratonward causing clastic starvation in on the shelf. This condensed section is associated with the presence of pyrite (Appendix 1) and increased TOC (Figure19) causing the gamma-ray curves to increase sharply. As the

TST of S1 was being deposited, conditions were favorable for the preservation of organic matter. This preservation was likely made possible by density and salinity stratification in the water column in conjunction with euxinic oxygen levels at the seafloor. The maximum flooding surface, MFS1 is placed at the peak of the gamma-ray curve and is supported by the presence of pyrite from XRD analysis (Appendix 1) (Figure 19). The remaining Union Springs Member resides in the highstand systems tract (HST) of S1 and is characterized by a general and gradual decrease in gamma-ray response with a corresponding increase in bulk densities as the depositional environments prograde basinward. The HST records slow base-level reduction and/or the increased rate of clastic influx as it transitions to exceed base-level rise. Starting at the MFS are a series of aggradational parasequences consisting of thin alternating layers of carbonate and pyrite-rich intervals that can be identified in the gamma-ray, bulk density, and photoelectric (PE) curves. These parasequences seem to be much better preserved in the HST than the underlying TST. Higher in the HST these parasequences begin to become more progredational as the facies shallow before the accumulation of the Cherry Valley Member lowstand carbonates. Bounding the upper extent of the HST of S1 is the erosional surface of SB2 that places the carbonate Cherry Valley Member directly over the basinal shales of the Union Springs Member.

4.2 SEQUENCE 2

S2 is bounded below by SB2 and above by SB3 (Figure 19). SB2 is placed at the last inflection point in the gamma-ray curve that also coincides with an increase in bulk density. The LST of S2 starts at the SB2 surface and extends to the first regional transgressive surface (TS2) above the carbonates of the Cherry Valley Member. The LST of S2 represents a prograding lowstand carbonate formed in response to a reduced base level or during a short period when sea-level was fairly stable. As seen in the well logs, the lithostratigraphic transition from the Cherry Valley Member to the overlying Oatka Creek Member is sharp. Sequence stratigraphically this rapid back stepping / increase in gamma-ray units is the transgressive surface TS2 (Figure 19). TS2 was formed as base levels began to increase and the transgressive carbonate deposits struggled to keep up with the rapid base-level rise. The TST of S2, similar to the TST of S1, starts at the TS2 surface and bounded above by the maximum flooding surface (MFS2) of S2 (Figure 19). The TST of S2 shows a general upward-increasing of gamma-ray readings and an upward-decrease in densities. However, unlike the highly radioactive basal Union Springs Member, the condensed section associated with SB2's TST is not as radioactive relative to the Union Springs (Figure 10B). This is evident in both the gamma-ray curve in the well logs and TOC analysis done on sidewall cores (Figure 7) (Figure 19). This apparent lack of organic enrichment could imply that the transgressive event lacked the extent of the Union Springs Member, preventing the facies belts to migrate far enough landward as to effectively isolate the basin. Alternatively the reduction in TOC seen in the Oatka Creek could just mean that the sediment source was better able to transport clastics farther into the basin. The TST of S2 is capped by MFS2 marked at a maximum in gamma-ray / minimum in bulk density curve and marks the beginning of the HST of S2 (Figure 19). The HST of S2 is bounded below by TS2 and above by the next regionally extensive erosional surface of SB3 (Figure 19). This HST, again, represents the maximum of base-level rise and the transition to a period of slow base-level fall represented by the gradual increase of sediment flux to the basin as facies moved basinward. Log curve character is similar to that seen in the HST of S1 with an inverse relationship of decreasing gamma-ray with respect to increasing densities (Figure 19).

4.3 SEQUENCE 3

The upper-bounding surface, SB3, of S2 comes in two forms. In a southwest-northeastern-trending band passing between the valley and ridge province and the upper northwest side of Pennsylvania is the Stafford Limestone of the Stafford Member (Figure 6) (Figure16). The Stafford Member is the lithostratigraphic basal unit of the Skaneateles Formation and where it is present marks the clear basinward shift in facies of lowstand carbonates resting on basinal shales (Brett and Baird, 1996). The sequence boundary is placed at the inflection point on the gamma-ray curve where there is an abrupt decrease to a local minimum in gamma-ray character correlating to an increase in the bulk density curve (Figure 7). However, as one can see from the Stafford Member isopach map from Figure 16, this carbonate occurs as a relatively restricted marker that may result from the effects of underlying faults that caused basinal warping of the basin at the time of deposition. The effects of basinal structures on Marcellus related deposition will be discussed further in the coming sections. In the deficiency of the Stafford Limestone, SB3 is placed at its stratigraphic equivalent which is just below the last local maximum of gamma-ray curve before a trending interval of an overall increase in gamma-ray values that can be correlated laterally into the Stafford Limestone. In the proximal basin the transition between the HST of Sequence 2 and the lower bounding surface, SB3, of Sequence 3 is represented as a very slight shift in gamma-ray baseline, usually on the order of a 15 to 20 API unit increase in gamma-ray values (Figure 11). This sometimes subtle bounding surface represents a landward shift in depositional facies into the organic-lean shales of the Skaneateles Formation (Figure 9). Overlying the Stafford Member is the Levanna Member of the Skaneateles Formation which contains the TST and HST of S3 (Figure 7). The TST of SB3 is placed at the gamma-ray minimum / bulk density maximum, marking the point just before the Stafford Member succumbed to rapid base level rise. The better developed organic-rich shales in the Levanna Member seem to be confined to the TST in the distal basin. Even when best developed, the Levanna Shale is not as organic rich as its older organic-rich counterparts of the Marcellus Formation (Figure 19). Correlation of the Levanna Member shows that it passes laterally into the undifferentiated organic-lean shales of the Skaneateles Formation and expands rapidly to the northeast proximal segment of the basin (Figure 17). The lack of enrichment likely has something to do with the duration of isolation and the dramatic increase in sediment flux proximal to sediment supply. The Levanna Member shows a point of base level maximum at the MFS placed at the point of gamma-ray maximum / bulk density minimum, marking the lower bounding surface of the HST of S3. This highstand systems tract is unique with respect to its predecessors. The HST of S3 show the most expansion of any of the systems tracts discussed thus far. The distal deposits of the highstand sediments in the upper Levanna Member behave similarly to the highstands that came before them; however, upon moving more and more proximal to sediment supply the parasequences lose the familiar "shallowing up" profile and adopt a profile of a distinctly aggradational nature. Sediment supply in the HST of SB3 appeared to match the rate of accommodation allowing for as much as 500 m of highstand deposits. Sequence 3 is bounded above by SB4 at a point of gamma-ray minimum /bulk density maximum at the top of the HST of S3.

4.4 SEQUENCE 4

Sequence 4 is the overall thickest deposits of the previous three sequences and is characterized by its general lack of gamma-ray/bulk density character. Sequence 4 is comprised of a lowstand deposit, bounded below by SB4, that passes rapidly into organic-lean shales. The TST is bounded below by the transgressive surface (TS4) that can be located using the same method used in picking the sequence boundary between sequences 2 and 3 but by using a decrease in base-line shift instead of an increase (Figure 11). Similarly, because of the general lack of character in the gamma-ray curves of this section of rock, MFS4 of S4 can only be picked by using the method shown in Figure 11 coupled with the bulk density curve. MFS4 occurs as a slight increase in gamma-ray values where there is a decrease in bulk density relative to the rock above and below. The HST of S4 shows an aggradation of parasequences until it is truncated by SB5 that marks a dramatic basinward shift in facies and places the Tully Limestone of the Tully Member directly on top of the vast expanse of organic-lean basinal shales. The Tully Member is the progradational basal member of the Genesee Formation (Figure 5).

4.5 DEPOSITIONAL SEQUENCES

The Marcellus Formation was deposited as one of several black shale-based depositional sequences, each representing shorter term base-level oscillations (Johnson et al., 1985; Brett and Baird, 1986; Van Tassell, 1994; Brett and Baird, 1996; Ver Straeten, 2007). These sequences fit inside a tectono-stratigraphic model explaining the Acadian Orogeny that entails four tectonic phases that shaped the Appalachian Basin (Ettensohn, 1985, 1987, 1994). The organic-rich black shales of the Union Springs and Oatka Creek Members formed in response to the collision of the Avalonian Terranes with the North American Craton that caused thrust-load induced subsidence and rapid deepening of the foreland basin. The foreland basin is deepest proximal to the thrust front and is the reason for the noticeable thickening of S1 and S2 (Appendix 2.1 and 2.3).

There has been debate whether this subsidence is eustatic in nature or just localized response to the thrust-induced loading (Johnson et al., 1985; Johnson and Sandberg, 1989). It is possible that both forms of subsidence plays a role in forming the Upper and Middle Devonian succession of rocks in the core region of Marcellus exploration activity but it is difficult to ascertain the contributions of each mechanism separately (Burton et al., 1987; Werne et al., 2002). On the onset of the Acadian Orogeny the Appalachian foreland basin was home to intermittently active basement structures that were remnant to the Precambrian breakup of Rodina (Lash and Engelder, 2011). The most prominent of these structures is the Rome Trough that enters Pennsylvania through its southwestern corner. The exact location of the Rome Trough is not as obvious in the rest of the state (Harper, 1989). Also, in one of the main fairways of the Marcellus play resides a series of northwest striking basement wrench faults (Figure

12) (Parrish and Lavin, 1982; Rodgers and Anderson, 1984; Harper, 1989). These faults are thought to have formed as strike-slip faults related to the formation of the proto-Atlantic Ocean in the Late Precambrian (Thomas, 1977). Although the Acadian foreland basin was chiefly formed in response to thrust-induced subsidence, it is likely that these inherited basement structures played some role in the foreland basin evolution (Lash and Engelder, 2011). For example, it has been shown that reactivation of preexisting structures in the time of foreland flexure can act to partition a foreland basin into regions of fault controlled depocenters (Tankard, 1986; DeCelles and Giles, 1996). The organic-rich Union Springs Member of the Marcellus Formation represents a sharp rise in sea level that resulted from the onset of the second tectonic phase of the Acadian Orogeny (Ettensohn, 1985, 1994). In more proximal basinal settings the transgressive surface is obscured by an increase in clastic flux and shows a more transitional trend into basinal black shales. In contrast, in the distal basin the rise in sea level is shown by a sharp transgressive surface that places organic-rich Union Springs Member directly over the Onondaga Formation’s limestones. These reactivated features may be responsible for the thinning and eventual total absence of S1 in a northeast-southwest oriented region in northwestern Pennsylvania (Figure 20). This absence of S1 may be due to warping and/or local flexing of the basin in this area induced by a displacement from a wrench fault known as the Lawrenceville-Attica and Home-Gallitzin fault (Lash and Engelder, 2011). The result of such displacement would be a local reduction in base level great enough allow for the erosion of S1. The Oatka Creek Member encompasses the entirety of S2 and like S1 thickens in relation to increasing proximity to the thrust to the east (Figure 21). The accommodation needed for this thickening would have been created

from the relaxation of the tectonic load (Ettensohn, 2004). In a similar manner, S2 also thins in the same northwest-southeast trending area in northwest Pennsylvania that locally places the Oatka Creek Member resting disconformably directly on top of the Onondaga Formation due to erosion (Figure 10). The thinning of the remaining sequences (S3 and S4) to the distal eastern basin may appear to also be lost to erosion; however, the complete sequences of all of these in areas of thinning, like the location of the R.E.#1 in southwestern Pennsylvania suggest that the thinning is due to lack of sedimentation in the distal basin rather than erosion (Figures 22 and 23). In all, the thickness trends of the sequences in the Marcellus Formation (S1 and S2) as well as the sequences outside of the Marcellus Formation (S3 and S4) seem to be controlled, somewhat, by reactivated basement structures at the time of deposition. This semi-syndepositional movement on wrench faults likely created localized depocenters and subtle ridges of a magnitude great enough to influence base level enough to encourage erosion and influence sedimentation (Lash and Engelder, 2011).

4.6 X-RAY DIFFRACTION AND TOC

Mineralogical analysis was performed on a suite of sidewall cores taken from a well in Washington County, Pennsylvania and used to tie the mineralogy of the separate members within the Marcellus Formation to its position in the sequence stratigraphic model (Figure 5: A-C; Figure 24) (Appendix 1).

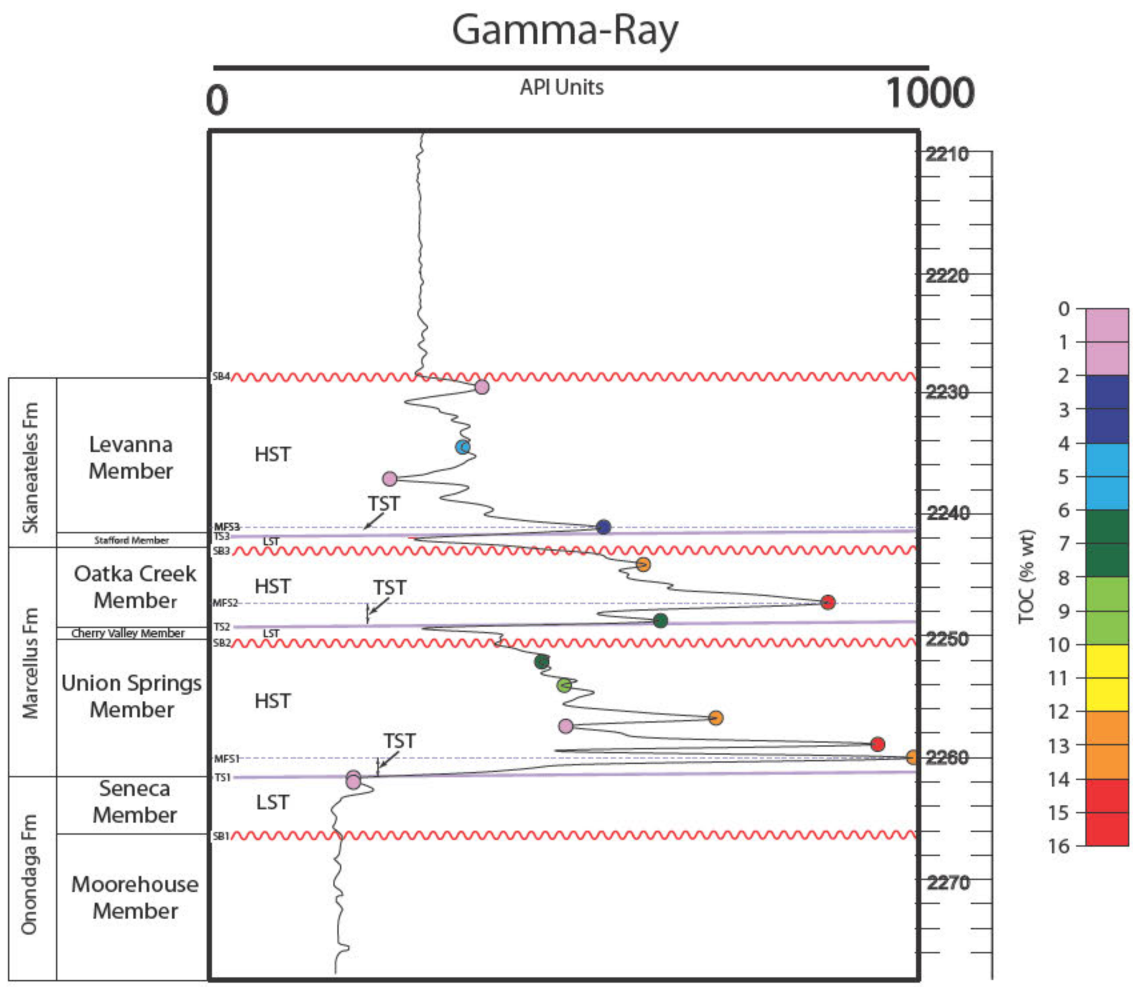

Figure 24: Sequence stratigraphic model applied to the R.E. # 1 well showing the relationship between TOC percentages (colored dots) and the corresponding systems tract. TOC weight percentages are generally greatest in the trasgressive systems tracts to lower highstand systems tracts and decrease upward as the system transitions to dominately highstand depositional conditionis.

A broad comparison of all the samples allows for the identification of trending data. The key observations made on these core points are as follows:

1. Quartz is present in every sample.
2. No dolomite when TOC is greater than 1%.
3. Pyrite occurs only in samples with TOC greater than 1%.
4. Pyrite, muscovite, and smectite are more likely to be missing when TOC content falls below 1%.

From the data it is apparent that in the lowstand systems tracts there tends to be a decrease in TOC (Table 2). The XRD data in this study shows the presence of calcite, and sometimes dolomite in each of the sampled LST's (Table 2). In Lash and Engelder (2011) the calcite content of their TST was found to be three times more abundant than in the overlying regressive sequence tract (RST) (Lash and Engelder, 2011; Figure21). The RST is roughly equivalent to this study's HST and the LST also used in this study is contained in the lower TST of Lash and Engelder (2011). Note that their sequence stratigraphic model is fundamentally different from this study. The systems tracts are based on maximum regressive surfaces rather than maximum flooding surfaces and the LST is incorporated within their lower TST. Even with the overlap in systems tract designation their data are still helpful as a comparison with the findings from this study.

	Sample #	Depth Meters	TOC (% wt)	Calcite	Dolomite	Illite	Muscovite	Pyrite	Smectite	Quartz
Sequence 5										
HST	1-1R	2096.72	**	x		x				x
HST	1-3R	2097.02	**			x	x		x	x
HST	1-4R	2124.46	**			x	x	x	x	x
TST	1-6R	2161.03	6.84			x	x	x	x	x
LST	1-7R	2164.69	0.16	x	x	x				x
LST	1-8R	2170.18	0.07	x	x	x				x
Sequence 4										
HST	No Sample									
TST	1-9R	2190 9	4.22			x	x	x	x	x
LST	No Sample									
Sequence 3										
HST	1-11R	2229.61	0.64			x	x	x	x	x
HST	1-13R	2234.18	4.23			x	x	x	x	x
HST	1-14R	2236.93	0.8	x	x	x				x
TST	1-16R	2241.19	3.49			x	x	x		x
LST	No Sample									
Sequence 2										
HST	1-18R	2242.11	12.75	x		x	x	x		x
TST	1-20R	2247.29	14.36			x	x	x	x	x
TST	1-22R	2248.81	6.49	x		x	x			x
LST	No Sample									
Sequence 1										
HST	1-23R	2252.17	7.42	x		x	x	x		x
HST	1-24R	2254 3	8.55	x		x	x	x		x
HST	1-26R	2256.74	12.92			x	x	x		x
HST	1-27R	2257.35	1.62	x						x
HST	1-28R	2258.87	15.76	x		x	x	x		x
TST	1-30R	2260.09	13.78	x		x	x	x		x
LST	1-31R	2261.62	0.3	x						x
LST	1-32R	2261.62	0.3	x						x
LST	1-33R	2261.92	0.09	x						x
LST	1-34R	2261.92	0.09	x						x

(HST) Highstand Systems Tract

(TST) Transgressive Systems Tract

(LST) Lowstand Systems Tract

** No TOC analysis

Table 2: Sidewall core samples broken into their respective sequence and systems tracts. TOC values greater than 1% highlighed in red. Black “x” indicates mineral present in sample.

In a transgressive systems tract deposit one would expect to see a mineral assemblage representative of the rising base level associated with TST deposits. The mineral assemblage of the transgressive samples shows the presence of clay minerals (illite and smectite), mica (muscovite), and pyrite. Lash and Engelder (2011) found that quartz content increases sharply with a decrease in clay content that was interpreted to be in response to the rapid landward shift in facies at the time. Pyrite content was also shown to increase with a peak at the MFS, indicating the development of a condensed section. The condensed sections in the Marcellus Formation serve as excellent reservoir rock. One would not expect to find such an abundance of quartz in an area of the basin supposedly starved of clastic material. This quartz content is likely from planktonic organisms living in the photic zone above the basin floor. This is supported by Lash and Engelder's (2011) scanning electron microscope and thin section analysis of core taken through the Marcellus Formation that found the quartz occurring as microcrystalline and lining the pore throats and coating detrital clay grains.

In a highstand sequence tract a mineral assemblage should reflect a period of base-level rise that gradually slows to a period of stabilization before the development of the overlying sequence boundary. Indeed, the mineral assemblages shown in the XRD data shows a grouping of minerals not out of the ordinary with TOC values typical of deep basinal deposition.

5 CONCLUSIONS

5.1 CONCLUSIONS

Sequence stratigraphic analysis of 821 wireline well logs shows that the Middle Devonian Hamilton Group is comprised of five sequences. The Marcellus Formation, which is the oldest of the Hamilton Group Formations, is itself made up of two sequences S1 and S2. Variations in thicknesses of S1 and S2 across the state of Pennsylvania appear to reflect an intertwined relationship of sedimentation rate, accommodation space, localized uplift, and proximity to a clastic source. Thrust loading from the collision of Avalonian terranes into the North American Craton created the accommodation space that allowed for the accumulation of both sequences (Ettensohn, 1985, 1994). The highstand systems tracts of both sequences reflect accommodation space and from regional isopach maps looks to be thickening the most in the northeast region of the basin near the Acadian thrust front. Elsewhere, both sequences seem to have a relative uniform thickness as they move into the distal part of the basin towards southwestern Pennsylvania. This uniform thickness may indicate that the influence of thrust loading was not felt as much distally because of decreasing accommodation. There is a northeast-southwest-trending region of northwest Pennsylvania in which both sequences experienced some erosion locally placing the Oatka Creek Member disconformably on top of the Onondaga Formation. Construction of a sequence stratigraphic model reveals a predictable framework that can be used for reservoir assessment regionally across Pennsylvania. X-ray diffraction analysis indicates that mineralogy within each depositional systems tract may be predicable. The sequence stratigraphic model constructed as a result of this study shows that the greatest amount of preserved malleable kerogen rich rock is within the TST and lower HST of both S1 and S2. A comparison of mineralogy and TOC shows that these same zones also are enriched in reservoir enhancing quartz, calcite, and pyrite.

This study was meant to answer two key questions:

1. Can mineralogy be predicted within specific zones of the Marcellus Formation?
2. Is there a relationship between mineralogy and TOC?

Through x-ray diffraction the mineralogy of rock strata within each sequence is found to be a predictable and cyclic deepening upward progression of lowstand carbonates (calcite, dolomite, quartz) to deepwater shales (illite, smectite, pyrite, muscovite, and quartz) in the transgressive and highstand sequence tracts.

Total organic carbon analysis performed on each of the sidewall core samples shows a range of weight percentages from a low of 0.07 % to a high of 15.76 %.

Comparison of XRD and TOC data shows that the relationship between mineralogy and hydrocarbon producing organic matter may vary predictably within each sequence. The most organic-rich sediments seem to be concentrated in the TSTs and lower-HSTs of each sequence analyzed. Also, associated with these organically enriched systems tracts is the presence of reservoir enhancing minerals (quartz, calcite, and pyrite) which makes a strong case that the ability of the rock to retain its permeability after hydraulic fracturing is predicable. Landing the horizontal segment of a well in the transgressive and lower highstand systems tracts in the Marcellus Formation may increase the efficiency of the completion method of hydraulically fracturing of such wells. By targeting these zones of enhanced reservoir in the TSTs and lower-HSTs the fracture design of a well could bypass zones of rock with mineralogy not conducive to fractures remaining open and thus optimizing hydrocarbon recovery.

This study provides solid evidence that the ability of the organic-rich shales of the Marcellus Formation to fracture efficiently and remain open is predictable on a broad and regional scale when targeting the TSTs and lower-HSTs of sequences S1 and S2. The sequence stratigraphic model presented in this study suggests that rock enriched in otherwise malleable organic matter may also be enriched in reservoir enhancing minerals (quartz, calcite, and pyrite) that control brittleness. What remains unknown is assessing how important the abundance of each compositional constituent is relative to each other. The interaction of the before-mentioned reservoir enhancing minerals with TOC on a nano-scale level in both the oil and gas windows remains unknown and could serve as an interesting potential for future research.

It is hoped that this study will encourage other geologists to respect organic rich shales for the tremendous resource potential they possess. Though shales are widely abundant, making up of almost 50% of all sedimentary rocks in the geologic record, they have been largely understudied historically (Boggs, 2006). This study serves as a reminder that our sequence stratigraphic understanding of shales, especially organic-rich shales, is just as important as other classes of sedimentary rocks particularly now that they are viewed as reservoir rock.

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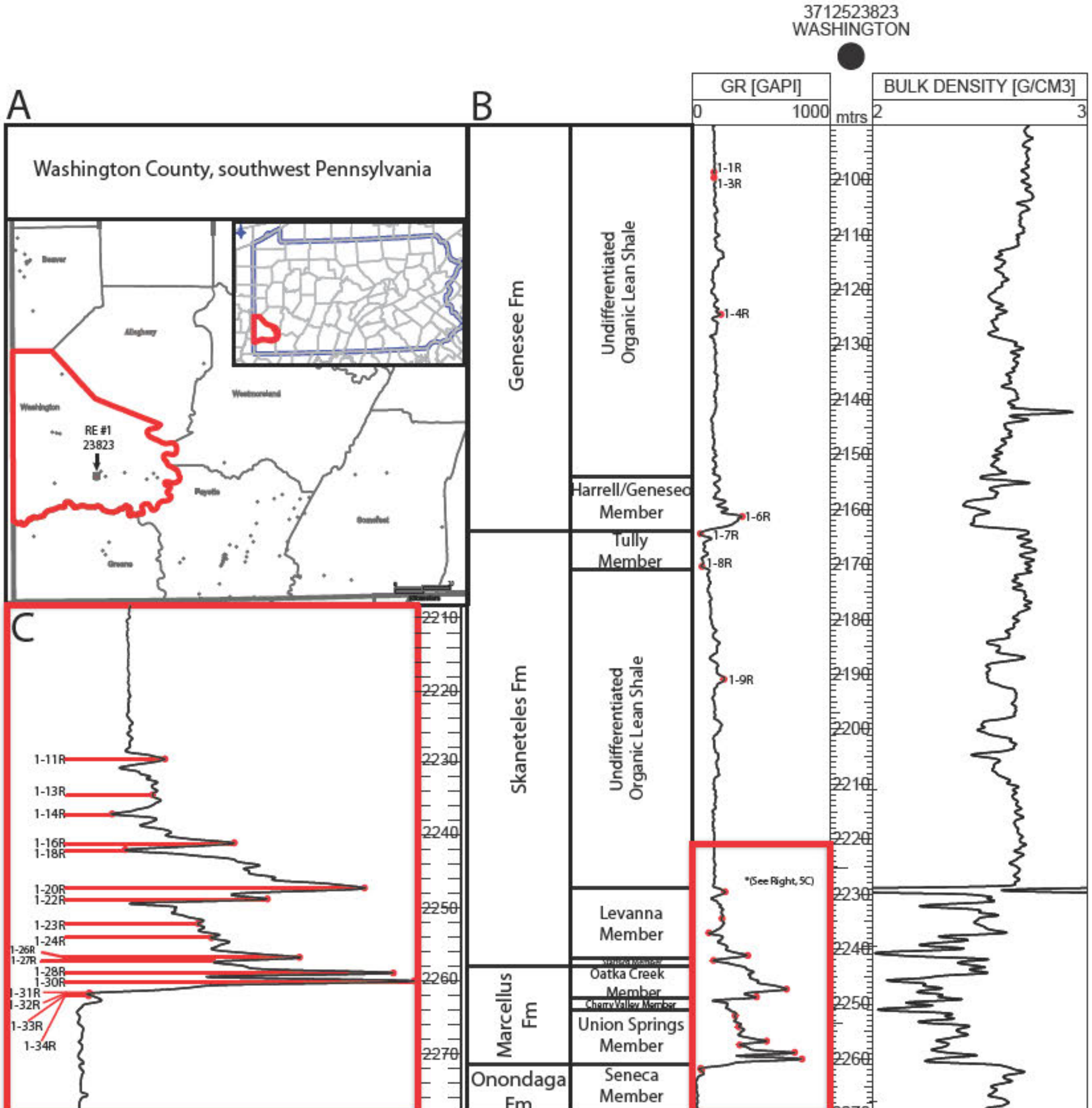
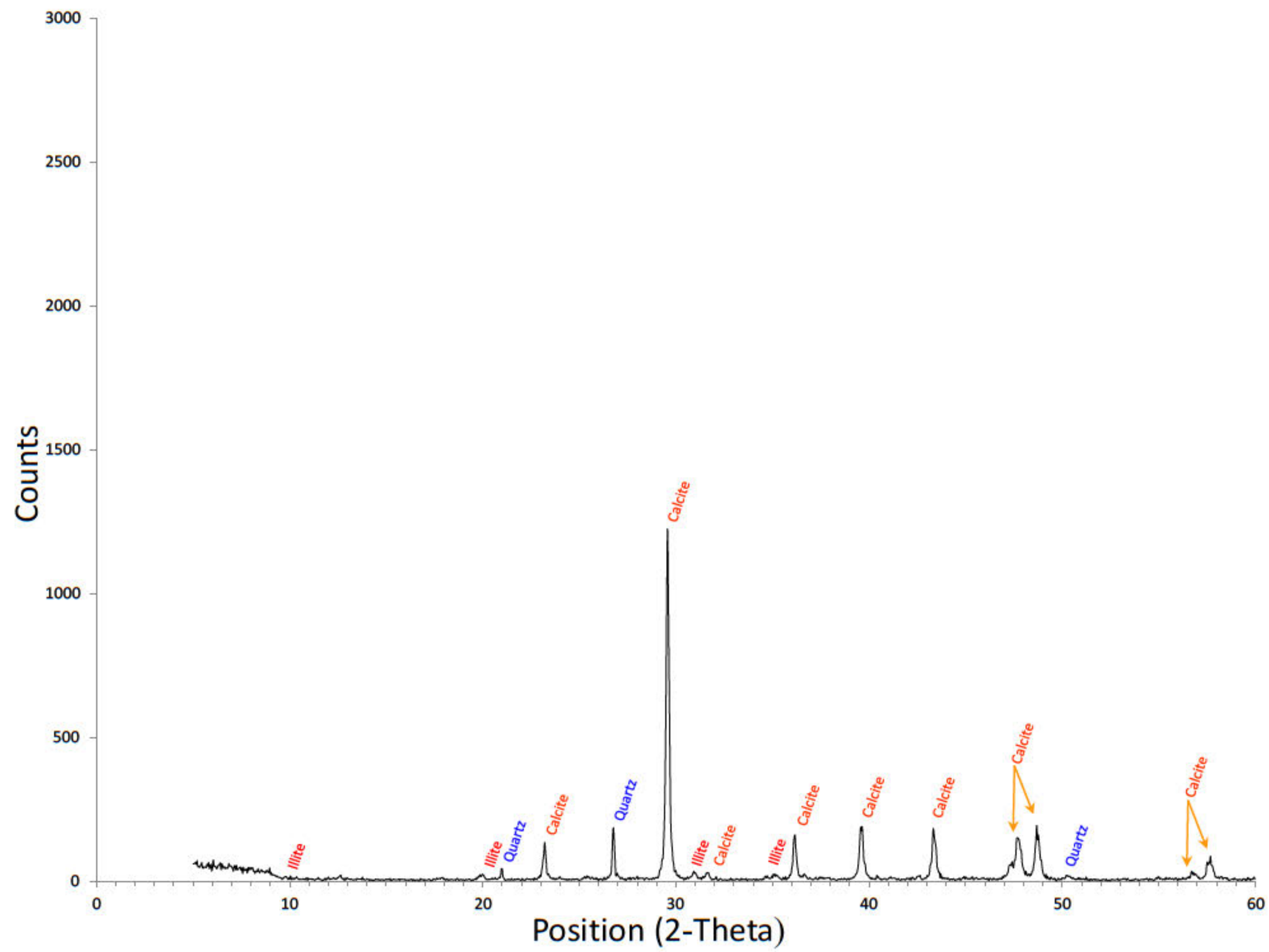
Appendix 1

X-ray Diffraction Results

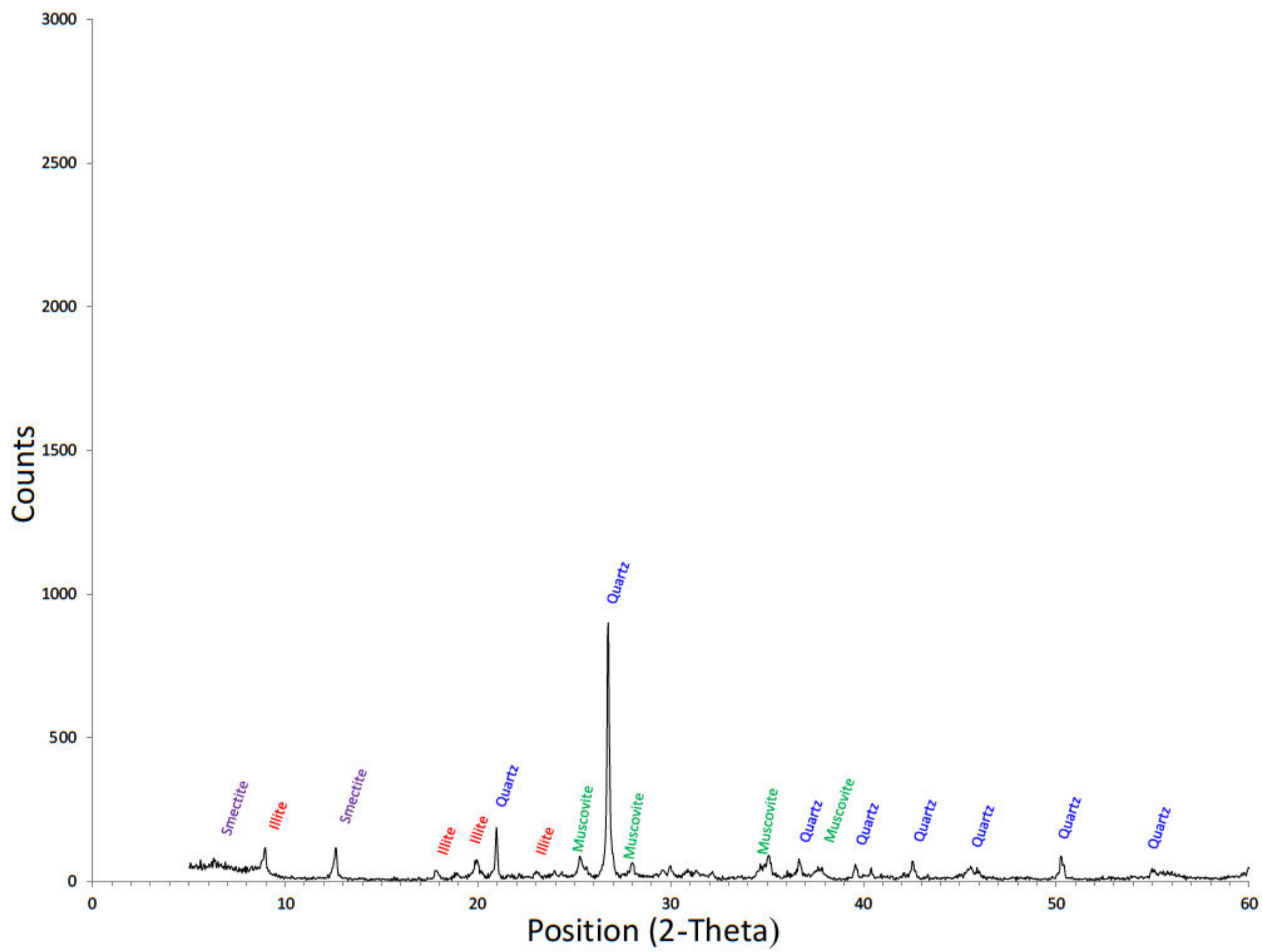


Appendix 1) Location of the RE #1, Washington County, Pennsylvania. **B)** Wireline type log of the RE #1 showing the depth at which each sidewall core was taken and its position relative to the stratigraphic section. Each red dot, on the gamma-ray curve (GR), corresponds to an x-ray diffraction data point as well as a measured TOC (weight %) value. **C)** Gamma-ray curve zoomed-in to the Marcellus Formation.

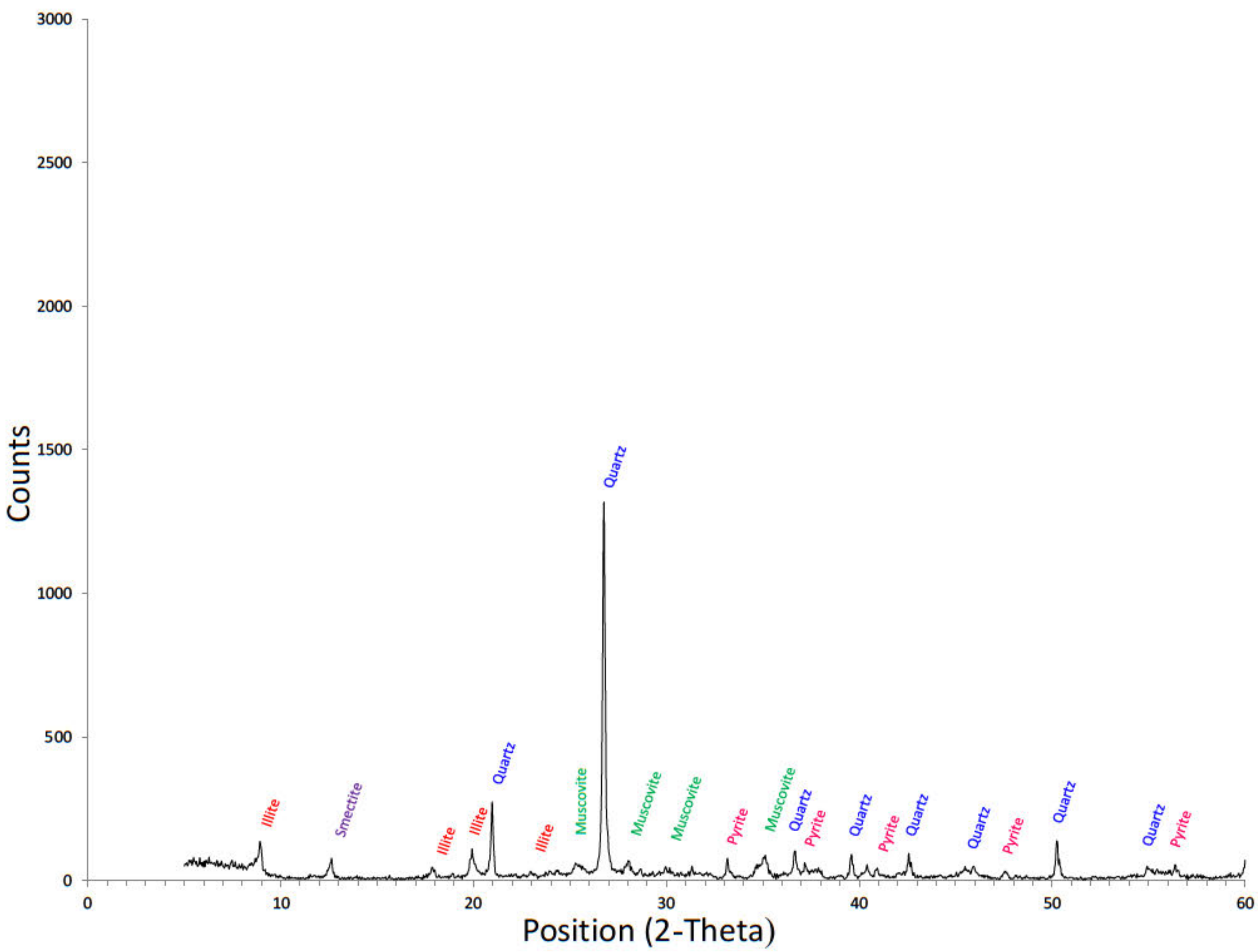
Sample 1-1R_05-60-04_2096.72 m



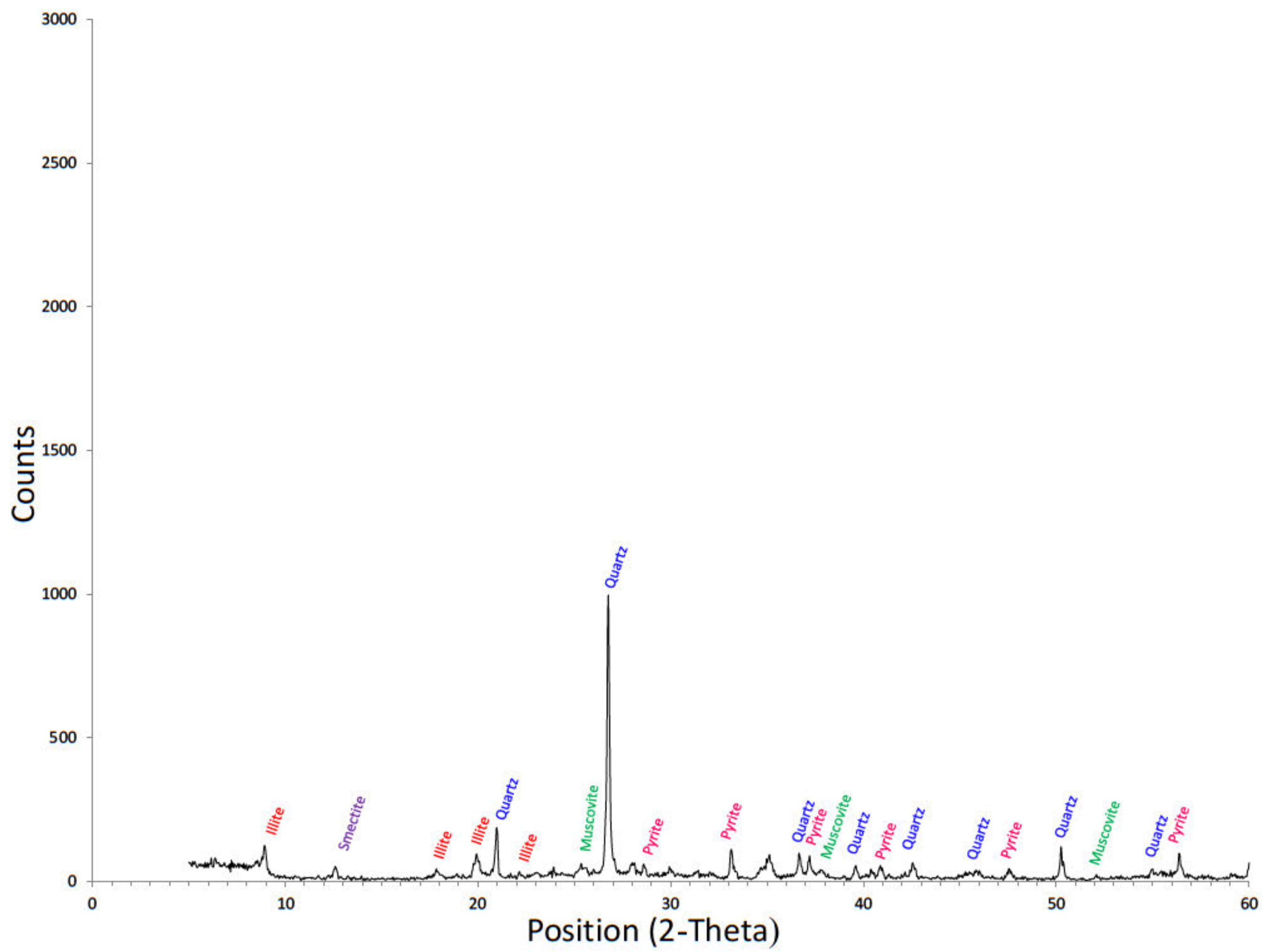
Sample 1-3R_05-60-04_2097.02 m

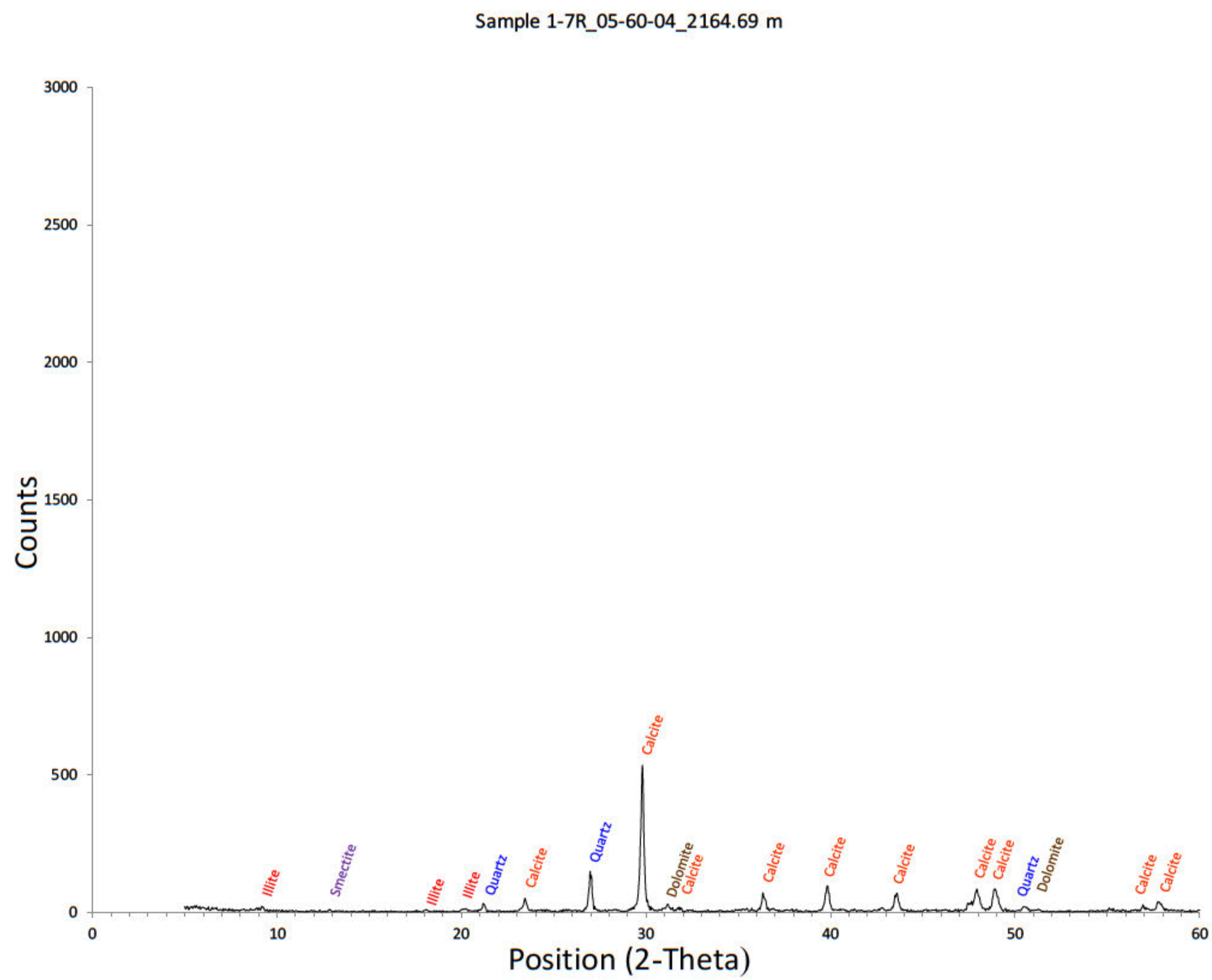


Sample 1-4R_05-60-04_2124.46 m

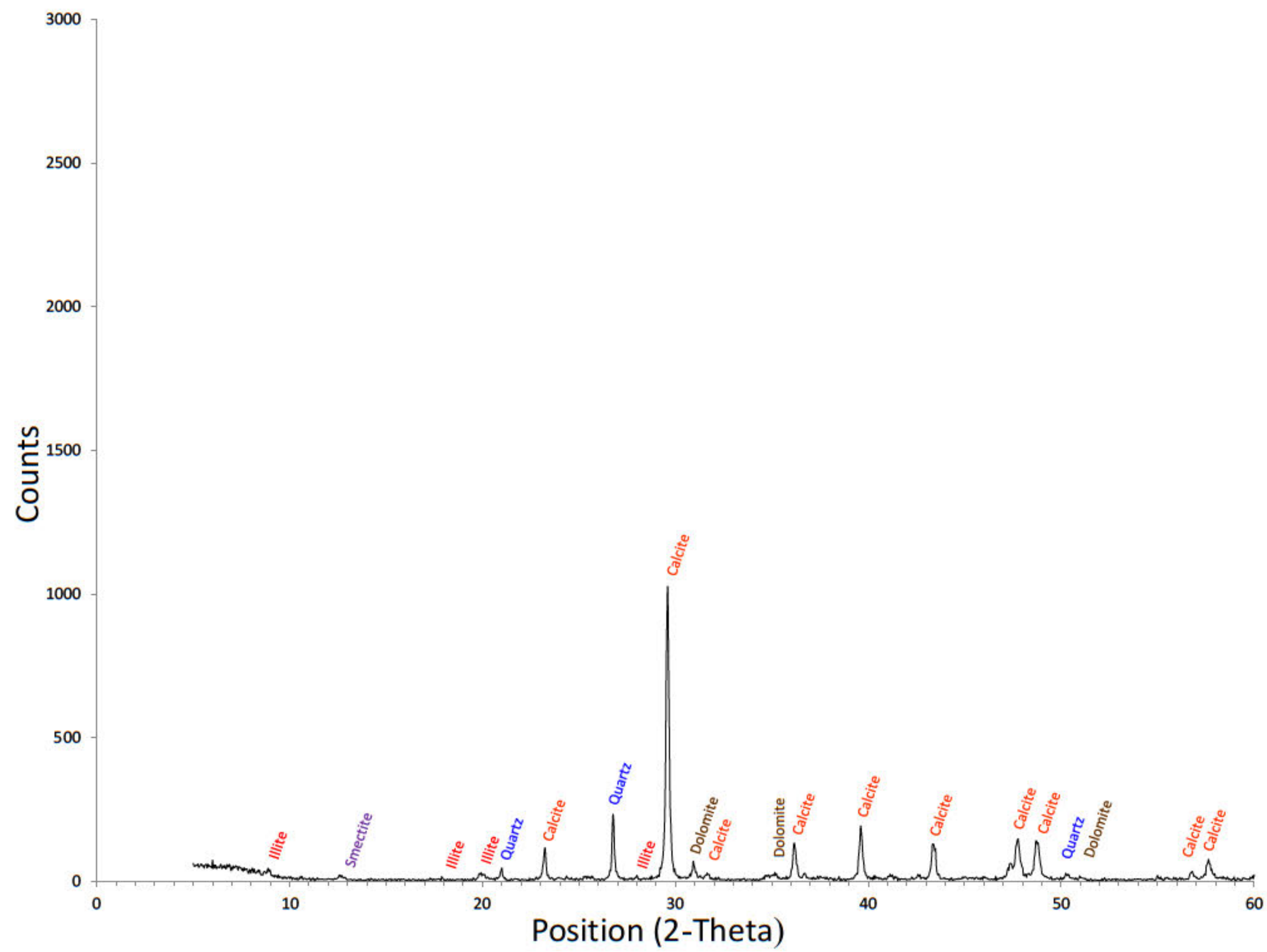


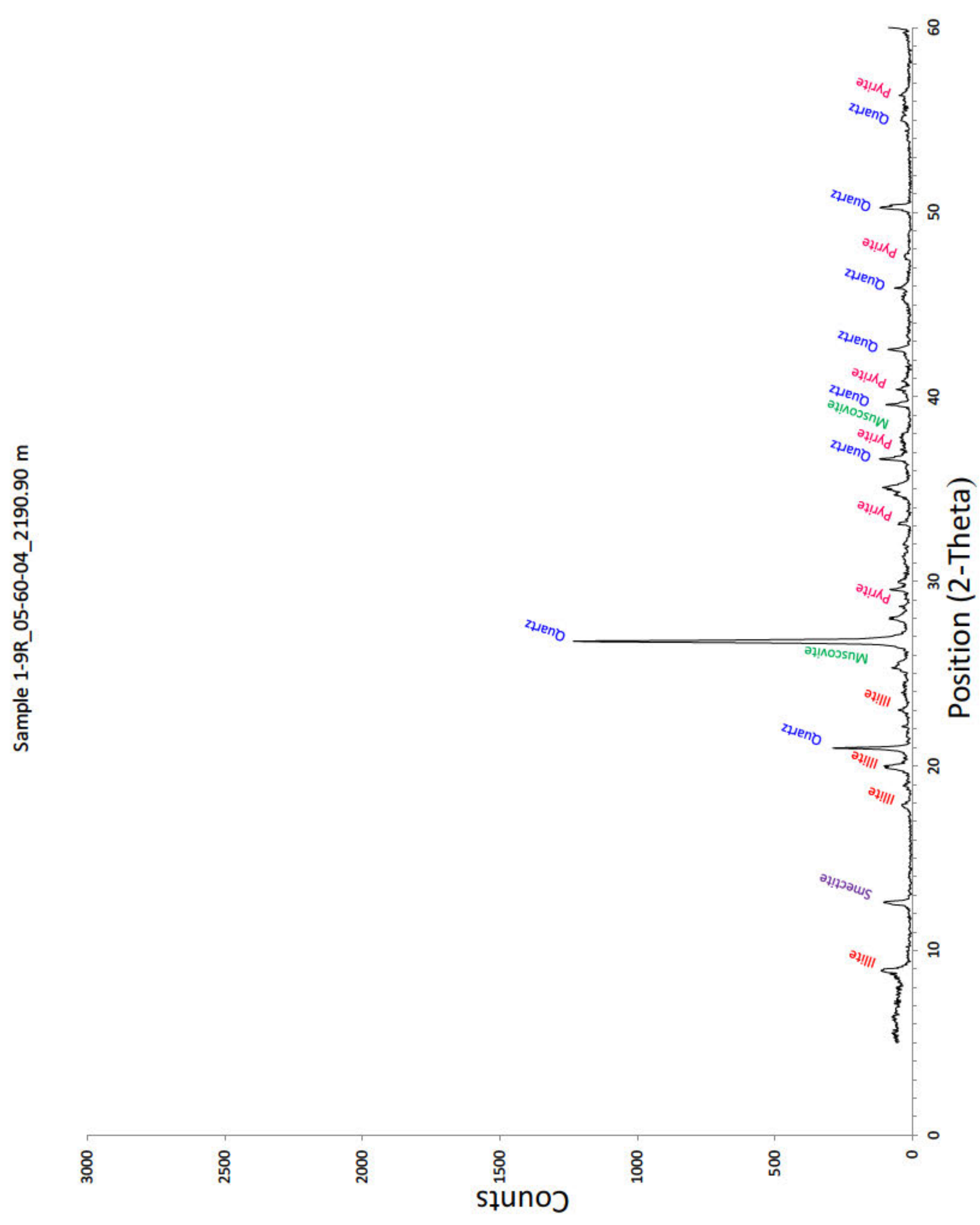
Sample 1-6R_05-60-04_2161.03 m



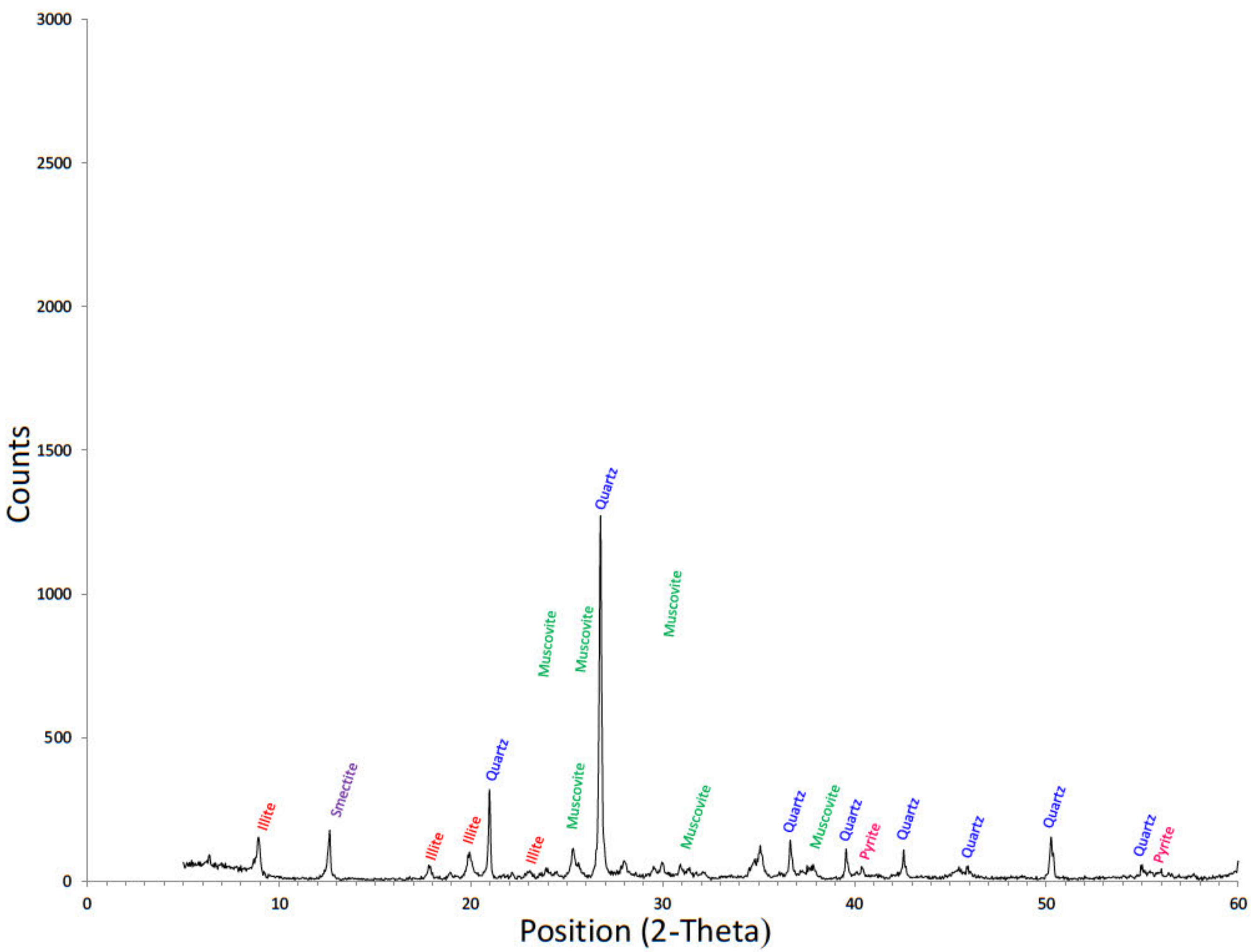

Sample 1-7R_05-60-04_2164.69 m
Counts
3000
2500
2000
1500
1000
500
0
0
10
20
30
40
50
60
Position (2-Theta)
Illite
Smectite
Illite
Illite
Quartz
Calcite
Quartz
Calcite
Dolomite
Calcite
Calcite
Calcite
Calcite
Calcite
Calcite
Quartz
Dolomite
Calcite
Calcite

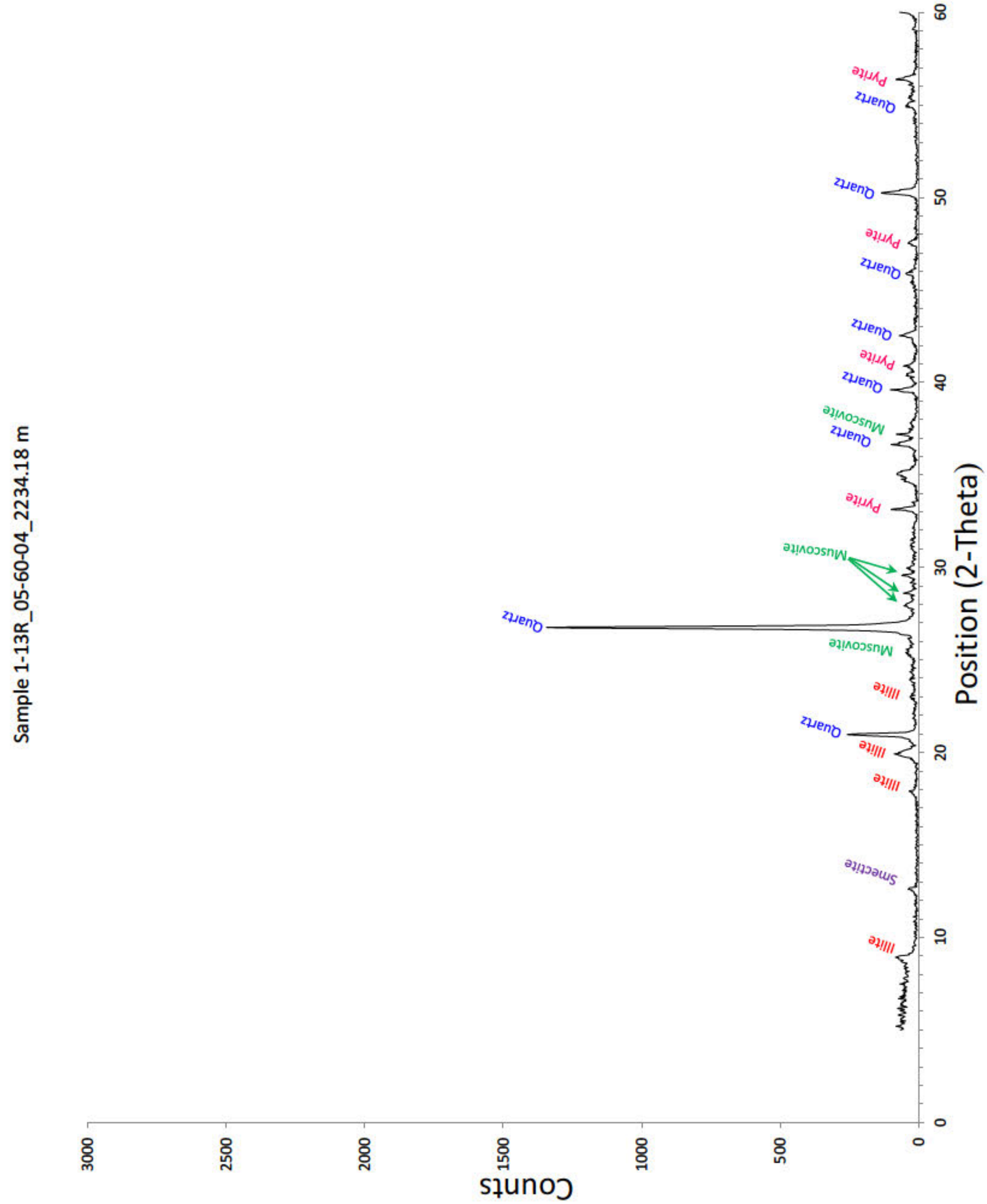
Sample 1-8R_05-60-04_2170.18 m



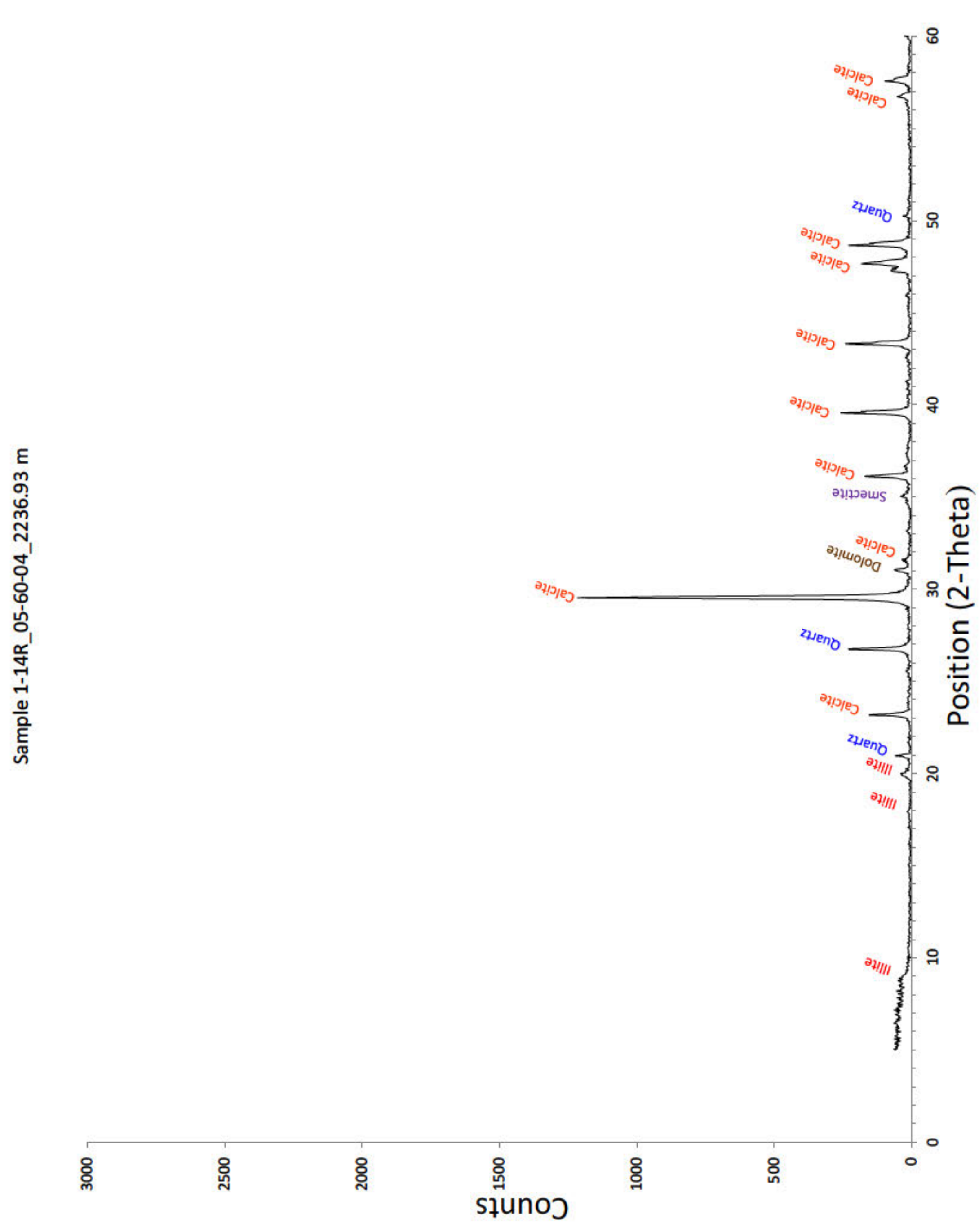

Sample 1-9R_05-60-04_2190.90 m
Counts
Position (2-Theta)
0
500
1000
1500
2000
2500
3000
10
20
30
40
50
60
Illite
Smectite
Illite
Illite
Quartz
Illite
Muscovite
Quartz
Pyrite
Pyrite
Quartz
Pyrite
Muscovite
Quartz
Pyrite
Quartz
Quartz
Pyrite
Quartz
Quartz
Pyrite

Sample 1-11R_05-60-04_2229.61 m



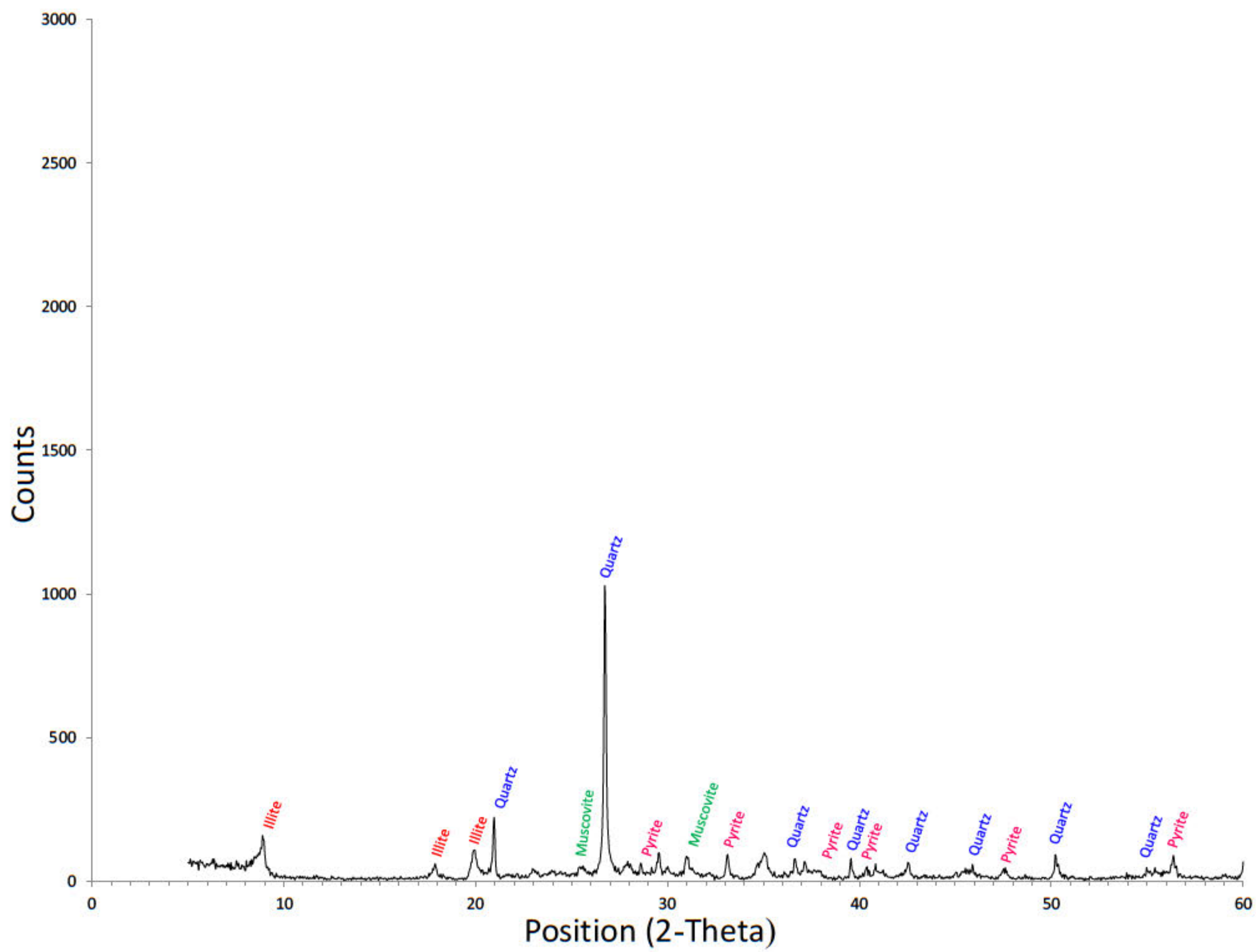


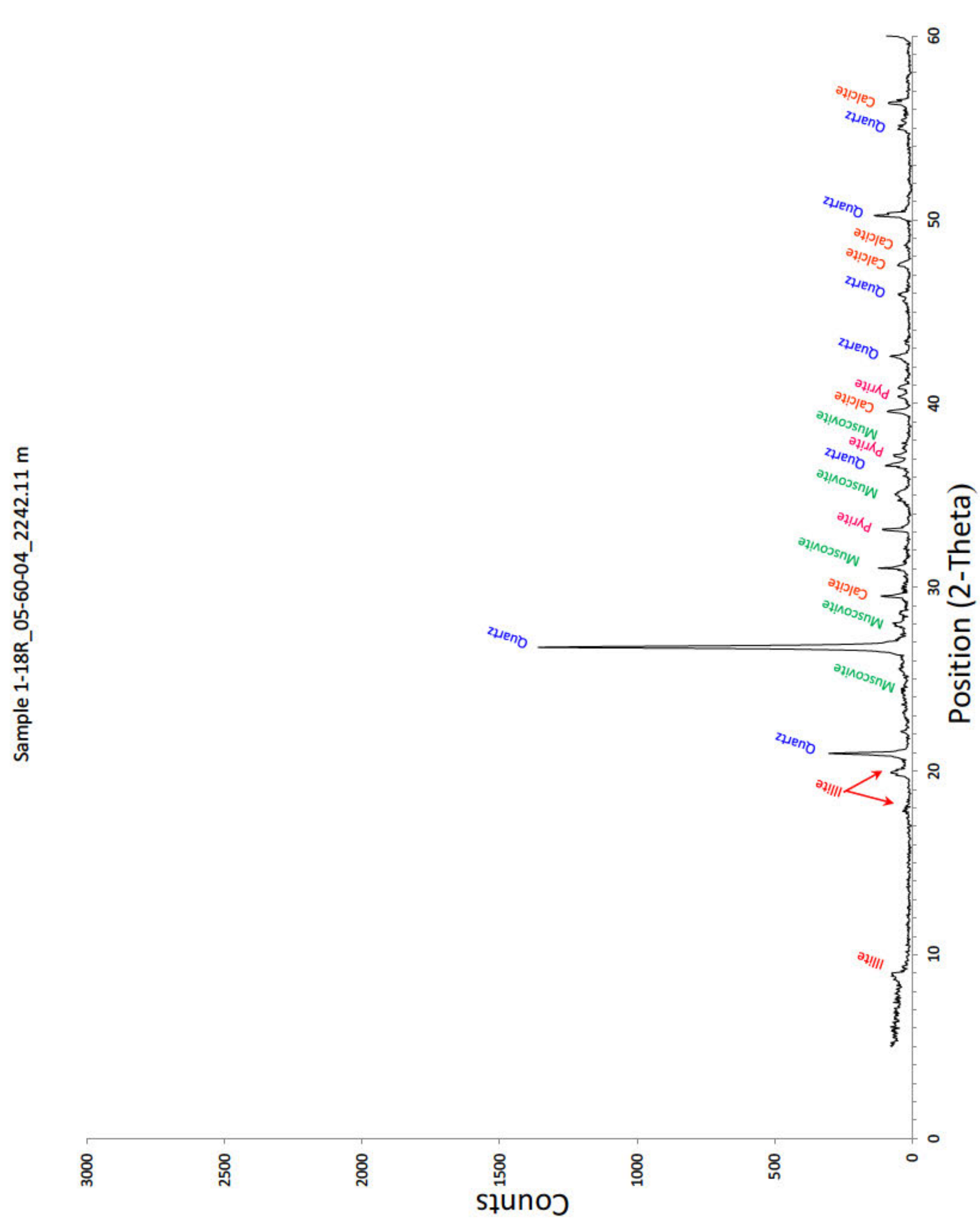
Sample 1-13R_05-60-04_2234.18 m
Counts
Position (2-Theta)
0
500
1000
1500
2000
2500
3000
0
10
20
30
40
50
60
Illite
Smectite
Illite
Illite
Quartz
Illite
Muscovite
Quartz
Muscovite
Pyrite
Quartz
Muscovite
Quartz
Pyrite
Quartz
Quartz
Pyrite
Quartz
Quartz
Pyrite



Sample 1-14R_05-60-04_2236.93 m
Counts
0
500
1000
1500
2000
2500
3000
Position (2-Theta)
0
10
20
30
40
50
60
Illite
Illite
Illite
Quartz
Calcite
Quartz
Calcite
Dolomite
Calcite
Smectite
Calcite
Calcite
Calcite
Calcite
Calcite
Quartz
Calcite
Calcite

Sample 1-16R_05-60-04_2241.19 m





Sample 1-18R_05-60-04_2242.11 m
Counts
Position (2-Theta)
0
500
1000
1500
2000
2500
3000
0
10
20
30
40
50
60
Illite
Illite
Quartz
Muscovite
Quartz
Muscovite
Calcite
Muscovite
Pyrite
Muscovite
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Pyrite
Muscovite
Calcite
Pyrite
Quartz
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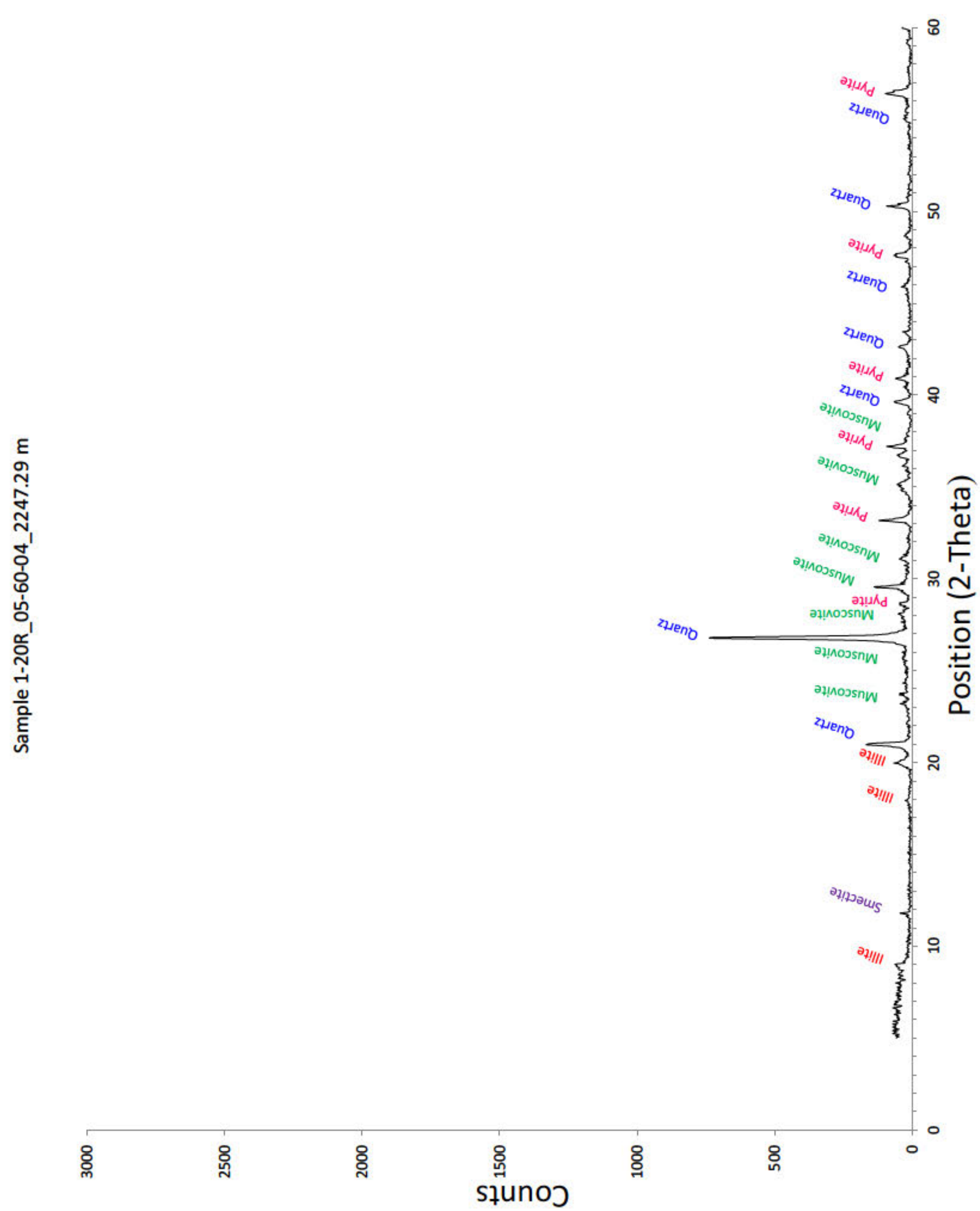
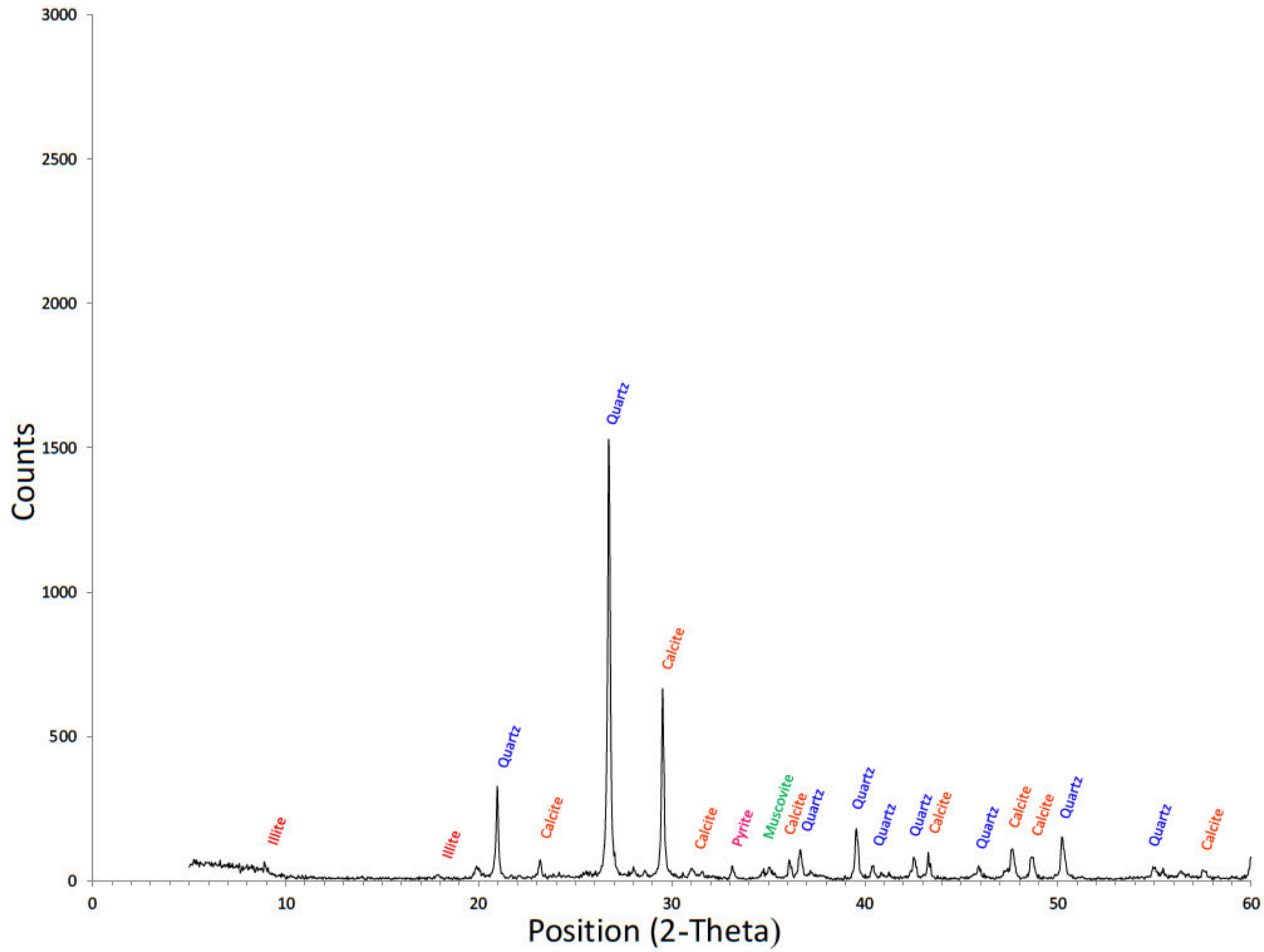
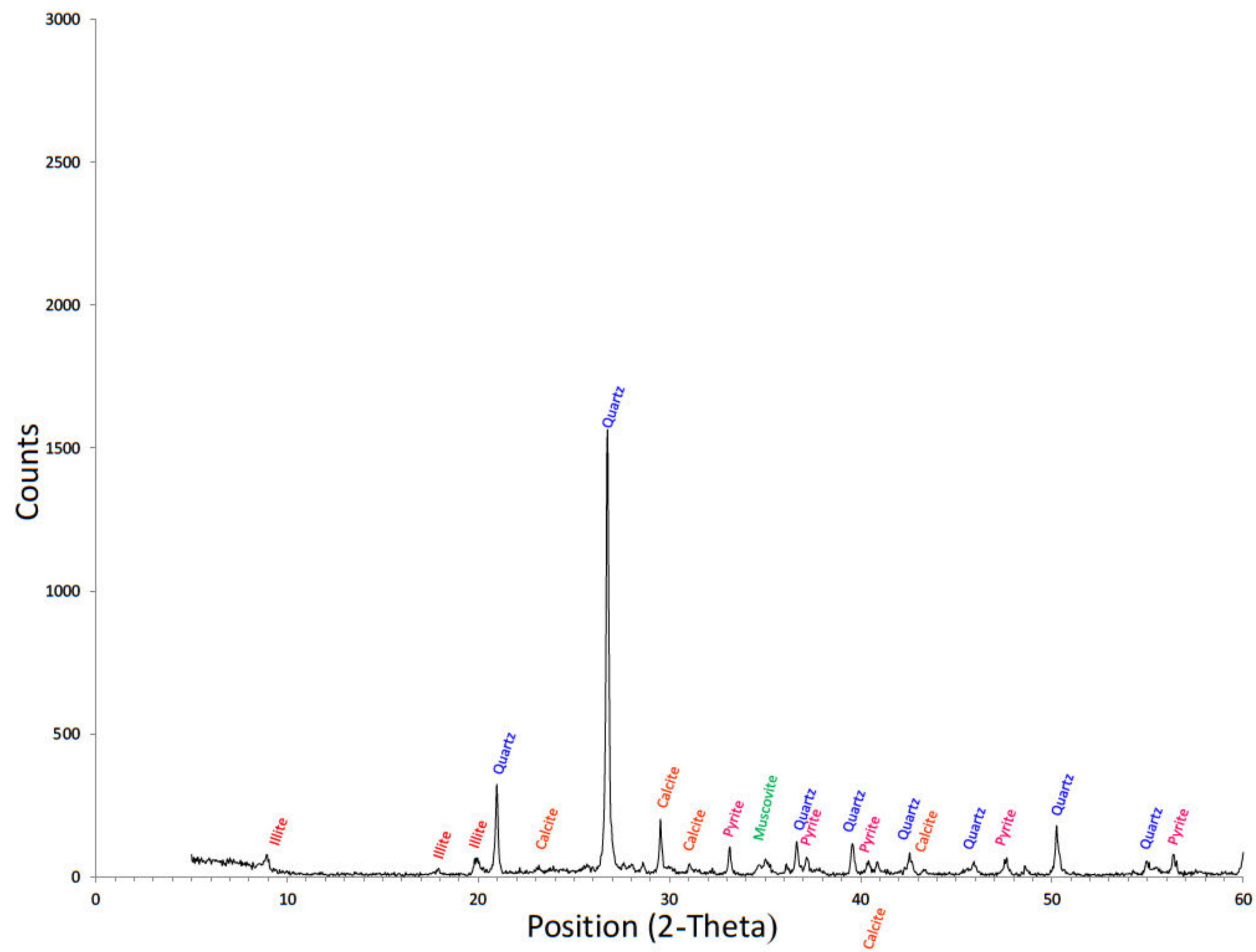
Calcite
Calcite
Quartz
Quartz
Calcite


Sample 1-20R_05-60-04_2247.29 m
Counts
Position (2-Theta)
Illite
Smectite
Illite
Illite
Quartz
Muscovite
Muscovite
Quartz
Muscovite
Pyrite
Muscovite
Muscovite
Pyrite
Muscovite
Pyrite
Muscovite
Quartz
Pyrite
Quartz
Quartz
Pyrite
Quartz
Quartz
Pyrite

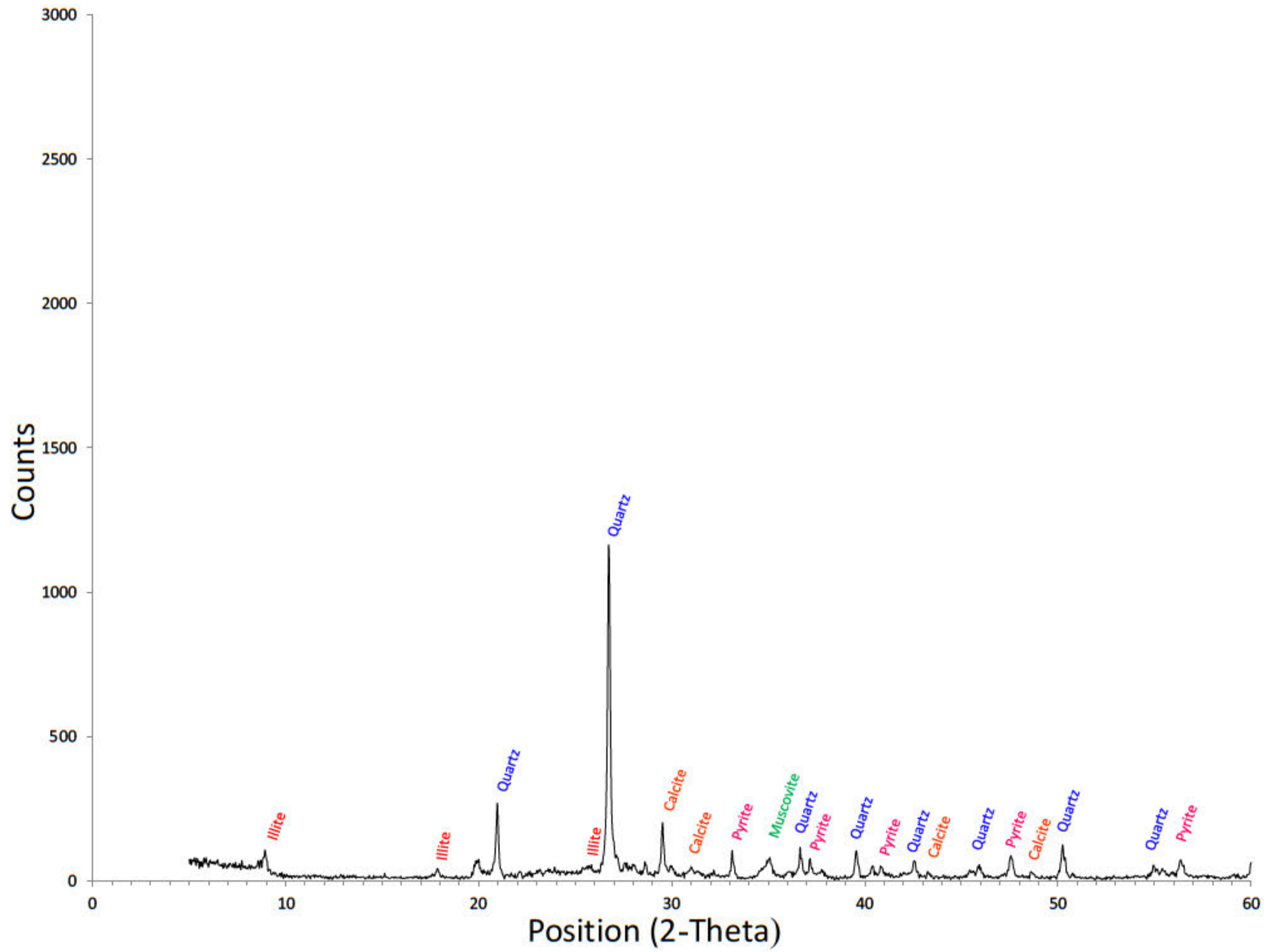
Sample 1-22R_05-60-04_2248.81 m



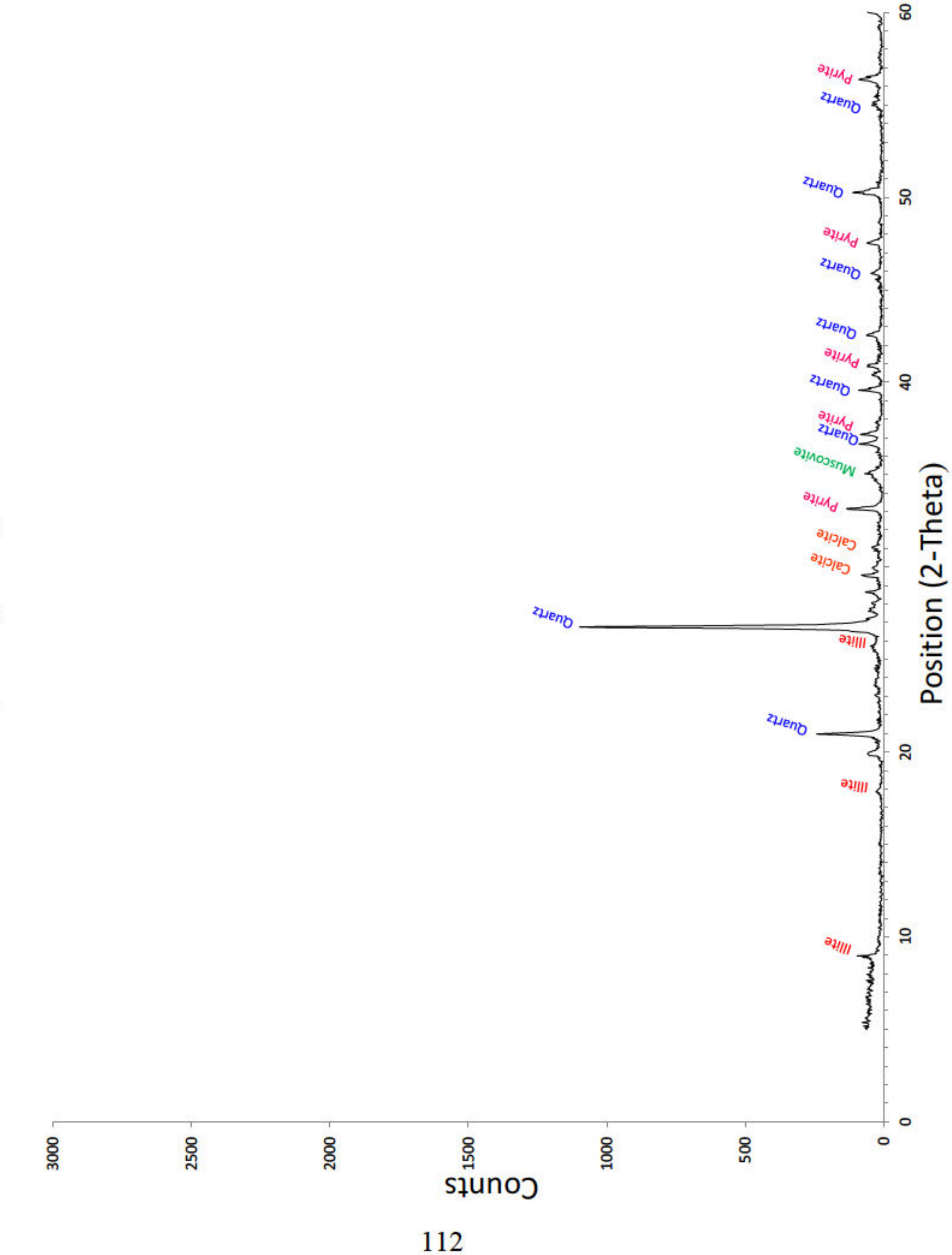
Sample 1-23R_05-60-04_2252.17 m



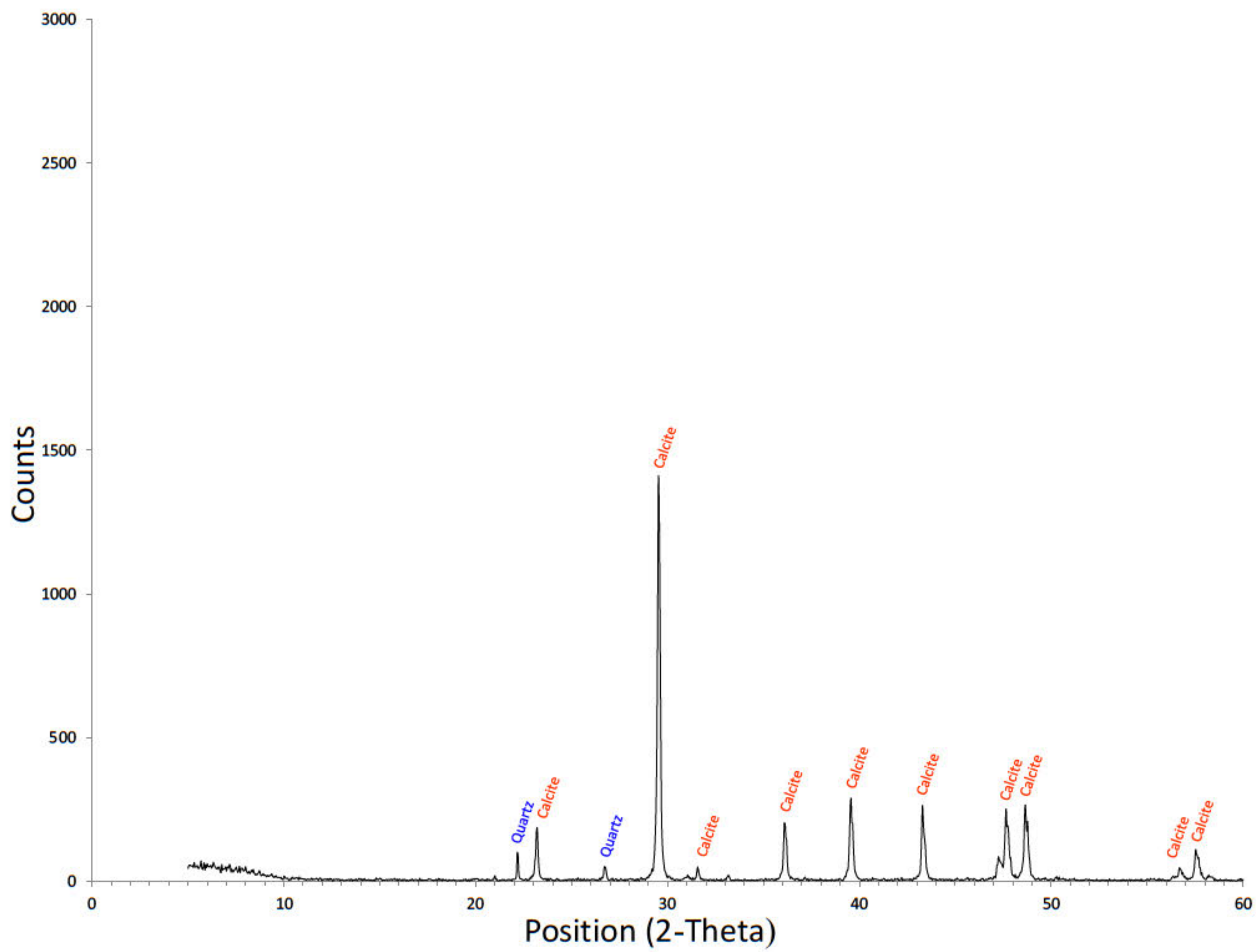
Sample 1-24R_05-60-04_2254.30 m

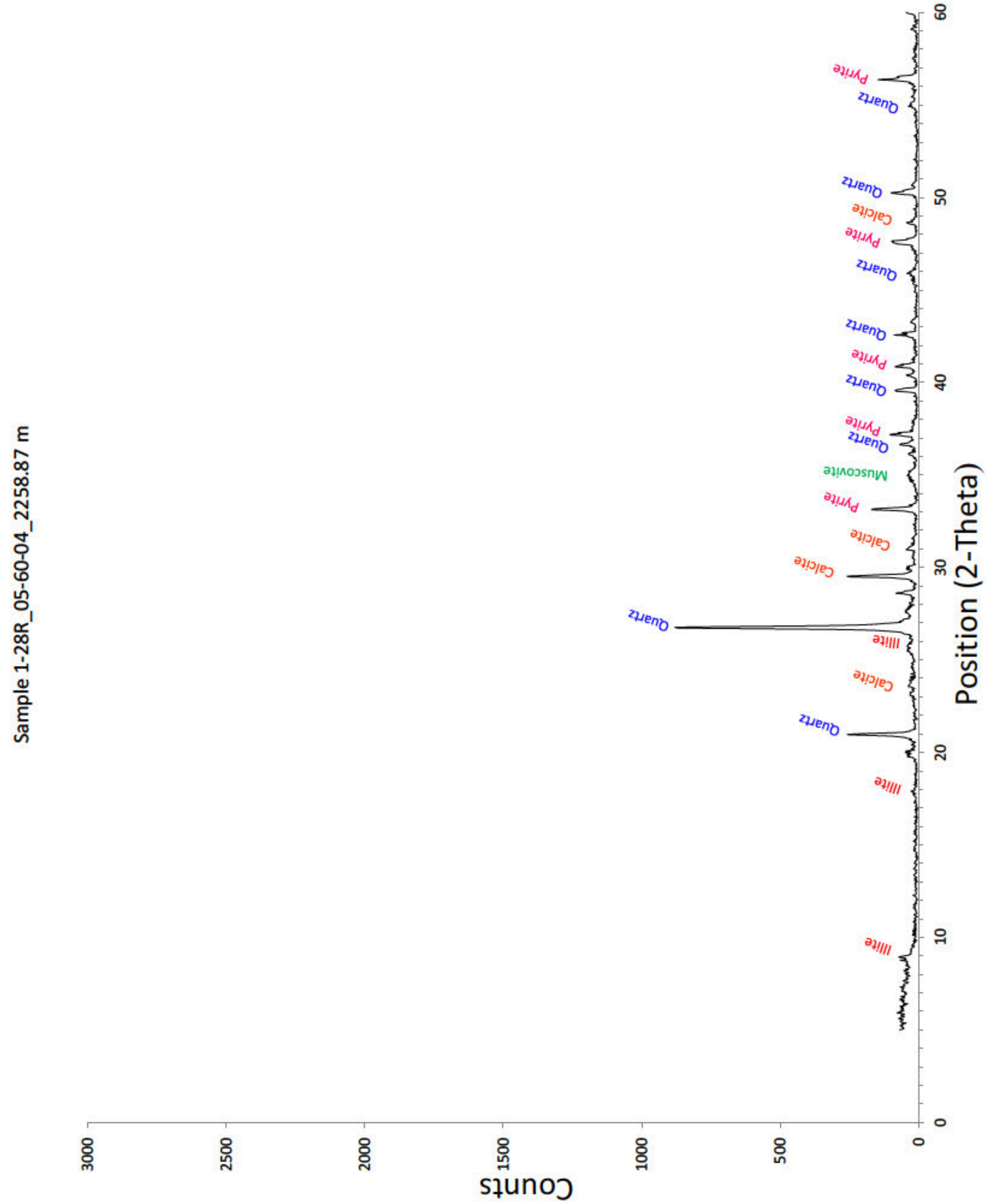


Sample 1-26R_05-60-04_2256.74 m

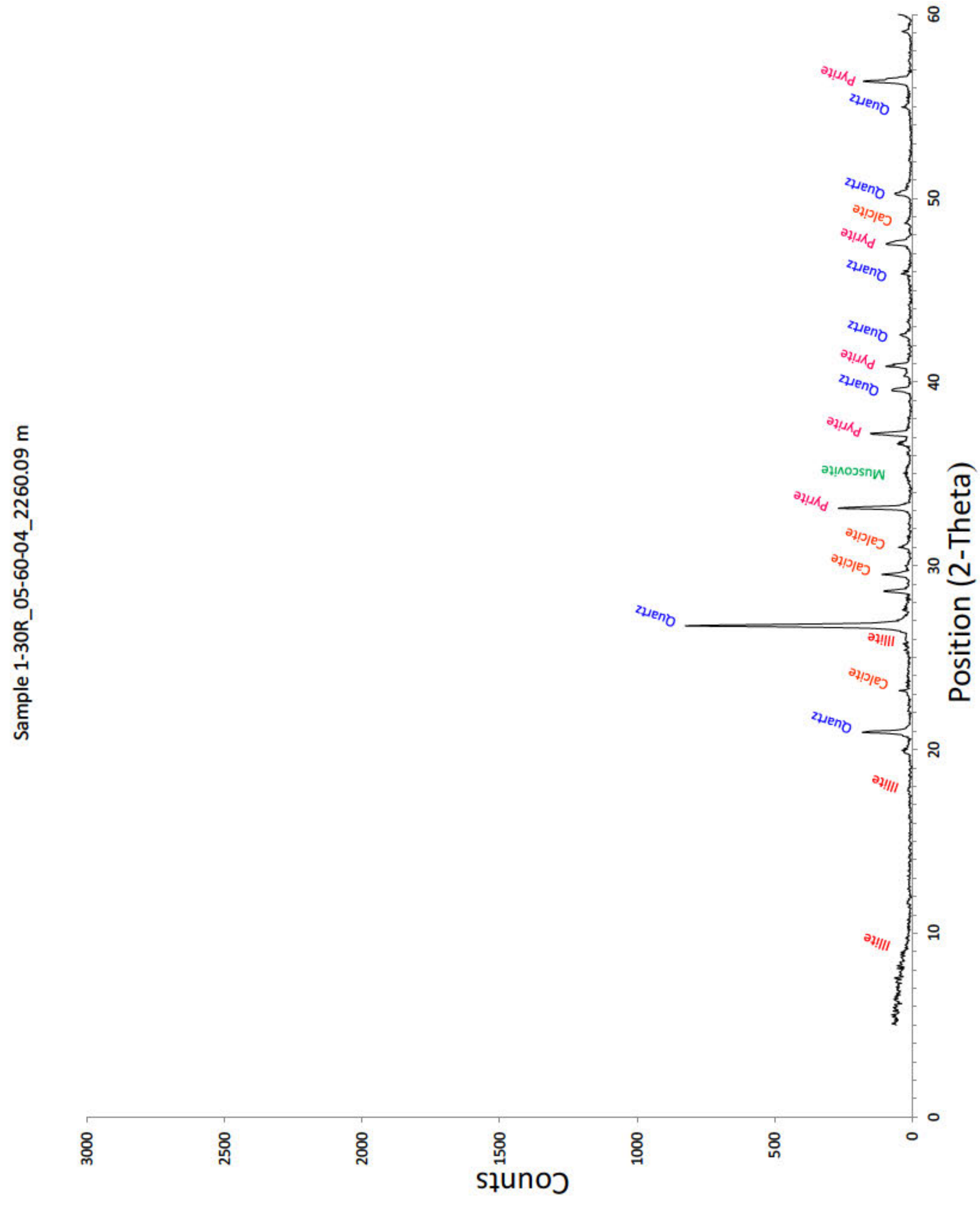


Sample 1-27R_05-60-04_2257.35 m

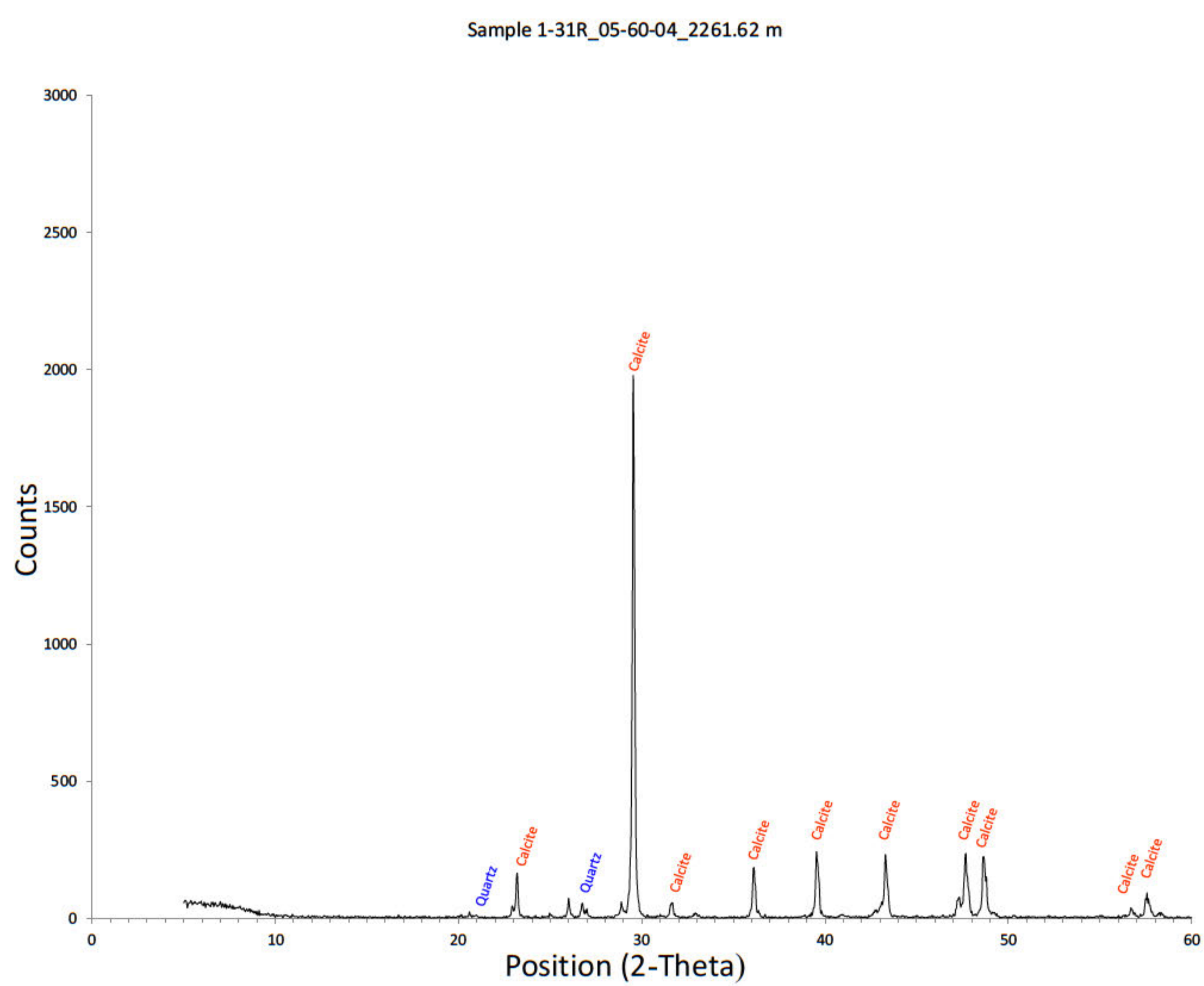




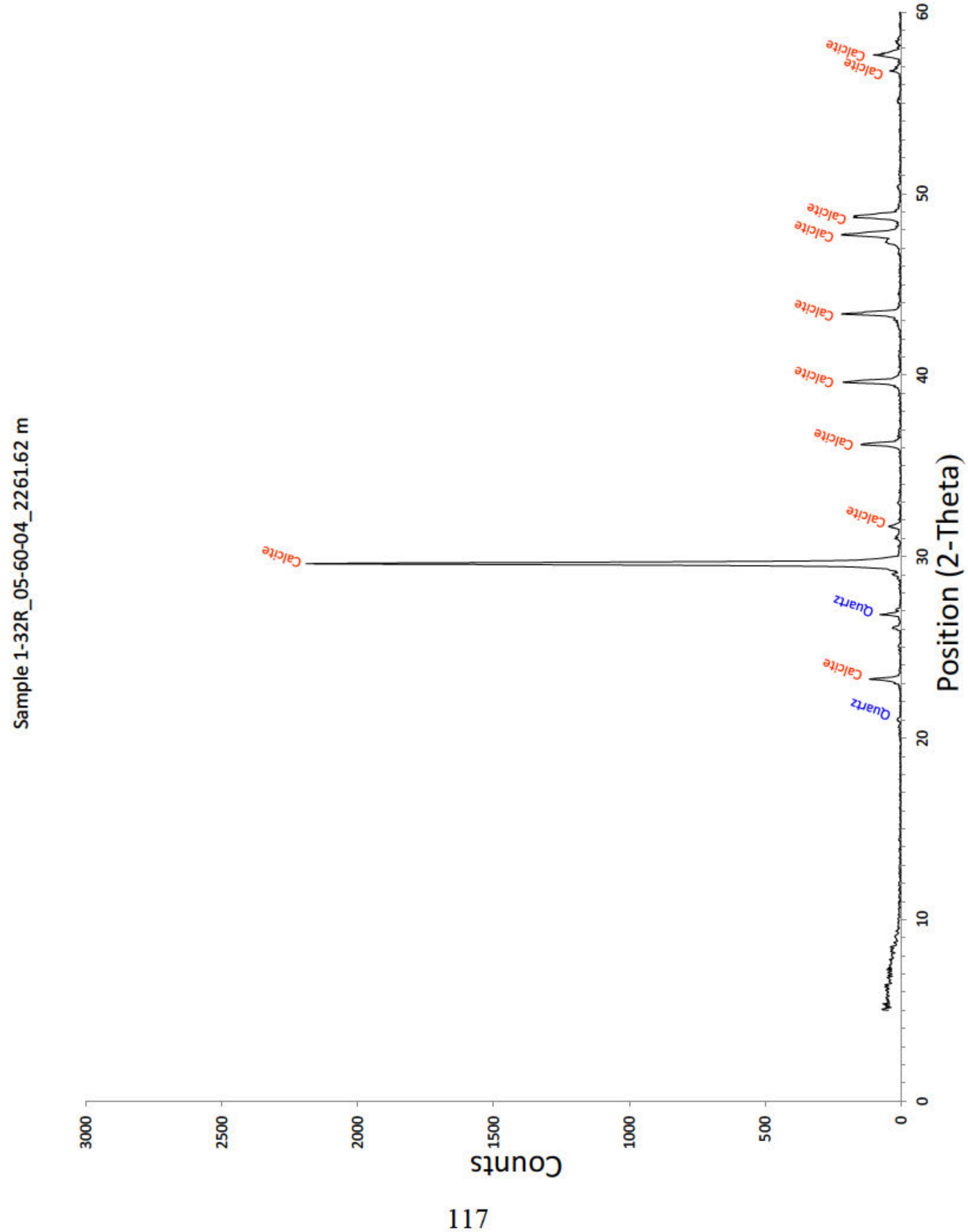
Sample 1-28R_05-60-04_2258.87 m
Counts
Position (2-Theta)
Illite
Quartz
Calcite
Illite
Quartz
Calcite
Calcite
Pyrite
Muscovite
Quartz
Pyrite
Quartz
Pyrite
Quartz
Quartz
Pyrite
Calcite
Quartz
Quartz
Pyrite

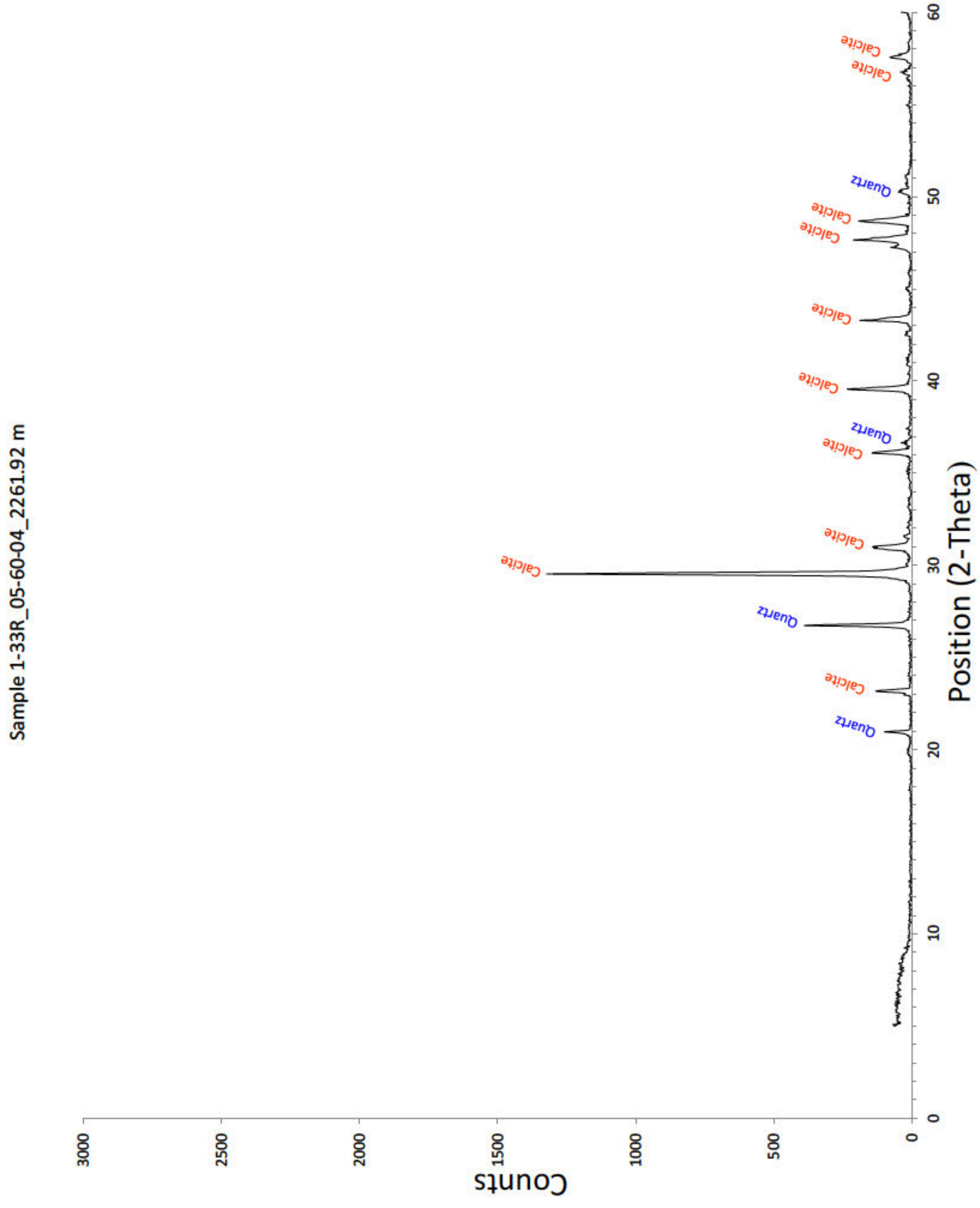


Sample 1-30R_05-60-04_2260.09 m
Counts
Position (2-Theta)
Illite
Illite
Quartz
Calcite
Illite
Quartz
Calcite
Calcite
Pyrite
Muscovite
Pyrite
Quartz
Pyrite
Quartz
Quartz
Pyrite
Calcite
Quartz
Quartz
Pyrite

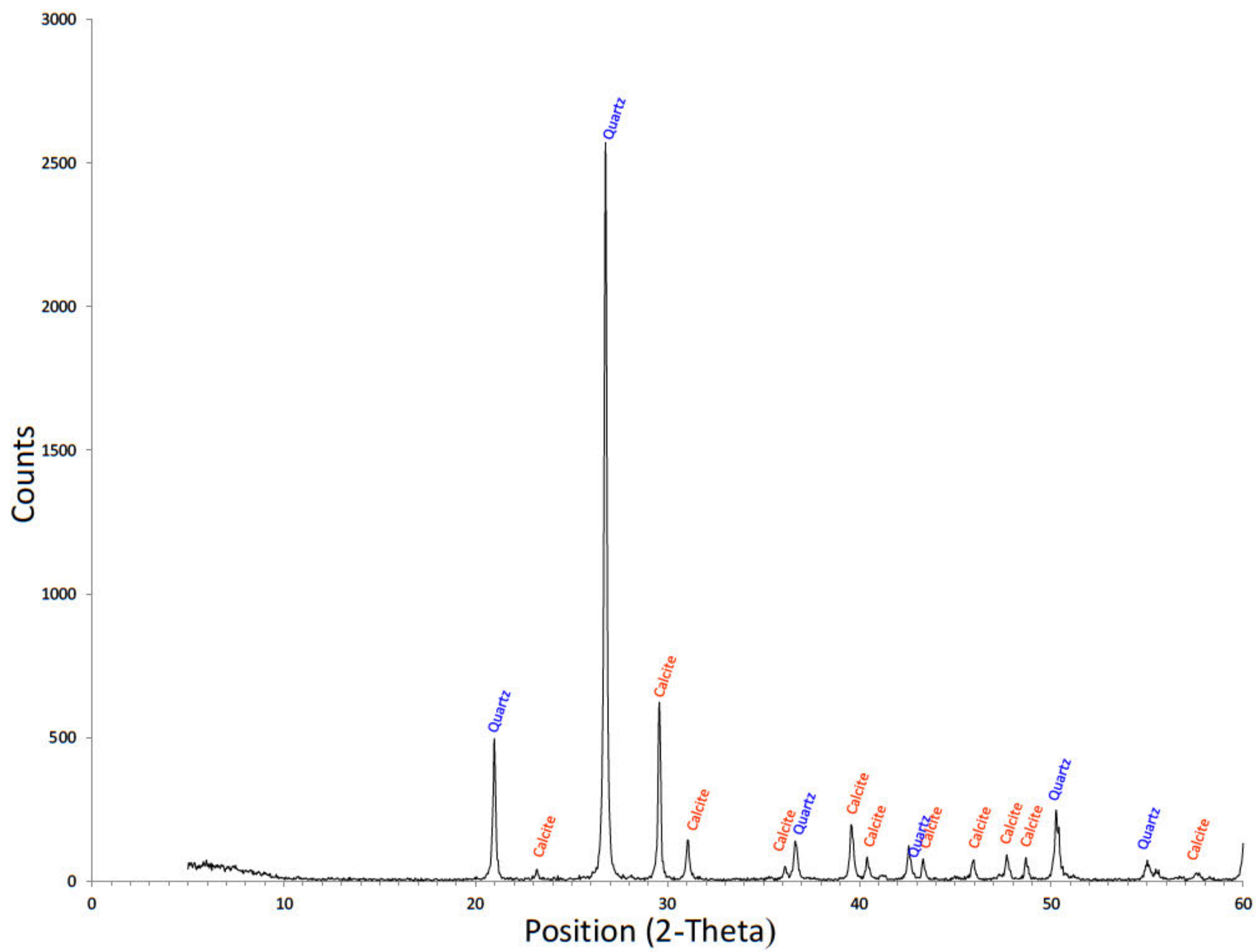


Sample 1-31R_05-60-04_2261.62 m
Counts
3000
2500
2000
1500
1000
500
0
Position (2-Theta)
0
10
20
30
40
50
60
Quartz
Calcite
Quartz
Calcite
Calcite
Calcite
Calcite
Calcite
Calcite
Calcite
Calcite
Calcite


Sample 1-32R_05-60-04_2261.62 m
Counts
Position (2-Theta)
Calcite
Quartz
0
500
1000
1500
2000
2500
3000
0
10
20
30
40
50
60

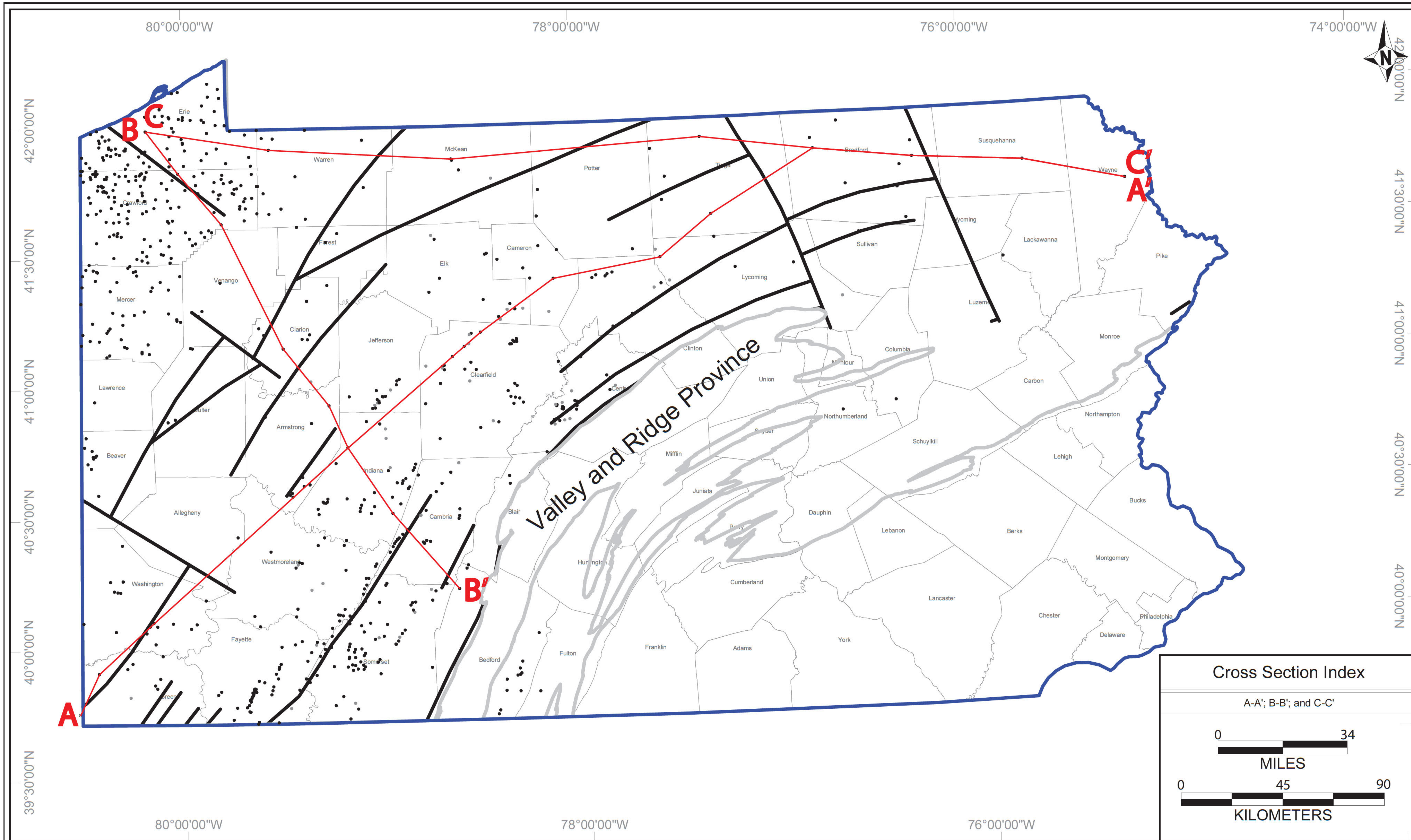

Sample 1-33R_05-60-04_2261.92 m
Counts
Position (2-Theta)
Quartz
Calcite
Quartz
Calcite
Calcite
Calcite
Quartz
Calcite
Calcite
Calcite
Calcite
Quartz
Calcite
Calcite
0
500
1000
1500
2000
2500
3000
0
10
20
30
40
50
60

Sample 1-34R_05-60-04_2261.92 m

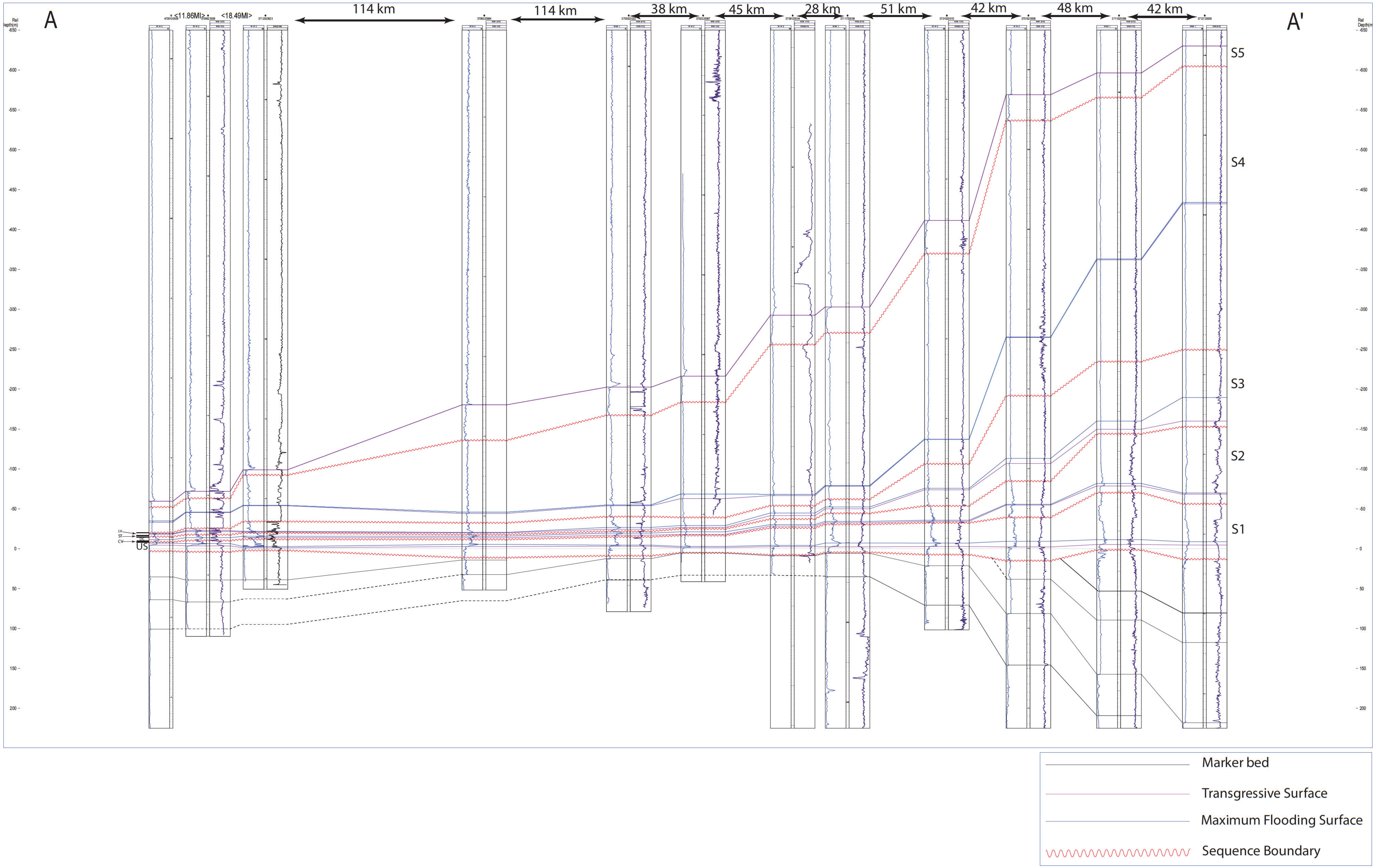


Appendix 2

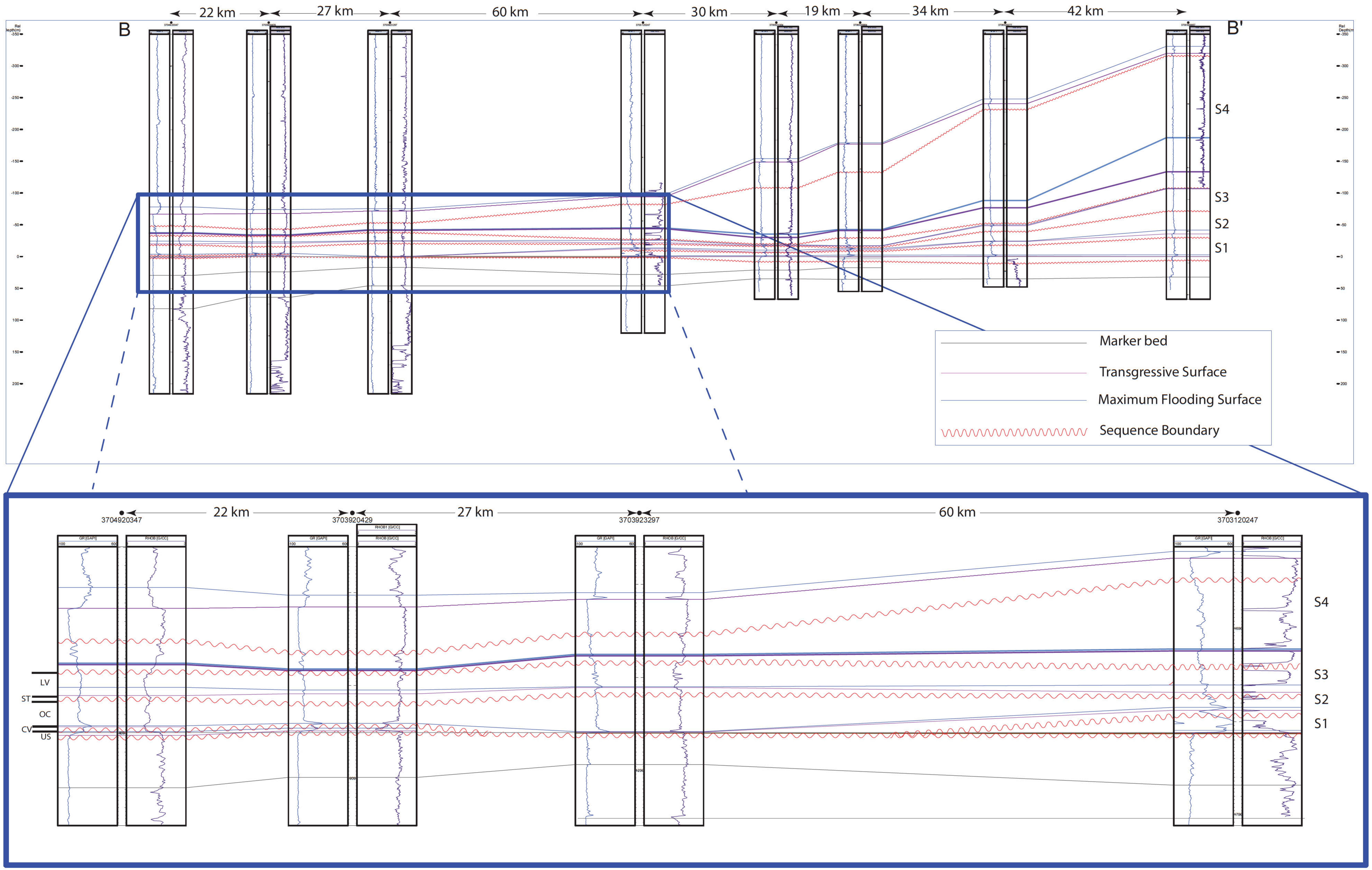
Cross Sections across Pennsylvania



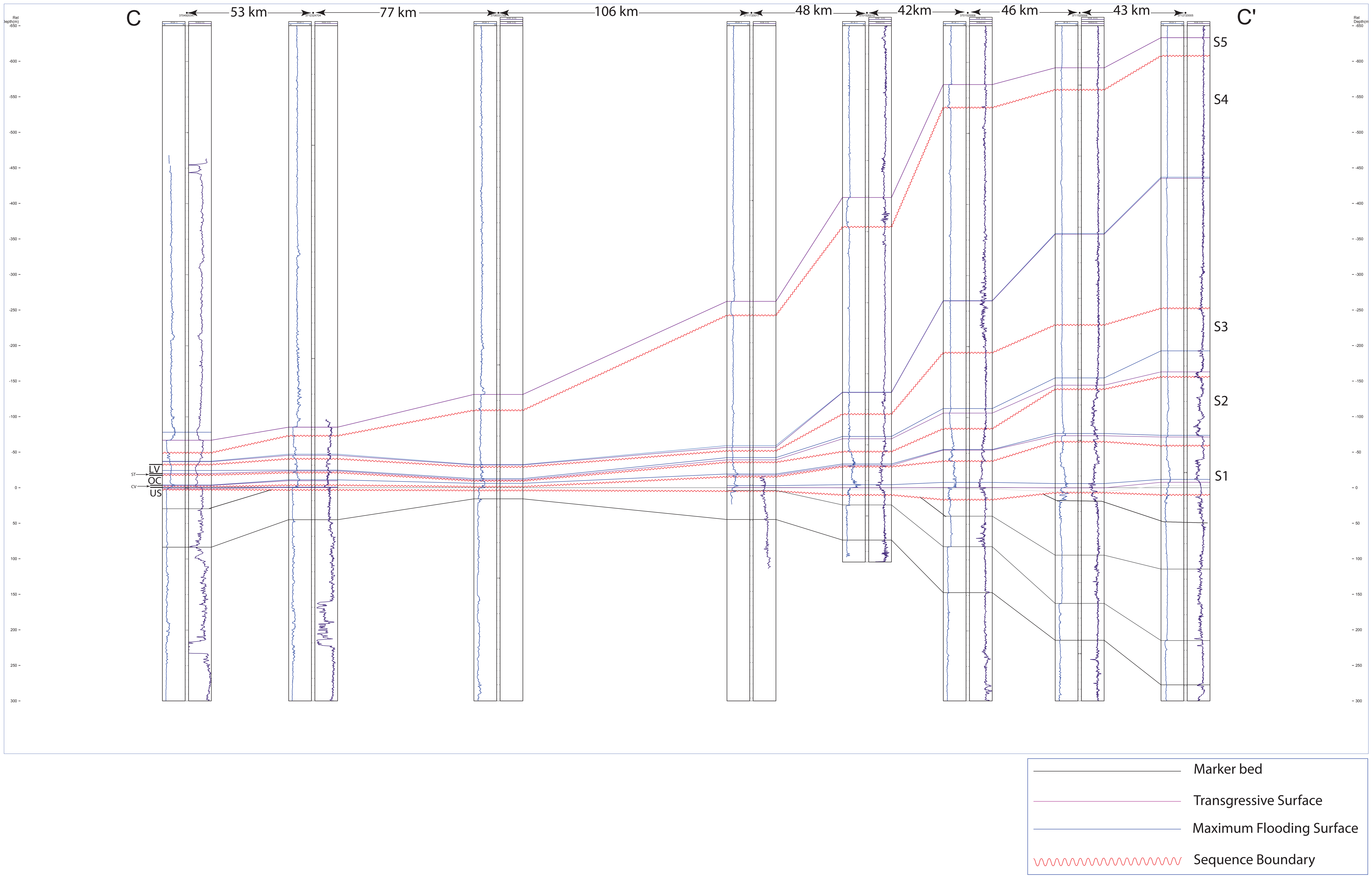
Appendix 2: Cross section index map. Well control is represented by solid black dots. Grey dots represent wells that did not penetrate and/or were not logged through sequences S1-S4. Black lines represent underlying regional basement faults (See text for discussion).



Appendix 2.1: Cross section A-A' showing thickening of all sequences (S1, S2, S3, S4, and S5) towards the eastern Acadian Thrust Front (Refer to Cross Section Index Map). This section is flattened on the Tioga B bentonite. A truncation surface below the lower sequence boundary of S1 indicates the Marcellus Formation was deposited after a regional erosion event took place. US=Union Springs Member, CV=Cherry Valley Member, OC=Oatka Creek Member, ST=Stafford Member, LV=Levanna Member.



Appendix 2.2: Cross section B-B' along dip showing thickening of all sequences (S1, S2, S3, and S4) towards the AcadianThrust Front (Refer to Cross Section Index Map). This section is flattened on the Tioga B bentonite. A truncation surface below the lower sequence boundary of S1 indicates the Marcellus Formation was deposited after a regional erosion event took place. S1, containing the Union Springs Member, shows progressive thinning due to erosion to the northwest of Pennsylvania before being completely absent in parts of Crawford and Eerie Counties placing the Oatka Creek Member (S2) disconformably on the Onondaga Formation (See text for discussion). US=Union Springs



Appendix 2.3: Cross section C-C' showing thickening of all sequences (S1, S2, S3, S4, and S5) towards the eastern Acadian Thrust Front along the New York - Pennsylvania borber(Refer to Cross Section Index Map). This section is flattened on the Tioga B bentonite. A truncation surface below the lower sequence boundary of S1 indicates the Marcellus Formation was deposited after a regional erosion event took place. S1, containing the Union Springs Member, shows progressive thinning due to erosion to the northwest of Pennsylvania before being completely absent in parts of Crawford and Eerie Counties placing the Oatka Creek Member (S2) disconformably on the Onondaga Formation (See text for discussion). US=Union Springs Member, CV=Cherry Valley Member, OC=Oatka Creek Member, ST=Stafford Member, LV=Levanna Member.