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Clay Minerals from the Perspective of Oil and Gas Exploration

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1. Introduction

The clay minerals e.g. kaolinite, smectite, illite, chlorite, etc. are ubiquitous in the targeting rocks of oil and gas exploration. During the early age (1940s) of worldwide oil exploration, clay minerals were studied to predict the quality of organic rich source rock and generation mechanism when scientists tried to investigate the origin of oil and gas (Grim, 1947, Brooks, 1952). Then the clay minerals analysis was used as a tool in terms of environmental determination, stratigraphic correlation and hydrocarbon generation zone identification to find exploration target interval, which was preliminarily and generally summarized by Weaver in 1960. By the 1970s, the clay minerals began to be widely studied for diagenesis and reservoir quality prediction due to the application of petrological analysis and quantitative mineralogical analysis by X-ray diffraction (Griffin, 1971; Pettijohn, 1975; Heald and Larese, 1974; Bloch et al., 2002). Since 1980s, the clay minerals analysis has been used to determine the hydrocarbon emplacement time and petroleum system analysis (Lee et al., 1985). These intermittent clay minerals research progresses are the result of exploration demands of conventional reservoirs (sandstone and carbonate rocks) at different times.

Despite their increasing importance in fundamental geological research and oil industry, clay minerals prove difficult to study in the past. Their sheet structure results in features that can only be resolvable at the sub-micron scale. They are also subtly variable in chemical composition (Fe, Mg, K, Al, etc) and can be confused with each other and other silicates. The recent innovative analytical tools and modern analysis techniques, e.g., QEMSCAN (Automated Mineralogy and Petrography), FIB/SEM (Focused Ion Beam/Scanning Electron Microscope), EDS (Energy-dispersive X-ray spectroscopy), etc., have the capability of quantitative and qualitative characterizing nano-pore and mineralogy of fine grained shale rocks (Lemmens et al., 2011), which creates new era of studying clay minerals for facilitating unconventional (shale) reservoir exploration.

Even though there were the numerous sporadic reports about the application of clay minerals in the oil and gas exploration. So far, relatively little work has been documented on the detailed summary of clay minerals from the perspective of oil and gas exploration. This paper is to systematically summarize the important role of clay minerals in oil and gas exploration from many points of view: basin tectonic evolution, depositional environment, thermal history and maturation history of organic matter in the source rock, hydrocarbon generation, migration and accumulation process, diagenetic history and reservoir quality prediction. The traditional and cutting-edge analytical tools and techniques are also be introduced to identify and characterize the clay mineralogy, rock fabrics property and micro- to nano-scale pores both conventional and unconventional oil and gas exploration.

2. The uses of clay minerals in oil and gas exploration

2.1. Indication of tectonics and sedimentation

During the evolution of petroliferous sedimentary basin, the clay minerals contained in the rocks undergo a series of changes in composition and crystal structure in response to tectonics and sedimentation. The amount and type of clay minerals are a function of the provenance of clastic minerals and of diagenetic reactions at shallow and greater depth in different tectonic and sedimentary settings. Clay minerals can be used to infer tectonic/structural regime, basin evolution history and the timing of various geologic events. This may even provide useful tool in helping to unravel the histories in tectonically complex area, e.g., Schoonmaker et al. (1986) found that the depth distribution of illite/smectite (I/S) compositions showed an irregular, zig-zag trend with depth. This trend is probably the result of multi-stage reverse faultings resulted from the compressional tectonic movement. I/S data were also used to infer several kilometers of uplift and subsequent erosion of the section. The depositional facies appears to be an important factor controlling the abundance of clays in the sediments. Fluvial facies generally possesses higher clay mineral abundance. Well-sorted clean aeolian sands typically have a low clay abundance (<15%).

2.2. Indicator of hydrocarbon generation and expulsion

For oil and gas exploration, we need at least to confirm the exploration area has potential source that generates the oil and gas. This drives geologists to study the potential source rocks (usually organic rich shales) to understand if the organic matter in the source rock can generate hydrocarbons at a given depth in a specific geologic time and when the generated hydrocarbons reach the expulsion peak. Organic geochemistry is the main discipline for studying oil and gas generation and expulsion. However, clay mineralogy is also important for evaluation of these parameters since clay minerals and organic matters usually coexist in the sedimentary rocks and the ultrafine clay minerals are sensitive to the changes in the rocks accompanying the hydrocarbon generation and expulsion processes. Association of clay minerals and organic matter in shales is a significant factor in petroleum genesis. Grim (1947) emphasized the likelihood that the clay minerals in shales concentrated organic

constituents by adsorption to form abundant source material, and subsequently acted as catalysts in petroleum generation (Brooks, 1952).

Many authors report the transformation of clay minerals during diagenesis is from montmorillonite to mixed-layer montmorillonite/illite to illite (Hower et al., 1976) and changes in the ordering of Illite/smectite (I/S) are particularly useful in studying the hydrocarbon generation because of the common coincidence between the temperatures for the conversion from random to ordered I/S and those for the onset of peak oil generation. Percentage of expandable layers in Illite/smectite decreases sharply where the T_{max} (from Rock-Eval pyrolysis) of S₂ hydrocarbon production peak and indicator of thermal maturation-production index (PI) [$PI = S_1 / (S_1 + S_2)$] indicate it is oil generation zone (Burtner and Warner, 1986). The use of mixed-layer illite/smectite (I/S) as a geothermometer and indicator of thermal maturity is based on the concepts of shale diagenesis that were first described in detailed studies of Gulf Coast (Powers, 1957; Hower et al., 1976; Hoffman and Hower, 1979). The good agreement between changes in ordering of I/S and calculated maximum burial temperatures or hydrocarbon maturity suggests that I/S is a reliable semi-quantitative geothermometer and an excellent measure of thermal maturity (Waples, 1980; Bruce, 1984; Pollastro, 1993). The clay mineral association even can be used to evaluate the hydrocarbon generation degree, e.g., the presence of illite-smectite-tobelite demonstrates that oil generation has taken place and absence of tobelite layers shows that the rock has not been heated sufficiently to generate large amounts of oil (Drits et al., 2002).

The significant changes of clay minerals during burial and their relations with diagenetic stages, temperature, organic matter maturity, hydrocarbon generation and expulsion can be summarized in Figure 1. During early diagenesis, the maturity of source rock indicated by vitrinite reflectance (R_o) is low and low percentage of illitic beds in illite-smectite mixed-layer clay minerals, e.g. $R_o = 0.5\%$ approximately corresponds to around 25% illite presence. The Clay minerals mainly experience loss of pore water and little oil is generated during this period. 25 to 50% illitic beds in illite-smectite mixed-layer clay minerals correspond to major oil generating zone ($R_o = 0.5$ to 1.0%). When more than 75% illitic layers are present in illite-smectite mixed-layer clay minerals, cracking of hydrocarbons form dry gas ($R_o > 1.5\%$). This general trend can be used to predict if the source rock is able to generate hydrocarbon in an area. For example, the smectite alters to illite at temperature of 80 to 120°C, which corresponds to the oil generation peak at the same temperature range. Figure 2 presents data from Liaodong Bay area in Bohai Bay Basin in Northeast China to this aspect showing the change in maturity of organic matter and reaction progress in the smectite to illite transformation, which indicates that the rapid increase in illite and decrease in smectite (montmorillonite) in I/S correspond to rapid oil generation.

The reaction of smectite to illite in these clays also can indicate the producing high pore-fluid pressures (Powers, 1967) and expulse hydrocarbons from the shales (Burst, 1959; Bruce, 1984). This can be demonstrated in Figure 2 that the overpressure development interval corresponds to the transformation of smectite to illite and hydrocarbon generation zone (Figure 2C, D, E).

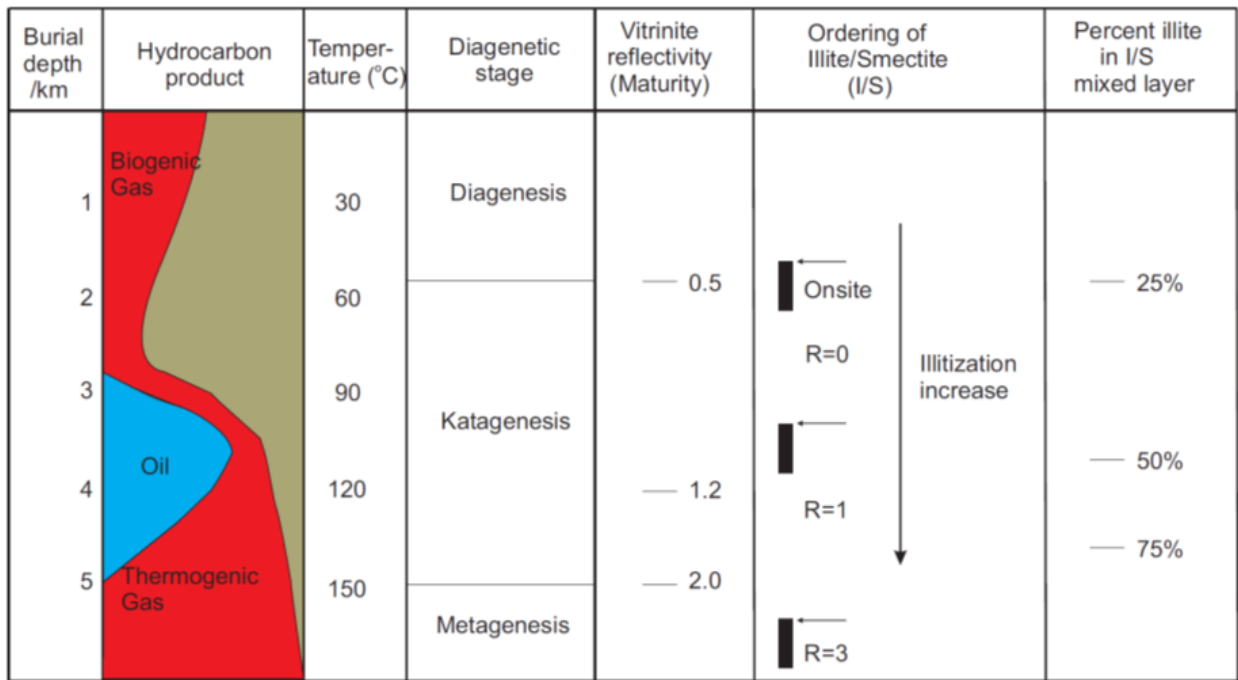


Figure 1. Generalized relationship between temperature, hydrocarbon generation, diagenesis, source rock maturity (vitrinite reflectance), changes in mixed-layer illite/smectite. Figure and data summarized from Foscolos et al (1976), Hoffman and Hower (1979), Waples (1980), Tissot and Welte (1984).

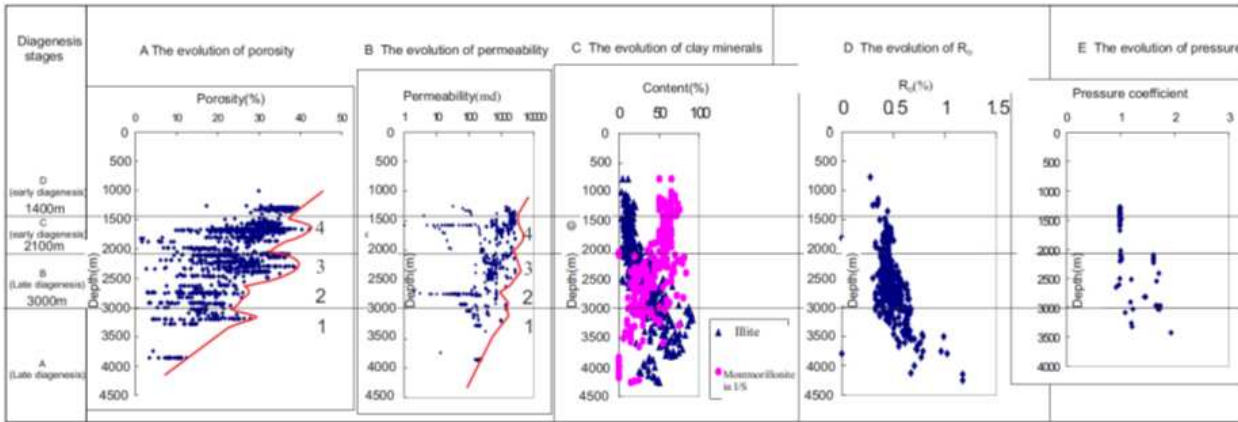


Figure 2. Five plots showing the relationships between diagenetic stages, porosity (A), permeability (B), clay minerals evolution (C), vitrinite reflectance (R_o) (D), and pressure (E) in Liaoqing depression, Liaodong bay sub-basin, Bohai Bay Basin, Northeast China. The secondary porosity zones are numbered upward from 1 to 4.

2.3. Indices for hydrocarbon migration and accumulation

It is critical to establish that hydrocarbon formation and migration occurred after the formation of the trap (anticline, etc.) that is to hold the oil. There is still very little known about the manner in which hydrocarbons formed in argillaceous source rocks migrate and accumulate in porous reservoirs. Some evidence exists, however, that the clay mineral-kerogen complex plays a role in modifying hydrocarbon compositions during migration.

Some time ago, Legate & Johns (1964) used gas chromatography to measure the affinity of montmorillonite clays for hydrocarbons of differing polarity, and suggested that during the migration of petroleum chromatographic effects might modify their composition. Young & Melver (1977) developed the chromatographic technique further and convincingly showed that they could in numerous instances predict oil compositions following migration, where the clay-kerogen complex was the chromatographic agent. "Organo-pores" proposed by Yariv (1976) could be migration paths for hydrocarbons in argillaceous source rocks.

A number of investigators (Powers, 1967; Burst, 1969) have focused attention on the late-stage dehydration which accompanies smectite to illite transformation during burial diagenesis. This firstly suggests that the replacement of kaolinite by illite or direct precipitation of illite indicates fluid flow where the chemical potential of the fluids is in disequilibrium within the reservoir sandstone. The existence of secondary illite does indicate aqueous fluid flow and thus can be used as indices of fluid movement and hence signal the possible hydrocarbon migration. Secondly, it indicates that the water release could create a flushing action responsible for the migration of petroleum hydrocarbons from the source rock through the migration paths to nearby reservoirs. Also, the water liberation can build up abnormal pressures in less permeable sediments, which can provide migration dynamic for hydrocarbons (Figure 2 C, E).

Abnormal Illite distribution has been used as an index to determine if certain rocks/strata/areas are a hydrocarbon migration pathway and its conducting capability (Zeng and Yu, 2006, Jiang et al., 2011). If there shows abnormal illite distribution, it indicates the hydrocarbon migration happened. The illite abnormal distribution of three wells from three different structure zones in Liaodong Bay Sub-basin of Bohai Bai Basin in Northeast China in Figure 3 suggests hydrocarbon migration happened in these three areas represented by three wells, but the conduiting capabilities are different in the three areas based on different abnormal magnitude of illite content. At the same depth of these three wells, illite content of well JZ25-1s-1 is the highest and the illite content of well JZ21-1-1 is the lowest, which indicates the hydrocarbon migration in the JZ25-1s-1 well area is the most active and the JZ21-1-1 area is the relatively least active area regarding to hydrocarbon migration (Figure 3). This result is consistent with current oil discoveries: The Liaoxi uplift (represented by well JZ25-1s-1) to the west of Liaodong Bay contributes to the most reserves in the Liaodong Bay sub-basin. Tan-Lu strike-slip area (represented by well JZ23-1-1) is emerging as the second largest hydrocarbon migration and accumulation area (Jiang et al., 2010, 2011). Almost no oil and gas discoveries in the rest area of Liaozhong depression (represented by well JZ21-1-1) away from strike-slip zone and Liaoxi uplift so far due to poor hydrocarbon migration pathway and poor conduiting capability.

The smearing of clay minerals can also prohibit the hydrocarbons' further migration and facilitate the hydrocarbon accumulation. When the soft clays are smeared into the fault plane during movement and they will provide an effective seal. In many cases, the presence of clay types and their proportions can even indicate if there is oil and gas accumulation.

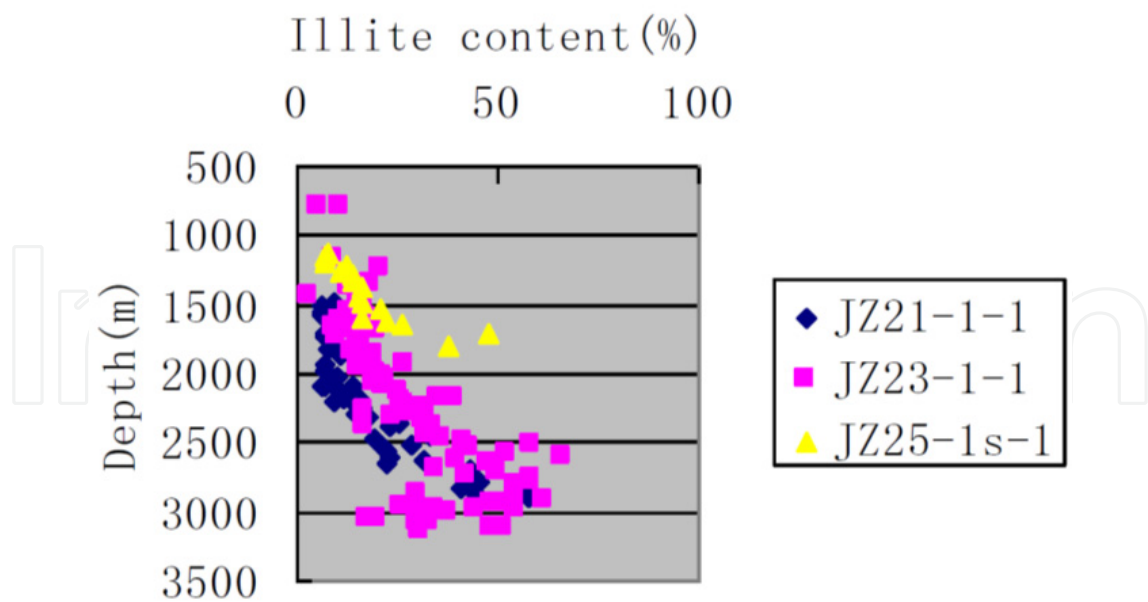


Figure 3. The illite content distribution versus depth from three wells in Liaodong Bay area, Bohai Bay Basin.

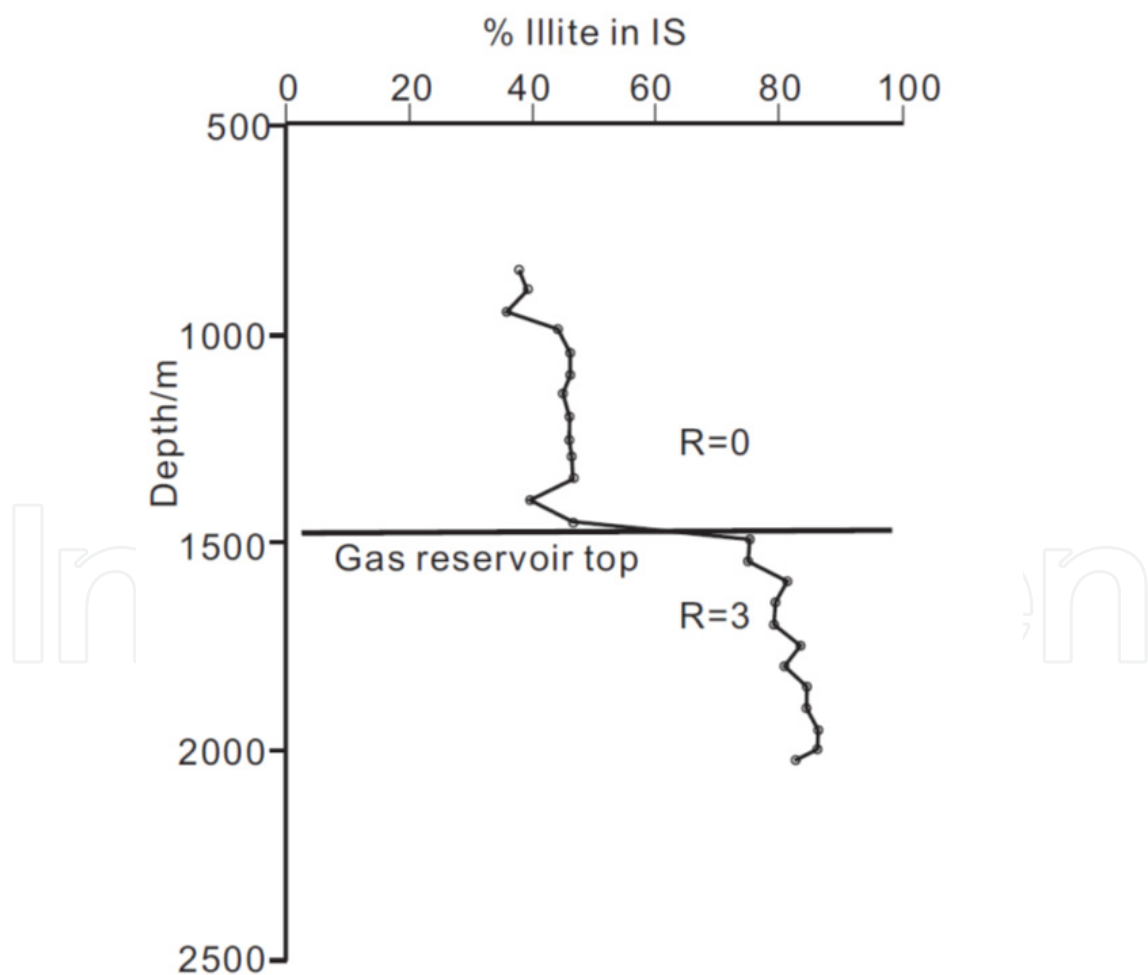


Figure 4. The abrupt changes in the percent illite in I/S and the ordering of I/S (R) in well Dongfang 6 in Dongfang Gas Field, Northern South China Sea.

Webb (1974) recorded that the Cretaceous sandstones of Wyoming generally contain abundant authigenic kaolinite where water saturated, but little if any authigenic clay is found where the sandstones are hydrocarbon saturated. Investigation on clay mineral and its relationship with gas reservoirs show that the clay mineral percentage and ordering of I/S can indicate the hydrocarbon reservoir, e.g., the high content of illite in I/S and higher ordering of I/S change indicate the gas reservoir interval in Dongfang 6 well from Dongfang gas field in Northern South China Sea (Figure 4).

2.4. Significance of clay mineralogy for reservoir Quality prediction

Porosity and permeability are the most important attributes of reservoir quality. They determine the amount of oil and gas a rock can contain and the rate at which that oil and gas can be produced. Most sandstones and carbonates contain appreciable fine-grained clay material including kaolinite, chlorite, smectite, mixed layer illite-smectite and illite. These clay minerals commonly occur as both detrital matrix and authigenic cement in reservoir sandstones. The reservoirs initially have intergranular pores that are main space for oil and gas accumulation. When the reservoirs are deposited, their primary porosity is frequently destroyed or substantially reduced during burial compaction. The clay minerals are usually assumed to be detrimental to sandstone reservoir quality because they can plug pore throats as they locate on grain surface in the form of films, plates and bridge and some clay minerals promote chemical compaction. Not only in sandstone reservoir, the clay content also greatly accelerated the rate of porosity loss in limestone reservoir (Brown, 1997). Generally, the porosity loss is mainly caused by the diagenetic process including mechanical compaction, quartz and K-feldspar overgrowths, carbonate cementing and clay mineralization. Especially, the diagenetic clay minerals play a very important role in determining the reservoir quality.

Authigenic clays from diagenesis in the sandstones studied occur as illite, illite-smectite and kaolinite. They form cements around the detrital minerals. During the period of intermediate to deep burial diagenesis, Illite and illite-smectite clays are the first cements. These early-formed clay films play an important role in reducing reservoir porosity and permeability during burial diagenesis. For example, pore-filling illite formed mainly at the expense of kaolinite. The illitic clays usually occur as pore-bridging clays to reduce the pore space and block the fluid movement by reducing permeability. For clay minerals that replaced rigid feldspar minerals are easily compacted and can be squeezed into pore throats between grains. This will also greatly influence the decrease of reservoir quality.

For oil and gas exploration, we expect the occurrences of high-quality reservoirs. Even though the porosity and permeability of reservoir generally decrease with the increase of burial depth due the diagenetic processes as state above, other diagenetic processes may enhance porosity through the forming of secondary porosity including fractures, removal of cements or leaching of framework grains, preexisting cements and clay minerals, limited compaction and/or limited cementation. The dissolution of authigenic minerals that previously replaced sedimentary constituents or authigenic cements may be responsible for

a significant percentage of secondary porosity. Some micropores are found in various clays regardless of whether the clay is authigenic or detrital in origin. Also, the existence of clay minerals does not always mean to reduce the reservoir quality, it may be good phenomenon to indicate good reservoir quality, e.g., coats of chlorite on sand grains can preserve reservoir quality because they prevent quartz cementation (Heald and Larese, 1974; Bloch et al., 2002; Taylor et al., 2004). Sometimes, the higher content zone of kaolinite is indicative of higher porosity. The reason is that porosity is created when the acid dissolves feldspar to produce kaolinite (Jiang et al., 2010). These all show the positive aspect to clay authigenesis.

The secondary porosity development and its relationship with clay minerals evolution has been investigated in many basins (Bloch et al., 2002; Taylor et al., 2004; Jiang et al., 2010). Let's use Liaodong Bay Sub-basin in Bohai Bay Basin in Northeast China as example again. There clearly exist four secondary porosity development zones for the Tertiary strata, whose depth intervals are 1600-1800 m, 2000-2500 m, 2700-2800 m and 3200-3300 m, respectively (Figure 2A). These intervals are named 1 upward to 4 informally. Their corresponding permeability zones have relative higher values (Fig.2B). The secondary and third secondary porosity zones have relatively larger scale. Correlation between porosity, clay minerals and R_o demonstrates that the secondary porosity zones are related to the rapid transformation of the clay minerals and hydrocarbon generation ($R_o > 0.5\%$) (Figure 2A, C, D). The relation between zones of secondary porosity and pressure distribution illustrated that No.3 secondary porosity is just right below the top surface of overpressure. This is probably because that the overpressure can retard compaction and avoid the excessive porosity reduction.

2.5. Petroleum emplacement chronology

Petroleum emplacement chronology is one of the frontier research subjects in both petroleum geology and isotope geochronology. Determining the oil or gas emplacement ages has important implications for oil or gas genesis and resource prediction. Typical relative chronology for oil or gas migration, emplacement, and accumulation is established by petrology, basin tectonic evolution, trap formation, and hydrocarbon generation from the source rock (Kelly et al., 2000; Middleton et al., 2000). So far, the illite K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating technique hold significant promise in establishing absolute constraints on the emplacement age of oil and gas.

Since the middle of the 1980s, authigenic illite K-Ar dating has been applied to determine the ages of petroleum migration in the North Sea oil fields and Permian gas reservoirs in Northern Germany (Lee et al., 1985; Liewig et al., 1987, 2000; Hamilton et al., 1989). The dating is based on the hypothesis that "illite is commonly the last or one of the latest mineral cements to form prior to hydrocarbon accumulation. Because the displacement of formation water by hydrocarbons will cause silicate diagenesis to cease, K-Ar ages for illite will constrain the timing of this event and also constrain the maximum age of formation of the trap structure" (Hamilton et al., 1989). Wang et al. (1997) investigated oil or gas emplacement ages in the Tarim Basin by this technique.

Recently, illite $^{40}\text{Ar}/^{39}\text{Ar}$ dating was considered better than traditional K-Ar dating. Among the advantages of $^{40}\text{Ar}/^{39}\text{Ar}$ dating over traditional K-Ar methods are that stepwise heating can distinguish contributions from authigenic illite and detrital K feldspar by interpreting their gas release characteristics. The K-Ar dating and total fusion $^{40}\text{Ar}/^{39}\text{Ar}$ dating, however, yield a meaningless mixing age of the authigenic illite and detrital K feldspar, e.g., gradually rising age spectra are obtained by $^{40}\text{Ar}/^{39}\text{Ar}$ laser stepwise heating of the illite samples from the Tertiary reservoir sandstones in the Huizhou sag, Pearl River Mouth Basin in South China Sea. The youngest ages at the first steps are interpreted as being caused by contributions from authigenic illite, suggesting that the petroleum emplacement occurred after 11 Ma. The high plateau ages in the high-temperature steps that are rather variable between the seven samples are interpreted as being caused by contributions of detrital K-feldspar in the sandstones (Yun et al., 2010).

2.6. Significance for petrophysical property study

The reservoir petrophysics e.g. porosity, permeability, water saturation and hydrocarbon saturation are the most important properties that define and control qualitatively and quantitatively the reservoir performance. The minerals present in the reservoir especially the clay mineral (Moll, 2001) can play the utmost role, which affects both the reservoir capacity and production because the grain size of clay minerals is generally very small and result in very low effective porosity and permeability, thus any presence of clay in a reservoir may have direct consequences on the reservoir properties (Said et al. 2003).

Characteristics of clays that strongly affect their electrical behavior are clay composition, internal structure, the tremendous surface to volume ratios of most clays and the charge imbalance along the surface of clay minerals. All these clay mineral manifestations have an impact upon the interpretative petrophysical parameters by well logging responses. In order to better understand the well logging response for petrophysical analysis, the type of clay minerals must be taken into account in reservoir evaluation, e.g., Potassium presence in the reservoir can increase radiation on Gamma Ray logs. Sometimes, the log response can indicate the hydrocarbon saturation and clay content, e.g., the high resistivity zone of resistivity log corresponds to intervals with low water saturation, a more restricted distribution of diagenetic clay (mainly chlorite) and the low resistivity zone corresponds to intervals with more widely distributed diagenetic clay and variably reduced permeability (Nadeau, 2000).

3. Traditional clay mineral characterization methods and their applications for conventional oil and gas exploration

The traditional methods e.g. XRD (X-ray Diffraction), petrographic microscope, XRF (X-ray Fluorescence) and SEM (Scanning Electron Microscopy) have been widely used for clay minerals characterization in conventional siliciclastic and carbonate reservoirs for many years. X-ray diffraction (XRD) is used to provide information on the rock mineral

composition and type of clay minerals and their content. Petrographic microscope can identify the reservoir mineralogy composition, pore types, authigenic clays and cements. Figure 5A illustrates that the Tertiary lacustrine turbidite reservoir in Jiyang Sub-basin of Bohai Bay Basin is mainly composed of quartz (Q), K-feldspar (Fs) and calcite based on thin section observation. The secondary porosities include the intergranular and intragranular pores caused by dissolution of kaolinite, feldspar and carbonate cement. Scanning electron microscopy (SEM) provides wide range of information about the morphology, mineral composition, distribution and paragenesis of the neoformed authigenic clay minerals, mechanically infiltrated clays, transformational clays and pedogenic mud aggregates. Since SEM has a very large depth of field, and can thus yield a three-dimensional image useful for understanding the structure of a sample. It will help understand the clay mineralogy and their effect on the porosity, permeability and other reservoir characteristics. Figure 5B shows secondary pores resulted from dissolution of authigenic kaolinite exist in the similar turbidite sandstone reservoir as that in Figure 5A in Jiyang sub-basin based on SEM observation.

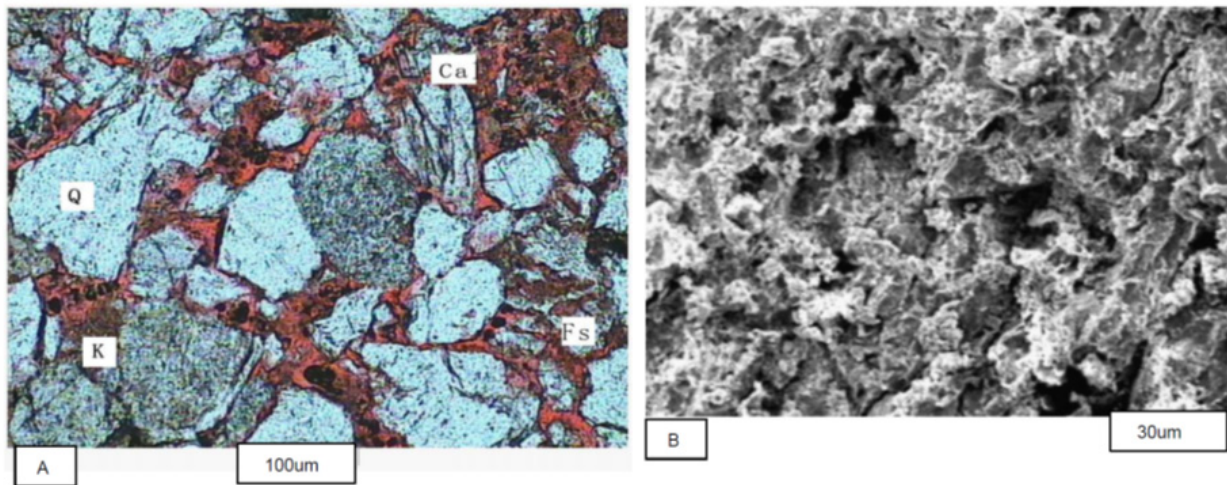


Figure 5. Photomicrography A illustrates secondary pores resulted from dissolution in feldspar (Fs) and kaolinite (K) and some intergranular secondary pores by carbonate cement dissolution based on thin section observation. The sample is from Tertiary lacustrine turbidite sandstone at the depth of 3012m of Well Niu-110; Photomicrograph B is a Scanning Electron Microscope (SEM) image showing secondary pores from dissolution of kaolinite the sample is from Tertiary turbidite sandstone at the depth of 2985.3m from well Niu-35. Both the two wells are both located in in Jiyang Sub-Basin, Bohai Bay Basin, Northeast China.

4. New techniques and their applications for unconventional oil and gas exploration

Over the past decade, interest in shale gas and shale oil reservoirs increased due to commercial success of gas-shale plays in North America. In contrast to conventional oil and gas reservoirs (sandstone and carbonate), these new identified reservoirs typically have very fine-grained rock texture (dominant grain size $\leq 62.5 \mu\text{m}$), low porosity ($\leq 10\%$) and very low permeabilities (in nanodarcy range). These rocks used to be considered as only source rocks with high organic content ($\geq 2\%$ weight fraction Total Organic Carbon, TOC), but now they

have been found as reservoir rocks through horizontal drilling and hydraulic fracturing. Gas and oil reserves in the tight shales are huge, US Energy Information Administration (EIA) released a major report in 2011 that there exists potential 6,622 trillion cubic feet (Tcf) of gas contained in shales around the world. Despite the commercial importance of shale formations, their physical properties especially porosity, pore-size distributions and clay mineral fabrics are still poorly understood. Porosity measurements in shales are complicated because of the very fine-grained texture, small pore sizes, extremely low permeability, and the strong interaction of water with clay minerals, which are often important component in these rock types. Shales exhibit dual-porosity structure and have a more complex pore-structure than the sandstones and limestones. One of the biggest challenges in estimating oil and gas transport and storage properties of shales has been a lack of understanding of clay type, clay content, free-gas content, porosity and their relationships. Brittleness of shale has an impact on proppant embedment and maintaining hydraulic-fracture connectivity to the wellbore. High clay-rich shales usually have low Young's Modulus and, by extension, low brittleness index and difficult to frac. So clay minerals play key role in shale gas and shale oil exploration.

Since shales are really fine and tight, estimating reservoir quality in gas shale requires a thorough understanding of pore structure and pore connectivity. MicroCT is a proven technique to resolve pore parameters with a resolution in the order of 1 micrometer. NanoCT technology has resolution down to 200nm but even that may not be enough for gas shale. Gas shales are known to contain finely-dispersed porous organic matter within an inorganic matrix. The porosity within the organic phase has pore and pore throat dimensions typically below 100 nanometers and even down to just a few nanometers, so new techniques are required to characterize the clay minerals in shales. The recent new clay mineral characterization methods include but not limited to FTIR (Fourier transform infrared spectroscopy), QEMSCAN (Automated Mineralogy and Petrography), FIB (Focused Ion Beam), EDS (Energy-dispersive X-ray spectroscopy), etc.

The advancements of special analytical techniques have made significant progress in clay mineral imaging, mineral identification and quantifying by using FEI company's QEMSCAN®, The clay mineral identification and quantification based on the QEMSCAN® EDS spectral analysis method is a reliable alternative to conventional methods. Furthermore, the automated SEM-EDS solution approach provides additional textural information, and the resulting mineral maps can be used to differentiate, in the case of conventional sandstone and unconventional tight shale reservoir rocks, pore linings, from granular mineral alteration products, from intergranular cements, and sedimentary laminations. Figure 6 illustrates QEMSCAN® mineral and texture maps of representative shale samples from China. The Silurian shale (Figure 6A) shows no bedding and has relatively low content of quartz (14.5%) and Cambrian shale (Figure 6B) shows bedding and high content of quartz (62%), dominant clay minerals of two samples are illite and no smectite detected, which indicates that among the two samples the Cambrian shale (Figure 6B) is more easier to frac to produce gas since it has high brittle quartz content and no expandable smectite.

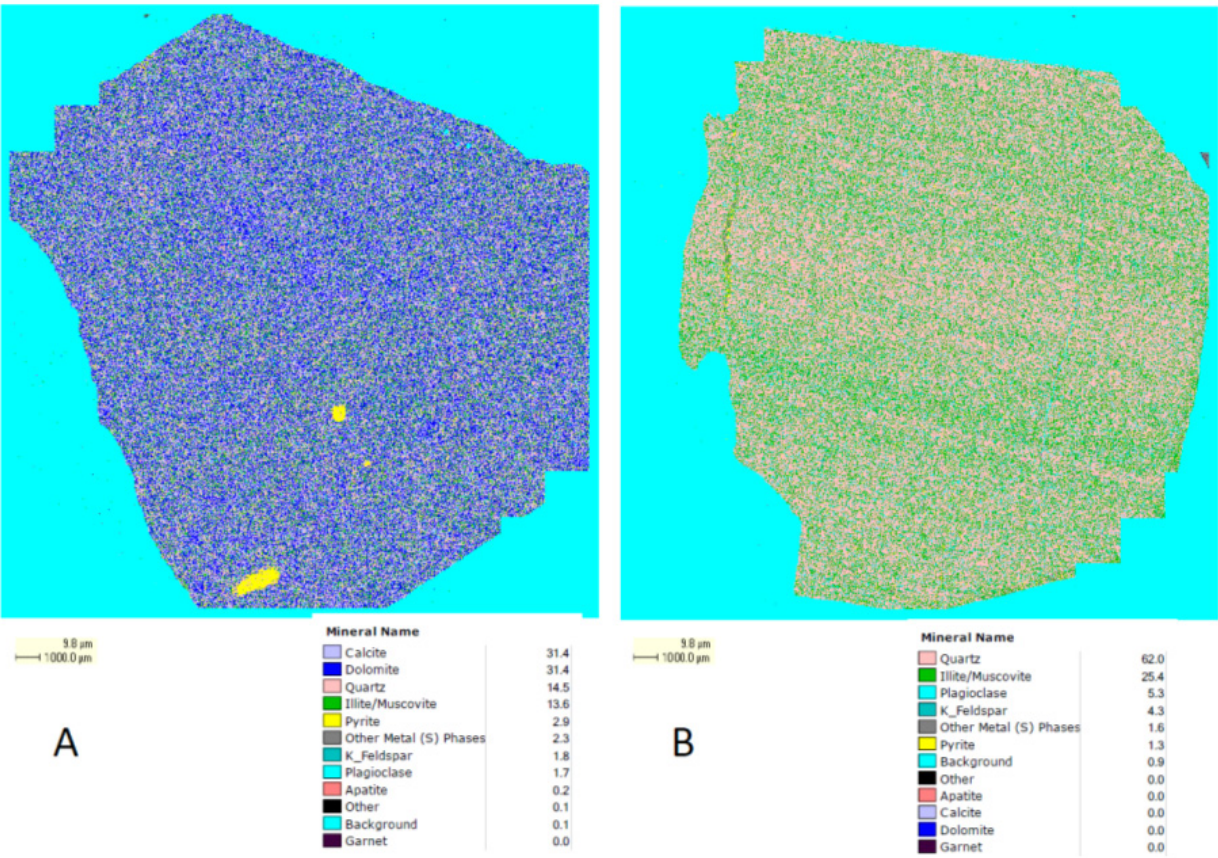


Figure 6. Slices from QEMSCAN showing the rock fabrics and quantitative mineral composition. A is from Silurian shale in Chongqing, China and B is from Cambrian shale in Guizhou, China.

The SEM/EDS has also recently been widely used to study shale reservoirs since SEM has a high resolution and EDS’s chemical element analysis can help identify mineral composition precisely through the combination of fabric and chemical composition analysis. Figure 7 illustrate this method to identify that a Silurian shale sample from Sichuan, China is mainly composed of quartz, albite, dolomite, illite, chlorite and kerogen by using the SEM/EDS method.

For the intuitive visualization of the nano-pore network and rock fabric architecture, FIB/SEM is the only technology so far with nanometer resolution in 3 dimensions to reveal the reservoir architecture of broad ion polished shale. The high resolution of a Scanning Electron Microscope (SEM) combined with the precise cutting capability of a Focused Ion Beam (FIB) enables rendering of 3D reconstructions with resolution of a few nanometers (Lemmens et al., 2011). The FIB is capable of removing a controlled amount of material to create a subsequent 2D section parallel and aligned with the previous one, with inter-section spacing of the order of 10nm, and having resolution of a few nanometers in the section plane. Figure 8 is an example of FIB/SEM slice of a Silurian shale reservoir in Sichuan Basin in China, which renders the intra-organic (kerogen) nano-scale pores and illite presence in the kerogen. These nano-scale pores can store huge amount of gas in the basin. In this way, after careful combination of the subsequent slices, a 3D model with nanometers resolution can be obtained. Figure 9 shows an example of 3D reconstruction for a US Paleozoic shale reservoir (Zhang and Klimentidis, 2011).

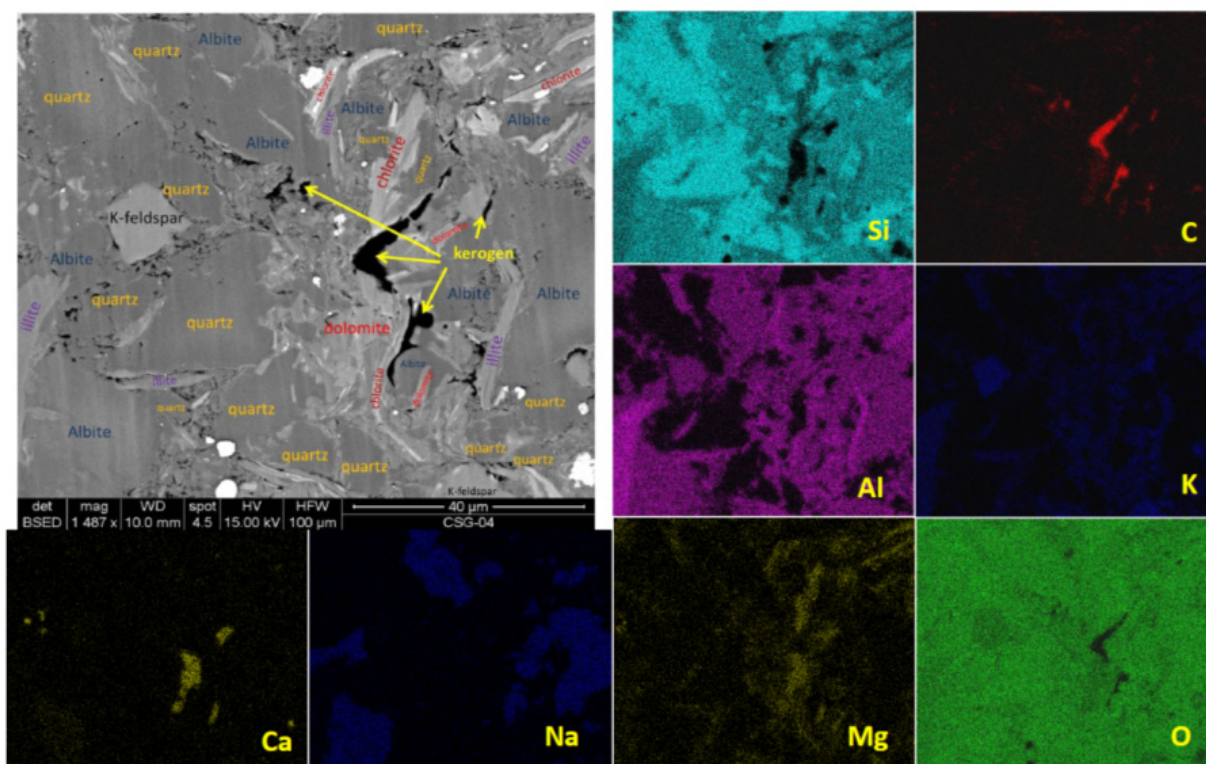


Figure 7. Mineral composition identification based on Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS). The sample is from Silurian shale in Pengshui, Sichuan, China. The upper left and the rest of the slices have the exact same view area under microscope even though their scales are different.

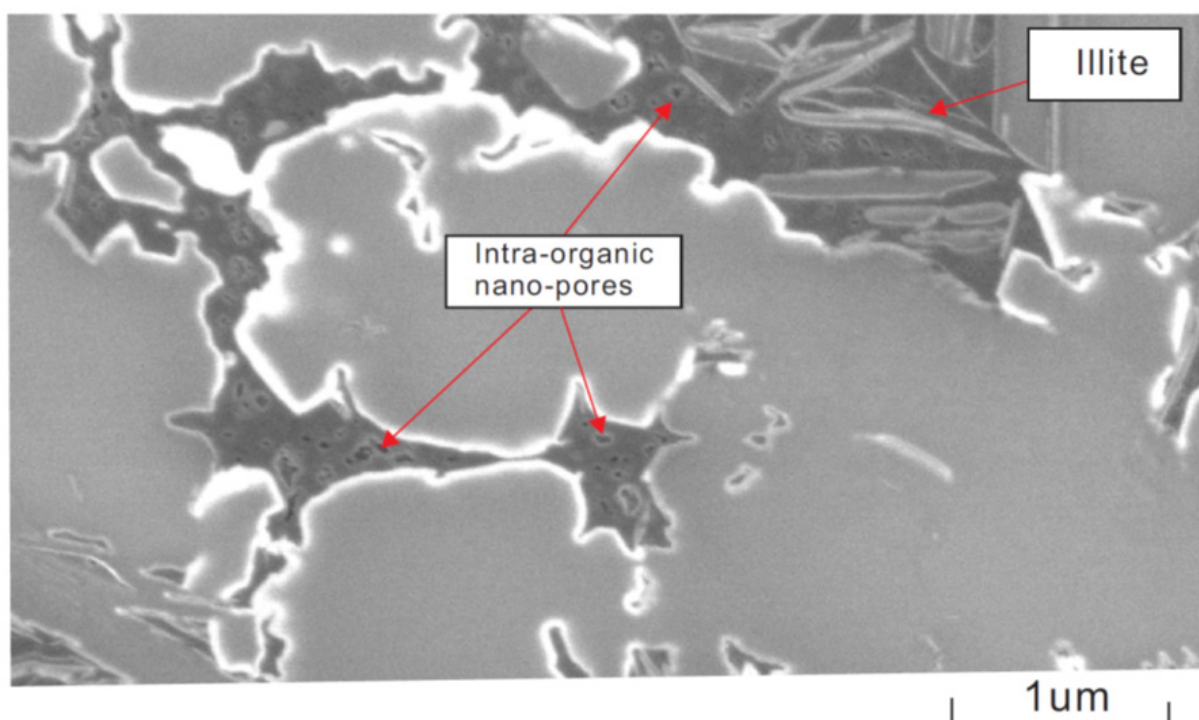


Figure 8. The FIB/SEM slice of Silurian shale reservoir from East Sichuan Basin, China. The sample depth is 2164.8m below surface.

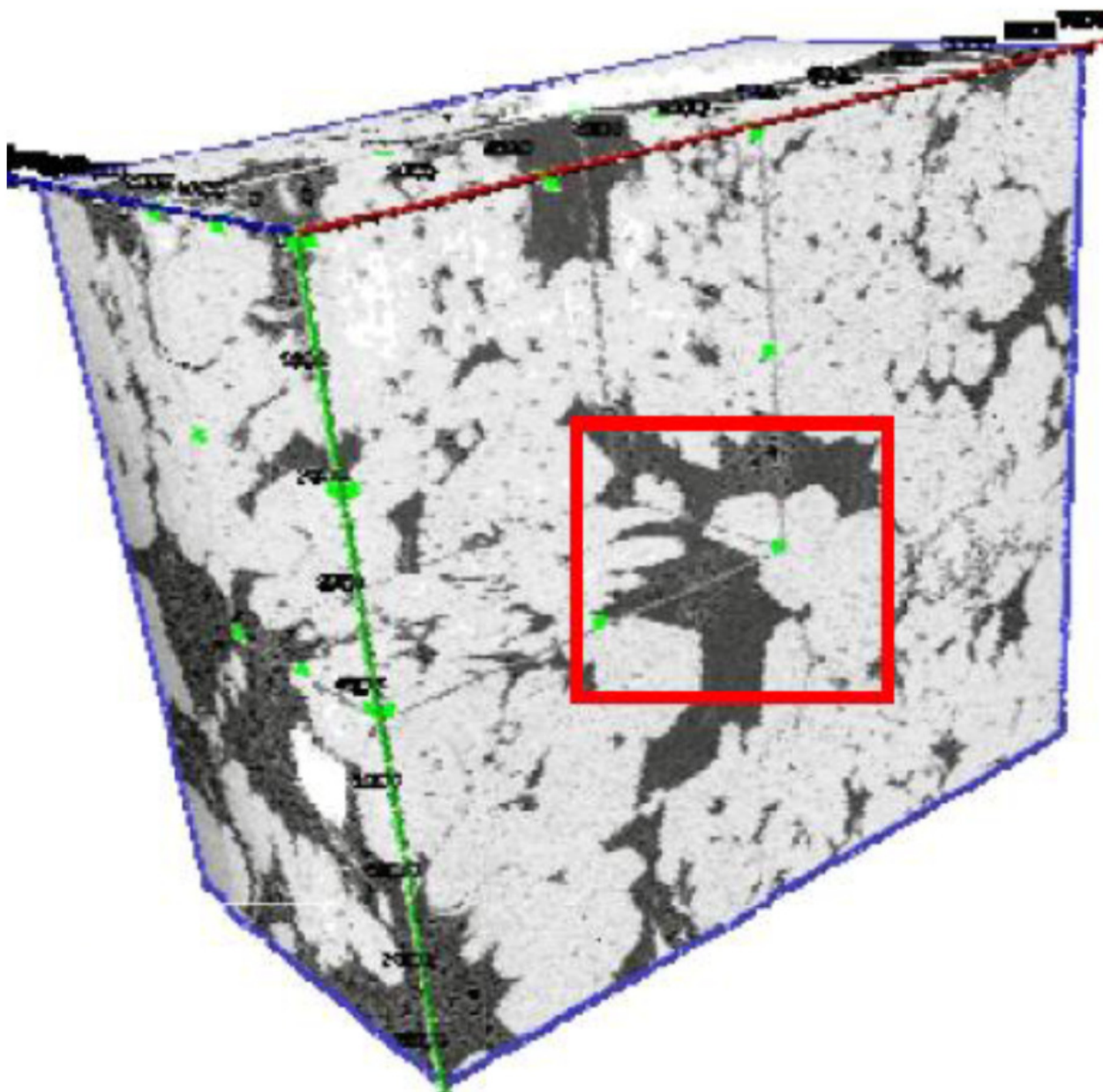


Figure 9. 3D reconstruction of a US Paleozoic shale core sample from a series of FIB/SEM imaging slices (from S. Zhang and R.E. Klimentidis, 2011). The red rectangle area with about 200nm in width shows the nano-pores developed in the kerogen.

5. Summary

The clay minerals are important compositions in source rocks and reservoir rocks that can generate and store oil and gas respectively. The presence of clay minerals strongly influences the physical and chemical properties of conventional sandstone, carbonate and unconventional shale.

Regionally, the clay minerals can be used to interpret and understand such perspectives as the basin evolution on tectonics, sedimentation, burial and thermal history, to infer the sedimentary environment and to correlate strata, etc.

For clay minerals in source rocks, they are important for quality evaluation of the hydrocarbon generation, expulsion and migration. Clay minerals help concentrate organic matter by adsorption and subsequently act as catalyst to generate petroleum. The transformation of montmorillonite to illite and increasing ordering of I/S can indicate the hydrocarbon generation and expulsion events.

For clay minerals in reservoir rocks, their presence has an important impact upon reservoir properties such as porosity and permeability and upon those measured physical data that are used to evaluate reservoir quality. Geologists use clay minerals information to decipher the burial diagenetic process and reveal the pore type and pore evolution. Even though they are usually considered to be detrimental to reservoir quality because they can plug pore throats and can be easily compacted, other diagenetic processes may enhance porosity through the forming of secondary porosity through providing porosity by clay dissolution, creating micropores in clays and coating of chlorite on grains to prevent quartz cementation.

The recent emerging shale oil and gas exploration requires state-of-art imaging and characterization techniques to study the application of clay minerals in the exploration of this unconventional resource. The modern innovative QEMSCAN® and FIB/SEM/EDS have been playing key roles in the identification and quantitative characterization of clay minerals, which help define the best brittle reservoir interval and avoid exploration failure by choosing the compatible drilling and hydraulic fluids.

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