INTRODUCTION
The recent proliferation of unconventional oil and gas plays in North America has prompted an interest in the diagenesis of shale systems, and specifically the factors that control reservoir quality and its mechanical behavior. This interest has also raised fundamental issues such as developing a better understanding of whether or not shales behave as open or closed systems (e.g., Bjorlykke, K. and Jahren, J., 2012; Land et al., 1997) and how diagenesis controls migration pathways. Furthermore, connecting scales of observation from basin-scale to the micro/nano-scale is also a crucial issue. Shales are recognized as very heterogeneous because of depositional factors (e.g., Schieber, 2016) as well as their diagenesis (e.g., Milliken and Day-Stirrat, 2013; Manning and Elmore 2015; and others). This paper will focus on the diagenesis of shales with an emphasis on the paragenesis of mineralized fractures. Shale diagenesis can be highly complex due to a myriad of variables operating across non-discrete spatial-temporal boundaries within sedimentary basins (Fig. 1). The paragenesis of a given shale is a function of the contribution of each variable and many are interconnected. As a result, their paragenesis is complex and can be difficult to predict. This complexity can allow for diagenetic studies to focus on the details, which are clearly important, but can also result in not seeing the forest for the trees (or leaves).

Our approach has been to conduct integrated diagenetic studies of shale units. A key element is the construction of a paragenetic sequence through thin section petrography and the use of scanning electron microscopy (SEM). Fluid inclusion microthermometry is used to determine temperatures of formation and composition of fluids and geochemical data (e.g., 87Sr/86Sr values) can help determine the origin of the alteration, particularly in mineralized fractures. X-ray computed tomography (XRCT) is crucial to determine the 3-D microstructural features (e.g. fracture geometry). We also use anisotropy of magnetic susceptibility (AMS) to better understand burial and tectonic processes operating on sediments and paleomagnetism to determine absolute timing of events.

PARAGENESIS OF SHALES
We have investigated the origin and timing of diagenesis in several shale units including the Marcellus Shale (Devonian) in Pennsylvania and West Virginia (Steullet and Elmore, 2014; Manning and Elmore, 2015), Barnett Shale (Mississippian) in Texas (Dennie et al., 2012), Wolfcamp Shale (Permian) in West Texas (Wickard et al., 2016), and Haynesville Shale (Jurassic) in Louisiana and Texas (Benton and Elmore, 2013). We are currently continuing to study the Wolfcamp Shale as well as the Woodford Shale (Devonian-Mississippian) in Oklahoma and the Antrim Shale (Devonian) in Michigan. Our objective in these studies is to understand the paragenesis within the individual units but also to compare the paragenesis and timing of diagenetic events between the units (Fig. 2).

Our studies show some similarities in the paragenetic sequences between each unit (Fig. 2). Authigenic calcite, dolomite, quartz, barite, celestine, anhydrite, sphalerite, and albite are found in the matrix and/or in mineralized fractures in all five shale units. Despite the ubiquitous occurrence of these minerals within all five shale formations, the timing of the precipitation events are variable.

Common events during early diagenesis include precipitation of pyrite, concretions (phosphatic and calcitic), dolomite, and sphalerite. Dissolution of siliceous microorganisms and precipitation of quartz is very common during early diagenesis (e.g. Milliken and Day-Stirrat, 2013). Early precompactional fractures, usually filled
with calcite, are common in some shales. Middle diagenesis is broadly characterized by clay diagenesis, specifically, the conversion of smectite to illite and in some cases chlorite precipitation. Middle and late diagenesis are commonly characterized by mineralization in fractures. The mineralized fractures show variable fracture habits and their mineral paragenesis can be complex. Fractures range from horizontal to vertical, can be anastomosing to relatively straight depending on the lithology they cut through (Fig. 3a). Some mineralized fractures are associated with breccias which can also have a very complex mineralogy. Common minerals filling fractures include calcite, ferroan calcite, dolomite, ferroan dolomite, barite (Fig. 3b), celestine (Fig. 3b), quartz, sphalerite (Fig. 3c), anhydrite, and pyrite. Other fractures are filled by witherite (Fig. 3d), magnesite, albite, and/or saddle dolomite which probably indicate alteration by low-temperature hydrothermal fluids. Hydrocarbons are also found in some fractures (Fig. 3e). Authigenic albite is not only present in fractures but also in the matrix (Fig. 3c) and is interpreted to form during late diagenesis (Fig. 2).

Fluid inclusions can also provide information on the origin of mineralized fractures. For example, in the Wolfcamp, entrapment temperatures of fluid inclusions in barite are approximately 100° C with salinities of ~25 Wt% CaCl₂. Various evolutions of the clay sheets (Fig. 3h).

Some barite-celestine fractures in the Wolfcamp contain pores, some of which are occluded by ferroan dolomite rhombs (Fig. 3f). This suggests that these pore networks were open and continued to allow fluids to pass through them after the initial mineralization event. Additionally, there is ferro dolomite alteration and calcite along the edge of fractures suggesting that fluids were also able to migrate along the matrix-fracture boundary. The presence of relic hydrocarbons also provides additional evidence for fluid migration through fracture networks in the Wolfcamp Shale (Figs. 3e, f, and h). XRCT provides nondestructive three-dimensional visualization and characterization through mapping the variation of X-ray attenuation, which relates to the density of minerals (e.g. Kercham and Carlson, 2001). This analysis is particularly useful for visualizing microstructural features such as mineralized fractures and replacement textures in allogens. Critically, it also allows one to scale up from SEM and petrographic work. Figure 4a shows a vertical fracture containing pyrite and pyrite-replaced allogens dispersed in the matrix (colored red) from the Haynesville Shale. Lower density minerals are colored in green and blue and likely correspond to clays, quartz and calcite. Closer examination of replaced allogens shows a preferential replacement by pyrite along growth lines and margins of brachiopod shells (Fig. 4b). XRCT scans of the Woodford show complex fracture networks (Fig. 4c). The major fracture networks are shown in blue and are dominantly composed of calcite (confirmed petrographically). These fractures were likely displacive, considering that the measured rock fabric inferred from AMS shows a near vertical inclination. Additional segmentation of the data shows fish-tail twinning that likely corresponds to authigenic gypsum/anhydrite. Complex suites of microfractures, largely comprised of...
barite and celestine, are found adjacent to larger fractures in the Wolfcamp Shale (Fig. 4e, f). This suggests that larger mm-scale fractures can trigger the formation of micro and perhaps nano-sized fractures. Closer examination of the large fracture shows a high degree of roughness along the fracture wall (Fig. 4g). These discontinuous surfaces can act as conduits for fluid migration and often serve as sites for the precipitation of later stage diagenetic minerals.

XRCT analysis is a valuable tool to better characterize the complexity of diagenetic features that would otherwise be missed using conventional petrographic analysis. In addition to porosity in fractures, other types of porosity occur in shales (e.g., Loucks et al., 2009; Slatt and O’Brien, 2011). For example, in the Wolfcamp Shale porosity occurs in organic matter, mineralized fractures, frambooidal pyrite, intergranular, between clay sheets, associated with dolomite, and as intraparticle and moldic pores in allochems and carbonates.

A new frontier in diagenetic research has been the use of magnetic fabric and paleomagnetic analysis to measure the timing and nature of physiochemical processes operating in shales (e.g., Elmore et al., 2012, Heij et al., 2016). AMS quantifies the preferred orientation and intensity of magnetic grains in rocks, thereby defining its fabric. (see Tarling and Hrouda, 1993 for review). AMS is represented by a symmetric second rank tensor with three mutually perpendicular principal axes $K_1$ (long axis), $K_2$ (intermediate axis) and $K_3$ (short axis). In addition, the degree of anisotropy, a proxy for mineral shape anisotropy and shape factor with end-members ranging from oblate to prolate can be computed (see Jelinek, 1981). Our studies (e.g. Heij et al., 2016) suggest that clays control the AMS signal and compaction shapes their orientation with the $K_3$ (short axis) of grains oriented perpendicular to the bedding plane (oblate). Sub-vertical $K_1$ tensors with prolate shapes occur in horizons with elevated ferroan carbonate fractions and pervasive mineralized fracture networks (e.g., Fig. 4e). Punctuated degrees of magnetic anisotropy and shape factors occur across many of the cores (e.g. Wolfcamp and Haynesville) and could suggest the presence of compactional disequilibrium (Schwehr et al., 2006). Preliminary results suggest that these zones show differential fluid-flow behaviors and as a result, could impact reservoir properties (e.g. distribution of released hydrocarbons). Paleomagnetic analysis of shales provides evidence for remagnetizations that are inferred to be chemical remanent magnetizations (CRMs). These CRMs can be related to burial diagenetic events and/or fluid-flow events (e.g., Elmore et al., 2012) such as migration of hydrothermal fluids in the Woodford (Roberts and Elmore, 2014). Establishing the timing of these events can help refine paragenetic sequences for each basin.

**Figure 2:** A combined paragenetic sequence from the Wolfcamp Shale - WP, Marcellus Shale – M (Steullet and Elmore, 2014), Woodford Shale – WD (Roberts and Elmore, 2014), Barnett Shale - B (Dennie et al., 2012), and the Haynesville Shale - H (Benton and Elmore, 2013). The number of formations that demonstrate the same diagenetic events are indicated by the number at the beginning of each line. The solid lines and dotted lines indicate the degree of certainty for the relative timing of diagenetic events.

DISCUSSION

The reasons for the similarities between the shale formations could be that many of the authigenic phases were sourced internally. Most of the elements in the authigenic minerals in the Wolfcamp Shale, for example, could have been derived from the mudstone and the minerals precipitated from internal fluids. Bacterial interactions during early burial may have facilitated decomposition of organic matter and precipitation of barite, sphalerite, and ferroan dolomite (González-Muñoz et al., 2003; Peltier et al., 2011; Selleck, 2014; Blättler et al., 2015). Barite is unstable in strongly reducing environments (Honor, 2000; Arndt et al., 2006) and it could migrate into fractures along with celestine. Sulfate reduction may have developed frambooidal pyrite and phosphate concretions. Biogenic silica micro-fossils dissolved during initial burial, providing silica for authigenic
quartz (Hesse and Schacht, 2011). Shale dewatering in the mudstones likely stimulated the migration of pore fluids that may have supplied magnesium, silica, and iron which could have been a source for ferroan carbonates and authigenic quartz (McHargue and Price, 1982; Coniglio and James, 1988). The smectite-to-illite conversion was likely a source for silica, iron, and magnesium (e.g., Coniglio and James, 1988), that formed chert and ferroan carbonates as well as for iron-rich chlorite during middle and late diagenesis. Authigenic albite is common in many sedimentary rocks and can from early to late diagenesis (Fishman et al., 1995). Authigenic albite formation can form isochemically from the constituents in the rock (Kastner, 1971). The Na could be derived from seawater or clay transformations and Si and Al from the smectite to illite transformation. Some workers have suggested that authigenic albite in carbonates can form from burial brines (Spötl et al., 1999).

Fracturing during burial probably allowed for migration of internal fluids in the mudstones (e.g. Millikan and Land, 1994). Strontium released from aragonite which formed in aragonite seas in the Permian (Hardie, 1996) is a likely source for the celestine in the fractures. Similarly, dissolution of allochems were probably a source for calcite in fractures.

Perhaps more intriguing than the similarities within shale formations are the differences. The variations between shale formations could be explained by differences in depositional environment, tectonic setting, and burial history. For example, the tectonic setting could trigger the migration of external hydrothermal fluids into the formation. Interestingly, each shale seems to have at least one major or minor authigenic mineral constituent which was not identified within the other shale units or one phase is found in much higher abundance than another. For example, the Woodford Shale (Roberts and Elmore, 2014) has significant variability within fracture
networks when compared to other shales, containing hydrothermal minerals in fractures. Within the Barnett Shale monazite and stillwellite are identified above the Barnett/Viola unconformity, which may indicate some hydrothermal contribution (Dennie et al., 2012). The results from these units suggests the systems were at least partially open to external fluids.

Fractures can also influence the mechanical behavior of mudstones because they are pre-existing planes of weakness that can reactivated during hydraulic fracturing (e.g., Gale et al., 2014). The type of fracture fill is another variable because, minerals such as calcite, dolomite, barite, and quartz are brittle and promote fracturing (Dehandschutter et al., 2005). The role of micro fractures which may not be fully recognized without XRCT analysis should be addressed.

An important question in shale diagenesis is what were the pathways for fluid migration? Mineralized fractures are one obvious pathway, and the presence of porosity, re fracturing, and replaced minerals in some fractures suggest they may have been a pathway for multiple fluid flow episodes after the initial mineralizing event. Thin horizontal intervals in mudstones with deformed prolate AMS fabrics (e.g., Heij and others, 2016) and thin carbonate intervals (Engle et al., 2016) are also hypothesized fluid conduits. In shale basins with high rates of subsidence, like the Midland Basin, differential overpressuring can aid pore fluid migration not just through fracture systems, but also by increasing permeability intervals within the mudstone matrix (e.g., Marshall, 1982).

The scale of the observations in shales is another issue that must be addressed. Many authors have discussed how nano scale porosity in organic matter is present in many shales (e.g. Loucks et al., 2009; Curtis et al., 2012) but other porosity types are also present. Few studies have devoted equal attention to each scale of observation. An important question is how to scale up from the nano scale to micron scale where porosity occurs in clays, fractures, pyrite, dolomitic intervals, and then upscaling further to larger features such as sedimentary structures and to basin-scale faults. One might assume that the different levels of porosity are interconnected but the nature of these connections is unclear and remains a fundamental question that should be addressed.
CONCLUSIONS

Mudstones can have a very complex diagenetic history that can show levels of intricacy equal to or greater than that of sandstones and carbonates. Shales can be either open or closed to external fluids, and it is possible that they evolve from closed to open during burial. In fact, shales are so complex that they may be open or closed at different times in their burial history. Many variables, which are not mutually exclusive, can influence their paragenesis. For example, thermal conditions can accelerate mineral transformations such as illitization and rapid burial rates can cause overpressuring. Tectonics can result in the introduction of external fluids which can precipitate hydrothermal minerals. Fluid chemistries also exert a control on the diagenesis such as the variability of authigenic minerals in fractures. The detrital input affects mineral stability and the presence of organic matter can influence mineral dissolution rates and the creation of porosity. Ocean chemistry can also influence mineral precipitation (e.g., higher strontium levels due to replaced aragonite). The interplay of these variables can add further complexity and obscure the diagenetic history.

Absolute timing of diagenetic events is a largely unresolved issue in many shales. Radiometric dating can provide dates for events like the smectite to illite transformation (e.g., Clauer et al., 2012) and paleomagnetism has also been successful in some shales (e.g., Dennie et al., 2012; Manning et al., 2015) to constrain the timing of fluid flow and burial diagenetic events but more work is clearly needed. AMS analysis may also prove useful in determining how some variables such as compaction and tectonism impact the spatial variability of rock fabrics (e.g. Pares, 1999; Heij et al., 2016). Many hypotheses about the diagenesis of shales remain untested and should be investigated. For example, are mineralized fractures an important conduit for later flow? How complex are fracture systems and what is the role of microfractures?

How does this complexity relate to the mechanical behavior of the shale? What is the nature of the contact between mineralized fractures and the matrix? Does roughness of the fracture wall effect fluid flow and the mechanical behavior? How do we connect scales of observations? Addressing these types of questions are important if we are to better understand shale diagenesis and move beyond concentrating on the leaves to focusing on the trees and see the whole forest.

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REFERENCES

The Sedimentary Record


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