LATE-DIAGENETIC ILLITIZATION IN MISSISSIPPIAN SANDSTONES OF THE MICHIGAN BASIN

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ABSTRACT

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Abundant authigenic clay minerals (illite, kaolinite, chlorite), detrital mica grains (biotite, muscovite), and phyllosilicate-bearing lithic fragments (mudstone, phyllite) have been identified in the Mississippian age Marshall and Michigan Stray Sandstones of the Michigan Basin. These phyllosilicates were identified and analyzed with optical petrography, scanning electron microscopy, transmission electron microscopy, and X-ray diffraction. Many of these phyllosilicates exhibit morphologies and textural relationships indicating extensive alteration (replacement, partial dissolution, neoformation) resulting from changing pore fluid conditions. Illite replacement of precursor kaolinite and illite neoformation are observed. Illite cement formation typically occurs at high temperatures (deep burial), but occurs in these strata at depths shallower than most illite-bearing sandstones. This cement formation requires an external source of potassium. Multiple hypotheses have been proposed to account for this potassium. Here these hypotheses are evaluated to determine the cause of illite cement formation in these Mississippian sandstones. Illite formation is made thermodynamically possible by the transport and mixing of deep saline brines in the Michigan Basin with Marshall pore fluids. Illite crystallinity data indicate that authigenic illite formed at temperatures exceeding 200° C. Converging evidence suggests that hot brines from deeper in the Michigan Basin mixed with Mississippian formation waters to initiate kaolinite illitization and the neoformation of illite. These brines likely moved vertically along reactivated faults and fractures in the basin.

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Introduction

Diagenesis describes the suite of physical and chemical modification to sediments and sedimentary rocks after deposition (Berner, 1980). Creation and destruction of porosity from grain compaction, detrital grain dissolution/alteration, and secondary mineral precipitation/dissolution determine the present petrophysical state of the rock. Diagenesis in sandstones has long been the focus of extensive research due to the control these processes have on reservoir quality in economically significant sedimentary basins. Understanding the diagenetic history of individual strata is integral to interpreting observations and managing resources within an entire basin due to implications regarding resource generation, migration, and storage. Analysis of clastic diagenesis is a critical component of overall reservoir quality evaluation (Taylor et al., 2010), and therefore remains essential to perform. Clay cements specifically have the potential to control porosity and permeability within sandstone units by occluding pore space and restricting pore apertures (Ehrenberg, 1990).

Abundant clay cements (illite, kaolinite, chlorite), and uncommonly abundant mica grains (biotite, muscovite) have been identified within the Mississippian age Marshall and Michigan Stray Sandstones of the Michigan Basin (Stearns, 1933; Westjohn and Weaver, 1998). Illite cement in sandstones typically occurs as grain-coating cement with a characteristic fibrous morphology (Wilson and Pittman, 1977). This cement is of interest to hydrologists and geologists due to the significant impact that widespread cementation of this type typically has on permeability - potentially decreasing permeability by orders of magnitude relative to noncemented sandstones (Worden and Morad, 2003).

Previous Work on Authigenic Illite in Sandstones

Precipitation of authigenic illite has a commonly present thermal property - heat to overcome the kinetic barrier for crystallization; and a fundamental mass requirement - a supply of potassium ions to fill interlayer cation sites (Lanson et al., 2002). Previous studies have suggested the possibility of illite cement precipitation in sandstones at temperatures as low as 50° C (Bjorkum and Gjelsvik, 1988). The majority of authigenic illite, however, is believed to form at temperatures exceeding 100° C (Lanson et al., 2002). The required heat is often provided by burial beneath overburden. The geothermal gradient increases with increasing burial, so authigenic illite is more commonly observed in deeply buried strata (Lanson et al., 2002).

In many instances diagenetic illite is known to form in closed systems as the result of a reaction involving precursor kaolinite and potassium feldspar. However, the destabilization of this kaolin-K-feldspar assemblage is only thought to be possible at high temperatures (Lanson, 2002). An alternative reaction pathway for the precipitation of illite at lower temperatures was proposed by Berger et al. (1997) which involves the formation of illite from precursor kaolinite facilitated by influx into the system of high K⁺/H⁺ ratio fluid. For this reaction to proceed a critical K⁺/H⁺ ratio must be reached (Berger et al., 1997). This ratio would need to be high enough that the fluid becomes highly supersaturated with respect to illite. If this requirement is met then the fluid would also be supersaturated with respect to K-feldspar, eliminating the possibility of an internal source of potassium (Lanson et al., 2002). If an internal source of potassium is not provided it would be impossible to form diagenetic illite without a pore-fluid compositional change.

Previous Work on Study Area

Two models have been previously proposed to account for the delivery of potassium into these strata: (1) Downward percolation of meteoric water interacting with potassium bearing aluminosilicates in the overlying Michigan Formation and transporting aqueous species into underlying porous sandstones (Zacharias, 1992). (2) Transport of potassium into porous sandstones via vertical cross-formational hot brines rising along faults and fractures in the underlying units (Cox, 2015).

This study aims to evaluate the feasibility of each proposed model using a combination of clay mineralogy, petrography, and aqueous geochemical modeling. Clastic diagenetic processes are results of the interactions between minerals and pore fluids; therefore a study of such a system should aim to consider both liquid and solid components (Garrels and Mackenzie, 1971). Correlating aqueous chemical evolution with diagenetic mineralogical changes should provide the most comprehensive description of late diagenesis possible (Worden and Burley, 2003). Additionally, increased understanding of late diagenesis in these strata would contribute to community understanding of basin-scale processes in the Michigan Basin and provide further analysis of porosity and permeability in strata with the potential for fluid storage.

Geologic Background

The Michigan Basin is an intracratonic basin encompassing the Lower Peninsula of Michigan and extending into parts of Ontario, Ohio, Indiana, and Wisconsin (Fig. 1). The basin contains dominantly Paleozoic siliciclastic, carbonate, and evaporitic strata overlying Precambrian basement rock. The southernmost limb of the Proterozoic Mid-Continent Rift



Figure 1: *Geologic map of the Michigan Basin*: Geologic map of the Michigan Basin showing bedrock. Mississippian units are outlined in the key to identify units of interest. Modified from Michigan Department of Natural Resources Land and Mineral Services Division (1999).



Figure 2: *Michigan Lower Peninsula structural features*: Map Indicating the location of the Mid-Continent Rift (MCR) as well as major fault structures in the Michigan Basin and the base of the Mississippian Marshall Sandstone. From Westjohn and Weaver (1998), modified from Budai and Wilson (1991).

(MCR) runs NW-SE through the basin (Hinze et al., 1975). Structural features in the Paleozoic strata such as the Howell Anticline and the Lucas and Albion-Scipio faults (Fig. 2) are thought to be associated with fault tectonics resulting from reactivation of basement faults in the MCR (Prouty, 1988).

The kinetics of illite formation commonly require some degree of heating. Often this is accomplished by heating resulting from burial beneath overburden sediment. In the Michigan Basin the thermal history is not fully understood (Velbel, 2009). There is almost no rock record during the basin's "Lost Interval" except for minor Jurassic red-beds between Carboniferous strata below and Pleistocene glacial till above (Velbel, 2009). Cercone (1984), and Cercone and Pollack (1991) reported signs of unexpectedly high temperatures in the basin based on vitrinite reflectance data from Silurian, Ordovician, and Devonian mudstone samples, and Pennsylvanian coal samples, which could not be accounted for by overburden models alone at normal midcontinent geothermal gradients. Further evidence of anomalous heating from apatite fission tracks completed on crystalline basement core samples (Crowley, 1991; Wang et al., 1994), dolomite fluid inclusion analysis completed on Devonian samples (Luczaj et al., 2006; Cox, 2015), and geothermal modeling (Nunn and Sleep, 1984; Vugrinovich, 1988; Wagenwelt, 2015) suggests that external sources of heat (hydrothermal activity) may be required to account for the observed phenomena.

Marshall Sandstone

The Marshall Sandstone is a Lower-Mid Mississippian sandstone unit overlying the Coldwater Shale (Fig. 3). Sedimentological features and sparse fossils as well as the presence of intercalated siltstone and mudstone suggest a shallow marine depositional environmental (Harrell et al., 1991). Attempts to reconstruct the subsurface geometry of the Marshall Sandstone from



Figure 3: *Michigan Basin stratigraphic column*: Stratigraphic column indicating units in the Michigan Basin. Mississippian units of interest, the Marshall Sandstone and Michigan formation, are outlined by the red box. Modified from Ma et al. (2009).

core analysis and core-log calibration reveal a maximum thickness of 320 feet (Monnett, 1948; Adducci, 2015). Marshall thickness is at a maximum near the center of the basin, with strata thinning to a minimum thickness of 130 feet as the strata pinch out to the north, south, and west (Monnett, 1948). The Marshall consists of two formally recognized, continuous sandstone "blankets" (Fig. 4). The Lower Member ranges from sublitharenite to very micaceous (up to 61%) fine grained 30-50 ft. basal layer of litharenite based on point-count data from this study. This basal layer is not observed in every Marshall well, and the exact subsurface geometry of this layer is not well established. The Napoleon Sandstone Member (or Upper Member) is predominantly fine-medium grained sublitharenite based on point-count data from this study. The presence of metamorphic phyllitic-schistose lithic fragments combined with evidence from detrital zircon signatures suggest metamorphic provenance of detrital grains likely originating from Carboniferous Appalachian highlands (Boothroyd, 2012).

Michigan Formation

The Upper Mississippian Michigan Formation overlies the Marshall Sandstone. Lithologies include interbedded mudstone, limestone, dolomite, gypsum, anhydrite, and a basal layer of sandstone lithologically identical to the Napoleon Sandstone and referred to informally as the "Michigan Stray" sandstone. The Michigan Stray sandstone occurs as interfingering deposits of sand, the maximum thickness of which is 70 feet (Monnett, 1948). The geometry of the Michigan Stray varies considerably throughout the basin, and at present there is no agreed upon interpretation for these thickness variations. Differentiation of the Michigan Stray from the Marshall is a subject of debate in the Michigan Basin geological community. The basis for this distinction is the presence of the "Stray Dolomite", a band of dolomite within the Michigan Formation that separates the Napoleon Sandstone from the Michigan Stray (Monnett, 1948). The



Figure 4: *Michigan Basin Mississippian stratigraphic column*: Detailed stratigraphic column of Mississippian rocks in the Michigan Basin. Not every member/unit identified in the stratigraphic column will be present in a given well because of the subsurface geometry of particular members.

most recent sedimentological interpretation of the Michigan Stray is that it is genetically related to the Marshall Sandstone (Adducci, 2015); it is for this reason included in this study. The occurrence of evaporites in the Michigan Formation indicates a transition of the Michigan Basin from shallow open marine to a partially closed sabkha environment (Harrell et al., 1991).

Clay Mineral Background

Illite

Illite is a 2:1 non-swelling dioctahedral potassium-bearing clay mineral (Środon and Eberl, 1984) with the general mineral formula:

(K)_{0.6-0.9}(Al,Fe,Mg)₂(Si,Al)₄O₁₀(OH)₂

The 2:1 structure of illite consists of two tetrahedral aluminosilicate sheets sandwiching one dioctahedral sheet with potassium ions in interlayer cation sites in order to balance the otherwise negative layer charge (Fig. 5). The amount of potassium in the mineral formula may vary due to changes in the charge of the 2:1 layer resulting from the varying cation substitution in the 2:1 layer.

Illite is commonly represented in reactions and thermodynamic problems as muscovite (another dioctahedral phyllosilicate). Pure muscovite has a layer charge of one, which comes from the 1:3 Al:Si ratio in tetrahedral sheets and octahedral sheets that are populated entirely with Al^{3+} . Muscovite represents the trisilicic endmember of the trisilicic-tetrasilicic series of dioctahedral micas, with the tetrasilicic endmember being celadonite (Eslinger and Pevear, 1988), which contains no Al^{3+} . Muscovite is chosen as the representative mineral for illite because of the Al^{3+} in the crystal structure of illite. However, illite has the capability to contain



Figure 5: *Illite mineral structure*: Hybrid polyhedral and ball-and-stick structural model of illite. Octahedral sheets are sandwiched between tetrahedral sheets. Interlayer cations show the location of potassium in the structure. Modified from Gualtieri et al. (2008).

divalent Fe²⁺ and Mg²⁺ cations in octahedral sites as well. Illite containing significant divalent substitution in octahedral sites would more closely resemble phengite, the midpoint mineral in the trisilicic-tetrasilicic dioctahedral mica series (Eslinger and Pevear, 1988). Phengite has a mineral formula (Bailey, 1980):

$$K(Al_{1.5}(Mg,Fe)_{0.5})(Al_{0.5}Si_{3.5})O_{10}(OH)_2$$

This strict formula more closely approximates illite than muscovite does. The difference between illite and phengite is the lower layer charge of illite, which is achievable by either decreasing the amount of divalent substitution in octahedral sheets or increasing the amount of Si⁴⁺ in tetrahedral sheets.

Illite is commonly a major component of detrital mudrocks, but it also occurs in sandstones as a detrital component or grain-coating cement (Wilson and Pittman, 1977). Diagenetic illite forms by way of one of two reaction mechanisms: transformation or neoformation. Transformation is a type of alteration common in phyllosilicate minerals in which a precursor mineral alters to a secondary mineral through the direct incorporation and reuse of part of the structure of the precursor mineral (Segonzac, 1970). Neoformation refers to the creation of a secondary mineral via dissolution of the primary mineral followed by subsequent crystallization of the secondary mineral with its own unique structure (Eberl, 1984). Neoformation of fibrous cements is common in clastic units containing abundant porosity, especially those with saline pore fluid (Meunier and Velde, 2004). Neoformation is the dominant mechanism of illite formation in sandstones; however, both mechanisms have been found to occur in these units.

Authigenic illite of transformation origin typically forms from a precursor clay mineral, usually either smectite or kaolinite (Machhi, 1987; Lanson, 2002). The alteration process

resulting in illite as the product mineral is referred to as illitization of the precursor mineral. Illite commonly occurs in interlayered illite/smectite (I/S) mixed layers in both detrital and diagenetic components. Pure illite is very rare; even diagenetically precipitated illite typically has at least 5% smectite mixed layers (Środon and Eberl, 1984). Determination of this smectite percentage is possible using X-ray diffraction (XRD) analytical techniques outlined in Środon (1980) and Środon and Eberl (1984).

The empirical observation of illite XRD peak narrowing with increasing temperature has resulted in the use of illite XRD peak characteristics as a rough geothermometer in diagenetic-tometamorphic pelitic systems (Kübler, 1969). The loss of smectite layers with increasing temperature causes a noticeable narrowing of the 001 illite XRD peak. Use of this "Kübler Index" of illite crystallinity (IC) is an empirical metric that began as an industry exploration technique prior to its increased usage amongst clay mineralogists in the academic community (Kübler and Jaboyedoff, 2000). Advances in XRD instrument accuracy and diffraction modeling software programs like NEWMOD and WILDFIRE have resulted in the continued use of the Kübler Index into the 21st century (Lee and Lee, 2001; Battaglia et al., 2004; Aldega et al., 2007; Doublier et al., 2010; Laughrey et al., 2011; Mählmann and Frey, 2012; Warr and Cox, 2016).

Kaolinite

Kaolinite is a 1:1 non-swelling aluminosilicate clay mineral with the mineral formula:

$Al_2Si_2O_5(OH)_4$

The 1:1 structure consists of alternating silicon tetrahedral sheets and aluminum bearing octahedral sheets. The 3+ charge of aluminum necessitates a vacancy in every third cation site in the octahedral sheet in order to balance charge, making kaolinite a dioctahedral clay. It is most

common as a weathering product in near-surface rocks rich in feldspars (Nesbitt and Young, 1989).

Kaolinite cements in sandstones have a distinct morphology (Wilson and Pittman, 1977). Cements form as a series of pseudo-hexagonal plates stacked on top of one another in a vermicular or "booklet" morphology (Fig. 6). These booklets are pore-filling cements, as opposed to grain-coating cements (Wilson and Pittman, 1977). Kaolinite cements are known to be precursor minerals for diagenetic formation of gibbsite, chlorite, and illite, although instances of kaolinite as a product in reactions involving aforementioned minerals are not uncommon (Bjorkum and Gjelsvik, 1988).

Kaolinite and Illite Thermodynamics

Phyllosilicate minerals exhibit a variety of morphologies and alteration textures in these units, the occurrences of which reflect diagenetic mineral-water interactions. Alteration of primary minerals into secondary product minerals is controlled by reactions in which reactant minerals interact with aqueous species in pore fluid to yield product minerals and new aqueous species (Berner, 1980). Each reaction that occurs alters the composition of pore fluid, adjusting the chemical conditions within the given unit and driving new minerals to react to eventually reach thermodynamic stability. The sequence of events in which these reactions, as well as physical processes like compaction, occur is referred to as the paragenetic sequence. A paragenetic sequence can be thought of as a solid-state record of geochemical alteration (in addition to other mechanical processes). Diagenetic formation of phyllosilicates comprises the last two stages of the paragenetic sequence within the Marshall/Michigan Stray Sandstones (Fig. 7). Authigenesis of kaolinite and illite are respectively the two most recent diagenetic events in this paragenetic sequence.



Figure 6: *Kaolinite morphology*: Secondary electron (SE) scanning electron microscope (SEM) image of vermiform booklet kaolinite cement morphology. Booklets consist of a series of pseudohexagonal plates stacked on top of one another. From Osborne et al. (1994).



Figure 7: *Michigan Stray/Marshall Sandstone paragenetic sequence*: Petrographically determined paragenetic sequence detailing the relative timing of diagenetic modifications to the Michigan Stray and Marshall Sandstones. Dashed lines indicate tentative interpretation. Red lines indicate events that are not present throughout all intervals of these units; chlorite (red) occurs only in intervals presently at 0 - 200 m depth, whereas illite (blue) occurs only in intervals presently at 400 - 450 m depth. Modified from Zacharias (1992).

Kaolinite chemical precipitation from a solution is heavily influenced by leaching of meteoric water into groundwater during shallow, early diagenesis (Blatt, 1979; Hurst and Irwin, 1982). Weathering and recharge environments with large quantities of rainfall and snowmelt will result in relatively ion-diluted naturally acidic meteoric water, which will favor the formation of kaolinite at the expense of K-feldspar by the reaction (Bjorkum and Gjelsvik, 1988):

$$2KAlSi_{3}O_{8} + 2H^{+} + 9H_{2}O \leftrightarrow Al_{2}Si_{2}O_{5}(OH)_{4} + 2K^{+} + 4H_{4}SiO_{4}$$
(1)

An alternative scenario resulting in kaolinite formation by this same reaction has been observed as a result of naturally acidic waters entering sandstones along contacts with adjacent shales due to hydrocarbon maturation and dehydration of these shales (Ehrenberg, 1991). In such instances, kaolinite is observed along the contacts, but not pervasive throughout the unit. In the presence of abundant atmospheric precipitation and high flushing rates, near-surface leaching will proceed to alter diagenetic kaolinite to aluminum hydroxide gibbsite (Velbel, 1985). This reaction, as well as reaction 1 and all other K2O-Al2O3-SiO2-H2O system reactions, are represented as boundary lines in mineral stability diagrams (Fig. 8), making these diagrams useful for evaluating chemical changes in systems containing these minerals. Groundwater composition may be plotted on these diagrams, and thermodynamic equilibria of the groundwater with one or more minerals may be inferred based on where the data plot. Authigenic kaolinite is common as a cement in sandstones, usually due to the availability of aluminum from feldspar in clastic rocks (Blatt, 1979; Hurst and Irwin, 1982). Reaction 1 is not kinetically inhibited by temperature (instances of the K-feldspar-kaolinite reaction at surface conditions are plentiful), so the reaction is free to proceed in porous rocks containing feldspar and dilute pore-fluid.



Figure 8: *K*₂*O*-*Al*₂*O*₃-*SiO*₂-*H*₂*O mineral stability diagram:* Activity-activity mineral stability diagram for the K₂O-Al₂O₃-SiO₂-H₂O mineral system. Boundary lines constructed using data from Robie et al., 1979 (corrected edition).

The potential for substitution in both the tetrahedral and octahedral sheets and the resulting variable composition make illite a difficult mineral to properly treat in terms of thermodynamic stability. Thermodynamic datasets often do not contain much information about illite, and those interested in performing calculations or writing reactions frequently use muscovite as a proxy. As previously discussed, this practice is often insufficient in representing the actual composition and layer charge of illite. One technique for studying potassium aluminosilicates involves using the K₂O-Al₂O₃-SiO₂-H₂O mineral stability diagram to graphically display mineral thermodynamic stability (Fig. 8). Attempts have been made by previous workers to include a discrete illite phase in this diagram (Sass et al., 1987; Aja et al., 1991; Yates and Rosenberg, 1996; Aja, 1997; Noguera et al., 2011). Such attempts are based on experimental reactions; therefore, they do not perfectly represent illite reactions in natural systems.

Preliminary Evaluation of Potassium-Delivery Hypotheses

Meteoric Water Infiltration

One potential mechanism of potassium delivery into Mississippian strata of the Michigan Basin is the infiltration of meteoric water enriched with potassium sourced from dissolution of K-feldspar in overlying clastic strata (Zacharias, 1992). The feasibility of this hypothesis relies on the following background information: age dates of the diagenetic illite in Mississippian strata (from previous work only), the presence of diagenetic kaolinite in Mississippian strata (previous work and this study), and the potential for a reaction in which kaolinite/aqueous aluminum and silica react with potassium to yield illite (this study). Unpublished K/Ar age dating of diagenetic illite from the Marshall Sandstone were reported by Cox (2015). Three size fractions (2-1 μ m, 1-0.5 μ m, and <0.5 μ m) from two sampling locations were dated. Analysis of diagenetic illite is conventionally performed using the smallest possible size fraction, as detrital illite particles are typically larger (>2 μ m) than diagenetically formed particles (Środon, 1984). Cox's (2015) age dates for the smallest size fractions in the two samples are 275 Ma and 294 Ma. This variability could represent either multiple illitization events or a gradual illitization process. Regardless, these dates constrain the timing of illite formation to the Early Permian. Assuming hydrological connectivity of units deposited in the Michigan Basin during this interval, the possibility of meteoric water dissolving K-feldspar in clastic units (Michigan Formation, Saginaw Formation, Grand River Formation, and any post-Grand River Group pre-Jurassic red-bed units that are now missing) and transporting that potassium downward into Mississippian strata should not be overlooked.

The formation of illite requires some source of aluminum and silica as well as potassium. The aluminum and silica are provided by a precursor mineral in transformation reactions, or the aqueous components of a dissolved precursor mineral in neoformation reactions. Conventional illitization of mudrocks involves smectite functioning as the precursor mineral and altering to illite by transformation (Segonzac, 1970). However, no discrete smectite has been observed by petrography or XRD analysis in Mississippian sandstones in the Michigan Basin. Therefore, illitization from a precursor would require a different mineral as a reactant.

Kaolinite may alter to illite by one of two possible reactions (Lanson et al., 2002). One potential reaction is expressed below (the author chose muscovite to represent illite):

$$KAlSi_3O_8 + Al_2Si_2O_5(OH)_4 \leftrightarrow K(Al_2)(AlSi_3)O_{10}(OH)_2 + SiO_{2(aq)} + H_2O$$
(2)

in which kaolinite reacts with dissolving potassium feldspar to yield illite, aqueous silica, and water. This reaction is only possible in the presence of kaolinite and actively dissolving K-feldspar. Both are present in the Marshall Sandstone and Michigan Formation, but the kaolinite-potassium feldspar assemblage is stable at temperatures greater than what would be expected from a burial geotherm in these strata (Lanson et al., 2002). A second kaolinite-illite forming process is possible via the reaction (the author chose muscovite to represent illite):

$$3Al_{2}Si_{2}O_{5}(OH)_{4} + 2K^{+} \leftrightarrow 2K(Al_{2})(AlSi_{3})O_{10}(OH)_{2} + 2H^{+} + 3H_{2}O$$
(3)

in which kaolinite reacts with aqueous K^+ ions to yield illite, excess hydrogen ions, and water. This reaction, proposed by Berger et al. (1997), has been suggested by Lanson et al. (2002) to occur in instances where kaolinite is already present within a sandstone, then K^+ -rich fluids invade the formation satisfying the thermodynamic requirement for the reaction to proceed. Reaction 2 is considered the conventional process resulting in authigenic illite formation in sandstones at high temperatures (Lanson et al., 2002), although reaction 3 is more feasible at lower temperatures provided invasion of K^+ -rich fluid occurs (Berger et al., 1997).

Previous reactions have expressed illite formation by transformation of kaolinite. Illite has also been neoformed in these strata. Neoformation of illite from ions in pore fluid would proceed by the reaction:

$$K^{+} + 3Al^{3+} + 3H_4SiO_4 \leftrightarrow K(Al_2)(AlSi_3)O_{10}(OH)_2 + 10H^+$$
 (4)

This reaction precipitates illite directly from aqueous ions in pore fluid. It should be noted that reaction 4 requires the same reactant ions as the previous transformation reactions, the difference being that reactants in reaction 4 are aqueous. Initiation of reaction 4 still requires an additional

source of potassium, aluminum, and silica. These reactants are supplied by dissolution of K-feldspar, or dissolution of kaolinite plus additional potassium.

Mobilization of enough K⁺ to initiate reactions 3 or 4 in the Marshall/Michigan would require sufficiently large amounts of K-feldspar in the overlying strata and a large enough flushing rate of meteoric water to destabilize this K-feldspar and transport the K⁺ down by percolation. Provided those requirements are met, K⁺ ions would certainly be introduced to the Mississippian strata.

If the proposed hypothesis of potassium enriched meteoric water infiltration were true then two lines of supporting evidence would exist: (1) aqueous geochemical mixing models should indicate that thermodynamic stability of illite is attainable by invasion of such water, and (2) the temperature of formation of the diagenetic illite would be firmly within the range of shallow diagenesis.

Vertical Deep Brine Movement

An alternative mechanism for potassium delivery to Mississippian-aged clastic strata is the vertical cross-formational movement of hot saline brines from older strata in the Michigan Basin. Previous researchers have suggested that deep brines migrate vertically into younger strata along faults and fractures in the Michigan Basin (Girard and Barnes, 1995; Luczaj et al., 2006; Castro et al., 2009). Such hot brine movement has been invoked as the cause of previously unexplained hydrothermal mineralization in some strata of the Michigan Basin (Machel and Lonnee, 2002). Evidence of some degree of brine mixing based on helium isotope concentrations and major element chemistry has already been observed in the Marshall aquifer specifically (Ma et al., 2005). Movement of this brine is thought to be possible due to the presence of basement



В



Figure 9: *Potassium delivery model schematic*: Graphic representations of two proposed K^+ delivery models. A: K^+ delivery by percolation of meteoric water enriched by dissolution of overlying K-feldspar. B: K^+ delivery by infiltration of hot brines from deep within the basin.

Mid-Continent Rift (MCR) faults and fractures which have been reactivated prior to the time of such hydrothermal mineralization. Vertical hot brine movement would also provide support for the idea that a hydrothermal event may be responsible for the high thermal indicators (vitrinite reflectance data, apatite fission track data, authigenic mineralization) observed in the Michigan Basin (Cox, 2015).

Helium and neon values of deep basinal brines analyzed by Castro et al. (2009) were found to be very similar to mid-oceanic ridge values, which suggests that these brines may have an upper mantle or deep basement source. Assuming hydrologic connectivity of Michigan Basin formations along preferential flow paths from fracturing/faulting as previous researchers suggest, fluid transportation to younger strata would be possible from any deeper formation. Aqueous geochemical analyses by Wilson and Long (1993) show that the Devonian and Silurian-aged units contain highly concentrated brines with TDS levels ranging from 200,000-450,000 ppm. Such highly concentrated brines may be sufficiently ion rich to drive kaolinite-illite reaction 3 or reaction 4 towards thermodynamic equilibrium and sufficiently hot to overcome the kinetic barrier of illite crystallization.

If the deep hot brine hypothesis were true then different supporting evidence would be expected: (1) aqueous geochemical mixing models should indicate that thermodynamic stability of illite is attainable by mixing of Marshall pore-fluid with known basinal brines, and (2) the temperature of formation of diagenetic illite should be greater than the shallow diagenetic regime (anchizone or epizone).

Research Objective

This project's objective is to combine new and existing data for solid and liquid phases in Mississippian sandstones of the Michigan Basin to better understand the reactions and processes influencing late diagenesis (epidiagenesis; terminology of Worden and Burley (2003)) of these strata. The Marshall Sandstone and Michigan Formation contain textbook examples of authigenic clay minerals, but with present depths and corresponding expected thermal conditions that deviate from the norm. This project aims to evaluate the feasibility of two previously proposed late-diagenetic processes to better constrain how the formation of authigenic illite in shallow (modern depth) sandstone was possible.
Methods

Sampling

Subsurface samples were obtained from cores housed at the Michigan Geological Repository for Research and Education (MGRRE) in Kalamazoo, Michigan. Marshall Sandstone and Michigan Formation cores of interest were identified through literature review and conversation with MGRRE faculty (William Harrison, personal communication, 2018) and selected with the goal of encountering diagenetic facies while maximizing variation in depth and pore fluid composition. Four cores were selected for analysis (Table 1, Fig. 10). Ten to fifteen evenly spaced intervals of interest within each core were cut and sampled to allow broad coverage of the Marshall and Michigan Stray Sandstones from each well (Table 2).

Optical Petrography

Traditional optical petrography was completed using a petrographic transmitted-light microscope. Forty-six thin sections (one thin section per sample collected) were produced and stained with blue-dye epoxy to identify open pore space. These thin sections were then analyzed and point-counted using 200 points per thin section to obtain quantitative mineral abundance data. Optical petrography was completed with the goal of initial identification of mineral grains, characterization of textures, and preliminary characterization of diagenetic processes (paragenetic sequence). Petrographic analysis was completed for every sample collected.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) provides multiple advantages over optical petrography when studying clay minerals and micron-scale mineral alteration. High resolution

Number	Well Name	County	Depth Range (m)	Strata	Pore Fluid TDS (ppm)
1	RASA 5	Crawford	153-186	Lower Marshall	1000-10000
2	W-1002	Clare	400-442	Napoleon, MI Stray	>100000
3	W-962	Clare	405-443	Napoleon, MI Stray	>100000
4	CH101	Calhoun	6-43	Napoleon	<500

Table 1: Wells sampled as part of this project



Figure 10: *Sample well locations*: Geographic location of sample wells. Numbers correlate to well numbers from Table 1. The location of the Mid-Continent Rift as well as major fault structures in the Michigan Basin and the base of the Mississippian Marshall Sandstone are indicated by the black lines. Modified from Westjohn and Weaver (1998).

Well Name	Depth (ft.)	Unit/Member	SEM	XRD	TEM
RASA 5					
1	503	Lower Marshall	Yes	No	
2	514	Lower Marshall	No	No	
3	519	Lower Marshall	Yes	No	
4	531	Lower Marshall	Yes	No	
5	588	Basal Lower Marshall	No	No	
6	592	Basal Lower Marshall	Yes	No	
7	598	Basal Lower Marshall	Yes	No	
8	604	Basal Lower Marshall	No	No	
9	607	Basal Lower Marshall	Yes	No	
10	609	Basal Lower Marshall	Yes	No	
11	611	Basal Lower Marshall	Yes	No	
12	612	Basal Lower Marshall	No	No	
W-1002					
1	1315	Michigan	Yes	No	
2	1328	Michigan	No	Yes	
3	1344	Michigan	Yes	Yes	
4	1356	Michigan	Yes	No	
5	1363	Michigan	Yes	Yes	
6	1382	"Stray Dolomite"	No	No	
7	1401	Napoleon	Yes	No	
8	1406	Napoleon	Yes	Yes	Х
9	1411	Napoleon	Yes	No	
10	1420	Napoleon	Yes	Yes	
11	1435	Napoleon	No	Yes	
12	1444	Napoleon	Yes	Yes	
13	1448	Napoleon	Yes	No	
W-962					
1	1328	Michigan	Yes	No	
2	1338	Michigan	Yes	Yes	
3	1343	Michigan	No	Yes	
4	1373	Michigan	No	No	
5	1382	"Stray Dolomite"	No	No	
6	1400	"Stray Dolomite"	Yes	No	
7	1420	Napoleon	No	No	
8	1425	Napoleon	Yes	Yes	Х
9	1430	Napoleon	Yes	Yes	
10	1448	Napoleon	Yes	Yes	
11	1453	Napoleon	Yes	No	
CH101					
1	20	Napoleon	Yes	No	
2	33	Napoleon	Yes	No	
3	58	Napoleon	Yes	No	
4	70	Napoleon	No	No	
5	85	Napoleon	Yes	No	
6	100	Napoleon	No	No	
7	114	Napoleon	Yes	No	
8	126	Napoleon	No	No	
9	133	Napoleon	Yes	No	
10	140	Napoleon	Yes	No	

Table 2: Marshall and Michigan Stray Sandstone sample depths

capabilities of SEM allow for determination of clay morphologies from polished thin sections and rock chip fragments (Wilson and Pittman, 1977). Subtle constituents of difficult-todistinguish clay matrix material, such as identification of silt sized detrital fragments and oriented fabric of detrital micas, are more easily visible using SEM relative to optical microscopy.

Polished thin sections and rock chip pairs were produced for 31 samples (each pair prepared from the same sample) spanning each of the four sampled cores (Table 2). Thin sections were coated using a carbon thread evaporator, attached to the metal stage using sticky carbon tabs, and then analyzed on a JEOL 6610LV SEM with backscattered electron (BSE) imaging and an Oxford Instruments energy dispersive X-ray spectroscopy (EDS) system. BSE imaging was conducted in high vacuum mode using an accelerating voltage of 20 kV, a working distance of 10 mm, a spot size of 53, and a 'z' height of 10 mm. The heterogenous nature of the brightness observed while viewing a flat (polished) surface in BSE mode is due to differences in Z contrast. In electron microscopy Z is the average atomic number for all elements in a phase. Materials with larger Z values appear brighter in the image, whereas materials with low Z values appear darker in the image. BSE imaging allows for rapid preliminary identification of mineralogy and determination of subtle compositional differences within individual grains (White et al., 1984). Energy dispersive X-ray spectroscopy (EDS) provides semi-quantitative compositional analysis at the micron scale (White et al., 1984). When paired with BSE, identification of single-grain alteration and subsequent determination of product phases are possible.

Secondary electron (SE) imaging of freshly fractured rock chips was completed to investigate in-situ mineral morphological relationships. Freshly fractured rock chips were broken

off from samples, coated in a gold sputter coater, attached to an aluminum stub (diameter 25 mm) using sticky carbon tabs, and analyzed using SE imaging and EDS. SE imaging was conducted in high vacuum mode using an accelerating voltage of 10 kV, a working distance of 25 mm, a spot size of 30, and a 'z' height of 25 mm.

X-ray Diffraction

Powder X-ray diffraction (pXRD) has long been the primary analytical method for clay mineralogists concerned with identification, composition, crystallography, or quantification of clay minerals (Moore and Reynolds, 1989).

Samples for pXRD analysis were selected using an illite morphology classification scheme to exclude samples in which dioctahedral potassium-bearing phyllosilicates are not diagenetic. Selected samples were required to contain observable illite with morphologies consistent with diagenetic neoformation (grain coatings/pore linings) based on SEM observations. Samples containing pseudomatrix or ambiguous morphologies were excluded from pXRD analysis to avoid contamination by detrital illite.

Sample preparation is outlined in Figure 11. Clay mineral XRD sample preparation begins with separating the clay size fraction (equivalent spherical diameter of $< 2 \ \mu m$) of bulk rock samples. . Disaggregation of bulk rock samples was completed by gentle crushing with a ceramic mortar and pestle. The samples were rinsed with deionized water and placed into an ultrasonic bath for five minutes to facilitate further disaggregation. The suspension was then set aside to allow separation of the clay size fraction ($< 2 \ \mu m$) using settling rates determined by Stokes law. The $< 2 \ \mu m$ clay size fraction was then decanted into the beakers, where the suspended clay size fraction was allowed to sediment onto the quartz disc. Sedimentation results



Figure 11: *XRD sample preparation flowchart*: Sample preparation procedure for powder X-ray diffraction of the clay size fraction.

in oriented XRD samples, as the platy crystal habit of clay minerals will cause them to settle out of suspension with their basal planes flat against the mount.

Clay coatings on the mounting medium are very thin when prepared using this method, and as a result the generated X-rays may interact with the crystal structure of the mounting medium itself. To mitigate this issue low background fused-quartz discs were used as the mounting medium. These discs still exhibit some degree of background noise, which is expressed on XRD patterns as a slight hump from ~6-11° 2 Θ . Discs were placed at the bottom of 250 ml beakers. The clay size fraction so prepared on a quartz/glass mounting medium was then ready for insertion into the diffractometer.

An X-ray beam is generated by a cathode ray tube (typically copper or chromium), then passed through a filter (typically nickel or iron) to produce a monochromatic beam of desired K_{α} radiation which is then aimed at a sample. The X-rays scatter upon interaction with the sample, and much of the scattering results in destructive interference. In the instrument configuration routinely used in clay mineralogy, the angle at which the beam interacts with the sample (Θ) is gradually changed to scan for instances when constructive interference of X-rays occurs, indicating that Bragg's Law is satisfied, and diffracted X-rays can be recorded by the detector. The intensities of diffracted rays are recorded by either a point or a slit detector over a range of angles. The peak positions of a sample are determined by the composition, geometry, and atom spacing of the sample's crystal structure. Clay minerals can be identified from diagnostic XRD peaks, provided peak overlap is not too severe. In bulk rock samples quartz typically cannot be separated entirely from the clay-size fraction, although this is not a problem as quartz may be used as an internal standard in pXRD analysis of clastic sedimentary rocks (Moore and Reynolds, 1989).

Prepared pXRD mounts were taken to Proto Manufacturing in Taylor, Michigan for analysis. XRD analysis was completed using a Proto Manufacturing AXRD Benchtop diffractometer with a Cu tube, a nickel filter, a slit receiving detector (0.1 mm), a divergence slit (0.5 mm), and a rotating stage to reduce the effects of textural heterogeneity within the sample. No anti-scatter slit was used. This instrument uses a voltage of 30 kV, and a current of 20 mA. The diffractometer was set to record XRD patterns from 4-40° 20 with a 5 second dwell time and $0.02^{\circ} 2\Theta$ step size (resulting in a scan speed of $0.24^{\circ} 2\Theta$ per minute) with binning set at 2. The sample was then inserted into a glycolation chamber overnight at 65°C and analyzed again the following day. Ethylene glycol is frequently used in pXRD studies of clay minerals to analyze potential swelling components of a sample (Moore and Reynolds, 1989). Glycolation results in expansion of interlayer sites in low layer charge smectite-group minerals and consequent modification of the (001) peak for smectite and mixed layer illite/smectite. This modification appears as a shift of the (001) peak to a lower angle due to expansion of the smectite layer spacing and can be analyzed to determine the degree of expandable material in the sample.

The Kübler Index of illite crystallinity (IC) was used to evaluate the temperature of illite authigenesis. The Kübler Index is an empirical metric determined by measuring the full width at half the maximum (FWHM) of the illite (001) diffraction peak in units of $^{\circ}2\Theta$. This value is then plotted on the formational regime graph (Fig. 12). The boundaries of the anchizone in Kübler Index are intended to be adjusted based on the XRD scan rate. The boundaries of the anchizone used in this diagram are after Weber (1972) and Teichmüller et al. (1979) and were determined using Kisch (1990).



Figure 12: *Kübler Index diagram*: Kübler Index usage diagram indicating thermal regime of illite formation. Boundaries for the anchizone defined using Kisch (1990).

Transmission Electron Microscopy

Transmission electron microscopy (TEM) is commonly used along with pXRD to characterize structure and crystallography of clay minerals (Mackinnon, 1990). TEM analysis provides a look at the crystal habit of individual illite fundamental particles (Nadeau et al., 1984), as well as high resolution compositional analysis and the potential to distinguish authigenic illite polytypes by selected area electron diffraction (SAED) (Grubb, 1991). Polytypism refers to a specific type of polymorphism in phyllosilicate minerals in which the chemical formula remains the same, but the layer-stacking sequence of individual sheets vary in their pattern of repetition (Smith and Yoder, 1956). Controls on illite polytypism are not yet fully understood, although there is a suggested relationship between specific polytypes and hydrothermal formation of authigenic illite (Grubb, 1991; Bauluz et al., 2002).

TEM samples were prepared by suspending the clay size fraction of bulk rock samples in water as for pXRD, then pipetting one drop of the suspended solution onto lacey carbon coated Cu TEM grids. The solution was then allowed to air-dry. Samples were analyzed on a JEOL 2200FS TEM equipped with an Oxford Instruments EDS. Samples were viewed in high-vacuum mode using bright-field imaging with an accelerating voltage of 10kV. Spot size was adjusted as needed. Images were captured using a Gatan digital camera. Acquisition time for EDS analysis was set to two minutes per sample to mitigate data quality reduction associated with low dead time. The duration of electron beam interaction with each sample varied.

Aqueous Geochemistry

Aqueous geochemical mixing and forward modeling was conducted to evaluate the feasibility of achieving illite-solution thermodynamic equilibrium under different geological scenarios.

Groundwater chemical data for 476 wells within the Michigan Basin were collected as part of the Regional Aquifer System Analysis (RASA) USGS program and published in USGS Open-File Report 90-368 (Dannemiller and Baltusis Jr., 1989). Many of these sample wells were in the Marshall Aquifer, so ample groundwater chemical data are available for this study. Data relevant to K₂O-Al₂O₃-SiO₂-H₂O systems were compiled from the 90 groundwater wells reported for the Marshall aquifer in the RASA report (Appendix).

Pore fluid compositions resulting from mineral-water interactions were modeled using the USGS software package PHREEQC. The Debye-Hückel equations were used for dilute solution calculations, and the Pitzer equations for brine solution (>10,000 ppm TDS) calculations. A database was constructed containing the appropriate information from the Debye-Hückel and Pitzer databases that are provided as default databases in PHREEQC. Real and hypothesized fluid compositions were used as initial inputs for aqueous mixing models run in PHREEQC.

Results

Sampling

Forty-two samples of Marshall (8 basal Lower, 4 Lower, 21 Napoleon) and Michigan Stray (9) Sandstone (plus three samples of "Stray Dolomite" and one mudstone sample) were collected from four wells (Table 2). Thin sections were prepared from every sample collected. Thirty-one polished thin sections were prepared for BSE SEM analysis (Table 2). Twelve XRD samples were prepared from two of the four wells (Table 2). Two samples were prepared for TEM (Table 2).

Optical Petrography

Optical petrographic examination was performed to characterize and screen all prepared samples, and to select samples for SEM thin section analysis. Diagenetic components identified include quartz overgrowths, feldspar overgrowths, authigenic carbonate, kaolinite cement, chlorite cement, illite cement, and pyrite cement. Individual thin section descriptions and raw point-count data are provided in the Appendix. These data were used to calculate quartz-feldspar-rock fragment (QFR) ratios for each sandstone sample following the methods of Folk (1974). QFR, mica abundance, and grain size/sorting data for all sandstone samples are presented (Table 3). Sandstone samples are very fine/fine-grained and are dominantly moderately well/well-sorted (Fig. 13). These QFR ratios were then plotted on a ternary diagram (Fig. 14) and used to classify each sample.

Lithologically, sandstone samples include sublitharenite, litharenite, feldspathic litharenite, and greywacke. Sublitharenite and litharenite are the dominant lithologies of these

Depth (ft.)	Q	F	R	Mica (%)	Average Grain-Size (φ)	s.d. (φ)	Sorting Class
W-1002							
1315	95	3.33	1.66	0	3.14	0.53	Moderately well
1328	81	2	17	0	2.50	0.39	Well
1344	61.6	1.7	36.6	3	2.80	0.40	Well
1356	66.3	1.2	32.5	3.5	2.70	0.39	Well
1363	66.8	2.3	30.9	2	2.78	0.39	Well
1382							
1401	78.2	9.7	12.1	2	2.54	0.37	Well
1406	84	1.2	14.8	0.5	2.58	0.38	Well
1411	94.4	2.8	2.8	2	3.05	0.49	Well
1420	70.2	2.4	27.4	1	2.82	0.57	Moderately well
1435	76.1	2.4	21.5	0.5	2.20	0.32	Very well
1444	70.3	10.3	19.4	1	2.43	0.35	Well
1448	/2.3	4.8	22.9	3.5	2.54	0.52	Moderately well
W-962							
1328	64.1	0	35.0	6	2 98	0.43	الم/٧/
1328	67.5	27	22.9	25	2.38	0.43	Well
12/2	07.5	1.5	20.0	1	1.07	0.40	Verywell
1343	64.4	1.5	3/1 1	2	2.90	0.32	
1373	04.4	1.5	34.1	2	2.50	0.40	Wen
1/00							
1400							
1420	80.3	3.6	16.1	1	2.45	0.36	W/ماI
1420	80.5	1.0	14.6	15	2.45	0.30	Verywell
1430	70	7.4	13.6	1.5	2.00	0.30	
1/153	77 5	/.4	17.8	0.5	2.50	0.35	Well
1455	77.5	4.7	17.0		2.50	0.50	Wen
RASA 5							
503	85	2.5	12.5	0	2.29	0.34	Verv well
514	72.4	4.1	23.5	2	2.55	0.36	Well
519	79.5	1.9	18.6	2	2.66	0.39	Well
531	81.2	2.6	16.2	0.5	2.41	0.36	Well
588	76.2	1.6	22.1	33	3.23	0.55	Moderately well
592	72.9	3.1	24	25.5	3.09	0.51	Moderately well
598	65.3	4.8	29.9	3.5	2.83	0.43	Well
604	61.7	4.3	34	39.5	3.17	0.62	Moderately well
607	68.1	3.4	28.5	30	3.17	0.55	, Moderately well
609	75	8.3	16.7	43.5	2.98	0.87	Moderate
611	70.8	0	29.2	61.5	3.06	0.82	Moderate
612	83.3	0	16.7	0	2.90	0.61	Moderately well
CH101							
20	74.1	11.1	14.8	1	2.00	0.29	Very well
33	77.2	3.5	19.3	1	3.26	0.57	Moderately well
58	69.2	2.6	28.2	2	3.09	0.47	Well
70	69.7	2.7	27.6	3.5	3.10	0.49	Well
85	68	2.7	29.3	3	3.26	0.51	Moderately well
100	67.7	3.7	28.6	1.5	3.16	0.48	Well
114	76.5	2.9	20.6	2	3.07	0.50	Moderately well
126	69.2	2.8	28	2	3.16	0.50	Moderately well
133	69.7	3.6	26.7	0.5	3.09	0.46 Well	
140	70.8	4.5	24.7	3.5	2.74	0.41	Well

Table 3: Selected results from thin section point counting.



Figure 13: *Grain size/sorting*: Sandstone sample grain size and sorting. Boundaries for grain sorting after Folk (1974).



Figure 14: *QFR ternary diagram*: Marshall and Michigan Stray sandstone quartz-feldspar-rock fragment (QFR) ratio ternary diagram. Fifty percent of all sandstone samples are classified as litharenites, and 40.5% of all sandstone samples are classified as sublitharenites. Lithological classifications are after Folk (1974).

units. Of the 42 sandstone samples point-counted, 40.5% were sublitharenites, and 50% were litharenites. There does not appear to be a relationship between depth and lithology, as most samples from all four wells plot within similar sublitharenite-litharenite ranges. Rock fragments consist primarily of slightly deformed mudstone and phyllite fragments as indicated by the high birefringence grains (Fig. 15). Feldspars consist of plagioclase and K-feldspar (microcline and orthoclase). Mica grains (biotite and muscovite) are present throughout all four wells but constitute between 25.5% - 61.5% of thin sections in certain intervals of the RASA 5 well (Fig. 16). Wells W-1002 and W-962 show intervals of very little porosity (0% - 0.5%), as pore space appears to be clogged almost entirely by deformed detrital pseudomatrix (Fig. 17). Classification of this material as pseudomatrix is based on SEM data and will be discussed in the SEM results section. Dissolution of K-feldspar grains is common and pervasive throughout all sample wells (Fig. 18).

Scanning Electron Microscopy

Scanning electron microscopic analysis was completed for all 31 polished thin sectionrock chip pairs with representation from all four sample wells (Table 2). The presence/absence of phyllosilicate minerals, as well as authigenic pyrite, was documented for each thin section and is presented (Table 4). Identifications of minerals are based on a combination of diagnostic morphology/crystal habit and EDS compositional analysis. EDS analyses of polished thin sections are generally considered semi-quantitative, while EDS analysis of minerals in rock chip fragments cannot be used to confidently determine mineralogy and are supportive evidence at best. Identification of textural relationships by scanning electron microscopy (combining rock chip and thin section data) is the basis for revision of the paragenetic sequence in these strata from Zacharias (1992) (Fig. 7).



Figure 15: *Abundant lithic fragments*: Optical PPL/XPL micrograph of lithic fragments in Marshall Sandstone A: Plane polarized light view B: Cross polarized light view. Lithic fragments consist primarily of mudstones and phyllites. High birefringence in XPL indicates detrital mica. From W-1002 well at 1356 ft. measured depth.



Figure 16: *Abundant mica grains*: Optical PPL micrograph of abundant detrital mica grains oriented with a preferential fabric. Deformation of mica grains, most likely due to compaction, nearly eliminates porosity. From RASA 5 well at 604 ft. (depth).



Figure 17: *Pseudomatrix*: Optical PPL view of detrital pseudomatrix consisting of reworked mudstone lithic fragments. From W-1002 well at 1315 ft. (depth).



Figure 18: *Skeletal K-feldspar*: Optical PPL view of skeletal K-feldspar grain indicated by the red circle. Blue dyed epoxy represents pore space. From W-962 well at 1430 ft. (depth).

Well Name	Depth (ft.)	Present pore-fluid salinity	Illite cement	Kaolinite cement	llt ps Kin	Chlorite cement	Muscovite	Biotite	Pyrite
Lower Marshall	503	Brackish		X		x	X		
Lower Marshall	519	Brackish		X		X			x
Lower Marshall	531	Brackish		X		X	X	х	X
Basal Lower	592	Brackish		X		X	X	X	X
Basal Lower	598	Brackish		X		X	X	X	X
Basal Lower	607	Brackish				X	X	Х	X
Basal Lower	609	Brackish					X	Х	X
Basal Lower	611	Brackish		X		X	X	X	Х
W-1002									
MI Stray	1315	Hyper-saline	X				X		X
MI Stray	1344	Hyper-saline	Х	X	Х		X		X
MI Stray	1356	Hyper-saline	Х	X	Х		X		Х
MI Stray	1363	Hyper-saline	Х	X			X		Х
Napoleon	1401	Hyper-saline	X				X		X
Napoleon	1406	Hyper-saline	X	X	Х		X		X
Napoleon	1411	Hyper-saline	X	X			X		X
Napoleon	1420	Hyper-saline	X				X		X
Napoleon	1444	Hyper-saline	X	Х	Х		X		X
Napoleon	1448	Hyper-saline	X	X			X		X
W-962									
MI Stray	1328	Hyper-saline		X			X		X
MI Stray	1338	Hyper-saline	X				X		X
Napoleon	1400	Hyper-saline							X
Napoleon	1425	Hyper-saline	X	X	X		X	X	X
Napoleon	1430	Hyper-saline	X	X			X	X	X
Napoleon	1448	Hyper-saline	X	X	X		X	X	X
Napoleon	1453	Hyper-saline	X	X	X		X	X	X
CH101									
Napoleon	20	Dilute		X			X		
Napoleon	33	Dilute		X		~	X	v	X
Napoleon	58	Dilute		X		X	X	X	X
Napoleon	85	Dilute				X	X	X	X
Napoleon	114	Dilute				X	X	X	X
Napoleon	133	Dilute				X	X	X	X

Table 4: Selected mineral occurrences in samples observed by SEM.

Illite

Illite was observed as detrital and diagenetic components in two of the four sample wells. Illite was present in wells W-1002 and W-962 (Table 4), both of which are located in the central part of the basin, in Clare County (Fig. 10). These two wells have nearly identical depth ranges and pore fluid compositions (Table 1) and are geographically close to one another. Additionally, these two wells are deeper than the two sample wells in which illite was not observed. Illite was observed with several different morphologies. A classification scheme consisting of four different groupings was created to differentiate between detrital and diagenetic morphologies. The morphologies comprising this illite classification scheme are (1) a constituent of detrital pseudomatrix, (2) illite with isotropic fabric of ambiguous origin, and fibrous cement, distinguishing between (3) complete grain-coating and (4) patchy distributions (Fig. 19). This textural classification was used to identify intervals containing only diagenetic neoformed illite for use in pXRD study. Table 5 displays the burial depths and morphological classifications of observed illite.

Detrital illite was observed in two forms: mudstone lithic fragments, and pseudomatrix. Mudstone lithic fragments are made up of small grains that exhibit different brightness when viewed in BSE mode due to differences in Z contrast, thereby showing the fine-grained material to consist of a mixture of multiple clay minerals and commonly including quartz (Fig. 20).. Detrital illite was also observed as pseudomatrix (Fig. 21). This material was determined to be of detrital origin due to the existence of silt sized quartz particles interspersed throughout the illite clay, and evidence of local fabric in small mica grains interspersed in the material (Fig. 22). This pseudomatrix is interpreted to be reworked mudstone and metasedimentary material, and porosity is negligible in intervals where it is observed (Fig. 23, Table 5).



Figure 19: *Illite morphological classification images*: Representative BSE/SE-SEM images of each illite textural group. A: Detrital pseudomatrix B: Isotropic illite of ambiguous origin. C: Authigenic fibrous illite (partial grain-coating distribution) D: Authigenic fibrous illite (full grain-coating distribution).

Table 5: Occurrence of dominant and minor illite morphologies based on SEM observation.

				Fibrous				
Domina	int Occurrence	X	trix		grain-coating	tribution	aolinite	
Minor C	Dccurrence	x	ma	<u> </u>	te 8	dist	ed I	
Absent			opr	rop	ple	γų	lac	
Well	Burial Depth (fe	eet)	Psei	lsot	Com	Pato	Rep	
W-1002	1315		Х		x			
	1328			х	Χ		x	
	1344			х	Χ		x	
	1356				x	Χ	x	
	1363				Χ			
	1382							
	1401				Χ	х		
	1406			Χ	х		x	
	1411		Χ					
	1420					x		
	1428			х	Χ			
	1435			х	Χ		x	
	1444				Χ		x	
W-962	1328							
	1338				Χ			
	1343				Χ			
	1373		Χ		х			
	1382							
	1400							
	1420							
	1425				Χ	x	x	
	1430				Χ	x		
	1448				Χ		x	
	1453		Χ		х		x	



Figure 20: *Detrital mudstone*: BSE-SEM thin section image. Detrital mudstone lithic fragment surrounded by quartz grains. From W-1002 well at 1448 ft. (depth).



Figure 21: *Pseudomatrix EDS*: BSE-SEM. EDS profile of detrital pseudomatrix. The location of the EDS analysis is shown by the yellow circle. From W-1002 well at 1315 ft. (depth).



Figure 22: *Pseudomatrix analysis*: BSE-SEM image of detrital pseudomatrix containing silt sized quartz grains and mica grains with a preferential orientation. The red arrows indicate the direction of the mica fabric. The white circle indicates the target area of EDS analysis. EDS analysis reveals chemical composition resembling K-bearing phyllosilicate minerals. From W-1002 well at 1315 ft. (depth).



Figure 23: *Pseudomatrix SEM*: BSE-SEM image of detrital pseudomatrix filling pore space and nearly eliminating porosity. Brighter grains indicate high atomic number (feldspar). From W-1002 well at 1315 ft. (depth).

Diagenetic illite has the classic fibrous morphology typical of illite cements in sandstones (Boles and Franks, 1979). Illite wisps form as grain coating cements on the surfaces of detrital grains (Fig. 24). The lengths of these wisps vary from 1-10 µm. These illite cements, although present, are difficult to observe in polished thin section and are more easily viewed in rock chips using SE imaging. Illite cement can be observed nucleating on authigenic kaolinite plates (Fig. 25), indicating that illite precipitation is occurring after kaolinite precipitation in the paragenetic sequence. These cements do not always coat the outsides of quartz overgrowths (Fig. 26), suggesting that quartz overgrowth precipitation may occur concurrently with or later than illite precipitation.

EDS compositional analysis of illite was attempted. The chemical composition of detrital illite is of limited importance to this project; therefore, only authigenic grain coatings were analyzed by EDS. The effectiveness of EDS analysis is dependent on an area within the field of view containing an object of interest large enough relative to surrounding features that the signal received by the EDS detector is generated only from the feature of interest. When viewing illite in thin section the difficulty lies in finding an area of illite cement large enough that a small portion can be selected without including the detrital grain it is coating. When viewing illite in rock chips the quality of the EDS analysis is considered qualitative at best due to the effects of geometric modifications. Sample topography can modify the X-ray absorption path to the detector, thus deviating from the ideal absorption path required for highest quality analysis (Newbury and Ritchie, 2013). Therefore, rock chip EDS data generated should be used cautiously. EDS analyses of grain coating illite cements were completed on 42 areas and revealed an average illite mineral formula of:

 $K_{0.735}(Al_{1.697}Fe(II)_{0.113}Mg_{0.18})(Si_{3.567}Al_{0.424})O_{10}(OH)_2$



Figure 24: *Authigenic illite fibrous morphology*: SE-SEM image from a fractured rock chip. Fibrous authigenic morphology of grain-coating illite cements. Small prismatic quartz overgrowths are also observed nucleating on the grain. From W-1002 well at 1406 ft. (depth).



Figure 25: *Illite-kaolinite relationship*: SE-SEM image of authigenic illite nucleating on and around authigenic kaolinite plates. From W-962 well at 1453 ft. (depth). Mineral abbreviations are after Whitney and Evans (2010) and will be used for the remainder of this study.



Figure 26: *Uncoated quartz overgrowth*: SE-SEM image of illite cement-coated quartz grain. Prismatic quartz overgrowths are not coated by illite, suggesting that they may have formed cogenetically or later than illite cements. From W-1002 well at 1406 ft. (depth).

Table 6: Comparison of relevant illite mineral formulae.

Generic illite formula (Środon and Eberl, 1984)	K _{0.6-0.9} (Al,Fe(II/III),Mg) ₂ (Si,Al) ₄ O ₁₀ (OH) ₂
Illite cement EDS (SEM)	$K_{0.735}(Al_{1.697}Fe(II)_{0.113}Mg_{0.180})(Si_{3.567}Al_{0.424})O_{10}(OH)_2$
Illitized kaolinite EDS (SEM)	$K_{0.738}(Al_{1.829}Fe(II)_{0.098}Mg_{0.107})(Si_{3.212}Al_{0.788})O_{10}(OH)_2$
Illite lath EDS (TEM)	$K_{0.645}(Al_{1.701}Fe(II)_{0.120}Mg_{0.255})(Si_{3.525}Al_{0.475})O_{10}(OH)_2$

This formula is displayed alongside other relevant illite mineral formulae (Table 6). It fits firmly within the generalized definition of illite (Środon and Eberl, 1984). Illite in this study has phengitic substitutions (tetrahedral Al:Si ratio and degree of substitution divalent cations in the octahedral sheet) to a limited extent that results in layer charge (and corresponding interlayer site occupancy) firmly within the illite range.

Kaolinite

Kaolinite was observed in all four of the sample wells. Kaolinite occurs as pore filling cement (Fig. 27) with a classic booklet-like vermiform morphology consisting of a series of plates stacked on top of one another (Fig. 28). Kaolinite cements were commonly observed near skeletal potassium feldspar grains (Fig. 29), suggesting that formation of kaolinite cement is occurring at the expense of K-feldspar as in reaction 1. This observation also suggests that conditions within this system do not allow the mobilization of the aluminum and silica from this K-feldspar and will result in the crystallization of kaolinite cement in close proximity to the dissolving grain, as suggested by Velbel (1983).

The thicknesses of individual kaolinite plates appeared to be 0.5-1 μ m for most cements observed. However, the RASA 5 well contained kaolin material (as determined by EDS) with significantly thicker plates. Individual plates comprising RASA 5 kaolin cements have thicknesses of ~5-10 μ m (Fig. 30). These observations correspond to the morphology of dickite, a high temperature kaolinite polymorph, as reported by Beaufort et al. (1998). This tentatively classified dickite is observed in the (intermediate depth range) RASA 5 well.

EDS analyses of kaolinite cements were conducted periodically to confirm the identification of vermiform material as kaolinite. Classification of a mineral as kaolinite from



Figure 27: *Kaolinite morphology thin section*: BSE-SEM image of pore-filling vermiform morphology of kaolinite cements. From CH101 well at 20 ft. (depth).



Figure 28: *Kaolinite morphology rock chip*: SE-SEM image of pore filling kaolinite cements. Vermiform morphology consists of a series of pseudohexagonal stacked plates. A mineral with a blocky morphology (possible dickite) is present as well. From CH101 well at 20 ft. (depth).



Figure 29: *Kaolinite-K-feldspar relationship*: BSE-SEM images of multiple instances of kaolinite cements forming adjacent to skeletal K-feldspar grains. From RASA 5 well at 519 ft. (depth).



Figure 30: *Possible dickite morphology*: A: SE-SEM image of kaolin cement. Note the increase in thickness of particular crystals. B: BSE-SEM image of kaolin cements. The yellow circle indicates an unusually thick kaolin crystal. From RASA 5 well at 519 ft. (depth).

EDS analysis is based on the atomic percentages of O, Si, and Al. Kaolinite will have < 1% of any other element, and the Si:Al ratio must be exactly or very close to one. Most kaolin cements exactly matched the mineral formula for kaolinite. However, occurrences of kaolinite morphology with anomalous composition were observed in wells W-1002 and W-962 (Fig. 31). Such occurrences were identified initially by particular booklets appearing brighter in BSE imaging mode, indicating a chemical composition with a higher average atomic number than kaolinite. EDS analysis of five anomalous booklets revealed an average mineral formula of:

$$K_{0.738}(Al_{1.829}Fe(II)_{0.098}Mg_{0.107})(Si_{3.212}Al_{0.788})O_{10}(OH)_{2}$$

which falls within the compositional range of illite (Srodon and Eberl, 1984). The octahedral cations of this formula resemble the average mineral formula of authigenic grain coating illite, but the tetrahedral cations differ (Table 6). Classification of these crystals as illite is based on EDS analyses indicating values very close to kaolinite, but with less Al and an atomic percentage value of > 3% for K. These observations suggest that the anomalous booklets are instances of pseudomorphic replacement of kaolinite by illite, confirming illitization of kaolinite has occured.

Chlorite

Chlorite was observed in all four of the sample wells. Detrital chlorite was observed in all sample wells, and diagenetic chlorite was observed in wells RASA 5 and CH101 (Table 4). Detrital chlorite was observed as components of detrital mudstone and phyllite lithic fragments. Diagenetic chlorite was observed as grain coating cements with individual crystals displaying a disc-like morphology. These pore linings are easily visible in thin section (Fig. 32) and in rock chips (Fig. 33). These cements are observed coating other diagenetic features such as carbonate



Figure 31: *Altered kaolinite crystals*: BSE-SEM images showing crystals with kaolinite morphology but anomalous composition. Abnormal crystals are indicated by red boxes. The difference in brightness is due to a higher average atomic number than the surrounding kaolinite. A: From W-1002 well at 1344 ft. (depth) B: From W-962 well at 1425 ft. (depth) C: From W-1002 well at 1356 ft. (depth) D: From W-1002 well at 1444 ft. (depth).



Figure 32: *Authigenic chlorite*: BSE-SEM images of authigenic grain-coating chlorite. From CH101 well at 85 ft. (depth).



Figure 33: *Chlorite cement morphology*: SE-SEM images of bladed morphology of authigenic grain-coating chlorite. From CH101 well at 85 ft. (depth).

rhombs (Fig. 34), indicating that chlorite cement precipitation occured after carbonate precipitiation (Fig. 7). Quartz overgrowths occur on uncoated sections of detrital quartz grains, and then crystalize over chlorite rims (Fig. 35) indicating that quartz overgrowth precipitation occured after chlorite cement precipitation in the paragenetic sequence (Fig. 7). Chlorite lines pores that contain pore-filling kaolinite (Fig. 36). The kaolinite itself is not coated by chlorite, indicating that chlorite precipitated before kaolinite (Fig. 7).

EDS analysis of chlorite was conducted solely to confirm the identification of chlorite rims once per thin section (Fig. 37). Chlorite was not the primary focus of this project so further investigation of chlorite's chemical composition was not conducted.

Muscovite

Muscovite is present as a detrital component in all four of the sample wells (Table 4). Muscovite can be observed as components of metasedimentary lithic fragments (Fig. 38) and discrete grains (Fig. 39). Grains of muscovite are often deformed around rigid detrital grains of quartz and feldspar, resulting in reduction of porosity. Exfoliation of muscovite grains (Fig. 40) is common.

Exfoliation of muscovite grains is commonly observed immediately next to diagenetic kaolinite (Fig. 41). This figure depicts what appear to be muscovite layers altering to kaolinite near exfoliated edges. The change in Z contrast along with EDS analysis indicate that layers are becoming depleted of potassium near the edges (Fig. 42). Additionally, distinct kaolinite booklets are observed within exfoliated layers and immediately surrounding the muscovite. These observations suggest the alteration of muscovite into kaolinite. Along with biotite, muscovite abundance increases dramatically in the deeper interval of the RASA 5 well (590-610 ft. depth). Muscovite and biotite comprise up to 50% of rocks in this interval (Table 3) and


Figure 34: *Chlorite-carbonate relationship*: SE-SEM image of authigenic chlorite coating an authigenic carbonate rhomb. From CH101 well at 114 ft. (depth).



Figure 35: *Chlorite-quartz overgrowth relationship*: BSE-SEM image of quartz overgrowth overlying grain-coating chlorite cement. The overgrowth nucleated in area of incomplete cement coverage and grew into open pore space. From CH101 well at 133 ft. (depth).



Figure 36: *Chlorite-kaolinite relationship*: SE-SEM image of authigenic chlorite coating a quartz grain. Authigenic kaolinite can be observed filling the pore space outside of the coated grain. Note that the kaolinite is not coated with chlorite. From RASA 5 well at 519 ft. (depth).



Figure 37: *Chlorite cement EDS*: BSE-SEM image of chlorite cement with an associated EDS chemical composition. The white circle indicates the location of the EDS analysis. From CH101 well at 85 ft. (depth).



Figure 38: *Muscovite in lithic fragments*: BSE-SEM images of lath shaped muscovite crystals in detrital metasedimentary lithic fragments. From W-1002 well at 1448 ft. (depth).



Figure 39: *Muscovite as grains*: BSE-SEM images of muscovite as the dominant component of discrete muscovite grains. From W-962 well at 1448 ft. (depth).



Figure 40: *Exfolitaion of muscovite*: BSE-SEM image of exfoliation of a muscovite grain along interlayer plane. From W-962 well at 1425 ft. (depth).



Figure 41: *Possible muscovite alteration*: BSE-SEM images of authigenic kaolinite forming immediately adjacent to exfoliating muscovite. A: From W-962 well at 1430 ft. (depth) B: From RASA 5 well at 598 ft. (depth).



Figure 42: *Muscovite alteration EDS*: BSE-SEM image and EDS analyses of different sections of a potentially altering muscovite grain. Note the difference in potassium between the two analyses. From W-962 well at 1430 ft. (depth).



Figure 43: *Abundant mica*: BSE-SEM image of mica-rich interval within the RASA 5 well. Detrital mica grains comprise >50% of the sample. From RASA 5 well at 607 ft. (depth).

have clear fabric in the horizontal direction parallel to bedding (Fig. 43).

Biotite

Biotite is present in three of the four sample wells (not present in W-1002). Biotite is observed only as discrete grains. As with muscovite, biotite grains are commonly deformed between rigid detrital grains (Fig. 44). Exfoliation of biotite grains along the interlayer is common (Fig. 45).

Biotite grains commonly show compositional alteration along individual layers, giving grains an internally mottled appearance when viewed with BSE imaging (Fig. 46). Terminations of individual layers are commonly associated with compositional changes within these grains. Some grains appear to have altered (compositionally and texturally) into poorly crystallized minerals of ambigous morphology with compositions similar to kaolinite (Fig. 47). Other grains show unusually wide (3-4 μ m) spacing between individual layers, with authigenic chlorite nucleating on and between these layers (Fig. 48). It is unclear whether this unique appearance in BSE imaging is due to chlorite cements precipitating on biotite layers and growing into the accomodation space produced by exfoliation, or alteration of biotite to chlorite.

Pyrite

Diagenetically formed pyrite is present in all four of the sample wells and can be observed in almost all samples analyzed. Pyrite is easily distinguishable in BSE imaging due to the high Z contrast caused by pyrite's high average atomic number. Diagenetic pyrite occurs as framboidal clusters precipitating in open pore spaces (Fig. 49), and pore filling cement (Fig. 50). One locality (depth of 33 feet) was identified within the CH101 well that contains pore space which is entirely cemented with pyrite, completely occluding porosity (Fig. 51).



Figure 44: *Deformed mica grain*: BSE-SEM image of detrital biotite grain deforming around more rigid detrital grains. From RASA 5 well at 531 ft. (depth).



Figure 45: *Exfoliation of biotite*: BSE-SEM image of exfoliation of biotite grains. From W-962 well at 1453 ft. (depth).



Figure 46: *Biotite heterogeneity*: BSE-SEM image of compositional heterogeneity of biotite grain. Different Z contrasts display differences in average atomic number. From W-962 well at 1453 ft. (depth).



Figure 47: *Possible biotite alteration to kaolinite*: BSE-SEM image of possible alteration of detrital biotite grain to kaolin composition material. The yellow oval represents the target area of EDS analysis. From RASA 5 well at 598 ft. (depth).



Figure 48: *Possible biotite alteration to chlorite*: BSE/SE-SEM images of authigenic chlorite forming on and around detrital biotite grains. Note that chlorite appearts to be forming in the interlayer space of biotite. It is unclear if biotite is altering to chlorite or chlorite cements are nucleating directly on biotite layers. The top two images are BSE from thin sections, and the bottom two images are SE from rock chips. From CH101 well at 114 ft. (depth).



Figure 49: *Framboidal pyrite*: BSE-SEM images of diagenetically formed pyrite clusters with framboidal morphology. A: From W-1002 well at 1356 ft. (depth) B: From CH101 well at 133 ft. (depth).



Figure 50: *Pore-filling pyrite*: BSE-SEM images of diagenetically formed pyrite with pore-filling morphology. A: From W-962 well at 1328 ft. (depth) B: From CH101 at 58 ft. (depth).



Figure 51: *Abundant pyrite cement*: BSE-SEM images of anomalously abundant diagenetic pyrite. Pore-filling cement completely occludes porosity. Grains appear darker on screen due to BSE saturation from pyrite's high Z contrast. From CH101 well at 33 ft. (depth).



Figure 52: *Quartz microstylolites*: BSE-SEM image of microstylolites along quartz grain contacts resulting from pressure solution. Microstylolites have no preferred orientation. From W-962 well at 1453 ft. (depth).

Quartz,

Detrital quartz constitutes the majority of grains in these units (Fig. 14, Table 3). Quartz grains are primarily subangular in shape. Many quartz grains display microstylolites as a result of pressure solution caused by compaction (Fig. 52).

Diagenetic quartz overgrowths are common in grains from all four sample wells. Overgrowths on these grains generally do not precipitate around the entirety of the grain surface. Rather, overgrowths are observed to be prismatic in shape and precipitate as smaller overgrowths that do not engulf the entire grain (Fig. 53). These overgrowths appear as euhedral blocky bulges with straight edges in thin section (Fig. 54).

Potassium Feldspar

Potassium feldspar is present in all four sample wells. K-feldspar is observed as detrital grains comprising between 0-11.1% of detrital grains throughout different intervals (Table 3). Diagenetic overgrowths are common in grains from all wells (Fig. 55), indicating previous supersaturation of pore fluid with respect to K-feldspar. Dissolution of K-feldspar is also common in grains throughout all sample wells. Dissolution of K-feldspar is inferred from the presence of skeletal K-feldspar grains (Fig. 56), indicating previous undersaturation of pore fluid with respect to K-feldspar and the presence of skeletal K-feldspar grains (Fig. 56), indicating previous undersaturation of pore fluid with respect to K-feldspar.

Many K-feldspar grains were observed with diagenetic overgrowths that appear to be preferentially dissolving relative to the detrital grain on which they precipitated (Fig. 57). This indicates that pore fluid became undersatured with respect to K-feldspar after the precipitation of diagenetic overgrowths. It is also possible that there were multiple periods of pore fluid undersaturation with respect to K-feldspar and the most recent period of such conditions occured after the precipitation of these overgrowths. This preferential dissolution could be a result of insufficient residence time of undersaturated pore fluid, insufficient circulation of pore fluid



Figure 53: *Prismatic quartz overgrowth*: SE-SEM image of quartz grain displaying prismatic overgrowths. Overgrowths are not nucleating around the entirety of the grain, but rather as prisms in select areas. From W-1002 well at 1356 ft. (depth).



Figure 54: *Quartz overgrowths*: BSE-SEM images of euhedral quartz overgrowths with sharp, well defined edges. From W-962 well at 1338 ft. (depth).



Figure 55: *Feldspar overgrowths*: BSE-SEM image of K-feldspar overgrowths forming on detrital grains. From W-962 well at 1425 ft. (depth).



Figure 56: *Skeletal K-feldspar*: BSE-SEM images of skeletal (partially dissolved) K-feldspar grains. From RASA 5 well at 519 ft. (depth).



Figure 57: *Preferential dissolution of K-feldspar overgrowths*: BSE-SEM images of K-feldspar grains with diagenetic overgrowths that seem to be preferentially dissolving. From W-962 well at 1430 ft. (depth).

through open pore space, or a structural/compositional feature of these overgrowths that resulted in increased susceptibility to dissolution relative to the intact detrital feldspar cores.

Additional Selected Observations

Diagenetically formed carbonate minerals were present in all four of the sample wells. Pore filling calcite cement and euhedral authigenic carbonate rhombs (Fig. 58) were observed. These rhombs appear to be nucleating on detrital grains (Fig. 59), although some of these rhombs appear in open pore space (Fig. 60), likely because the thin section did not intersect the grain contact. These rhombs were determined to be ankerite based on their iron and magnesium content. Figure 58 shows rhombs displaying clear zoning as indicated by the difference in the brightness contrast in BSE imaging and supported by EDS analysis. These zoned regions contain varying Fe/Mg ratios and are likely caused by fluctuations in the pore fluid composition as the rhombs were gradually precipitating.

Titanium oxide minerals with skeletal and replacement textures (Fig. 61) occured locally throughout samples. The presence of these minerals is interpreted to be associated with remobilization of titanium from detrital biotite and rutile in sandstone systems (Morad and Aldahan, 1986; 1987).

X-ray Diffraction

Twelve samples of clay sized (<2 µm equivalent spherical diameter) material from the Marshall Sandstone and Michigan Formation were analzed by pXRD. Samples for XRD analysis were selected using the illite morphological classification scheme (Table 5) to identify samples containing only fibrous authigenic illite. Careful consideration was given to exclude samples containing detrital illite pseudomatrix material. Previous workers (Zacharius, 1992; Cox, 2015) have conducted XRD analysis of Marshall and Michigan clay sized fractions to idenify clay



Figure 58: *Authigenic carbonate morphology*: SE-SEM images of authigenic carbonate rhombs. EDS analysis suggests that rhombs are ankerite. From CH101 well at 114 ft. (depth).



Figure 59: *Zoned ankerite rhombs*: BSE-SEM images of authigenic carbonate rhombs nucleating on quartz grains. Rhombs are likely ankerite based on EDS analysis. Ankerite rhombs display zoning based on heterogeneity in Fe/Mg ratios. From CH101 well at 114 ft. (depth).



Figure 60: *Carbonate rhombs*: BSE-SEM image of authigenic carbonate rhombs in open pore space. From W-1002 well at 1356 ft. (depth).



Figure 61: *Ti-O mineralization*: BSE-SEM images. A: Ti-O mineral grain displaying a skeletal texture. From W-1002 well at 1406 ft. (depth) B: TiO mineral occurring as part of a metasedimentary lithic fragment. From RASA 5 well at 519 ft. (depth).

minerals, although none of the aforementioned work gave consideration to the seperation of detrital and diagenetic illite. As a result, previous XRD patterns generated from these clays likely include components of detrital clays. Such patterns are successful at identifying illite, but do not accurately represent XRD properties of the authigenic illite alone.

One representative diffractogram from each illite-bearing well is displayed (Fig. 62). All other diffractograms are included in the Appendix. Illite was found in all twelve of the XRD samples analyzed (Table 7). Kaolinite was found in all twelve samples (Table 7). Chlorite was found in seven samples (Table 7). Quartz was found in every sample (Table 7). Potassium feldspar was found (typically with low intensity peaks) in nine samples (Table 7). Minerals were identified using the presence of diagnostic peaks (Table 8). Sample preparation by sedimentation onto the mounting medium biased the distribution of minerals at the surface of the mount in favor of smaller clay particles (Moore and Reynolds, 1997). As such, peak intensities for illite cements are heightened, but quantifications of mineral abundances would not be accurate and therefore were not attempted.

No discrete smectite component was found in any XRD sample analyzed. However, the smectitic component of highly illitic IS mixed-layered minerals may be determined based on differences betwen illite peaks from air-dried and ethylene glycol saturated samples, due to the expansion of smectite interlayers during glycolation (Środon, 1980). Attempts were made to determine the smectitic component of diagenetic illite samples in this study using the methods of Środon (1980) and Środon (1984). However, the results were inconclusive. The problems with applying these techniques to these samples were as follows: the illite (004) peak used for one method was not within the range of the XRD runs in this study; the intermediate angle illite (002) and (003) peaks used with these methods were subject to quartz peak overlap (003) and not





Figure 62: *Representative diffractograms from clay sized fraction*: Representative diffractograms from both wells found to contain diagenetic illite. A: From W-1002 well at 1363 ft. (depth) scanned from 4-40° 20 B: From W-962 well at 1430 ft. (depth) scanned from 4-35° 20. Mineral abbreviations are those of Whitney and Evans (2010).

Well Name	Depth (ft.)	Illite	Kaolinite	Chlorite	Quartz	K-Feldspar
W-1002	1328	Х	Х	Х	Х	Х
	1344	Х	Х	Х	Х	
	1363	Х	Х	Х	Х	Х
	1406	Х	Х		Х	Х
	1420	Х	Х		Х	Х
	1435	Х	Х		Х	Х
	1444	Х	Х		Х	Х
W-962	1338	Х	Х	Х	Х	
	1343	Х	Х	Х	Х	Х
	1425	Х	Х		Х	Х
	1430	Х	Х	Х	Х	Х
	1448	Х	Х	Х	Х	

Table 7: Minerals observed in powder XRD analysis.

Table 8: Diagnostic peaks for mineral identification in oriented mounts of clay-size fractions by pXRD.

Illite d(Å)	Kaolinite d(Å)	Chlorite d(Å)	Quartz d(Å)	Microcline d(Å)	Sanidine d(Å)
10 (001)	7.16 (001)	14.2 (001)	4.26 (100)	3.24 (001)	4.25 (101)
5(002)	3.58 (002)	7.1 (002)	3.34 (011)	2.89 (010)	
3.35 (003)		4.74 (003)	2.46 (110)		
		3.55 (004)			

of sufficent intensity to be useful (002). Weakness of the (002) peak intensity is unusual and may be a product of Fe substituation in octahedral sites attenuating the Cu signal. This test was initially developed for use in analyzing bentonites and shale samples, and perhaps does not apply easily to sandstone cements. Środon's samples were analyzed up to higher angles, and the quantity of clay content available was much greater considering the sample types used.

The illite Ir (intensity ratio) number analysis of Środon (1984) was completed for every sample. This analysis approximates the degree of smectite mixed-layering by comparing intensity ratios of illite peaks from air-dried and ethylene glycolated samples using the equation:

$$Ir = \frac{\frac{I(001)}{I(003)}}{\frac{I(001)}{I(003)}} \frac{airdried}{glycol\ treated}$$

where Ir = 1 for pure illite. Larger Ir numbers (> 1) indicate that a swelling component (e.g., a smectite-group mineral) is present in the sample. This technique is not intended to provide definitive percentages, but rather to be used as an indicator of the presence/absence of expandable material and thus an additional consideration to the interpretation of illite crystallinity data. The calculated Ir numbers are shown in Table 9. Peak measurements used in the Ir calculation are shown in the appendix. Ir results should be interpreted with caution, keeping in mind that the theoretical minimum Ir number possible should be one, and yet four samples resulted in calculated Ir values below one. This may be due in part to error associated with determining the exact peak maximum intensity, or background overlap caused by the mounting medium background. The average Ir number from XRD samples was calculated to be 1.062 (Table 9). This value is statistically indistinguishable from unity, based on the standard deviation of 0.171, indicating a negligible component of expandable material.

Sample	Depth (ft.)	Ir (air-dried)	Ir (glycol)	lr	FWHM (° 2 0)
W-1002 (2)	1328	0.761	0.740	1.028	0.215
W-1002 (3)	1344	0.367	0.374	0.981	0.208
W-1002 (5)	1363	0.210	0.157	1.338	0.210
W-1002 (8)	1406	0.233	0.201	1.159	0.203
W-1002 (10)	1420	1.215	0.976	1.245	0.203
W-1002 (11)	1435	0.287	0.234	1.220	0.168
W-1002 (12)	1444	0.419	0.540	0.776	0.198
W-962 (2)	1338	1.121	1.093	1.026	0.212
W-962 (3)	1343	0.747	0.633	1.180	0.182
W-962 (8)	1425	0.186	0.192	0.971	0.180
W-962 (9)	1430	0.299	0.298	1.002	0.279
W-962 (10)	1448	0.184	0.225	0.816	0.232
Average				1.062	0.208
s.d.				0.171	0.029

Table 9: Calculated Ir numbers and full width at half maximum (FWHM) values of illite (001) peaks for samples containing authigenic illite.



Figure 63: *Michigan/Marshall illite crystallinity data*: FWHM values of authigenic illite samples plotted on the Kübler Index formational regime diagram. The average FWHM value is represented by the red line, and the range of FWHM values are represented by the yellow bar.

Illite crystallinity was investigated using the Kübler index, which is based on measuring the full width at half maximum (FWHM) of the illite (001) peak. Illite (001) peaks were fitted using Gaussian models in the software package PD Analysis, provided by Proto Manufacturing. FWHM measurements from all samples are displayed in Table 9. The average value of FWHM from XRD samples was $0.208^{\circ} 2\Theta$ (Table 9). This average value, along with the upper and lower bounds of the range of FWHM values, were plotted on a Kübler Index temperature regime chart (Fig. 63) with the boundaries defining the anchizone adjusted following the recommendations of Kisch (1990). FWHM values straddle the anchizone-epizone boundary on the diagram, indicating high crystallinity and suggesting high temperature of formation (~265° C - 315° C) for authigenic illite.

Transmission Electron Microscopy

Transmission electron microscopic analysis was completed on two samples, one from each of the two wells containing fibrous authigenic illite (W-1002 and W-962). The sample from well W-1002 was from a depth of 1406 feet, and the sample from well W-962 was from a depth of 1425 feet. Samples were selected using the illite morphology classification (Table 5) to eliminate all samples containing detrital illite. Next, samples were chosen based on SEM observations in an attempt to select samples that contain large amounts of fibrous authigenic illite. Transmission electron microscopic bright field imagery was acquired from both samples. Diagenetic illite was observed as groups of laths which were commonly clumped together (Fig. 64). These laths ranged from 30-90 nm in width and 200-1000 nm in length (Fig. 65). The arrangement of these laths in clumps may be due to the high layer charge of illite, such that individual laths became attracted to one another while in suspension and remained clumped on the TEM grid. Diagenetic kaolinite was also observed. Kaolinite occurs as pseudohexagonal



Figure 64: *Illite TEM crystal habit*: TEM micrographs taken with a Gatan digital camera of clumps of authigenic illite crystallites displaying a lath-shaped crystal habit. The large darker shapes on the micrographs are the lacy carbon grid. From W-1002 well at 1406 ft. (depth).



Figure 65: *Illite lath sizes*: Authigenic illite laths measured using the measuring tool built into the TEM software. The narrow lath crystal habit suggests formation conditions that limited crystal growth. From W-1002 well at 1406 ft. (depth).

plates, significantly larger than illite laths (Fig. 66). Larger muscovite grains were observed in the W-1002 sample. The determination of mineralogy was based on high resolution EDS analysis of individual grains throughout both samples (Appendix).

EDS analysis was completed for four different clusters of illite laths to determine the chemical composition of fibrous illite cements. Evidence of beam damage was present on some illite clusters after prolonged analysis. This evidence included blurring of previously sharply defined cleavage planes and crystal edges. EDS analysis of illite laths revealed an average mineral formula of:

$$K_{0.645}(Al_{1.701}Fe(II)_{0.120}Mg_{0.255})(Si_{3.525}Al_{0.475})O_{10}(OH)_2$$

This mineral formula is slightly different than that of the SEM illite average (Table 6). This is perhaps because SEM EDS analysis included components of detrital grains, or perhaps due to differences between the specific SEM and TEM instruments. The illite laths appear to contain slightly less potassium than the average SEM illite compositions. Once again the tetrahedral Al:Si ratio and degree of divalent octahedral substitution are similar to phengite.

Selected area electron diffraction was used to observe electron diffraction patterns for illite laths. Electron diffraction patterns were taken from larger illite laths in an attempt to produce the sharpest patterns as possible. Electron diffraction patterns from two grains are presented in Figures 67 and 68. Clear discrete diffraction spots on the SAED pattern from both samples indicate well-defined single crystal patterns, instead of a powder-like pattern that would be expected from random orientation about the c* axis (Freed and Peacor, 1992). This suggests that some degree of ordered stacking must be present in these illite crystals.



Figure 66: *Kaolinite TEM crystal habit*: TEM micrograph showing pseudohexagonal plate crystal habit of kaolinite. The darker features are the lacy carbon grid. From W-1002 well at 1406 ft. (depth).



Figure 67: *Selected area electron diffraction pattern #1*: Clump of illite laths and the resulting selected area electron diffraction pattern. The combination of discrete spots and faint rings indicate some disorder in an otherwise ordered stacking pattern. From W-1002 well at 1406 ft. (depth).



Figure 68: *Selected area electron diffraction pattern #2*: Larger illite lath and the resulting selected area electron diffraction pattern. Discrete spots resemble a single-crystal pattern rather than a powder-like pattern. From W-962 well at 1425 ft. (depth).

Aqueous Geochemistry

Pore fluid compositions from all 90 Marshall Aquifer groundwater wells were compiled from USGS Open-File Report 90-368 (Dannemiller and Baltusis Jr., 1989). Data for relevant aqueous species were extracted and are shown in the Appendix. Values were plotted on a log scale α (K⁺/H⁺) *vs* α (Si) diagram representing thermodynamic mineral stability fields (Fig. 69). Thermodynamic data used in the creation of this activity-activity diagram come from USGS Survey Bulletin 1452 (Robie et al., 1979). These same data were then plotted on the stability diagram which now includes the approximate position of an experimentally determined illite thermodynamic stability field (Fig. 70). The illite stability field on Figure 70 represents the full range of positions on the diagram where previous researchers have placed the boundaries of the illite stability field as determined experimentally (Aja, 1991; Aja et al., 1997; Yates and Rosenberg, 1997; Noguera et al., 2011). The majority of the data plot within the overlapping kaolinite-illite stability fields, while some data plot in the kaolinite stability field just below the illite stability field.

USGS aqueous geochemical software package PHREEQC (version 3) was used for mixing and forward modeling. The composition of a Marshall aquifer well from Lake County, Michigan (Well #3 from Lake County in USGS Dannemiller and Baltusis, 1988), was selected as the initial input to represent the modern pore fluid composition of the Michigan Basin in intervals found to contain either fibrous illite cements or authigenic replacement illite. This well was selected because it most closely approximates the depth and location within the basin of the sample wells containing aforementioned illite (Fig. 71). The representative well from Lake County was the deepest Marshall well near the center of the basin that was sampled as part of Dannemiller and Baltusis (1988). Using PHREEQC, the composition of groundwater in this well



Figure 69: *Marshall groundwater data*: Groundwater chemistry from the Marshall aquifer plotted on the $K_2O-Al_2O_3-SiO_2-H_2O$ system mineral stability diagram. Thermodynamic data used in production of boundaries from Robie et al. (1979). The least-squares regression line is displayed in blue.



Figure 70: *Marshall groundwater data with illite stability field*: Marshall aquifer groundwater chemistry plotted on illite inclusive mineral stability diagram. The illite stability field is represented by the blue square. This field represents all previous experimentally determined positions of illite stability.



Figure 71: *Geographic locations of relevant wells*: Geographic locations of wells relevant to completion of aqueous geochemical modeling.

was brought to undersaturation with respect to muscovite to represent (as well as possible) the composition of pore fluid prior to illitization (Appendix). Muscovite is frequently used as a proxy for illite in thermodynamic calculations given the poorly defined thermodynamic properties of illite (Bjorkum and Gjelsvik, 1988). The compositional adjustment representing undersaturation with respect to muscovite is made by fixing the saturation index of illite (K-mica) at -1 (undersaturation) and adjusting the chemical composition of relevant aqueous species in the solution to fit the fixed value. The saturation index is a value used to determine whether a fluid is saturated, undersaturated, or supersaturated with respect to a mineral phase. This value is the log of the ratio of the ion activity product (IAP) to K_{sp} for the illite (K-mica) dissociation reaction displayed below:

$$K(Al_2)(AlSi_3)O_{10}(OH)_2 + 10H^+ \leftrightarrow K^+ + 3Al^{3+} + 3H_4SiO_4$$
 (5)

using the equations:

$$SI = log_{10}(\frac{IAP}{K_{sp}})$$

where $log_{10}(K_{sp}) = 12.703$ (at 25° C) (PHREEQC internal database). The K_{sp} value comes from the equation:

$$K_{sp} = \frac{[K^+][Al^{3+}]^3[H_4SiO_4]^3}{[H^+]^{10}}$$

and is provided in the PHREEQC internal database, and the IAP is calculated by PHREEQC from the equation:

$$IAP = \frac{\{K^+\}\{Al^{3+}\}^3\{H_4SiO_4\}^3}{\{H^+\}^{10}}$$

PHREEQC will calculate the activities of K^+ , Al^{3+} , H_4SiO_4 , and H^+ required to make the SI equal the user-defined value, and then provide an output containing the composition of this new solution. The resulting pre-illite pore fluid should suffice to represent the slight chemical difference between modern pore fluid and pore fluid prior to fluid invasion and fibrous illite cement precipitation (Appendix). The precipitation of fibrous authigenic illite would have altered the composition of the pore fluid, and this modeled solution was created to account for the slight variation in composition. This modeled pre-illite composition was then plotted on the K₂O-Al₂O₃-SiO₂-H₂O mineral stability diagram (Fig. 72). This pre-illite composition was used as an input for aqueous mixing modeling.

The hypothesis that illite formed by downward percolation of meteoric water (Zacharias, 1992) was tested first. The composition of meteoric water used for mixing modeling was selected from USGS Water-Supply Paper 1535 (Carroll, 1962). Using PHREEQC this solution was brought to thermodynamic equilibrium with potassium feldspar at 25°C to represent enrichment of K⁺ resulting from the interaction of potassium feldspar with meteoric water (Appendix). An incremental mixing model was then initiated at 25°C using modeled pre-illite pore fluid and K⁺-enriched meteoric water as end member solutions. Potassium-enriched meteoric water was introduced at increments of 2%, 4%, 6%, 8%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100%. Compositions of each of the resulting mixed solutions were recorded and plotted along with the modern Marshall groundwater dataset (Fig. 73). Increasing the amount of meteoric solution being mixed with the pre-illite solution results in dilution of Marshall brine with respect to the K⁺/H⁺ ratio and Si activity, and subsequent movement of data points away from the illite stability field along both the X and Y axes and into the kaolinite stability field.

Two deep basin brine mixing models were created to investigate the hypothesis of precipitating illite by mixing with different compositions of deep formation waters. To test the hypothesis of upwardly mobile deep brine mixing, a Michigan Basin brine was required as an



Figure 72: *Modeled pre-illite solution*: Composition of the modeled "pre-illite" solution plotted on the illite-inclusive mineral stability diagram.


Figure 73: *Meteoric water mixing model results*: A: Results from K⁺-enriched meteoric water mixing model. B: Close-up on the data of interest. The arrow indicates the trend of the modeled pore fluid composition with increasingly larger percentages of K⁺-enriched meteoric water being introduced. The blue square represents the illite stability field.

input. The solution used for the first deep brine input was Devonian age well ID 4069 from the Richfield member (part of the Lucas Formation) in the Michigan Basin, sampled and reported by Wilson and Long (1993). This well was selected because the groundwater solution is saline, the composition has been described in detail, and geographically this well is very close to the sample wells that contain fibrous authigenic illite. Assuming that the flow path of these brines is dominantly vertical, groundwater from this Devonian well would be the most reasonable solution to use as a brine end member for mixing. The location of all wells used for modeling, as well as the Marshall sample wells containing fibrous authigenic illite are displayed (Fig. 71). Additional information regarding these wells is presented in the Appendix.

An incremental mixing model was then implemented at 25°C using modeled pre-illite Marshall pore fluid and Devonian well 4069 as end member solutions. Devonian brine was introduced at increments of 2%, 4%, 6%, 8%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100%. Compositions of each of the resulting mixed solutions were recorded and plotted along with the modern Marshall groundwater dataset (Fig. 74). Increasing the amount of Devonian brine being mixed with pre-illite solution results in movement of the data away from the illite stability field and into the kaolinite stability field. This trend is similar to that of meteoric water mixing, although the slope of the trend is much closer to zero than the meteoric model (Fig. 73).

The Devonian brine mixing model failed to provide a feasible illite-producing scenario, so another mixing model was defined. The composition of the second deep brine solution was calculated by averaging the compositions of two Silurian-age wells from the Niagara Group in the Michigan Basin as reported by Wilson and Long (1993). Preference in selection of these wells was given to wells located as near to the middle of the basin as possible for which values



Figure 74: *Devonian brine mixing model results*: A: Results from the Devonian brine mixing model. B: Close-up on the data of interest. The arrow indicates the trend of the modeled pore fluid composition with increasingly larger percentages of Devonian brine being introduced. The blue square represents the illite stability field.

of pH, K⁺, and H₄SiO₄ were reported. This eliminated many options. The Silurian-age Niagara Group was selected due to the known existence of highy concentrated brines that have been described in detail by Wilson and Long (1993). Wells 2090 and 2091 were selected because they most closely met all desired criteria (close to center of basin; pH, K⁺, H₄SiO₄ reported). The locations of these wells in relation to the two illite-bearing sample wells are displayed in Figure 71.

An incremental mixing model was then implemented at 25° C using a composition calculated by using the average of the two Silurian brines and the pre-illite Marshall brine as end member solutions. The Silurian brine solution was introduced at increments of 2%, 4%, 6%, 8%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100%. Compositions of each of the resulting mixed solutions were recorded and plotted along with the modern Marshall groundwater dataset (Fig. 75). Increasing the amount of Silurian brine being mixed with the preillite solution increases the K⁺/H⁺ ratio, resulting in movement of the data up the Y-axis within the illite stability field. This result is in contrast to previous mixing models.



Figure 75: *Silurian brine mixing model results*: A: Results from the Silurian brine mixing model. B: Close-up on the data of interest. The arrow indicates the trend of the modeled pore fluid composition with increasingly larger percentages of Silurian brine being introduced. The blue square represents the illite stability field.

Discussion

Well Log Interpretations

Well log profiles which include gamma ray (GR), caliper, neutron porosity, and bulk density data were provided by MGRRE for the Consumers Energy Winterfield W-1002 PN 61260 well and the Michigan Gas Storage Co. 25462 -W-962 observation well (the illite-bearing wells). The positions of the Marshall and Michigan Stray sandstones are easily apparent. The Stray Dolomite provides a recognizable low-GR, high-density signature that can be used to determine the contact between the two units (Fig. 76). The Marshall Sandstone and the Michigan Stray Sandstone have near identical signatures for all four of the included logs. Slight variation in density, neuron porosity, and gamma ray values exist within these sandstones. These variations occur intermittently and likely represent unsampled thin intervals of interbedded mudstone.

Paragenetic Sequence

Thin section and rock chip petrography (optical and SEM) comprise the basis for the paragenetic sequence (Fig. 7). Textural relationships between diagenetic minerals allow for the establishment of different stages of mineral dissolution and precipitation. The paragenetic sequence as presented here agrees relatively well with previous researchers (Zacharias, 1992). Minor modifications to previous work were made based on contrasting observations.

Compaction

The deformation (bending) of detrital mica grains demonstrates early mechanical compaction of rigid grains around the mica (Fig. 7, 44). Compaction by pressure dissolution is observed in quartz and feldspar grains (Fig. 52) from all sample wells except CH101, the

Consumers Energy Winterfield W-1002 PN 61260



Figure 76: *Representative well log*: Well log profile for the Marshall/Michigan interval of the Winterfield W-1002 well. The large bulk density and low neutron porosity signatures of the Stray Dolomite indicate the contact between the Marshall Sandstone and the Michigan Formation. This log was provided by MGRRE.

shallowest well. Quartz grains displaying pressure dissolution often show grain-coating cements nucleating along the entire exterior of these grains except points of contact with other grains. This implies that those points of contact existed prior to the formation of any type of grain-coating or pore-filling cement.

Mudstone lithic fragments and detrital mica grains in the Marshall and Michigan Stray Sandstones have been subjected to compressive forces resulting from overburden. In response to stress these grains deformed plastically around rigid detrital grains like quartz and feldspar (Fig. 22). Intervals containing large abundances of either mudstone lithic fragments or mica grains contain very little (0.5% - 7.5%) to no porosity (Fig 16, 17, 23, 43; Table 5). Physical deformation of detrital phyllosilicates constitutes the largest porosity-reducing factor in these strata.

The mica grains and mudstone fragments deform in different ways. In response to compressive stresses mudstone lithic fragments appear to lose any internal structure and rigidity, resulting in the formation of pseudomatrix. This pseudomatrix has an EDS signature identical to illite (Fig. 21), likely because illite is the dominant component of these detrital mudstone fragments. As a result, localities containing this pseudomatrix are litharenites, but also pseudogreywackes (24-36.6% pseudomatrix). Micaceous intervals in the Marshall are very micaceous (up to 61.5%). Mica grains in these intervals show less exfoliation and alteration than mica grains in intervals with normal low detrital mica abundances and significant porosity. It is likely that reduction of porosity by compaction and grain deformation inhibited alteration of these mica grains by restricting the amount of pore fluid and reactant solutes coming into contact with them.

Carbonate

Carbonate cements were observed primarily as diagenetic rhombs in these samples. Many of these rhombs were coated with chlorite cements (Fig. 34); therefore, the formation of these rhombs had to have occurred prior to the precipitation of chlorite cements (Fig 7). The later interval of carbonate formation on the paragenetic sequence was proposed by previous researchers. No evidence was found in this study to refute this position, so no changes were made to the previously established episode in the paragenetic sequence. The presence of Febearing carbonates indicates reducing conditions at the time of ankerite formation.

Feldspar

Feldspar overgrowths are commonly observed preferentially dissolving (Fig. 57). Feldspar overgrowth precipitation must have occurred prior to feldspar dissolution. Selective destruction of feldspar overgrowths relative to cores is unusual (Land and Milliken, 1981); this deserves further consideration. Kaolinite cements were observed precipitating adjacent to partially dissolved feldspar overgrowths (Fig. 29). This indicates that these overgrowths existed prior to the formation of kaolinite cements.

Chlorite

Chlorite cement precipitation occurred near the middle of the paragenetic sequence (Fig. 7). This is based on the observation that quartz overgrowths (Fig. 35) and pore-filling kaolinite cements (Fig. 36) are superposed upon grain coating chlorite cements. Zacharias (1992) reported instances of authigenic illite superposed on authigenic chlorite (in unspecified sample wells), although this was not observed in this study. The Fe^{2+} state of iron within the chlorite mineral

formula indicates that redox conditions were reducing, and the environment was anoxic at the time of chlorite formation.

Quartz Overgrowths

It is likely that multiple generations of quartz overgrowth precipitation occurred. Quartz overgrowths engulfing chlorite cements (Fig. 35) indicate that precipitation of these overgrowths occurred after chlorite (Fig. 7). Pore filling kaolinite cements and pyrite cements are observed superposed upon quartz overgrowths, indicating that an earlier generation of quartz overgrowths occurred between chlorite formation and pyrite formation (Fig. 7). A second generation of quartz overgrowths is inferred based on multiple instances of prismatic overgrowths precipitating on illite-coated grains, but not coated by illite (Fig. 26). This suggests that a later generation may have formed cogenetically with illite cements (Fig. 7).

Pyrite

Based on the morphological variation in diagenetic pyrite (Fig. 49, 50, 51) it is likely that multiple episodes of pyrite cement formation occurred in these rocks. Framboidal pyrite occurs in pore space directly outside of chlorite cement rims (Fig. 49-B) indicating that at least one generation of pyrite must have formed after chlorite cement precipitation. Raiswell and Berner (1985) suggest that pore-filling pyrite is Fe limited, and that significant supersaturation would be required for the formation of this texture. Carstens (1986) proposes that framboidal pyrite formation is a result of direct precipitation of pyrite crystals without the existence of a precursor sulfide and may be inhibited by the competitive growth of adjacent crystals. Regardless of texture, the occurrence of authigenic pyrite indicates that redox conditions during stages of pyrite formation were reducing, and the environment was euxinic (Berner, 1980).

Kaolinite

Pore-filling kaolinite cements precipitated near the end of the paragenetic sequence (Fig. 7). Kaolinite is observed filling pore space between chlorite-coated grains (Fig. 36). The kaolinite booklets themselves are not coated by the chlorite, indicating that kaolinite formed after the chlorite cements were in place. Some kaolinite booklets are observed transforming to illite (Fig. 31). Neoformed illite is also observed nucleating on and around kaolinite booklets (Fig. 25), indicating that illite formed after kaolinite cements were already in place (Fig. 7).

Illite

Precipitation of grain coating illite cements occurred very late in the paragenetic sequence (Fig. 7). Illite is observed nucleating (neoforming) on kaolinite (Fig. 25) and detrital quartz grains (Fig. 24). Illite is also observed as a transformation product of kaolinite (Fig. 31). There is no evidence of any type of cement superposed upon illite cements. Illite precipitation may have been cogenetic with a late generation of quartz overgrowth precipitation (Fig. 7, 26). The compositions of both varieties of authigenic illite (Table 6) – illite of transformation, pseudomorphic after authigenic kaolinite, and neoformed pore-lining fibrous illite – have mixed illitic-phengitic character, including specific tetrahedral substitutions consistent with illite, phengite-like substitutions of divalent cations – (Mg, Fe(II) – in octahedral sites, and overall layer charge and interlayer site occupancy of illite.

Detrital Phyllosilicates

Petrographic evidence suggests that many phyllosilicate minerals identified in these rocks either were not or are currently not in equilibrium with pore fluids. Alteration of mica grains is common. Alteration of detrital mica in porous intervals contributed to a minor extent to the

formation of secondary clays. Alteration of detrital muscovite to secondary kaolinite is strongly suggested by the formation of kaolinite cements between exfoliating muscovite layers which appear to be gradually depleted of potassium along grain edges (Fig. 41, 42). This style of alteration has been documented in soil profiles (Singh and Gilkes, 1991) and kaolinitic altered granites (Robertson and Eggleton, 1991) demonstrating that this reaction is common in a variety of conditions. TEM work of Robertson and Eggleton (1991) shows evidence of a transformation reaction of muscovite to kaolinite. This reaction shown below:

$$2KAl_{3}Si_{3}O_{10}(OH)_{2} + 2H^{+} + 3H_{2}O \leftrightarrow 3Al_{2}Si_{2}O_{5}(OH)_{4} + 2K^{+}$$
(6)

proceeds by removal of tetrahedral sheets and depletion of K⁺. This K⁺ depletion is observed in Marshall/Michigan samples (Fig. 42). Additionally, grains exhibiting this alteration show K⁺ depletion predominantly along edges that extend into open pore space. It is likely that porosity and fluid flow (or, at a minimum, solute transport) are critical in facilitating this reaction in muscovite grains in sandstones. This hypothesis would explain why alteration of grains in micarich intervals remained minimal. This reaction is represented by the muscovite-kaolinite boundary on the K₂O-Al₂O₃-SiO₂-H₂O stability diagram. This reaction could be initiated by the invasion of porosity by dilute waters. This process would dilute the Marshall pore fluids, expressed as a change in the K⁺/H⁺ ratio. If the composition of Marshall pore fluid were to initially plot within the muscovite stability field and then become diluted by the invasion of fresh water, movement of the data points toward the muscovite-kaolinite boundary would be expected and the alteration reaction may proceed. Evidence of this reaction in Marshall/Michigan strata may represent a previous period of meteoric water infiltration into Mississippian strata. This meteoric infiltration could have occurred at any point in time between the formation of authigenic chlorite and the formation of authigenic illite in the Early Permian (Cox, 2015).

Biotite can alter to a variety of different secondary minerals depending on the conditions of the system. Alteration of detrital biotite to secondary kaolinite was observed (Fig. 47). Individual layers of biotite appear to lose internal structure while becoming gradually depleted of potassium, iron, and magnesium where the grain extends into open pore space (Fig. 47). The alteration of biotite to kaolinite is well documented. The reaction can occur in soil profiles (Rebertus et al., 1986), igneous rocks (Dong et al., 1998), schists (Ahn and Peacor, 1987), and sedimentary rocks (Morad and Aldahan, 1986). Multiple mechanisms have been proposed for this reaction, from a transformation reaction of one biotite to two kaolinite layers (Dong et al., 1998) to a complete neoformation reaction in which kaolinite crystallizes at biotite layer boundaries (Ahn and Peacor, 1987). This process would proceed by the reaction:

$$K(Fe_{1.5}Mg_{1.5})Si_{3}AlO_{10}(OH)_{2} + 3Al^{3+} + Si^{4+} + 6H_{2}O \leftrightarrow$$
$$2Al_{2}Si_{2}O_{5}(OH)_{4} + K^{+} + 1.5Fe^{2+} + 1.5Mg^{2+} + 6H^{+}$$
(7)

...

A metastable intermediate stage consisting of altered biotite and halloysite may occur in systems where the reaction proceeds slowly due to low temperatures (Dong et al., 1998). As with muscovite, this reaction proceeds in part with depletion of K⁺. Biotite alteration to kaolinite by reaction 7 also involves substitution of 2+ octahedral cations with aluminum.

Evidence suggesting possible alteration of biotite to chlorite was observed at present depths ranging from 70-140 feet. Biotite is known to alter to chlorite in sedimentary systems (Veblen and Ferry, 1983; Banfield and Eggleton, 1988). This alteration is typically associated with the metamorphism of sedimentary pelitic rocks to low grade metamorphic greenschist facies. This reaction is believed to proceed by transformation, which would result in a morphology similar to the primary biotite grain. The potentially altering grains observed here

display unique textural relationships (Fig. 48). Bladed chlorite crystals can be seen on top of and in between biotite layers (Fig. 48). It may be that chlorite is nucleating on and in between exfoliated biotite layers rather than biotite altering to chlorite by transformation.

Detrital mica certainly contributes to the formation of diagenetic clay in these rocks. The initial stimulus for this project was the potential for such large amounts of detrital mica to provide an internal source of potassium for illitization. However, after thorough petrographic analysis, no illite cements were observed in samples that contain abundant (> 25.5%) mica (Table 4, 5). Intervals of abundant mica have been compacted to the point of nearly eliminating porosity (maximum of 5.5% porosity in mica-rich samples) (Table 4, 5). A similar lack of illite cement is noted in phyllitic rock-fragment-rich litharenite pseudogreywacke samples (maximum 0.5% porosity) (Table 4, 5). No illite cements are observed coating grains in samples with minimal porosity. This suggests that significant porosity may be a requirement for illite formation. If true, illite is interpreted to be a product of solute transport and not internally sourced.

Diagenetic Chlorite and Kaolinite

A graphic representation of the depth relationships between sample wells in this study, as well as the depth relationships of major diagenetic clay minerals is provided (Fig. 77).

Diagenetic chlorite occurred as a significant (> 5%) clay mineral in the two shallower wells (RASA 5 and CH101). Chlorite in deep wells did not occur as pervasive grain coating cements, but rather as detrital components of rock fragments. Petrographic results from this study disagree with the previous observations of Zacharias (1992) that chlorite abundance increases with depth. Significant diagenetic chlorite was found at modern depths as shallow as 58 feet and absent in both deeper wells. However, Zacharias' sampling included more wells



Figure 77: *Sample well and authigenic clay depth distribution*: Graphic representation of the depth distribution of major authigenic clay cements, as well as the depth relationship between sample wells. Well locations and unit names are placed only within sampled intervals and may not represent the entirety of the unit(s) at each location.

(19 total), which spanned all the stratigraphic intervals of Mississippian Sandstones. Perhaps this discrepancy comes from analyzing different sample wells with different chlorite depth distributions. Petrographic results from this study also disagree with the suggestion of Zacharias based on Land and Dutton's (1978) model that distribution of chlorite in sedimentary systems is strongly linked to the presence of detrital micas. Chlorite cements did occur in the RASA 5 well which contained abundant detrital mica (Table 3, 4), but chlorite was also found in significant abundances in the CH101 well which contained very little (maximum of 3.5%) mica (Table 3, 4).

Oxygen isotopic analysis of chlorite cements by Zacharias (1992) indicate that the original diagenetic fluid from which chlorite formed was similar in composition to sea water. To reconcile this information with the depth distribution of chlorite cements it should be noted that the deepest part of the Marshall Sandstone in the center of the basin has very little hydrological connectivity with the rest of Carboniferous strata (Ging et al., 1996). It is possible that evapo-concentrated marine formation waters from the Michigan Formation percolated down into the Michigan Stray and Marshall Sandstones and initiated the precipitation of chlorite cements. This model is attractive because it would explain the absence of pervasive chlorite in deep wells in the center of the basin where pore fluids are more saline. The presence of such abundant authigenic chlorite in shallow wells and the absence of similar abundance in deeper wells is difficult to fully explain without further study focusing specifically on this chlorite.

Pore filling kaolinite cements were pervasive throughout the entire depth range of all four sample wells (20-1450 feet). Kaolinite cements formed relatively late in the paragenetic sequence, but the final stage of paragenetic sequence (illite) has been dated to 294-275 Ma (Cox, 2015), meaning that the formation of diagenetic kaolinite likely occurred in the Late Carboniferous or Early Permian. Kaolinite commonly forms as a result of dilute acidic meteoric

water infiltration (Blatt, 1979; Hurst and Irwin, 1982). The Marshall Sandstone and Michigan Formation were deposited in a shoreline environment, meaning that formation waters in these depositional environments were marine. Hydrological connectivity of much of the Marshall/Michigan with overlying Pennsylvanian strata as established by the USGS Michigan Basin RASA study (Westjohn and Weaver, 1998) means that percolation of meteoric waters through overlying strata and into Mississippian strata was certainly possible. Dilute water infiltration into marine formation waters would result in a mixing scenario that would favor the formation of diagenetic kaolinite at the expense of dissolving K-feldspar by reaction 1. Petrographic evidence of this reaction is observed in the form of kaolinite cements commonly occurring immediately adjacent to skeletal K-feldspar grains (Fig. 29). This relationship is consistent with mixing of meteoric and marine waters initiating the formation of kaolinite cements during Late Carboniferous epidiagenesis.

Kaolinite-Illite Reaction

Marshall aquifer pore fluids plot on the K₂O-Al₂O₃-SiO₂-H₂O mineral stability diagram in the kaolinite stability field and the overlapping region of the experimentally determined illite stability field. Furthermore, the data seem to plot along a noticeable trend line, the slope of which is similar to the experimentally determined slopes of the kaolinite-illite stability field boundaries determined by Aja et al. (1991), and Yates and Rosenberg (1996) (Fig. 78). This strongly suggests that the aqueous geochemistry in the Marshall aquifer is influenced by a reaction which results in pore fluid compositions in equilibrium with kaolinite and illite. This observation conforms with the paragenetic sequence which places kaolinite precipitation and illite precipitation as the two most recent diagenetic events. SEM analysis revealed evidence of



Figure 78: *Experimentally determined kaolinite-illite stability boundaries*: Experimentally determined kaolinite-illite stability boundaries. A: Equilibration experiments at 25°C, from Aja et al., 1991 B: Equilibration experiments at 100°C, from Yates and Rosenberg, 1996.

kaolinite replacement by illite (Fig. 31), further supporting the hypothesis that a kaolinite-illite reaction occurred in these strata.

According to Aja et al. (1991), and Yates and Rosenberg (1996), the boundaries defining kaolinite-illite-solution equilibrium can be calculated for illite of composition:

$$K_xAl_2(Al_xSi_{4-x})O_{10}(OH)_2$$

from the reaction:

$$K_{x}Al_{2}(Al_{x}Si_{4-x})O_{10}(OH)_{2} + xH^{+} + \left(1 + \frac{x}{2}\right)H_{2}O \leftrightarrow$$

$$\left[\frac{2+x}{2}\right]Al_{2}Si_{2}O_{5}(OH)_{4} + xK^{+} + (2 - 2x)SiO_{2}$$
(8)

using the equilibrium constant expression:

$$\log\alpha\left(\frac{K^{+}}{H^{+}}\right) = \left[\frac{2x-2}{x}\right]\log\alpha(SiO_{2}) + \frac{1}{x}\log K$$

The slope of the kaolinite-illite stability boundary in this format is then:

$$m = \left[\frac{2x-2}{x}\right]$$

where x refers to the stoichiometry of illite (specifically, the amount of Al for Si substitution in tetrahedral sites). The linear regression of Marshall groundwater data on the $K_2O-Al_2O_3-SiO_2-H_2O$ mineral stability diagram has an equation of y = -2.0578x - 4.3459 (Fig. 69). The slope (m = -2.0578) of this trendline can then be used to calculate an x value of 0.493 for the Marshall data. When compared to x values derived from EDS analysis of illite in this study (x = 0.735, 0.738, 0.645) (Table 6) it is apparent that the linear regression value does not match observed values. The x value derived from illite lath TEM-EDS data most closely resembles the linear regression value. The Marshall linear regression x value is most similar to the calculated value of

x = 0.5 from the experimental results of Yates and Rosenberg (1996) at temperatures of 100° C and 150° C, and x = 0.52 from Aja et al. (1991) at 150° C. The data of Yates and Rosenberg show an increase in the x value with higher temperatures, with a maximum x value of 0.88 at 250° C. This contrasts with the results of this study. Illite crystallinity data from Marshall/Michigan samples suggest illite formation at temperatures between 250-300° C (Fig. 63), and yet the x value calculated for Marshall groundwater was only 0.493.

Marshall groundwater data from Figure 69 are not tightly clustered ($R^2 = 0.2835$). Groundwater compositions were replotted revealing a more apparent trend to the data defining the upper limit of the overall data distribution, and a linear regression line was calculated (Fig. 79). These data are more tightly clustered ($R^2 = 0.58$). The equation for this linear regression line is y = -0.847x + 0.713 (Fig. 79). The slope (m = -0.847) of this trendline can be used to calculate an x value of 0.702. This x value is much closer to illite EDS values from this study (Table 6). Marshall groundwater data from USGS report (Dannemiller and Baltusis, 1986) included sample wells throughout the entire lower peninsula, not just the portion of the Marshall that may contain illite. Based on the similarity between the new calculated x value and illite EDS data, groundwater data within the compositional range that was used to calculate the linear regression line (Fig. 79) may represent the portion of the basin where illite formation has occurred. The linear regression line from Figure 78 would then represent the position of the kaolinite-illite stability boundary for the Marshall system, and the groundwaters plotted along the regression line would indicate three-phase (solution-kaolinite-illite) solution-mineral equilibrium. The position of a stability field boundary (the y-intercept of the line) is determined by all the factors that influence the equilibrium constant for the reaction as written (e.g., standard Gibbs free energies of formation of all phases and species; solid-solution effects (e.g., Merino, 1975); P; T).



Figure 79: *Marshall groundwater trend*: Linear regression trendline of a portion of the Marshall groundwater data. The blue square indicates the portion of the data used to calculate the trendline.

However, the slope of a stability field boundary depends only on the stoichiometry of the reaction describing the equilibrium. The (1) slope of the regression line for the highest $\alpha K^+/\alpha H^+$ Marshall Sandstone groundwaters in Figure 79 and the corresponding x value in equation (8) above for the K-Al-Si proportions of a simplified illite (specifically, the stoichiometric subscript for tetrahedral Al-for-Si substitution and consequent layer charge and charge-balanced interlayer K occupancy) *inferred* from the slope of the regression line (Fig. 79) and (2) *measured* stoichiometric proportions of K, Al, and Si in illite of both neoformation and (especially) transformation origin in this study conform closely. This conformity of inferred and measured stoichiometric values suggests that a three-phase (illite-kaolinite-solution equilibrium) for (phengitic) illite of the measured composition in the Marshall (Napoleon) and lower Michigan Stray Sandstones existed. This equilibrium does not necessarily exist at present-day T, but it existed when the kaolinite transformed to illite (at temperatures of 200 – 300 °C, according to the results of this study's illite crystallinity results), and the solution chemistry has not changed upon cooling to present-day T at 400 – 450 m depth.

There are multiple issues with using this analysis. Calculation of x using this method is only accurate in the case of no divalent cation substitution in octahedral sheets. This method does not consider the presence of Fe^{2+} or Mg^{2+} in the illite mineral structure. This is problematic given that all EDS analyses in this study indicate the presence of divalent cation substitution in (phengitic) illite cements (Table 6). Additionally, x values may be caused by the influence of other factors on Marshall groundwater chemistry. It is also possible that the experimental data of Aja et al. (1991) and Yates and Rosenberg (1996) do not transfer exactly to kaolinite-illite thermodynamic equilibrium in natural systems. Two reactions have been proposed to describe kaolinite-illite-solution equilibrium in nature (reaction 2 and reaction 3). Reaction 2 assumes a closed system and relies on an internal source of potassium by dissolution of K-feldspar. K-feldspar is certainly present, but petrographic evidence suggests that K-feldspar dissolution ceased prior to illite precipitation, and the K-feldspar-kaolinite mineral assemblage should remain stable to temperatures greater than those achievable by simple burial in these strata (Lanson, 2002). Reaction 3 is more feasible at low temperatures, provided an additional potassium input exists. This reaction requires a significant increase in pore fluid K⁺/H⁺ ratio to proceed (Berger et al., 1997). Achieving such an increase by mica dissolution alone would require large amounts of mica to be altered/dissolved. Large amounts of mica are present in the Marshall/Michigan, but not in intervals containing illite cements. Illite formation would be expected in micaceous intervals if detrital micas were playing a large role in the reaction.

X-ray Diffraction

Among the diffractograms acquired for this study, the (001) (d = 10 Å) illite peak is probably the only illite peak of sufficient quality to interpret with any illite-centered techniques. Higher angle illite peaks, while present, are either obscured by peak overlap or too small due to high diffraction intensities from more abundant minerals (quartz and kaolinite).

In agreement with the work of Zacharias (1992) and Cox (2015), no smectite was identified in the Marshall/Michigan from XRD. The possibility of a smectitic mixed-layer component within illite cements was investigated by saturating XRD samples with ethylene glycol to encourage expansion of smectite layers. In the presence of smectite interlayering one would expect to see shifting of the (001) illite peak in the glycolated sample to slightly lower $^{\circ}$ 2 Θ than the (001) peak in the unglycolated sample. Such a shift was not observed in these

samples. An alternative method of investigating smectite mixed layering is calculation of the Ir number (Środon, 1980). Perfect 100% illite would have an Ir number of one. The larger the Ir number, the greater the component of smectite mixed layering. Difficulties with the Ir number calculation for these samples were described in the Results section, but the average Ir number of all samples was found to be 1.062. Extrapolation of Ir number to determine the percentage of smectite mixed layering is not encouraged as a confident means of determination (Środon, 1980). Instead, this number indicates a small, minor (<10 % smectite) presence of smectite mixed layering. In combination with the lack of peak shifting upon glycolation it is inferred that the presence of smectite layers within these illite cements is minimal.

Intensities of illite (001) peaks varied considerably. This is due to a combination of variable illite abundance in different samples and variable degrees of efficiency in sample preparation. Regardless of (001) peak intensity differences, the FWHM values throughout all samples spanned a narrow range ($\bar{x} = 0.2075^{\circ} 2\Theta$, $\sigma = 0.0286^{\circ} 2\Theta$). No trend of FWHM as a function of increasing depth was identified (Table 9).

Placement of the anchizone boundary positions varies among different workers within the illite crystallinity community. Original anchizone boundaries by Kübler (1969) were placed at FWHM 0.42° 2 Θ (low-grade) and 0.25° 2 Θ (high-grade) based on a scan speed of 1° 2 Θ /minute. Thorough analysis and attempted calibration of these boundaries over various scanning conditions was conducted by Kisch (1990). Kisch determined that slower scanning speeds resulted in slight narrowing of the (001) peak. Use of slow scan speeds without adjustment of the anchizone boundaries may result in placement of IC data in a higher-grade thermal regime. Therefore, these boundaries should be adjusted based on scanning speeds. The scan speed in this study (0.24° 2 Θ /minute) was initially selected to optimize signal to noise ratio and is on the

slower end of the spectrum of scan speeds used in crystallinity studies. Use of Kübler's anchizone boundaries (or anchizone boundaries used by workers using similar scan speeds as Kübler) would result in conclusions that may not be realistic due to peak narrowing from slow scan speeds. To adjust for the slow scan speed used in this study anchizone boundaries were selected after Weber (1972) and Teichmüller et al. (1979) who used near-identical scan speeds of $0.25^{\circ} 2\Theta$ /minute. These boundaries are $0.38^{\circ} 2\Theta$ (low-grade) and $0.19^{\circ} 2\Theta$ (high-grade).

FWHM values in this study plot in the anchizone and along the epizone-anchizone boundary, with the average value plotting just within the anchizone range. The temperatures associated with these boundaries are not exact, as different researchers have different working definitions of what constitutes the anchizone. The anchizone is the name assigned to the transition zone between diagenesis and metamorphism, and is defined by Kisch (1990) as a zone of weak to very weak metamorphism associated with the sub-greenschist facies. Assignment of exact temperature values to the boundaries on the Kübler Index would be misleading (Kisch, 1990), so the boundaries are used for qualitative analysis of the thermal regime in which illite forms. All FWHM data from authigenic illite in the Marshall and Michigan plot in high thermal regimes on the Kübler Index. In the context of the two previously proposed models for K⁺ delivery these results align more with the model of hot brine movement up through the basin. Meteoric water and formation waters of overlying strata would not reach temperatures close to those required to place illite crystallinity on the anchizone-epizone boundary. Although it is not definitive that authigenic illite formed at temperatures of 200-300° C, these results indicate that significant heating was required to account for such well crystallized illite.

Transmission Electron Microscopy

Many transmission electron microscope studies of clay minerals orient their samples with the basal planes perpendicular to the sample grid (parallel to the electron beam) in order to view the silicate layering. Doing so allows one to image layer spacings, layer sequences, and variations in polytype. Sample preparation in this study consisted of depositing a drop of suspended powdered clay onto the sample grid. This method results in orientation of individual flakes with their basal (001) planes parallel to the sample grid. As a result, lattice fringe imaging was not possible. Rather, crystal habit, composition, and stacking order were the focus of investigation.

Illite crystallites have two commonly reported habits: lath shaped crystallites and euhedral pseudohexagonal crystallites (Grubb and Peacor, 1991). The dominant habit in mudrocks is understood to be controlled by polytypic variation associated with formation conditions, although illite habit is not yet fully understood. TEM studies of illite in sandstones are less common. Nadeau et al. (1985) and Güven (2001) present images of fibrous cements from sandstones obtained with an identical sample preparation method as used in this study. All samples from five fibrous illite cemented sandstone units display lath morphology. Sizes of laths vary between units, but it appears that the lath crystal habit is dominant for fibrous cements. Güven presented evidence of authigenic illite laths nucleating on kaolinite cores; however, no such phenomenon was observed within Michigan/Marshall samples in TEM, although it was seen in SEM (Fig. 25).

Selected area electron diffraction (SAED) data from illite cements prepared using identical sample preparation procedure as this study were presented by Freed and Peacor (1992). Freed and Peacor (1992) demonstrated the effect of illite stacking disorder on SAED patterns.

Coherent ordered stacking of illite cement layers results in SAED patterns with sharp, discrete spots as expected from a single crystal pattern, whereas disordered layer stacking results in ringed patterns that resemble powder SAED patterns. Illite cement SAED data presented in this study display patterns with discrete spots and slight traces of rings (Fig. 67, 68), indicating dominantly ordered stacking with minor amounts of disorder. Ordered layer stacking is not fully understood, but is thought to be associated with higher temperature formation (Grubb, 1991; Bauluz et al., 2002).

Illite Cement Morphology

Calculations completed by Wilkinson and Haszeldine (2002) conclude that the growth of authigenic illite fibers as seen in sandstones is a process controlled by nucleation kinetics rather than growth kinetics. Based on observation of laths and fibers there appears to be a maximum size to which an illite fundamental particle can grow, and once that size is reached growth of the fiber can only proceed if nucleation of another fundamental particle occurs (Wilkinson and Haszeldine, 2002). This situation requires geological conditions that provide a high degree of pore fluid supersaturation with respect to illite. Thermodynamic stability is not sufficient to form illite fibers; the conditions must allow for continual, rapid fundamental particle nucleation. According to Wilkinson and Haszeldine (2002) these conditions must be more rigorous than slight supersaturation. They suggest that high temperatures and abnormally high pore fluid supersaturations are required for fibrous cement growth. These conditions are more readily met by the deep brine K^+ delivery model.

Geochemical Modeling

The geochemical scenarios resulting from the two proposed models of K^+ delivery can be simplified and modeled using modeling software. The goal of mixing modeling was to use

compositional inputs from Michigan Basin pore fluid data and plot results on illite-inclusive $K_2O-Al_2O_3-SiO_2-H_2O$ mineral stability diagrams to evaluate whether geologic scenarios representing the proposed K⁺ delivery hypotheses would allow for thermodynamic stability of illite.

The first step of modeling these scenarios was selection of a solution to represent Marshall pore fluid in sections of the basin where illitization has occurred. Illite was not present in the shallow sample well (CH101) or the intermediate depth sample well (RASA 5). Illite was only identified in the two deep wells which are both located in the middle of the basin. Unfortunately, USGS Open-File Report 90-368 did not collect groundwater samples at this depth in the Marshall. This is because the USGS report was part of the Michigan Basin Regional Aquifer-System Analysis program (RASA) which focused on sampling aquifers within the basin. The deepest central part of the Marshall/Michigan is not considered part of the aquifer, and therefore was not targeted for sampling during the RASA program. To compensate for this, the well selected to represent solute chemistry in the illite-bearing section of the Marshall/Michigan (Lake County Well #3) was the deepest and among the most saline of all Marshall wells sampled in the report.

Using PHREEQC the composition of Lake County Well #3 was brought to undersaturation with respect to illite (K-mica). A similar calculation was completed to bring meteoric water to equilibrium with respect to K-feldspar in order to represent enrichment in K⁺ from K-feldspar dissolution. The deep brine compositions used were selected based on location and data availability and were unmodified.

According to Lanson (2002), kaolinite-illitization reaction 3 and illite neoformation reaction 4 both require an influx of fluid with a high K^+/H^+ ratio to initiate. When plotting the

results from mixing models the data should be interpreted in the context of movement of the solution composition within/out of the illite stability field and movement along the Y-axis which represents the K^+/H^+ ratio. Regardless of movement along the X-axis, the formation of illite will not be possible unless mixing causes an increase in the K^+/H^+ ratio.

The meteoric water mixing model shows that increasing the amount of meteoric water entering the system (despite the minor K^+ enrichment) dilutes the Marshall brines with respect to the K^+/H^+ ratio. The compositional trend of the data decreases along the Y-axis, indicating that this model fails to provide the thermodynamic conditions necessary for illite formation.

The Devonian brine mixing model yielded similar results as the meteoric model. The slope of the mixing line is much nearer to zero, indicating that the Devonian brine is not diluting the Marshall brine, but is still failing to provide an increase in the K^+/H^+ ratio. Failure to move datapoints up the Y-axis into the illite stability field indicates that this model also fails to provide a large enough K^+/H^+ ratio increase to initiate an illite-forming reaction.

Failure of the Devonian brine mixing model necessitated that another brine mixing model be considered. Higher salinity Silurian brines were selected as an input to address the issue of insufficient K⁺/H⁺ ratio with mixing. The Silurian brine mixing trend has a very steep slope through 50% mixing. After 50% mixing the data begins to plot outside of the illite stability field and in the muscovite stability field. This is not an issue however, because movement of the mixing line up the Y-axis while remaining within the illite stability field indicates that mixing with Silurian brines could provide the K⁺/H⁺ ratio increase required to initiate illitization reaction 3. Once initiated this reaction will consume K⁺ and release H⁺, the combination of which would begin to move compositions down the Y-axis, toward where present Marshall groundwater data plot.

If mixing of pre-illite Marshall brines with Silurian brines were to occur, the resulting solution would plot increasingly upward along the Y-axis. When a K^+/H^+ ratio large enough to initiate reaction 3 or reaction 4 is reached the(se) reaction(s) would initiate and proceed to drop the K^+/H^+ ratio along the Y-axis and into the range of modern data. What is not accounted for in this scenario is the slightly greater silica concentration observed in modern data than such a mixing-reaction path would provide. To reconcile this, consider illite-forming reaction 2. This reaction was initially determined infeasible because it is understood to occur only at high temperatures (Lanson et al., 2002). Illite crystallinity data indicate that high temperature formation of illite was likely. It is also possible that, contrary to the paragenetic sequence, minor amounts of K-feldspar dissolution could have occurred later than expected. The possibility of this late K-feldspar dissolution should not be ruled out, as skeletal K-feldspar grains are observed in open pore space (Fig. 18) and may be contributing to the aqueous silica activity. The coexistence of K-feldspar, kaolinite, and hot saline fluid could potentially initiate reaction 2 in addition to reactions 3 and 4. Reaction 2 yields aqueous silica as a product phase, which could account for the X-axis increase our modeled data would require to return to modern groundwater chemistry. It is worth noting again that the slopes of experimentally determined kaolinite-illite stability boundaries are oriented in a top-left to bottom-right direction (Fig. 78), similar to the trend of modern data and the expected outcome of reaction 2 occurring concurrently with reactions 3 and 4.

Re-evaluation of Potassium-Delivery Hypotheses

The potassium-enriched meteoric water hypothesis is refuted by previous work and results presented here. The enriched meteoric water hypothesis relies on the ability of these waters to percolate down through overlying strata in order to deliver potassium as K^+ aqueous

ions. Ging et al. (1996) report that the deepest portion of the Michigan/Marshall is hydrologically isolated from meteoric water recharge based on trends of isotopic data. δ^{18} O values for much of the Marshall aquifer are interpreted as a mixture of meteoric water and formational brine (Ging et al., 1996); however, values from the deeper central part of the basin become isotopically heavier (Ging et al., 1996), indicating that meteoric water did not make it to this interval. Authigenic illite cements were only located in the deepest part of the Michigan/Marshall; therefore, enriched meteoric water recharge could not provide the K⁺ ions.

The location of illite cementation in the center of the basin likely has little to do with the overburden pressure or maximum burial depth that this interval was subjected to. The Marshall Sandstone has a maximum present depth of \sim 1500 ft. (\sim 400 – 450 m; Table 1), which according to Lanson et al. (2002) is not sufficient burial depth to destabilize the K-feldspar-kaolinite mineral assemblage (e.g., 3 - 5 km, 10,000 - 16,000 ft. in the North Sea). Past burial depths of Paleozoic strata in the Michigan Basin may have been greater at some point in the past. However, in the absence of almost any post-Carboniferous and pre-Pleistocene strata throughout the Michigan Basin (except ~100 m of Jurassic redbeds), burial history curves cannot be constructed. Instead, maximum burial depths of Paleozoic strata in the Michigan Basin must be inferred from thermal maturity indicators, which in turn must be interpreted invoking assumptions about the nature and thermal conductivity of the missing strata (see references in the Introduction, and review by Velbel, 2009). Previous estimates of maximum burial depth by such approaches have ranged from 300-2000 m (1000-6540 ft) of post-Pennsylvanian sediment, which would have had to have been completely eroded by the Jurassic (see review by Velbel, 2009). The timing of heating along the geothermal gradient at maximum burial (between Late Pennsylvanian and Jurassic; Velbel, 2009) is consistent with the previously acquired K-Ar dates

for the smallest Marshall Sandstone fine fraction of 294 and 275 Ma (Early Permian) (Cox, 2015). However, even with the maximum previously proposed thickness of now-missing former overburden (2 km), the maximum burial depth of the Marshall Sandstone would have been ~2.5 km (8,000 ft.), shallower than the depth interval of illite authigenesis in sandstones (Lanson et al., 2002). The available evidence does not favor the hypothesis that a burial model could account for temperatures required to initiate illitization in the 1500 ft. present depth range of the Marshall/Michigan.

The spatial distribution of illite cementation within the Marshall Sandstone could be a function of proximity to shallow structures formed by reactivation of faults in the Mid-Continent Rift, as previously proposed by Cox (2015). Some structures in Michigan Basin Paleozoic strata are inferred to have formed by post-depositional and post-lithification reactivation of faults in the MCR beneath the Paleozoic strata (Ma et al., 2009). Such fracture and fault systems may have served as conduits by which hydrothermal fluids could have been introduced into overlying strata (Luczaj et al., 2006; Velbel, 2009). Cox (2015) observed authigenic illite in all four sample wells near the Albion-Scipio and Lucas faults. The two samples wells from this study in which authigenic illite was observed were both located near the MCR in Michigan (Fig. 10). Invocation of deep hot brine movement along MCR associated faults/fractures does an acceptable job of explaining authigenic illite spatial distribution within the basin. This correlation is supported by evidence of hydrothermal dolomitization occurring along faults interpreted to be associated with the MCR (Luczaj et al., 2006).

The precise origin of the suspected hydrothermal fluid is difficult to determine. A large K^+/H^+ ratio increase is required to initiate illite-forming reactions. Such an increase is possible from mixing with Michigan Basin Silurian brines, although not possible from mixing with

other brines. Enrichment of formation fluids in K⁺ along upwardly mobile hydrothermal brine flow paths may be possible considering the presence of sylvite in the Silurian age Salina Group (Nurmi, 1977). Specific to the Michigan Basin, interaction of sylvite with hydrothermal fluid may allow less saline brines to reach K⁺/H⁺ ratios large enough to initiate illitization.

Recommendations for Future Work

XRD analysis remains a useful tool to investigate clay minerals and could be relied on as the primary analytical technique for further study. Use of the Kübler Index for crystallinity is still recommended, but a more thorough XRD investigation of authigenic illite would prove useful to determine whether crystallinity values vary throughout the basin. Increasing the spatial distribution and the number of samples may provide a better understanding of authigenic illite occurrence in the Michigan Basin, provided that proper selection of anchizone boundaries is considered and results are interpreted with caution. Identification of authigenic illite in sample wells more widely distributed throughout the basin, and XRD analysis of a larger number of those samples, may reveal trends in illite crystallinity that could be used to investigate potential heterogeneity of illitizing hydrothermal flow events. Perhaps illite crystallinity varies considerably between illite cement-bearing wells. Further investigation of illite polytypism and stacking order, although not fully understood, would provide supportive evidence and reveal information about the nature of these hydrothermal events. Polytypism may be investigated by randomly oriented clay XRD, as well as TEM analysis of samples with basal planes parallel to the electron beam.

TEM analysis of samples extracted from thin sections would allow imaging of lattice spacing in detrital grains experiencing alteration. This would resolve uncertainties regarding the degree of alteration in detrital biotite and muscovite. These alteration reactions would help to explain diagenetic changes in pore fluid composition, which can be incorporated into a more complete evaluation of Michigan Stray and Marshall Sandstone diagenesis.

Stable isotopic analysis of illite cements would yield an isotopic signature that would provide strong support regarding the origin of formation fluid. This analysis would be difficult,

however, because complete separation of illite from clay sized quartz would be required for accurate results, and such a complete separation is difficult and time consuming. Any degree of quartz contamination would reduce the usefulness of the results.

Mass-balance calculations using quantitative mineralogy and Marshall/Michigan pore fluid inputs can be applied to determine whether the abundance of K-feldspar and detrital mica in the Michigan/Marshall are sufficient to act as an internal source of K⁺ for the observed amount of authigenic clay material. This calculation would definitively prove whether an external K⁺ source is required for illitization.

Due to the thermodynamic dataset used in this study, K₂O-Al₂O₃-SiO₂-H₂O mineral stability-field boundaries and mixing models were generated for 25°C. Illite crystallinity data indicate that formation temperatures of authigenic illite were much greater than 25°C. Rerunning mixing models at more appropriate temperatures (200-300°C) and plotting data on a stability diagram constructed using high temperature thermodynamic data, and explicitly taking into account the effects of phengitic solid-solution effects in illite thermodynamics would allow for a more realistic treatment of illite thermodynamic stability at the temperature at which it formed.

In addition to illite cementation, intriguing questions regarding other clay minerals in the Marshall/Michigan exist. Kaolin material, identified in the Marshall as dickite based on morphology, was observed at depths much shallower than expected. The kaolinite-to-dickite reaction is kinetically limited by temperature (Beaufort et al., 1998). We know that hydrothermal activity occurred within these strata, but dickite was not observed co-occurring with illite (our hydrothermal indicator) in this study. Investigation of Marshall dickite by XRD and TEM may provide further insight into controls on hydrothermal activity, as well as contribute to the kaolin community.

Authigenic chlorite was observed as a pervasive diagenetic component in shallow portions of the Michigan/Marshall but absent in such abundance in deeper portions. Focused study of chlorite cements (including chlorite crystallinity XRD work) would be useful to determine whether the distribution of chlorite cement is a function of depth, spatial position, hydrology, aqueous geochemistry, mineralogy, or some combination of factors. Constraining the factors affecting authigenic chlorite distribution is a major component of reservoir quality evaluation, so perhaps the Michigan/Marshall could serve as a unique study area and an analog for similar systems.
Conclusions

Late diagenesis in the Michigan/Marshall Sandstones consisted of pore-filling kaolinite cement formation, followed by subsequent illitization of that kaolinite and neoformation of fibrous illite cements. Detrital phyllosilicates, while abundant in some intervals of these strata, are likely not providing the sole K⁺ ion source for illitization; this interpretation is based mainly on the lack of co-occurrence of these grains with illite cements. Mixing of pre-illite Marshall pore fluid with Silurian brine allows for illite thermodynamic stability and provides the K^+/H^+ ratio increase that initiates illite-forming reactions, whereas mixing with enriched meteoric water dilutes Marshall pore fluid with respect to this ratio. Illite crystallinity as determined by the Kübler Index indicates that authigenic illite formed in a high-temperature thermal regime. These lines of evidence converge to support the previously proposed hypothesis that deep, hot brines in the Michigan Basin moved vertically across formations along reactivated faults and fractures to provide the potassium required for the formation of illite. Faults and fracture systems above the Mid-Continent Rift probably served as conduits for hydrothermal flow, based on spatial distribution of illite cements within the basin. These hot brines reacted with kaolinite cements to form illite pseudomorphic after kaolinite by transformation (reaction 3) and directly precipitated fibrous illite (neoformation; reaction 4). It is possible that high temperatures associated with this hydrothermal activity resulted in destabilization of the K-feldspar-kaolinite mineral assemblage and initiated an illite-forming reaction (reaction 2) in which K-feldspar and kaolinite are both consumed.

APPENDICES

APPENDIX A: Point-count data

Table 10: *Point-count data*: Data from point counting 200 points for each thin section. MQz – monocrystalline quartz, PQz – polycrystalline quartz, CQz – chert, Kfs – K-feldspar, -Pl – plagioclase, SRf – sedimentary rock fragment, MRf – metamorphic rock fragment, Carb – unspecified carbonate, Ms – muscovite grain, Bt – biotite grain , Py – pyrite, Chl – chlorite, Kln – kaolinite, Pseudo – pseudomatrix, Dol – dolomite, Clay – clay sized material (deemed not to be pseudomatrix).

Sample	MQz	PQz	CQz	Kfs	Pl	SRf	MRf	Carb
W-1002								
1315	95	19	0	4	0	1	1	0
1328	99	18	0	3	0	11	14	22
1344	78	24	4	3	0	7	56	0
1356	85	22	3	2	0	2	52	5
1363	97	17	3	4	0	2	52	2
1382	0	0	0	0	0	0	0	0
1401	99	18	12	16	0	0	20	0
1406	102	24	10	2	0	0	24	0
1411	116	12	4	4	0	0	4	0
1420	99	15	4	4	0	3	43	0
1435	101	20	3	4	0	0	35	1
1444	98	16	2	15	2	0	32	0
1448	106	10	4	6	2	0	38	0
W-962								
1328	96	11	2	0	0	9	52	0
1338	88	20	2	4	2	4	43	0
1343	84	16	2	2	0	2	26	18
1373	75	8	4	2	0	0	46	0
1382	0	0	0	0	0	0	0	0
1400	0	0	0	0	0	0	0	0
1420	50	4	2	0	0	0	0	18
1425	124	11	0	6	0	2	25	0
1430	127	2	3	8	0	0	24	8
1448	122	6	0	12	0	0	22	0
1453	114	15	2	6	2	0	30	0

Table 10 (cont.)

Sample	Ms	Bt	Ру	Chl	Kln	Pseudo	Porosity	Dol	Clay
W-1002									
1315	0	0	7	0	0	72	1		
1328	0	0	7	0	3	1	22		
1344	6	0	2	1	1	1	17		
1356	7	0	2	1	2	3	14		
1363	4	0	2	0	1	0	16		
1382	0	0	7	0	0	0	30	163	
1401	4	0	14	0	0	0	17		
1406	1	0	14	0	2	0	21		
1411	4	0	8	0	0	48	0		
1420	2	0	16	0	3	0	11		
1435	1	0	15	0	0	0	20		
1444	2	0	11	0	1	0	21		
1448	7	0	5	0	4	0	18		
W-962									
1328	12	0	6	0	4	0	8		
1338	7	0	10	0	0	0	20		
1343	2	0	18	0	2	0	28		
1373	4	0	40	0	0	0	21		
1382	0	0	22	0	0	0	46	132	
1400	0	0	19	0	0	0	1	180	
1420	0	0	6	0	0	0	0		120
1425	2	0	10	0	0	0	20		
1430	3	0	2	0	2	0	21		
1448	1	0	10	0	2	0	25		
1453	6	2	5	0	0	0	18		

Table 10 (cont.)

Sample	MQz	PQz	CQz	Kfs	Pl	SRf	MRf	Carb
RASA 5								
503	114	20	2	4	0	2	18	0
514	104	16	3	7	0	4	36	0
519	106	16	2	3	0	2	27	0
531	112	12	1	2	2	5	20	0
588	76	13	4	2	0	0	27	0
592	76	14	4	4	0	0	31	0
598	62	24	10	7	0	6	38	3
604	50	8	0	4	0	2	30	3
607	68	11	2	4	0	0	34	0
609	24	12	0	4	0	0	8	3
611	20	12	2	0	0	8	6	0
612	38	21	6	0	0	4	9	46
CH101								
20	105	11	4	11	7	2	22	0
33	81	7	0	4	0	0	22	0
58	99	5	4	4	0	0	44	0
70	79	18	4	4	0	0	40	0
85	83	17	2	4	0	4	40	15
100	90	19	0	6	0	0	46	4
114	91	13	0	4	0	4	24	27
126	80	15	4	2	2	6	34	25
133	101	12	2	4	2	2	42	3
140	86	14	9	7	0	12	26	1

Table 10 (cont.)

Sample	Ms	Bt	Ру	Chl	Kln	Pseudo	Porosity	Dol	Clay
RASA 5									
503	0	0	0	0	7	0	33		
514	4	0	6	0	0	0	20		
519	4	0	5	7	2	0	26		
531	1	0	4	6	12	0	23		
588	23	43	2	0	0	0	10		
592	22	29	2	8	0	0	10		
598	7	0	6	20	2	0	15		
604	26	53	12	0	0	6	6		
607	22	38	6	1	0	6	8		
609	29	58	51	0	0	0	11		
611	47	76	26	0	0	0	3		
612	0	0	23	40	2	0	11		
CH101									
20	2	0	0	0	10	0	26		
33	2	0	83	0	0	0	1		
58	4	0	8	11	5	0	16		
70	6	1	5	3	2	0	38		
85	6	0	3	12	2	0	12		
100	3	0	2	10	1	0	19		
114	4	0	2	8	0	0	23		
126	4	0	5	10	2	0	11		
133	0	1	1	14	2	0	14		
140	6	1	15	0	0	0	23		

APPENDIX B: Thin section descriptions

Thin section descriptions

W-1002 Well:

1315 feet:

Sample consists of moderately well-sorted, very fine to fine-grained greywacke. QFR is 95:3.33:1.66. Almost all porosity is occluded by detrital pseudomatrix. Pseudomatrix comprises 36% of the entire sample, leaving 0.5% of porosity remaining. Authigenic pyrite comprises 3.5% of the sample.

1328 feet:

Sample consists of well-sorted, fine-grained sublitharenite. QFR is 81:2:17. Rock fragments consist of mudstones and metasedimentary fragments. The sample contains 11% porosity, and 11% authigenic carbonate cement. Much of the carbonate cement is partially dissolved, resulting in microporosity within the cemented areas.

1344 feet:

Sample consists of well-sorted, very fine to fine-grained litharenite. QFR is 61.6:1.7:36.6. Rock fragments consist primarily of metasedimentary fragments. This sample contains 8.5% porosity. Muscovite grains comprise 3% of this sample.

1356 feet:

Sample consists of well-sorted, very fine to fine-grained litharenite. QFR is 66.3:1.2:32.5. Rock fragments consist primarily of metasedimentary fragments. This sample contains 7% porosity. Muscovite grains comprise 3.5% of this sample, and authigenic carbonate cements comprise 2.5% of the sample.

1363 feet:

Sample consists of well-sorted, very fine to fine-grained litharenite. QFR is 66.8:2.3:30.9. Rock fragments consist of metasedimentary fragments. This sample contains 8% porosity. Muscovite grains comprise 2% of this sample. Authigenic carbonate comprises 1%, and authigenic pyrite 1% of the sample.

1382 feet:

This sample, from the "Stray Dolomite" is primarily dolomite. Silt-sized dolomite comprises 81.5% of the sample. Authigenic pyrite comprises 3.5% of the sample. This sample has 15% porosity.

1401 feet:

Sample consists of well-sorted, fine-grained sublitharenite. QFR is 78.2:9.7:12.1. The feldspar is entirely K-feldspar, and the rock fragments are entirely metasedimentary fragments. This sample contains 8.5% porosity. Authigenic pyrite is pore filling and framboidal and comprises 7% of the sample. Muscovite grains comprise 2% of the sample.

1406 feet:

Sample consists of well-sorted, fine-grained sublitharenite. QFR is 84:1.2:14.8. The feldspar is entirely K-feldspar, much of which has been partially dissolved. The rock fragments are entirely metasedimentary lithic fragments. This sample contains 10.5% porosity. Authigenic pyrite is pore-filling and framboidal and comprises 7% of the total sample.

1411 feet:

Sample consists of well-sorted, very fine to fine-grained greywacke. QFR is 94.4:2.8:2.8. No porosity is remaining in the sample as a result of deformed pseudomatrix comprising 24% of the sample. Framboidal authigenic pyrite comprises 4% of the sample, and muscovite grains comprise 2%.

1420 feet:

Sample consists of moderately sorted, very fine to fine-grained litharenite. QFR is 70.2:2.4:27.4. All of the feldspar is K-feldspar, and the rock fragments consist of sedimentary and metasedimentary fragments. This sample contains 5.5% porosity. Authigenic pyrite framboids comprise 8% of the sample. Muscovite grains comprise 1% of the sample.

1435 feet:

Sample consists of very well-sorted, fine to medium-grained sublitharenite. QFR is 76.1:2.4:21.5. The feldspar is K-feldspar, the rock fragments are metasedimentary fragments. This sample contains 10% porosity. Authigenic pyrite, occurring as framboids and pore-filling cement, comprises 7.5% of the sample.

1444 feet:

Sample consists of well-sorted, fine-grained feldspathic litharenite. QFR is 70.3:10.3:19.4. The feldspar is dominantly K-feldspar. Much of the K-feldspar grains display overgrowths, many of which have been preferentially dissolved relative to the cores. The rock fragments are metasedimentary fragments. This sample contains 10.5% porosity. Framboids of authigenic pyrite comprise 5.5% of the total sample.

1448 feet:

This sample consists of moderately well-sorted, fine-grained litharenite. QFR is 72.3:4.8:22.9. The feldspar is K-feldspar (some of which has been partially dissolved), and the rock fragments are metasedimentary. This sample contains 9% porosity. Authigenic pyrite framboids comprise 2.5% of the total sample. Muscovite grains comprise 3.5% of the total sample.

W-962 Well:

1328 feet:

Sample consists of well-sorted, very fine to fine-grained litharenite. QFR is 64.1:0:35.9. The rock fragments are sedimentary mudstone and metasedimentary fragments. This sample contains only 4% porosity. Muscovite grains comprise 6% of the total sample.

1338 feet:

Sample consists of well-sorted, fine-grained litharenite. QFR is 67.5:3.7:28.8. The feldspar is plagioclase and K-feldspar, and the rock fragments are dominantly metasedimentary fragments, with some mudstone fragments. This sample contains 10% porosity. Authigenic pyrite cements (pore-filling and framboidal) comprise 5% of the sample, and muscovite grains comprise 3.5% of the total sample.

1343 feet:

Sample consists of very well-sorted, medium to fine-grained sublitharenite. QFR is 77.3:1.5:21.2. The rock fragments dominantly metasedimentary lithic fragments. This sample contains 14% porosity. Significant amounts of authigenic framboidal pyrite (9%) and authigenic carbonate (9%) occlude pore space.

1373 feet:

Sample consists of well-sorted, very fine to fine-grained litharenite. QFR is 64.4:1.5:34.1. The rock fragments are metasedimentary fragments. This sample contains 10.5% porosity. This sample contains anomalously large amounts of pyrite cement. Framboidal and pore-filling authigenic pyrite comprises 20% of the total sample.

1382 feet:

This sample is part of the "Stray Dolomite". Dolomite comprises 66% of the total sample. Much of this dolomite is silt sized, however some crystals are up to 0.55 mm in length. This sample contains 23% porosity. Authigenic framboidal pyrite comprises 11% of the total sample.

1400 feet:

This sample is part of the "Stray Dolomite". Dolomite comprises 90% of the total sample. This dolomite is made up entirely of silt sized crystals. This sample has almost no porosity remaining (0.5%). Framboidal authigenic pyrite comprises 9.5% of the total sample.

1420 feet:

This sample is a claystone. It consists of 60% clay sized grains with very fine-grained quartz (28%) and carbonate (9%) grains interspersed. Authigenic framboidal pyrite comprises 3% of the total sample.

1425 feet:

This sample is a well-sorted, fine-grained sublitharenite. QFR is 80.3:3.6:16.1. The feldspar is K-feldspar which has been partially dissolved, and the rock fragments are metasedimentary and mudstone fragments. This sample contains 10% porosity. Authigenic pyrite framboids comprise 5% of the total sample.

1430 feet:

Sample is a very well-sorted, fine to medium-grained sublitharenite. QFR is 80.5:4.9:14.6. The feldspar is K-feldspar, many of which contain overgrowths that appear to be preferentially dissolved. The rock fragments are metasedimentary fragments. This sample contains 10.5% porosity. Authigenic carbonate comprises 4% of the sample.

1448 feet:

Sample is a well-sorted, fine-grained sublitharenite. QFR is 79:7.4:13.6. The feldspar is entirely K-feldspar, and the rock fragments are entirely metasedimentary fragments. This sample contains 12.5% porosity. Authigenic pyrite (framboidal and pore-filling) comprises 5% of the total sample.

1453 feet:

Sample is well-sorted, fine-grained sublitharenite. QFR is 77.5:4.7:17.8. The feldspar is K-feldspar and plagioclase, the rock fragments are entirely metasedimentary lithic fragments. This sample contains 9% porosity. Detrital mica grains comprise 4% of the total sample (muscovite 3%, biotite 1%).

RASA 5 Well:

503 feet:

Sample is a very well-sorted, fine to medium-grained sublitharenite. QFR is 85:2.5:12.5. The rock fragments are metasedimentary and mudstone fragments. This sample contains 16.5% porosity. Kaolinite cements comprise 3.5% of the total sample. Very minor amounts of muscovite were observed, but not counted.

514 feet:

Sample is a well-sorted, fine-grained litharenite. QFR is 72.4:4.1:23.5. The rock fragments are mudstone and metasedimentary fragments. This sample contains 10% porosity. Authigenic pyrite comprises 3% or the sample, and detrital muscovite 2% of the total sample.

519 feet:

Sample consists of well-sorted, very fine to medium-grained sublitharenite. QFR is 79.5:1.9:18.6. Rock fragments consist of metasedimentary and mudstone fragments. This sample contains 13% porosity. Authigenic components include pyrite, chlorite, and kaolinite. Muscovite comprises 2% of the total sample.

531 feet:

Sample is well-sorted, fine-grained sublitharenite. QFR is 81.2:2.6:16.2. The feldspar is K-feldspar and plagioclase, and the rock fragments are metasedimentary and mudstone fragments. This sample contains 11.5% porosity. Pore-filling kaolinite cements comprise 6% of the total sample. These cements contain microporosity within.

588 feet:

This sample consists of moderately well-sorted, very fine to fine-grained micaceous sublitharenite. QFR is 76.2:1.6:22.1. The rock fragments are entirely metasedimentary fragments. This sample contains 33% detrital mica grains. 11.5% of the total sample is comprised of muscovite, and 21.5% of the total sample is biotite. The mica grains are all oriented in the same direction. This sample only contains 5% porosity.

592 feet:

Sample consists of moderately well-sorted, very fine to fine-grained micaceous litharenite. QFR is 72.9:3.1:24. The rock fragments are entirely metasedimentary fragments. This sample contains 25.5% detrital mica grains. Muscovite comprises 11% of the total sample, and biotite comprises 14.5% of the total sample. The mica grains are all oriented in the same direction. This sample contains only 5% porosity.

598 feet:

Sample consists of well-sorted, very fine to fine-grained litharenite. QFR is 65.3:4.8:29.9. The rock fragments are metasedimentary and mudstone fragments. This sample contains 7.5% porosity. Chlorite (some weathered to a brown color) comprises 10% of the total sample. There are multiple types of authigenic cement in this sample, including pyrite, carbonate, chlorite, and kaolinite.

604 feet:

Sample consists of moderately-well sorted, very fine to fine-grained micaceous litharenite. QFR is 61.7:4.3:34. The rock fragments are metasedimentary and mudstone fragments. Detrital mica grains comprise 39.5% of the total sample. Biotite (26.5%) and muscovite (13%) are preferentially oriented. Pyrite cement comprises 6% of the total sample, and porosity only 3%.

607 feet:

Sample consists of moderately-well sorted, very fine to fine-grained micaceous litharenite. QFR is 68.1:3.4:28.5. The rock fragments are entirely metasedimentary fragments. Detrital mica grains comprise 30% of the total sample. Biotite (19%) and muscovite (11%) are preferentially oriented. This sample contains only 4% porosity.

609 feet:

This sample consists primarily of detrital mica grains and authigenic pyrite with a preferred orientation. Biotite (29%) and muscovite (14.5%) comprise the majority of minerals in this sample. These mica grains are oriented with a fabric parallel to bedding. Authigenic pyrite comprises 25.5% of the total sample. QFR make up only 24% of the total sample. QFR is 75:8.3:16.7. Authigenic siderite micro-nodules comprise 1.5% of the sample. This sample contains 5.5% porosity.

611 feet:

This sample consists of 61.5% detrital mica grains. Biotite (38%) and muscovite (23.5%) grains are all preferentially oriented. Authigenic pyrite comprises 13% of the total sample. Much of the authigenic pyrite is also preferentially oriented along the same plane as the mica grains. QFR combine for 24% of the total sample. QFR is 70.8:0:29.2. The rock fragments are mudstone and metasedimentary fragments. This sample contains only 1.5% porosity.

612 feet:

This sample consists of moderately well-sorted, very fine to fine-grained sublitharenite. QFR comprises only 39% of the total sample. QFR is 83.3:0:16.7. Chlorite comprises 20% of the total sample. This chlorite is brownish green in color and occurs as discrete grains, many of which resemble the typical shape of mica grains. Authigenic carbonate comprises 23% of the total sample. The carbonate is pore-filling calcite cement. Authigenic pyrite comprises 11.5% of the total sample. This pyrite is both pore-filling, and framboidal. This sample contains 5.5% porosity.

CH101 Well:

20 feet:

Sample consists of very well-sorted, fine to medium-grained feldspathic litharenite. QFR is 74.1:11.1:14.8. Feldspar grains are K-feldspar and plagioclase, and rock fragments are entirely metasedimentary fragments. Kaolinite cements with microporosity comprise 5% of the total sample. This sample contains 13% porosity.

33 feet:

This sample consists of moderately well-sorted, very fine to fine-grained pyrite cemented sublitharenite. QFR is 77.2:3.5:19.3. The rock fragments are entirely metasedimentary fragments. This sample is cemented by authigenic pyrite. This pyrite cement comprises 41.5% of the total sample. As a result, this sample contains only 0.5% porosity.

58 feet:

This sample consists of well-sorted, very fine to fine-grained litharenite. QFR is 69.2:2.6:28.2. Rock fragments consist entirely of metasedimentary fragments. This sample contains 8% porosity. Authigenic components include pyrite, kaolinite, and chlorite.

70 feet:

This sample consists of well-sorted, very fine to fine-grained litharenite. QFR is 69.7:2.7:27.6. Rock fragments consist entirely of metasedimentary fragments. This sample contains 19% porosity. Many of the grains are not in contact with one another. Detrital muscovite comprises 3% of the total sample. Authigenic components include pyrite, chlorite, and kaolinite.

85 feet:

Sample consists of moderately well-sorted, very fine-grained litharenite. QFR is 68:2.7:29.3. The rock fragments consist entirely of metasedimentary fragments. Authigenic carbonate comprises 7.5% of the total sample. This carbonate consists of rhombs that nucleate on detrital grains. Authigenic chlorite comprises 6% of the total sample. This chlorite is green in color and coats detrital grains. Other authigenic components include pyrite and kaolinite. This sample contains 6% porosity.

100 feet:

Sample consists of well-sorted, very fine to fine-grained litharenite. QFR is 67.7:3.7:28.6. The feldspar is entirely K-feldspar, and the rock fragments are metasedimentary and mudstone fragments. Grain-coating authigenic chlorite comprises 5% of the total sample. Other authigenic components include carbonate, pyrite, and kaolinite. This sample contains 9.5% porosity.

114 feet:

Sample consists of moderately well-sorted, very fine to fine-grained sublitharenite. QFR is 76.5:2.9:20.6. The rock fragments are metasedimentary and mudstone fragments. Authigenic carbonate occurs as both pore-filling cement and rhombs nucleating on grains and comprises 13.5% of the total sample. Authigenic chlorite occurs as grain-coatings and comprises 4% of the total sample. This sample contains 11.5% porosity.

126 feet:

Sample consists of moderately well-sorted, very fine-grained litharenite. QFR is 69.2:2.8:28. The feldspar is K-feldspar and plagioclase, and the rock fragments are metasedimentary and mudstone fragments. Authigenic carbonate rhombs comprise 12.5% of the total sample. Authigenic grain-coating chlorite comprises 5% of the total sample. Other authigenic components include pyrite and kaolinite. This sample contains 5.5% porosity.

133 feet:

Sample consists of well-sorted, very fine to fine-grained litharenite. QFR is 69.7:3.6:26.7. The feldspar is K-feldspar and plagioclase, and the rock fragments are metasedimentary and mudstone fragments. Authigenic grain-coating chlorite comprises 7% of the total sample. Other authigenic components include carbonate, kaolinite, and pyrite. This sample contains 7% porosity.

140 feet:

Sample consists of well-sorted, very fine to fine-grained litharenite. QFR is 70.8:4.5:24.7. The feldspar is K-feldspar, and the rock fragments are metasedimentary and mudstone fragments. Authigenic pyrite comprises 7.5% of the total sample. This pyrite is pore-filling and framboidal. Muscovite grains comprise 3% of the total sample. This sample contains 11.5% porosity.

APPENDIX C: Marshall aquifer groundwater data

Table 11: Marshall aquifer groundwater data: Selected aqueous geochemical data from the
Marshall aquifer (compiled from USGS Open-File Report 90-368).

Depth (ft.)	рН	Temp (°C)	K (mg/L)	SiO2 (mg/L)	Log(K/H)	Log(SiO2)
251	7.39	12	1	16	2.7978455	-3.574646
100	7.65	13	2.4	16	3.4380567	-3.574646
200	7.3	12.5	0.9	16	2.662288	-3.574646
330	7.61	11	0.8	14	2.9209354	-3.632638
320	7.41	11	6.9	8	3.6566945	-3.875676
257	7.26	11.5	4.2	11	3.2912947	-3.737373
300	7.24	11.5	3.5	12	3.1919135	-3.699585
470	7.04	11	5.6	11	3.1960335	-3.737373
339	7.39	11	2	17	3.0990754	-3.548317
144	7.23	11	2	17	2.9388755	-3.548317
330	7.33	12	1.1	15	2.7792381	-3.602675
254	7.32	12	1.2	14	2.8072267	-3.632638
100	7.24	11	0.9	13	2.602088	-3.664823
149	7.43	12	0.9	14	2.792088	-3.632638
140	7.55	13	0.9	12	2.912288	-3.699585
480	6.95	12	8	11	3.2609354	-3.737373
410	7.47	13	13	7.1	3.9917888	-3.927508
556	7.41	12.5	17	7.9	4.0484944	-3.881139
500	7.66	12	6.9	8.9	3.9066945	-3.829376
484	6.96	26	100	120	4.3678455	-2.699585
115	7.26	13	1.5	16	2.8441367	-3.574646
120	7.59	11	0.7	9.1	2.8429435	-3.819725
380	7.48	11.5	2.4	14	3.2680567	-3.632638
225	7.62	11	2.9	12	3.4904434	-3.699585
260	7.48	12	2.4	12	3.2680567	-3.699585
216	7.54	12.5	1.7	12	3.1782944	-3.699585
82	7.44	11.5	2	15	3.1490754	-3.602675
100	7.56	12	11	7.3	4.0092381	-3.915443
237	7.52	10.5	1.8	11	3.183118	-3.737373
44	7.37	12	0.7	9.3	2.6231435	-3.810283
315	7.43	13	4.7	6.7	3.5099433	-3.952691
418	8.1	14	2.5	6.9	3.9057855	-3.939917
340	7.21	10.5	3.9	11	3.2091101	-3.737373
397	7.35	11.5	2.6	12	3.1728188	-3.699585

Table 11 (cont.)

295	7.89	12	2	12	3.5988755	-3.699585
110	8.08	10	2.9	9.9	3.9504434	-3.783131
190	7.7	10	8.7	8.3	4.0473647	-3.859688
40	7.08	11	1.6	16	2.6919654	-3.574646
131	6.75	12	1.5	16	2.3341367	-3.574646
65	7.66	11	1.4	15	3.2139735	-3.602675
72	7.59	12	0.8	8.6	2.9009354	-3.844268
100	7.11	11	1	14	2.5180454	-3.632638
385	7.24	11	3	15	3.1249667	-3.602675
78	7.03	11	1.8	13	2.693118	-3.664823
393	7.2	12	1.5	20	2.7841367	-3.477736
250	7.33	13	0.3	18	2.2149667	-3.523494
425	7.2	12	5.5	12	3.3482081	-3.699585
569	6.43	13.5	180	7.5	4.093318	-3.903705
220	7.2	11	1.6	14	2.8119654	-3.632638
132	7.49	11.5	2.8	9.8	3.3450035	-3.78754
360	7.44	11	3.2	7.7	3.3531954	-3.892275
250	7.38	12	2.4	9.1	3.1680567	-3.819725
400	7.58	11.5	2.1	8.2	3.3100648	-3.864952
400	7.38	10.5	4.9	7.6	3.4782415	-3.897952
195	7.69	16	7.5	9.7	3.9729067	-3.791994
225	7.69	16	6.5	9.5	3.9107588	-3.801042
238	7.79	12.5	5.2	11	3.9140488	-3.737373
204	7.54	13.5	9.6	10	3.9301167	-3.778766
254	7.85	14	4.5	10	3.911058	-3.778766
262	7.84	11.5	4	10	3.8501054	-3.778766
275	7.81	12	4.7	12	3.8899433	-3.699585
501	6.68	16	10	6.2	3.0878455	-3.986374
207	7.35	11.5	1.8	14	3.013318	-3.632638
300	7.32	11	1.5	21	2.9039367	-3.456547
165	7.8	13	1.3	13	3.3217888	-3.664823
195	8.15	11	2.1	13	3.8802647	-3.664823
180	7.77	13	2	13	3.4788755	-3.664823
162	7.5	12	0.2	10	2.2088755	-3.778766
300	7.4	12	1.7	17	3.0384944	-3.548317

APPENDIX C – CONT.

Table 11 (cont.)

170	7.55	11.5	8.6	9.9	3.8923439	-3.783131
200	7.81	11	3.4	12	3.7493244	-3.699585
245	7.74	10.5	4	12	3.7501054	-3.699585
238	7.84	16	3.5	12	3.7919135	-3.699585
210	7.84	13.5	3.7	12	3.8160472	-3.699585
172	7.66	12	5.7	11	3.8239203	-3.737373
303	7.56	13.5	3.1	15	3.4592072	-3.602675
263	7.4	10.5	2.3	8.3	3.1695733	-3.859688
220	7.67	11	2.9	7.6	3.5404434	-3.897952
168	7.38	11	2.5	10	3.1857855	-3.778766
198	7.52	11	2.6	13	3.3428188	-3.664823
135	7.67	9	2.7	8.2	3.5094092	-3.864952
145	7.8	10	2.3	12	3.5695733	-3.699585
175	7.48	11	2.1	17	3.2100648	-3.548317
110	7.53	12	2	12	3.2390754	-3.699585
191	7.5	11	1.9	13	3.1865991	-3.664823
240	7.58	15.5	1.8	16	3.243118	-3.574646
185	7.7	12	2	13	3.4090754	-3.664823
120	7.3	12	1.4	15	2.8539735	-3.602675
116	7.44	11	1.2	17	2.9270267	-3.548317

APPENDIX D: Aqueous geochemical modeling well information

Table 12: *Aqueous geochemical modeling well information*: Additional information regarding wells involved in geochemical modeling.

Well Type	Well Name	Location
Marshall Sample Well	Consumers Energy Winterfield W-1002	TWN: 20N, RNG: 7W, SEC: 36
Marshall Sample Well	Michigan Gas Storage Company W-962	TWN: 20N, RNG: 6W, SEC: 7
Representative Marshall Well	USGS Lake County #3	44"01'25"N, 85"56'40"W
Devonian Well	Wilson & Long ID 4069	TWN: 19N, RNG: 6W, SEC: 19
Silurian Well	Wilson & Long ID 2090	TWN: 26N, RNG: 10W, SEC: 10
Silurian Well	Wilson & Long ID 2091	TWN: 26N, RNG: 10W, SEC: 12

Well Type	County	Depth (ft.)	Pore Fluid TDS (ppm)
Marshall Sample Well	Clare	1315-1448	>100000
Marshall Sample Well	Clare	1328-1453	>100000
Representative Marshall Well	Lake	569	81400
Devonian Well	Clare	5056	386780
Silurian Well	Grand Traverse	6345	422130
Silurian Well	Grand Traverse	6781	280140

APPENDIX E: Pore fluid analyses used in aqueous geochemical modeling

Table 13: *Pore fluid analyses used in aqueous geochemical modeling*: All analyses used in modeling work. Compositions denoted with a * are initial inputs into mixing models.

Composition	Depth (m) TDS (ppm)	Temp (°C)	Ca(ppm)	Mg (ppm)	Na (ppm)
Existing Data						
Mississippian Lake County #3	174	81400	13.5	3700	880	20000
Devonian ID 4069*	1541	386780	44.7	86100	10700	34100
Silurian ID 2090	1934	422130	53.8	106000	12600	21200
Silurian ID 2091	2067	280140	56.8	67700	8670	21000
Silurian Average*	2000.5	351135	55.3	86850	10635	21100
Rain Water	NA	NA	25	1.42	0.39	2.05
Model Generated						
Enriched Rain Water*	NA	NA	25	56.91	9.48	47.13
K-mica Undersaturated*	NA	NA	25	3981.75	947.16	21523.24

Composition	K (ppm)	Si (ppm)	рН	Cl (ppm)	Br (ppm)	SO4 (ppm)	Alk (ppm as CaCO3)
Existing Data							
Mississippian Lake County #3	180	7.5	6.43	44000	130	1900	140
Devonian ID 4069*	8700	2.4	4.3	242000	1200	0	240
Silurian ID 2090	21200	2.3	4.5	253000	2940	85	374
Silurian ID 2091	14200	4	5	190000	1820	28	207
Silurian Average*	17700	3.15	4.75	221500	2380	56.5	290.5
Rain Water	0.35	0	5.47	3.47	0	2.19	0
Model Generated							
Enriched Rain Water*	14.64	0	6.82	123.01	0	210.37	0
K-mica Undersaturated*	193.73	3.78	6.43	47361.2	0	2045.117	140

APPENDIX F: XRD diffractograms





Figure 80: *W-1002 XRD diffractograms*: Diffractograms from ungylocated (top) and glycolated (bottom) samples.



Figure 80 (cont.)





Figure 80 (cont.)





Figure 80 (cont.)





Figure 80 (cont.)





Figure 80 (cont.)





Figure 80 (cont.)











Figure 81: *W-962 XRD diffractograms*: Diffractograms from unglycolated (top) and glycolated (bottom) samples.

Figure 81 (cont.)







Figure 81 (cont.)





Figure 81 (cont.)





Figure 81 (cont.)





APPENDIX G: X-ray diffraction illite Ir number peak measurements

Sample	Depth (ft.)	001 AD	003 AD	001 Glyc.	003 Glyc.
W-1002 (2)	1328	51.65	67.86	379.34	512.59
W-1002 (3)	1344	52.41	142.8	202.84	542.02
W-1002 (5)	1363	60.71	308.73	345.58	2350.66
W-1002 (8)	1406	59.49	255.42	343.92	1708.01
W-1002 (10)	1420	214.78	176.71	88.73	90.88
W-1002 (11)	1435	58.09	202.52	404.95	1729.3
W-1002 (12)	1444	163.8	391.06	144.39	267.5
W-962 (2)	1338	209.35	191.52	193.52	172.58
W-962 (3)	1343	200.58	316.91	196.27	262.71
W-962 (8)	1425	69.53	373.88	351.61	1836.28
W-962 (9)	1430	168.54	563.26	196.66	659.01
W-962 (10)	1448	171.58	934.25	136.93	594.11

Table 14: *X-ray diffraction illite Ir number peak measurements*: XRD Ir number peak measurements: Raw measurements of peak intensities used to calculate the Ir number.

APPENDIX H: Transmission electron microscopy EDS data



Spectrum processing : Peaks possibly omitted : 8.036, 8.896 keV
Quantitation method : Cliff Lorimer thin ratio section. Processing option : All elements analyzed (Normalised) Number of iterations = 3
Standardless

Element	Weight%	Atomic%	
OK	47.99	62.62	
Mg K	1.54	1.32	
AIK	14.78	11.44	
Si K	27.49	20.43	
SK	0.31	0.20	
Cl K	0.25	0.15	
КK	6.08	3.25	
Fe K	1.56	0.58	
Totals	100.00		

Sample: illite clump Type: Default ID:

Sample thickness: 20.0 nm Sample density: 3.00 g/cm3 Density estimate: 1.93 g/cm3 Beam broadening: 0.37 nm Detector efficiency : Calculation Pulse pile up correction performed.

Figure 82: *W-1002 transmission electron microscopy EDS data*: TEM-EDS data for illite lath at 1406 ft. (depth).

APPENDIX H – CONT.

Figure 82 (cont.)



Spectrum processing : Peaks possibly omitted : 8.036, 8.896 keV

Quantitation method : Cliff Lorimer thin ratio section. Processing option : All elements analyzed (Normalised) Number of iterations = 3

Standardless

Element	Weight%	Atomic%	
ОК	50.28	64.68	
Mg K	1.32	1.12	
AIK	16.53	12.61	
Si K	24.42	17.90	
КK	6.07	3.19	
Fe K	1.37	0.51	
Totala	100.00		

Sample: larger lath Type: Default ID:

Sample thickness: 20.0 nm Sample density: 3.00 g/cm3 Density estimate: 1.91 g/cm3 Beam broadening: 0.36 nm Detector efficiency : Calculation Pulse pile up correction performed.

APPENDIX H – CONT.

Figure 82 (cont.)



Spectrum processing : Peaks possibly omitted : 8.036, 8.896 keV

Quantitation method : Cliff Lorimer thin ratio section. Processing option : All elements analyzed (Normalised) Number of iterations = 3

Standardless

Element	Weight%	Atomic%
OK	48.68	63.46
Mg K	1.95	1.67
AľK	15.32	11.85
Si K	24.29	18.04
SK	0.78	0.51
КK	6.36	3.39
Ca K	0.63	0.33
Cr K	0.40	0.16
Fe K	1.59	0.59
Totals	100.00	

Sample: Laths 2 Type: Default ID:

Sample thickness: 20.0 nm Sample density: 3.00 g/cm3 Density estimate: 1.94 g/cm3 Beam broadening: 0.37 nm Detector efficiency : Calculation Pulse pile up correction performed.
APPENDIX H – CONT.

Figure 82 (cont.)



Spectrum processing : Peaks possibly omitted : 4.490, 5.415, 8.036, 8.901 keV

Quantitation method : Cliff Lorimer thin ratio section. Processing option : All elements analyzed (Normalised) Number of iterations = 3

Standardless

Element	Weight%	Atomic%	
ОК	53.77	66.79	
AlK	22.23	16.37	
Si K	23.44	16.58	
SK	0.15	0.09	
Ca K	0.15	0.08	
Fe K	0.25	0.09	

Totals 100.00

Sample: kaolinite Type: Default ID:

Sample thickness: 20.0 nm Sample density: 3.00 g/cm3 Density estimate: 1.94 g/cm3 Beam broadening: 0.34 nm Detector efficiency : Calculation Pulse pile up correction performed.

APPENDIX H – CONT.



Spectrum processing : Peaks possibly omitted : 8.036, 8.895 keV

Quantitation method : Cliff Lorimer thin ratio

(Normalised) Number of iterations = 3

Standardless

Element	Weight%	Atomic%	
OK	52.82	67.12	
Mg K	1.33	1.11	
AĨK	14.54	10.95	
Si K	23.52	17.02	
ΚK	6.14	3.19	
Fe K	1.65	0.60	
Totals	100.00		

Sample: single lath Type: Default ID:

Sample thickness: 20.0 nm Sample density: 3.00 g/cm3 Density estimate: 1.90 g/cm3 Beam broadening: 0.36 nm Detector efficiency : Calculation Pulse pile up correction performed.

Figure 83: W-962 transmission electron microscopy EDS data: TEM-EDS data for illite lath at 1425 ft. (depth).

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