PETROLOGIC AND PETROPHYSICAL CHARACTERISTICS: MISSISSIPPIAN CHERT, OKLAHOMA

By

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2009

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
December, 2011

PETROLOGIC AND PETROPHYSICAL

CHARACTERISTICS: MISSISSIPPIAN CHERT,

OKLAHOMA

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INTRODUCTION

Purpose of Study

The Mississippian chat is an informal name widely used by the petroleum industry. It is a weathered and/or detrital interval of highly porous or hard, low porosity chert at or near the top of the Osagean, Mississippian Series. Chat generally occurs along the unconformity between the Pennsylvanian and Mississippian subsystems in north-central Oklahoma and south-central Kansas (Rogers, 2001). The weathered chert reservoirs in the Mississippian chat can be highly porous and permeable, which makes them significant products of oil and gas. The Mississippian chat has been explored and developed for more than 80 years, but the origin of silica is still poorly understood, sources of silica in the chert have not been confirmed, and the formation of the chert is debated. Since Mississippian "chat" is an informal name, "chert" will be used in place of it in this study.

The purpose of this study is to analyze selected samples of the Mississippian chert and (1) confirm sources of silica; (2) provide rock architecture and petrophysical data for chert reservoirs and aquifers; (3) improve our understanding of formation of cherts from carbonates in other chert-carbonate associations; (4) analyze possible controls that cause the petrophysical differences evident between the Mississippian chert and Mississippian cherty limestones; and (5) improve the understanding of diagenetic processes that form the Mississippian chert, which can provide a template for other cherty shelf carbonates in the Mid-continent region or perhaps elsewhere in the world.

Objective

A series of objectives were formulated to provide a systematic approach to conducting this research. These objectives are outlined below.

1. Locate cores containing the Mississippian chert.
2. Correlate cores to wireline well logs to establish petrophysical signature for cherty limestone and the typical Mississippian chert.
3. Select samples from cores for thin section, core plug and other analyses.
4. Determine and compare lithologies and compositions of the Mississippian chert and Mississippian cherty limestones using core and thin sections.
5. Examine and analyze the rock and petrophysical properties of the Mississippian chert, including porosity, permeability and grain density.
6. Characterize the sources of silica, porosity and permeability of chert and the Mississippian chert reservoirs, and understand diagenetic processes that form reservoirs.

Methods

Cores containing the Mississippian chert and Mississippian cherty limestones were described, sampled and analyzed. Core analysis includes depositional grain types and textures, morphology of cherts, ratios of chert to matrix, relative density, and sedimentary structures. Further information regarding petrophysical properties were acquired by analysis of well logs, and measurement of porosity, permeability and density on core plugs. In particular, well logs across these intervals were examined to determine variations in gamma ray, spontaneous potential (SP), resistivity, density and neutron porosity, and bulk density signature. Thin-sections of core were used to determine the mineral composition, pore types, confirm the possible sources of silica, and determine the relationship between cherts and limestones. A key component of this section was to determine if the chert was biogenic.

Previous Work

Mississippian "chat" is an old oil field term for weathered or tripolitic cherts that occur in many oil producing areas of the Mid-continental region (Duren, 1960). Though the term chat has been used for decades, it is rarely discussed in the scientific literature.

Duren (1960) first reported the presence of sponge spicules in the Mississippian chat at Glick Field, Kansas. He believed that secondary porosity in the chert was likely the result of leaching of siliceous sponge spicules rather than leaching of carbonate from a siliceous limestone. He determined that the tripolitic chert with fine-grained chalky matrix exhibited high porosity, permeability and water saturation in Glick field.

Mikkelson (1967) attempted to establish a clear and universal definition of the Mississippian chat, which was "a highly weathered product of erosion of Mississippian limestone, highly variable in lithology". He suggested the Mississippian chat mainly formed from weathering and erosion during pre-Pennsylvanian exposure, and contains two different intervals in some locations.

Rogers (1996) explained that porosity in the chat formed through several diagenetic steps, including initial dissolution of skeletal debris, in particular sponge spicules, followed by dissolution of matrix and dolomite, then precipitation and recrystallization of silica, and finally compaction and fracturing after burial. Rogers (1996) and Montgomery et al., (1998) related the primary origin of the chat to subtidal sponge spicule bioherms along a subtle shelf break. Montgomery et al. (1998) further suggested that fracturing played an important role in porosity and permeability enhancement, and differentiated transported chert conglomerates from in-situ spiculitic cherts in the Mississippian chat.

In 2001, Rogers systematically described the depositional and diagenetic processes of the Mississippian chat in Oklahoma, and concluded the diagenetic processes included two stages: replacement of calcite by chert molecule by molecule, and dissolution of remaining calcite by meteoric water. Pore fluid chemistry was crucial to the diagenesis, and that the dissolution of calcite in the second stage resulted in most of the secondary porosity, rather than dissolution of siliceous material as previous suggested by Duren (1961) and Meyers (1977). Rogers (2001) emphasized the role of dissolution of siliceous sponge spicules as the source of silica. Other possible sources of silica included hydrothermal emanations, dissolution of volcanic ash, eolian dust, and weathering of silica-rich rocks (Rogers, 2001; Dolbier, 2010).

Mazzullo (2009) described the four lithofacies, diagenetic processes and depositional model of the Cowley facies in Kansas, a similar spiculitic interval to the Mississippian chat in Oklahoma. The paragenetic sequence of diagenetic events included three generations of silicification with multiple episodes of dissolution and a final precipitation of dolomite.

The literature contains a limited discussion of the diagenetic history of cherty carbonate analogues. In the Lindström Formation (Late Permian) in Canada, dissolution of carbonate bioclasts in spicule-rich chert beds were thought to increase calcite pore-fluid concentration (Emerson and Bender 1981; Baker and Burns 1985; Compton 1988), and favor dolomite precipitation that locally replaced matrix and siliceous spicules (Reid, et al., 2008). In Devonian tripolitic chert in west Texas, Saller et al. (1991) indicated that reprecipitation of silica was prior to deep burial, and that most silica mobilization and silicification occurred before dolomitization and anhydrite cementation. Wilson (1996) described the development of the Cherty Series in upper Jurassic limestones in the Portland Beds in southern England as the failure in calcitization in the early stage of silicification. He suggested that the formation of chert nodules was the result of uneven removal of spicular silica and accompanied silicification of micrite, followed by pervasive silicification, accompanied by calcitization.

CHAPTER II

GEOLOGICAL BACKGROUND

Geological Setting

The Mississippian chert occurs on and around the Nemaha uplift and the Cherokee platform in central Oklahoma (Figure 1), and extends northward into southern Kansas (Rogers, 2001). Cherty Mississippian sediments were deposited at the shelf margin of the Burlington shelf, which was a thin but extensive carbonate wedge during early and middle Osagean (Lane, 1978), and the shelf edge west of the Ozark dome (Lane, 1978; Guschick and Sandberg, 1983; Rogers, 2001).

The Nemaha uplift is a major structural element that forms the western boundary of the Cherokee platform, and extends northward from Oklahoma into Kansas and Nebraska (Hudson, 1973). The Nemaha uplift formed mainly in Late Mississippian-Early Pennsylvanian time, contemporaneously with the elevation of the Ancestral Rocky Mountains in Colorado (Ye and others, 1996; Gay, 2003). Subsequent weathering and erosion of exposed Mississippian carbonate created the unconformity evident between the Pennsylvanian and Mississippian strata.

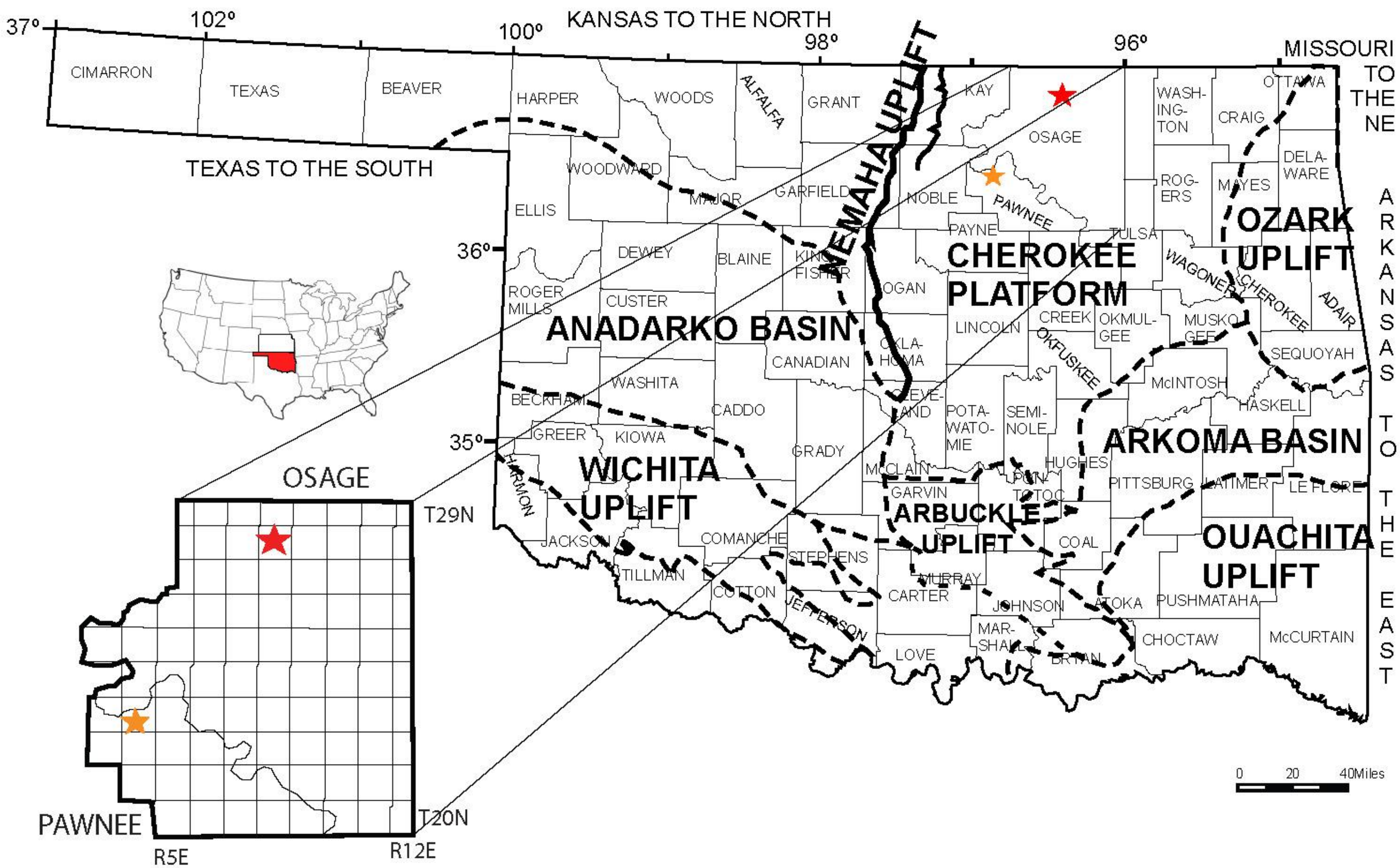


Figure 1. Location of the Nemaha Uplift, Cherokee Platform, where the Mississippian chert is widely distributed. Red star marks the location of cored Mississippian chert, yellow star the Mississippian cherty limestone.

Stratigraphy

The Mississippian chert was deposited along the unconformity between Mississippian and Pennsylvanian (Cherokee), and represents subaerial exposure and erosion of the Mississippian cherty limestone during post-Mississippian or pre-Pennsylvanian erosion of the southern Mid-continent.

During Mississippian (Kinderhookian-Osagean), a shallow sea covered most of Oklahoma, depositing shallow shelf to marine carbonate including shallow water, clean grainy carbonate, and deeper water, argillaceous silica rich ones. Recent work by Mazzullo et al. (2011) shows that the cherty facies are diachronos, which calls into question previous stratigraphic frameworks for the Mississippian subsystem. In north central Oklahoma, Mississippian strata have traditionally been separated into four units, in ascending order, termed Kinderhookian, Osagean, Meramecian, and Chesterian, based on lithologic and electric log characteristics of rock sections in wells (Jordan, 1959). In the northern Oklahoma, Mississippian limestone is believed to be mainly Osagean and Meramecian, and that Chesterian rocks are absent as a result of truncation prior to Pennsylvanian deposition (Jordan, 1959). In the study area, these traditional Osagean units consist of interbedded light- and dark-colored, dolomitic and argillaceous, cherty limestone (Jordan, 1959).

During the pre-Pennsylvanian, uplift, surface and/or near-surface erosion or in-situ weathering of the Mississippian limestone resulted in diagenetic alteration of the top of the unit, occasionally resulting in a Mississippian tripolitic chert facies (Elebiju, 2011), referred to as Mississippian chat. The Mississippian deposits were overlain by Pennsylvanian sediments of different ages. On the Cherokee platforms, Mississippian strata are overlain by strata interpreted to be of the Desmoinesian Series, Cherokee Group.

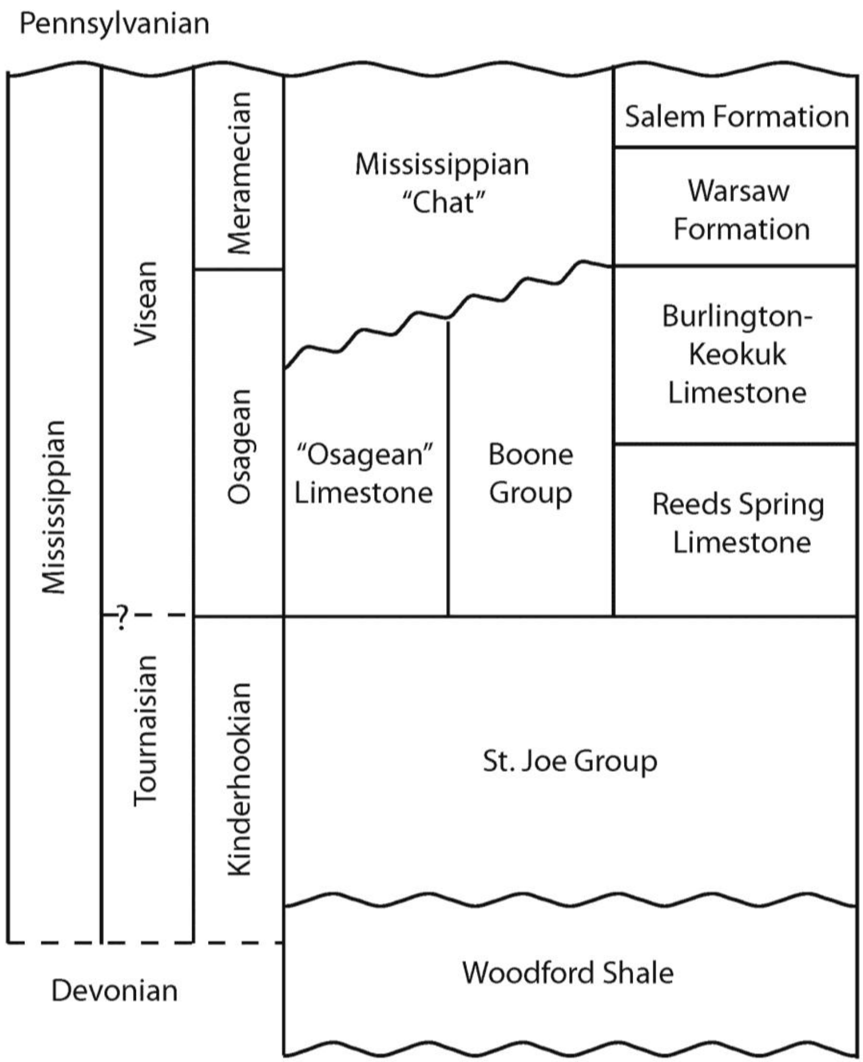


Figure 2. Stratigraphic column in study area. Modified from Mazzullo et al. (2011).

CHAPTER III

PETROLOGIC CHARACTERISTICS OF MISSISSIPPIAN CHERT AND MISSISSIPPIAN CHERTY LIMESTONE

Lithology of the Mississippian Chert

The Mississippian chert core is from the Chapman Barnard Ranch #14 well that was operated by Venezuelan Sun-Golden Oil Company. This well is located in the N/2 NW, Sec. 28, T.28N., R.8E., Osage County, Oklahoma (Figure 1). The total cored interval is 115 feet, and extends from 2633 ft to 2518 ft.

Based on rock texture, compositional changes, density, color, percentage of chert, and the degree of weathering, this interval is divided into four major zones, in ascending order: tripolitic chert (2633 ft ~ 2603.5 ft), cherty light colored (LC) limestone (2603.5 ft ~ 2562 ft), less weathered, lower porosity chert(2562 ft ~ 2535 ft), and tripolitic, high porosity chert (2535 ft ~ 2528 ft). Figure 3 is a petrolog showing the lithology and properties of this core. Though the petrologic properties in these four divisions are markedly different, the boundaries between them are gradational, and no abrupt changes are apparent.

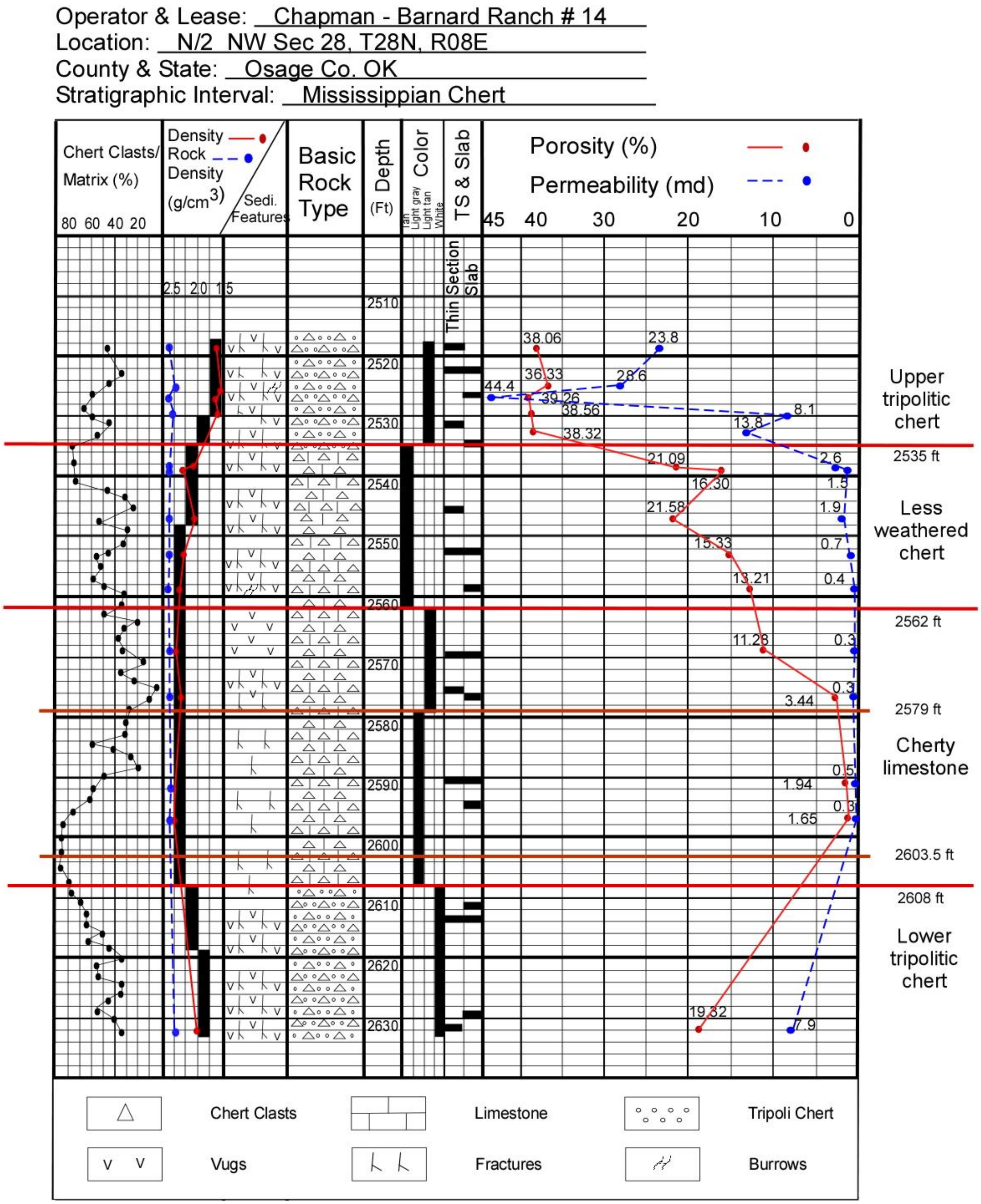


Figure 3. Petrolog of the Mississippian chert showing lithology and various rock properties, including porosity, permeability, rock density, and bulk density.

1. Lower tripolitic chert, 2633 ft ~ 2603.5 ft

The lowest part of the cored interval is tripolitic chert that is weathered, and entirely silicified. These rocks are white, porous, oil stained, tripolitic cherts, with unsorted, white to grey chert clasts (Figure 4). Chert clasts are mostly 1.5 ~ 3 cm, occasionally >10 cm, and are highly deformed by the combined effects of brecciation and dissolution. Black oil residues fill the micro-porosity to give some chert clasts a darker color. The rocks are also slightly pyritic, stylolitic, fractured and contain dissolution vugs (millimeter-size) in both core samples and thin sections. Overall, dissolution features seem more dominant than brecciation in this interval.

Thin section examination revealed that the tripolitic chert matrix is the result of leaching of the original spicular matrix (Figure 5 A&B). Leaching and dissolution removed matrix and enlarged pores between spicules, leading to high porosity. Spicules in the thin section are densely packed in the matrix and within chert clasts, all monaxon type, detached from demosponges (Mazzullo, 2009). Dissolution of cherty spicules is preferred in some chert clasts, creating moldic porosity. Subangular to subrounded silt-size quartz grains are sparsely distributed, and usually concentrated along stylolites. Small patches of relict calcite, partly replaced by microcrystalline quartz and full of spicules, occur, but are rare. Chert clasts are commonly composed entirely of siliceous spicules (Figure 5), cemented by microcrystalline quartz. Brecciation of chert clasts created fractures, most of which are open or partially cemented by microcrystalline quartz. Dissolution created micro-size vuggy porosity at the interfaces between chert clasts and matrix, blurring the boundaries. Some of these chert clasts have black bitumen or oil residue rims, marking the multiple stages of chertification. Fractures also occur in the porous matrix, and dissolution enlarged some fractures in the matrix and within chert clasts.

In the upper part of the tripolitic chert interval, the carbonate becomes less weathered and silicified. Lime mud content becomes evident and increases upwards. Calcite relicts are more common in the thin sections, and some fractures are filled by calcite cement (Figure 5 C&D). Dissolution features are still obvious, including stylolites, and numerous small vugs (millimeter-size), with some centimeter-size larger ones. Larger chert clasts (>10 cm) are more common as the carbonate content increases. Some thinner (around 1inch thick), relatively solid, lower porosity chert intervals are present, and become more frequent upwards. These relatively solid intervals show less dissolution features, contain chert clasts over 10 cm, have a white matrix that is entirely silicified, and are fractured but have few visible dissolution vugs. In some brecciated zones, larger chert clasts were brecciated into small angular pieces with sharp margins.

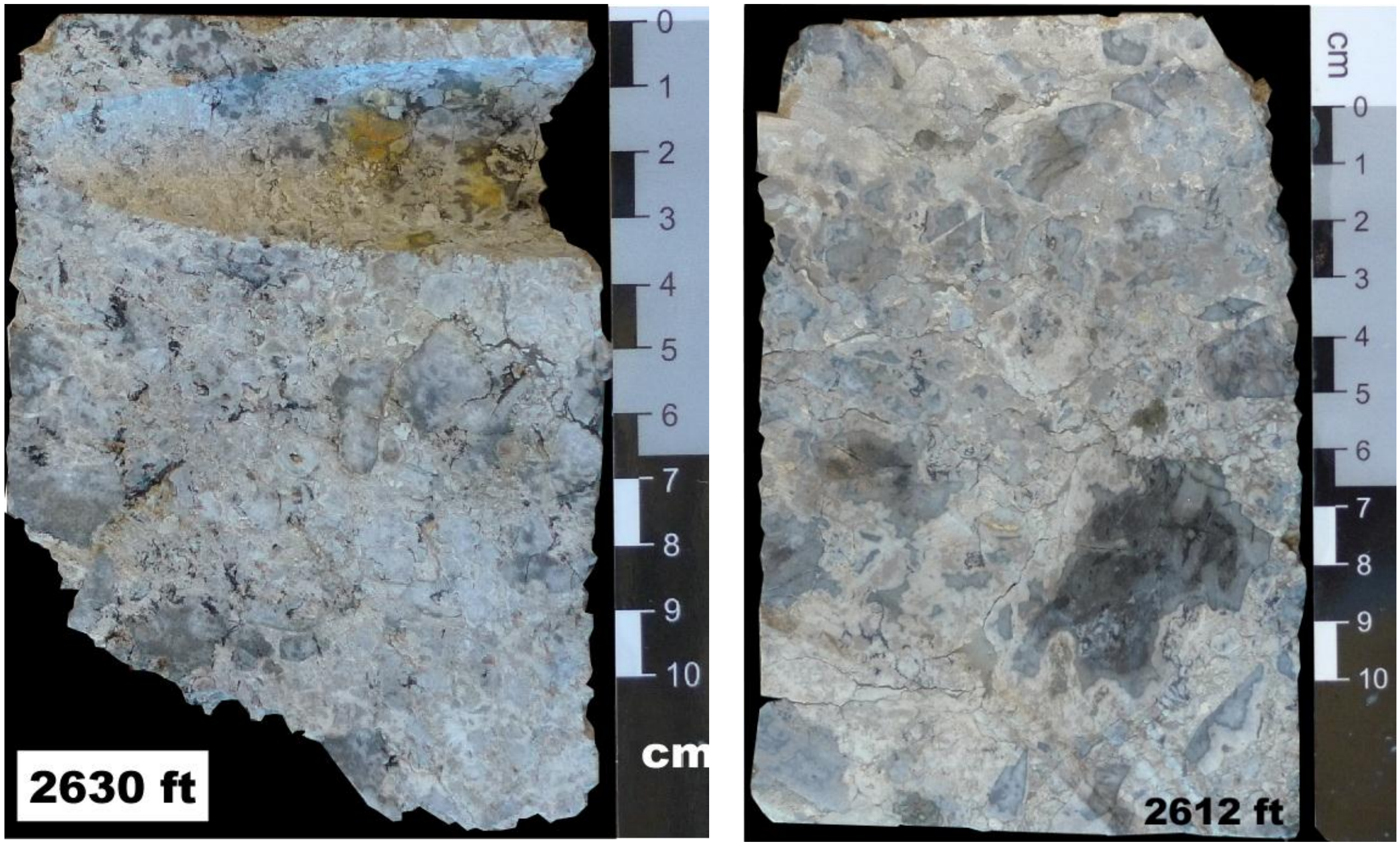
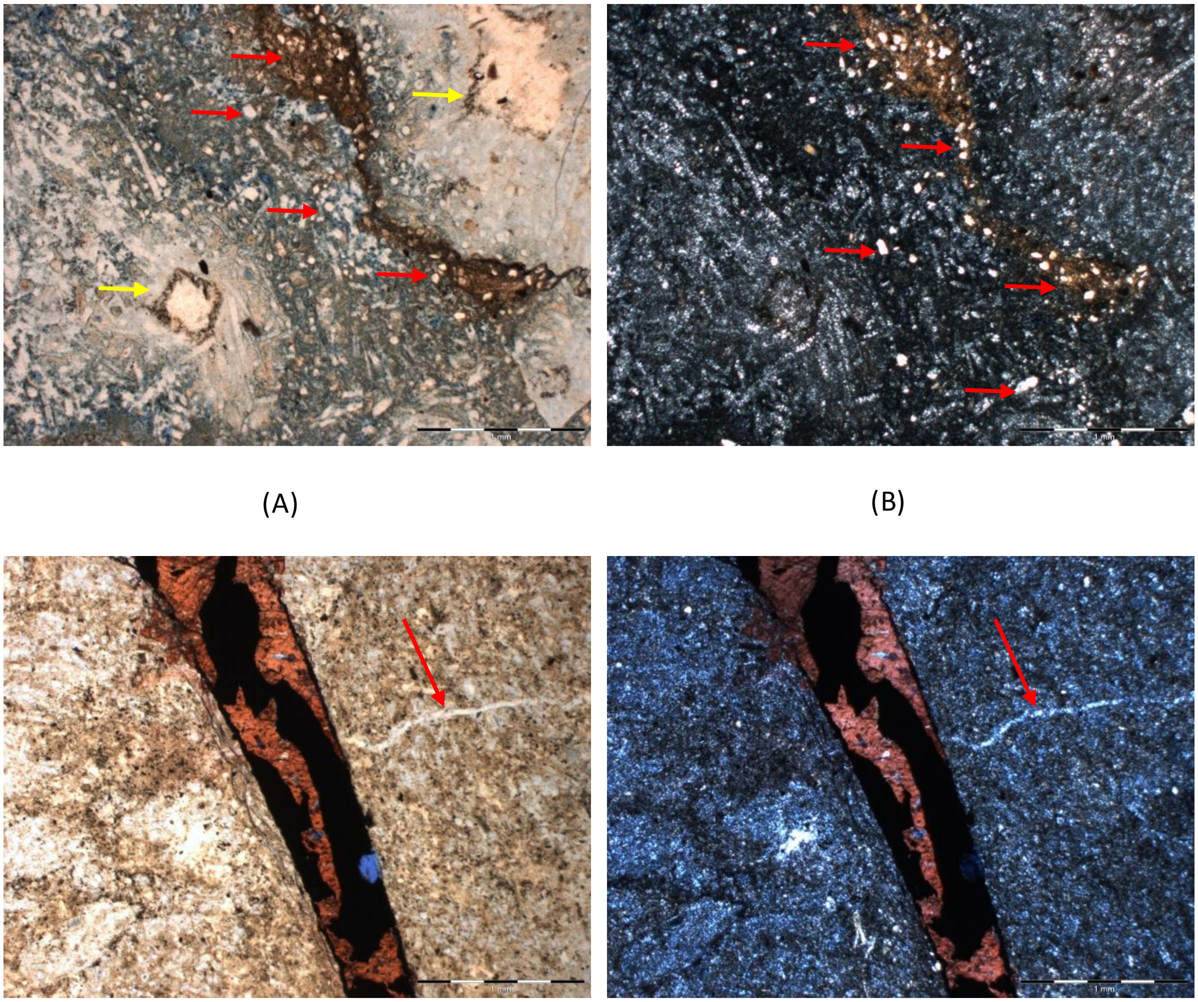


Figure 4. Core photographs of the tripolitic chert. Left: white tripolitic matrix with white to grey chert clasts, fractures and visible vugs. Depth: 2630 ft. Right: same texture as A, but slight less weathered, with fewer and smaller vugs; the black and dark grey chert clasts are caused by bitumen residues filling pores. Depth: 2612 ft. Note the deformed shape of chert clasts.



(A) (B)

(C) (D)

Figure 5. Thin section photomicrographs of the lower tripolitic zone, 2632 ft. A & B: Chert clasts in the tripolitic cherty matrix, with stylolites and silt-size quartz, some are marked by red arrows; spicules are densely packed in the matrix and chert clasts. Black bitumen residues (yellow arrows) form rims inside the chert clasts. Scale bar in lower right image represents1mm in length. A. Plane Polarized Light (PPL), B. Cross Polarized Light (CPL). C & D: In the upper transition zone, calcite cement and bitumen are filling fracture that crosscuts a healed fracture cemented by microcrystalline quartz (red arrow); scale bar is 1mm, C. PPL, D. CPL.

2. Cherty, low porosity, light colored (LC) limestone (2603.5 ft ~ 2562 ft)

a. Lower transition zone: 2608 ft ~ 2603.5 ft

Above the lowermost chert zone, the rock gradually changes from tripolitic chert to cherty limestone. The limestone is rich in chert, but light grey lime mud content increases upwards, as does the size of chert clasts, and the frequency of stylolites.

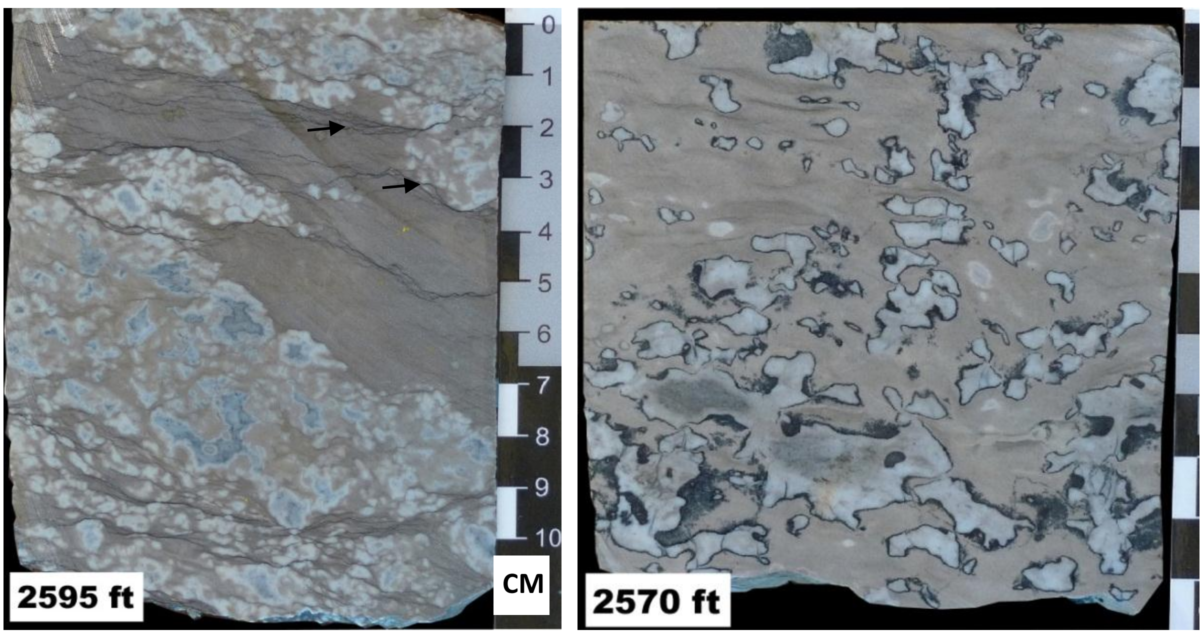
b. Cherty low porosity light colored (LC) limestone: 2603.5 ft ~ 2579 ft:

This interval is non-to-slightly weathered, solid cherty limestone with low porosity and permeability. These rocks (Figure 6 A) are light grey spicular wackestone with grey chert clasts and stylolites, but without obvious vugs. Lime mud content continuously increases upwards. Most chert clasts are 4~10 cm in diameter, and occasionally >15 cm. Chert clasts commonly display white rims. Others are black due to bitumen residue. They are highly brecciated in certain zones, and sometimes fractured into small pieces. These clasts are mostly elongated, nodular or flaser shaped, but highly brecciated clasts are angular.

The spicular wackestones consist of micritic matrix with siliceous spicules (<10%), and chert clasts (Figure 7 A&B), which are full of spicules and entirely silicified. Calcite is precipitated in the matrix, in fractures within the brecciated chert clasts, and is especially pervasive at the interface between micritic matrix and chert clasts. Euhedral dolomite rhombs occur inside chert clasts. Some carbonate cements show wavy extinction, typical of dolomite or partially dolomitized calcite. Peloids are common in the matrix (Figure 7); some appear aggregated. Porosity is minimal in thin sections.

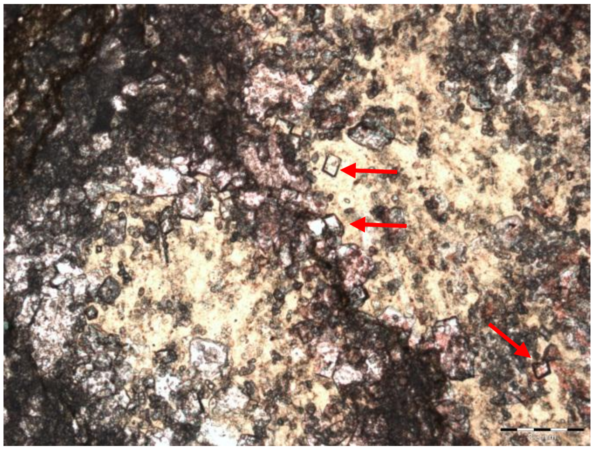
c. Upper transition zone: 2579 ft ~ 2562 ft:

The Mississippian section transitions up section from cherty limestone to chert. Rocks in this zone (Figure 6 B) are slightly to moderately weathered, with occasional vugs (Figure 7 C) and open fracture porosity. Chert clasts greatly decrease in both size and number, typically 1~2 cm in length with rare large ones, and nodular to flaser shaped. Specific intervals, such as 2573.9 ft~2574.2 ft, 2567.5 ft~2568 ft, contain more chert clasts, and the matrix in this interval is almost entirely lime mudstone. Stylolites are concentrated in certain zones, and some small fractures within chert clasts have yellow clay infill. Pyrite is more common in the upper transition zone.

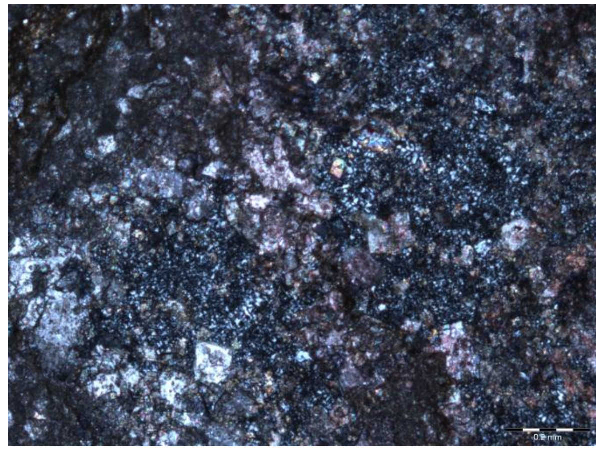


(A) (B)

Figure 6. Core photographs of LC cherty limestone. A: Light grey limestone, with nodular, flaser chert clasts. Stylolites are at the bottom and top of this interval. The white rims of the chert clasts are calcite cement, according to thin section analysis. Pyrite is marked by arrows. 2595 ft. B: Chert-rich zone of the upper transition limestone: light tan limestone matrix with nodular, flaser chert clasts. Bitumen or oil residues give chert clasts black rims. 2570 ft.



(A)



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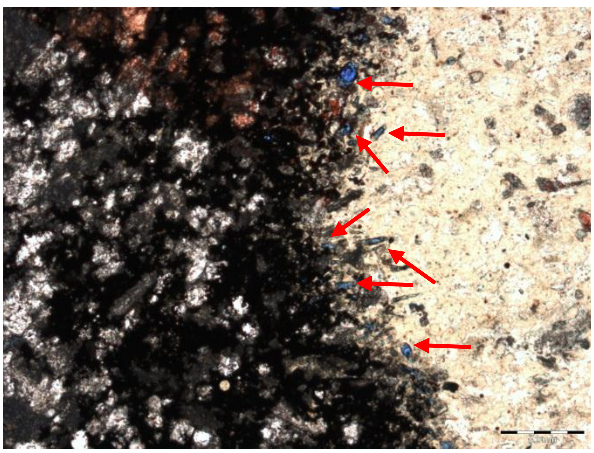
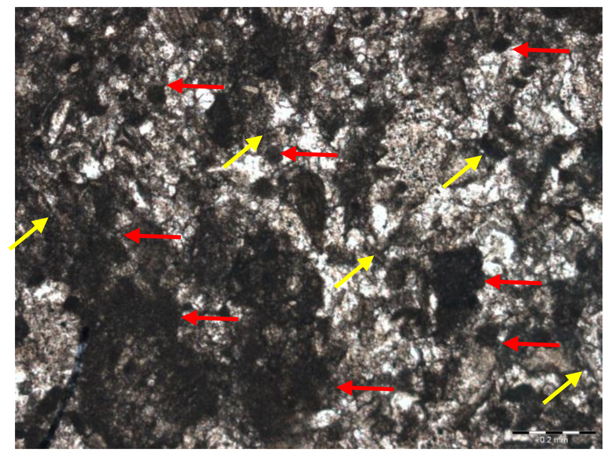


(C)



(D)

Figure 7. Thin section photomicrographs of LC cherty limestone. A & B: Micritic matrix (black) with chert clasts (light color); calcite cement is precipitated at the interface between chert clasts and the matrix, and some dolomite rhombs (red arrows); 2591 ft, scale bar is 0.2 mm, A. PPL, B. CPL. C: Pore space that is resulted from dissolution at the interface between chert and the matrix, marked by red arrows; 2576 ft, scale bar is 0.2 mm, PPL. D: Micritic matrix with calcite (white), pellets (red arrows), and a few small spicules (yellow arrows); some pellets are aggregated; note the size of spicules are much smaller than that in the chert. 2576 ft, scale bar is 0.2 mm, PPL.

3. Less weathered chert: 2562 ft ~ 2535 ft:

These rocks are moderately weathered chert (Figure 8), which are less weathered than the lower and upper tripolitic chert. Porosity increases upwards according to well logs, and ranges from 20% to 10% based on core plug measurements, indicating increasing weathering upwards. These rocks are tan, spicular wackestone with white, unsorted, flaser chert clasts that are deformed by dissolution and compaction. Chert clasts occur more frequently and are larger than in the underlying transition zone. Chert clasts are 1~2 cm in diameter with larger ones ranging up to 4~5 cm, and occasionally >5 cm. Burrow-mottled texture occurs in certain intervals, such as 2542.3~8 ft, 2546.4~5 ft. Fractures at various scales occur in the chert clasts and the matrix. Some fractures are filled by white calcite cements, others by dark bitumen residues. Stylolites and pyrite are present. As the depth decreases, the chert is increasingly weathered and leached, more fractured, with larger vugs, and smaller chert clasts.

The abundance of spicules in the micritic matrix is <10 percent. Thin section examination of less weathered chert reveals the micritic matrix is leached, contains micro-vug porosity (Figure 9 A&B), and sometimes is saturated with bitumen. Calcite, dolomite and partially dolomitized calcite occur at the interface between chert clasts and matrix, and along stylolites (Figure 9 C). Chert clasts are rich in siliceous spicules, some of which are dissolved to form vuggy porosity (Figure 9 A&B). Fractures are common in compacted and brecciated zones. Some fractures are open, and probably enlarged by dissolution, others are cemented by calcite (Figure 9 D). Silt-size quartz is sparsely distributed in the matrix of the less weathered chert, but concentrated along the stylolites.

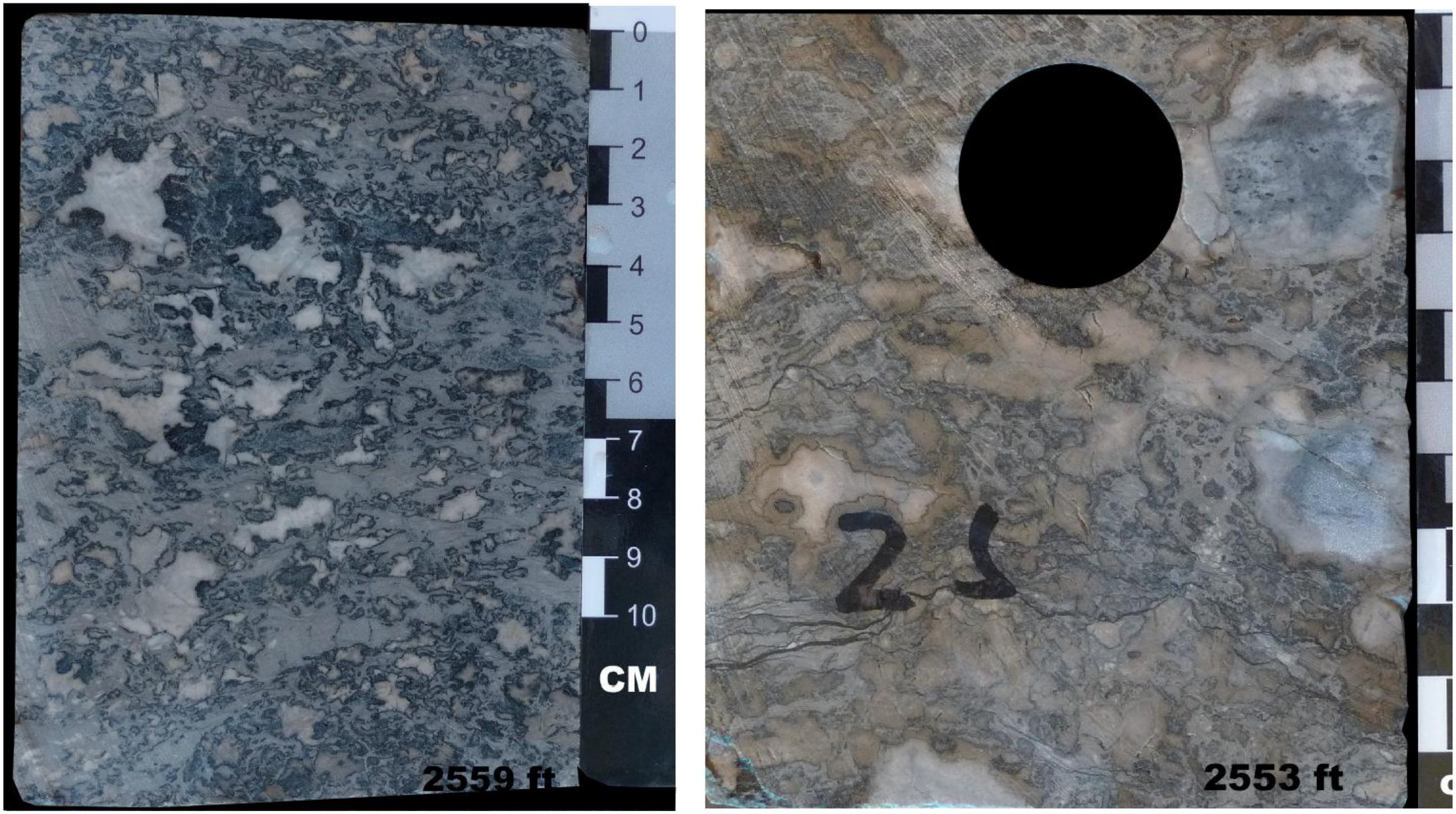
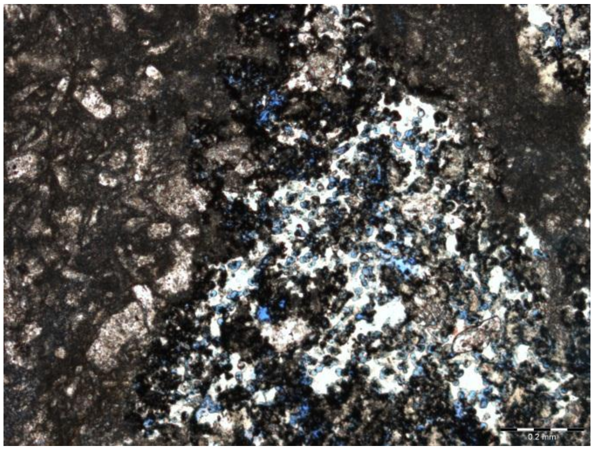
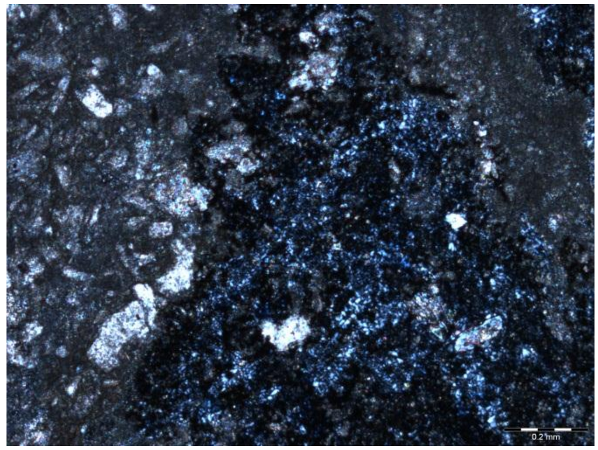


Figure 8. Core photographs of less weathered chert in the middle zone. Note in this interval, there are more chert clasts than the transition zone, but in smaller size. The rock texture is not as porous and highly weathered as the tripolitic chert, but it is distinct from the underlying cherty limestone, which has fewer chert clasts and less porosity. Left 2559 ft, Right 2553 ft.



(A)



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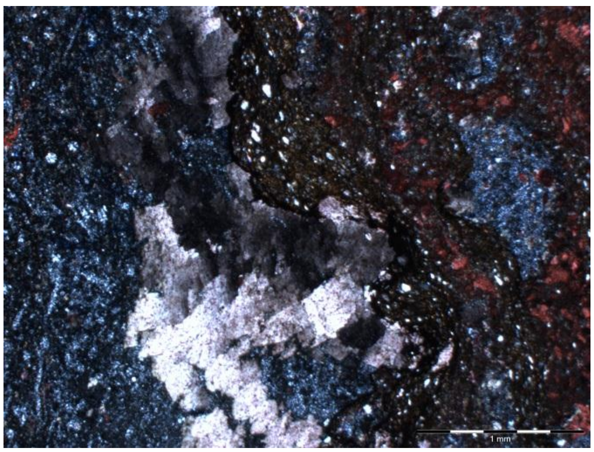

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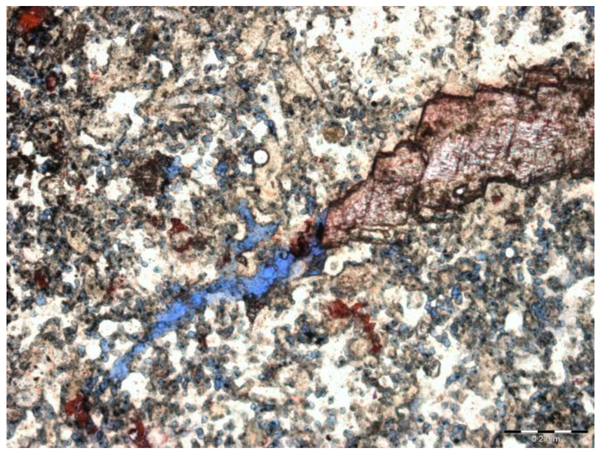


(D)

Figure 9. Thin section photomicrographs of less weathered chert. A & B: Micritic matrix with chert clasts; the matrix is similar to cherty limestone below, but the chert clasts are porous, with bitumen infills. 2553 ft, scale bar is 0.2 mm, A. PPL, B. CPL. C: Dolomite precipitated along stylolites. Depth 2553 ft, scale bar is 1mm, CPL. D: Calcite cement in the chert clast that is partially dissolved by weathering. Depth 2553 ft, scale bar is 0.2 mm, PPL.

4. Upper tripolitic chert: 2535 ft ~2518 ft:

The uppermost tripolitic chert zone in the Chapman Barnard #14 is extensively weathered, and contains high porosity (up to 40%). This interval is light tan, oil stained, and contains highly leached spicular matrix, with unsorted, dark colored, bitumen saturated, sub-angular to sub-rounded chert clasts (Figure 10). These chert clasts are generally 2~3 cm in diameter, whereas larger ones are about 5~8 cm in length. Dissolution features include abundant vugs in various sizes, from millimeter-size to several centimeters in diameter, and large quantities of micro-vugs, and stylolites.

These rocks are similar to the lower tripolitic chert of the cored interval, but more weathered, and show the highest porosity. The tripolitic matrix is highly weathered and very porous chert (Figure 11). Silt-size quartz grains are sparsely but widely distributed (Figure 11 B). This interval is entirely silicified, without any calcite or dolomite. Dissolution of spicules within chert clasts created abundant moldic porosity (Figure 11 D), differentiating this interval from the tripolitic chert at the base of the cored interval.

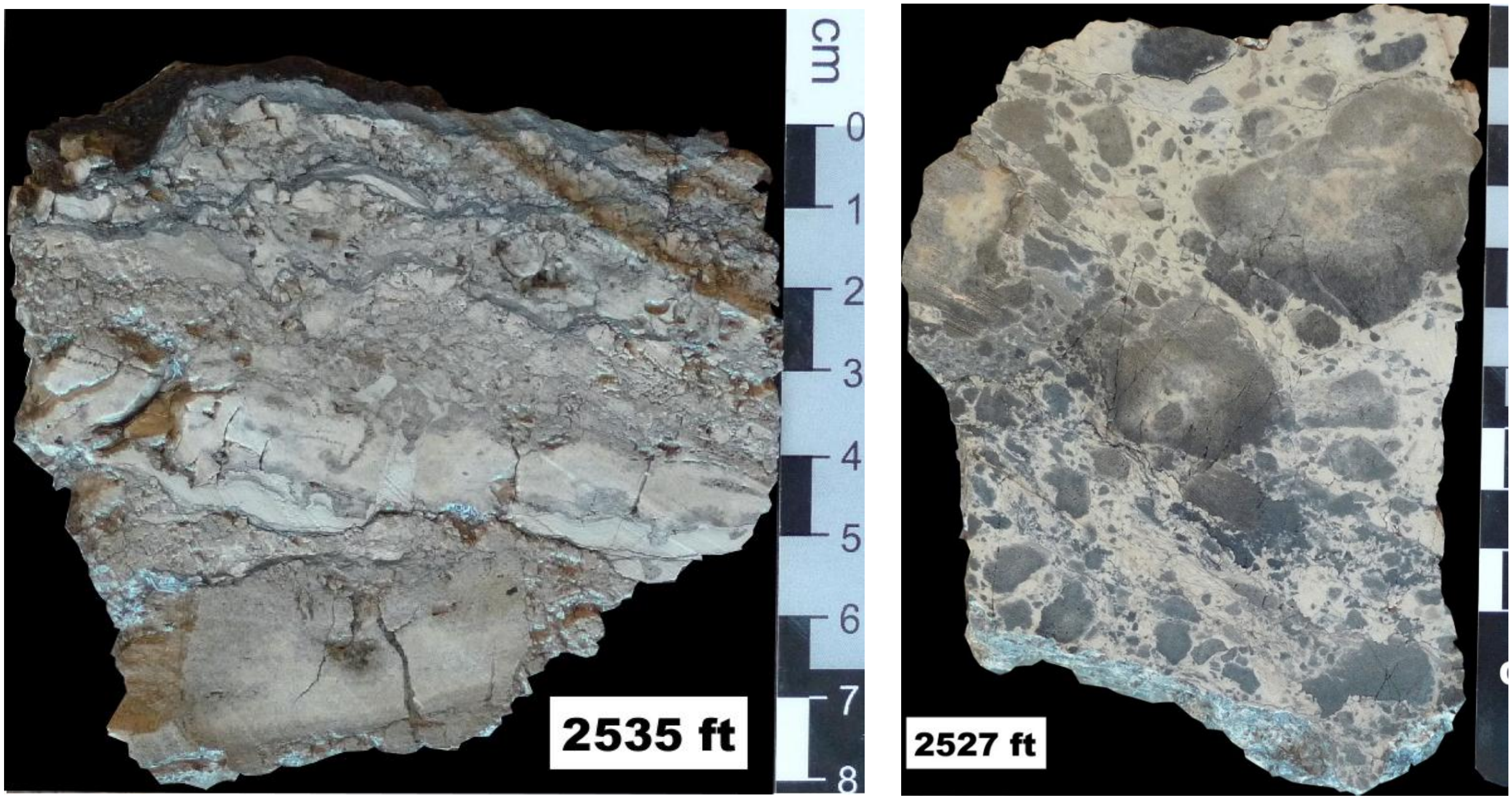
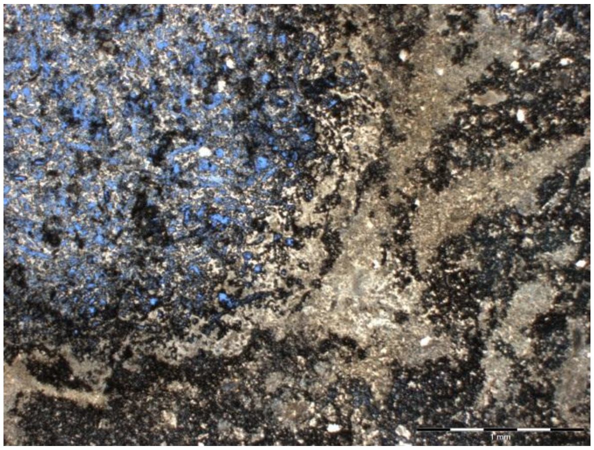
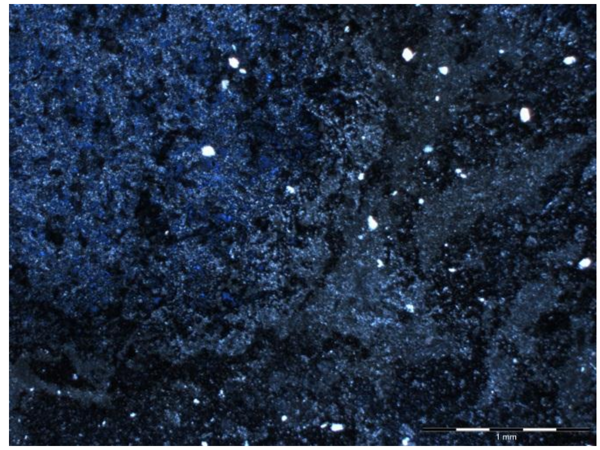
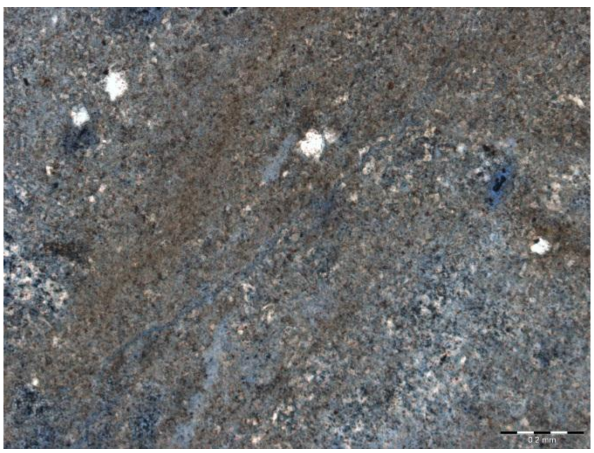


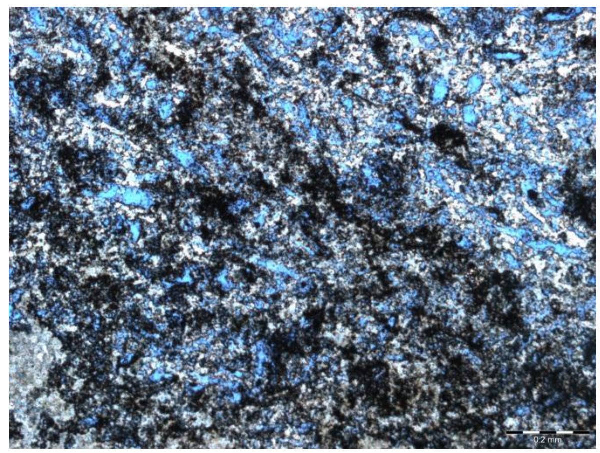
Figure 10. Core photographs of the upper tripolitic chert. These rocks are highly weathered, low density, with pervasive vugs and fractures. Chert clasts are oil stained to give them dark color.





(A) (B)





(C) (D)

Figure 11. Thin section photomicrographs of the upper tripolitic chert. A & B: Porous tripolitic chert matrix with porous chert clasts (up left corner), andsilt (white grains in B). Depth 2519 ft, scale bar is 1 mm, A. PPL, B. CPL. C: Highly weathered matrix in a larger scale; the matrix contains abundant micro-size pores. Depth 2532 ft, scale bar is 0.2 mm, PPL. D: Part of chert clast in a larger scale, full of molds, and bitumen residues. Depth 2519 ft, scale bar is 0.2 mm, PPL.

Mississippian Cherty Limestone

The second core examined consists of dark colored cherty Mississippian limestone that was cored in the Lone Star Anderson #1, located in the NWSE, Sec. 27, T.23N., R.04E., Pawnee County, Oklahoma (Figure 12). The cored interval extends from 3781 ft to 3528 ft, for a total of 253 ft. This interval is grey, spicular, peloidal, partially silicified limestones, with minimal porosity. Fractures are rare and mostly confined to the cherty zones. Based on the compositional change and depositional features, the Mississippian cherty limestone in this core was divided into 6 lithofacies: 1. grey shaley limestone; 2. light grey limestone; 3. black calcareous shale; 4. bedded shaley limestone; 5. bedded cherty limestone; 6. burrow-mottled cherty limestone. In the interval of 3766.5 ft to 3578 ft, shaley limestone is interbedded with cherty limestone (4 and 5). The lower (3766.5 ft ~ 3711 ft) and the upper part (3621 ft ~ 3578 ft) of this interval are more shaley, less cherty and contain more bioclasts and burrows, whereas the middle part (3711 ft ~ 3621 ft) is more cherty, less shaley, with more bedded and nodular cherts. A petrolog showing lithology, bioclasts and rock properties is shown in Figure 12.

Lithofacies Descriptions:

1. <u>Grey shaley limestone:</u> lithofacies 1 (Figure 13 A) first occurs from 3781 ft to 3770 ft, at the bottom of the cored interval. It is slightly stylolitic, pyritic, non-cherty to slightly cherty wackestone (Figure 14), which is wavy bedded, with sparsely distributed crinoids and rare brachiopods. A chert bed occurs at 3770 ft~3770.5 ft, with vertical and horizontal open fractures. Except in this thin bed, no obvious open fractures or nodular or bedded chert are observed. However, the cored interval contains a few narrow healed

fractures cemented by white calcite. Thin section analysis identifies chert cement in the

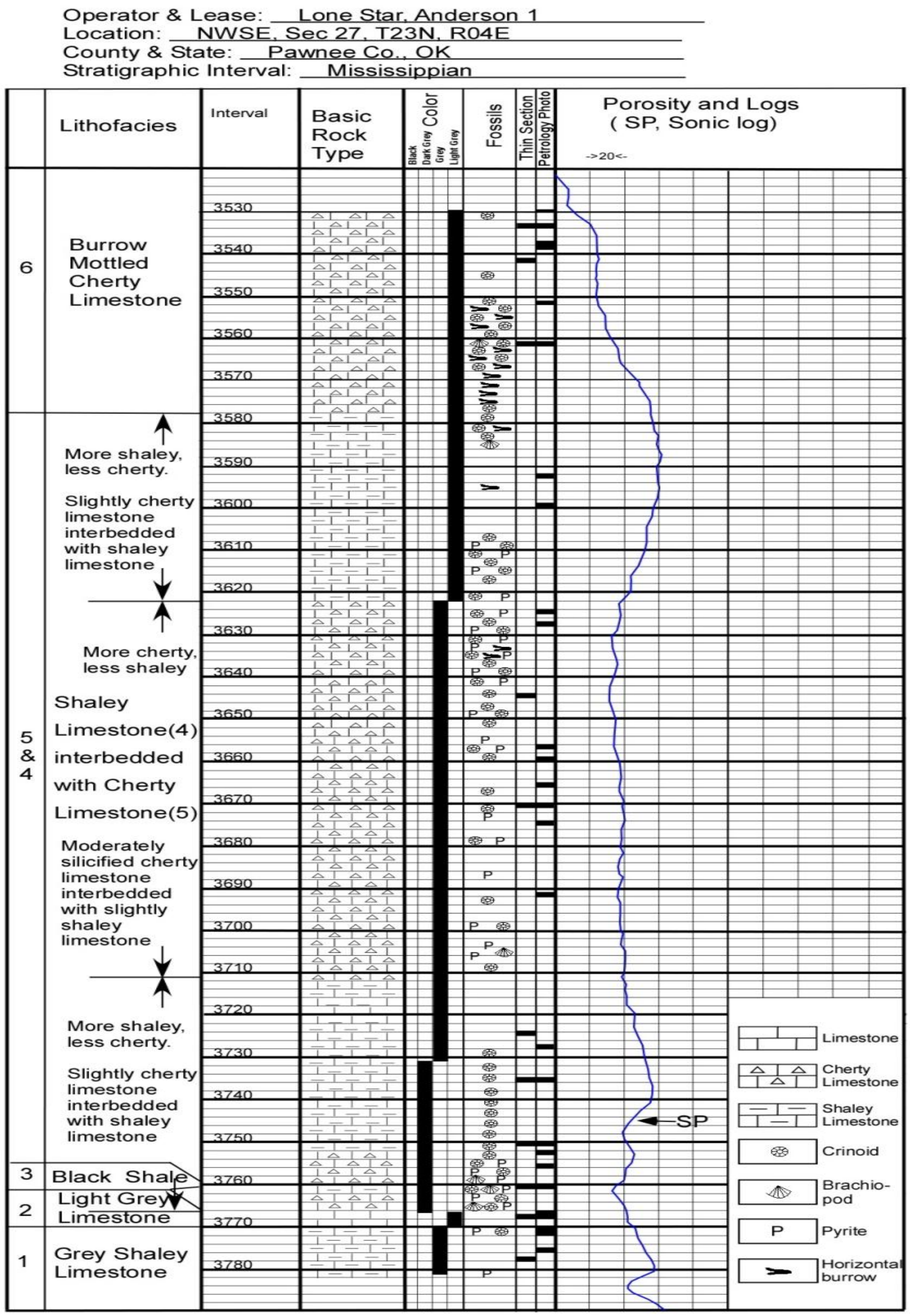


Figure 12. Petrolog of the Mississippian limestone showing lithologies, fossil occurrence and types, and the wireline log SP curve

micritic matrix, along with 20~30% spicules, 10% silt-sized quartz grains, and small patches of calcite. Quartz grains are 0.03 - 0.04 mm in diameter, and calcite is partially replaced by microcrystalline quartz. Later generation calcite crystals and/or dolomite rhombs precipitated in the chert cemented regions of this interval.

2. Light grey limestone: lithofacies 2 (Figure 13 B), which is first observed from 3770 ft 1in to 3766.5 ft, is clean, wavy bedded wackestone (Figure 15). It contains scattered chert nodules and a few long, sinuous, vertical fractures filled with white calcite cement. The texture of lithofacies 2 is very similar to the shaley limestone below (lithofacies 1), and consists of micritic matrix with 10% spicules, some 5% silt-size quartz grains, and small patches of calcite and chert cement. Crinoids comprise less than 1% of the rock volume, as determined by thin section analysis, and original calcite is partially replaced by microcrystalline quartz.

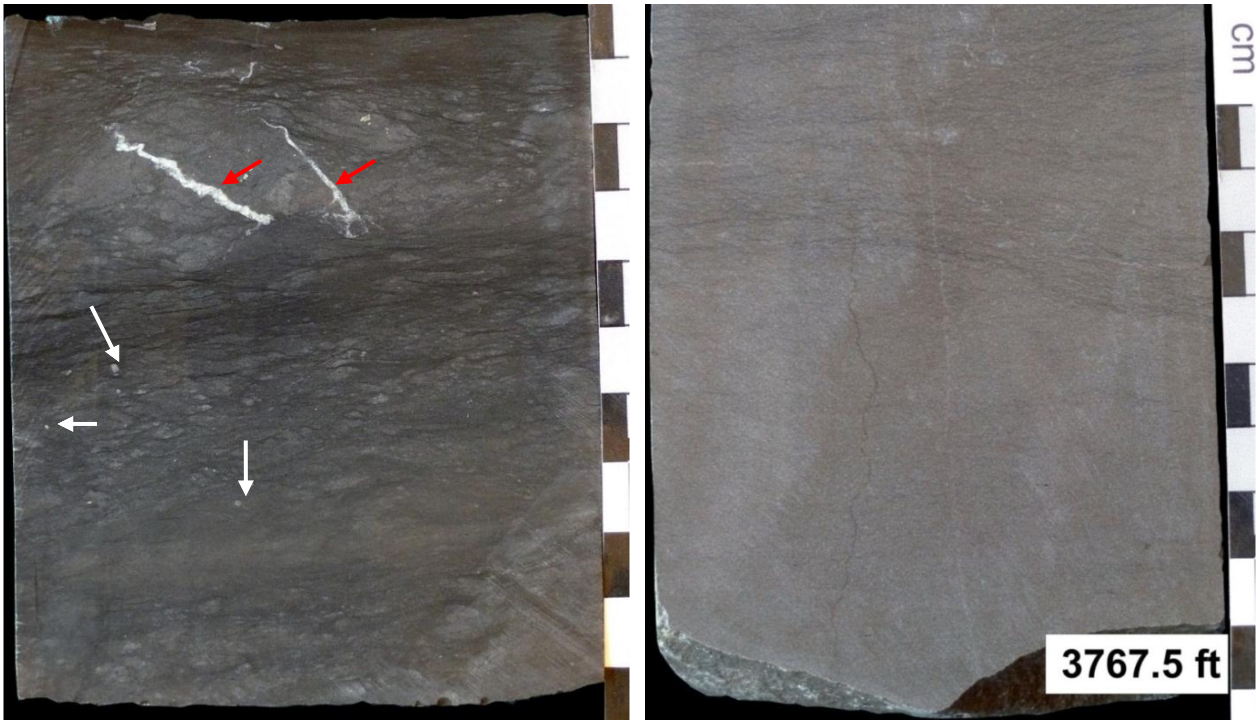
3. Black calcareous shale: lithofacies 3 (Figure 17 A), which occurs as one thin bed (about 0.5 ft) at the 3760 ft interval, is fossil-rich calcareous shale or clay-rich wackestone (Figure 16), with silt-size quartz grains (0.04 mm), and phosphate. Fossil fragments make up more than 25% of the volume and include brachiopods, ostracodes, sponge spicules and crinoids, some of which are partially replaced by microcrystalline quartz and chalcedony (Figure 17 B). These fossil fragments are mainly in two size populations: larger ones are about 0.5 - 1 cm in length, and smaller ones are about 1mm. Pyrite is associated with the larger fossil fragments. Phosphate is 3 – 5 mm in diameter and appears to be of organic origin (Figure 17 C).

4. Bedded shaley limestone: lithofacies 4 (Figure 18 B) is found from 3766.5 ft to 3578 ft, and consists of black to dark grey, laminated, or wavy bedded, clay-rich

mudstone to wackestone (Figure 19 A) with spicules (10%), and fossil fragments in micritic matrix. It appears peloidal, but the peloids are difficult to identify in the clay-rich micritic matrix, many interpreted peloids appear as aggregates. More argillaceous limestones typically contain more fossil fragments, mostly crinoids, along with lesser numbers of brachiopods and ostracodes, than cherty limestones. Some silt-size quartz grains (about 2~5% in the matrix) form laminae of micritic silty carbonate alternating with clay-rich carbonate. Most intervals are burrowed to give a mottled texture, and vertical fractures or cherty regions are not apparent.

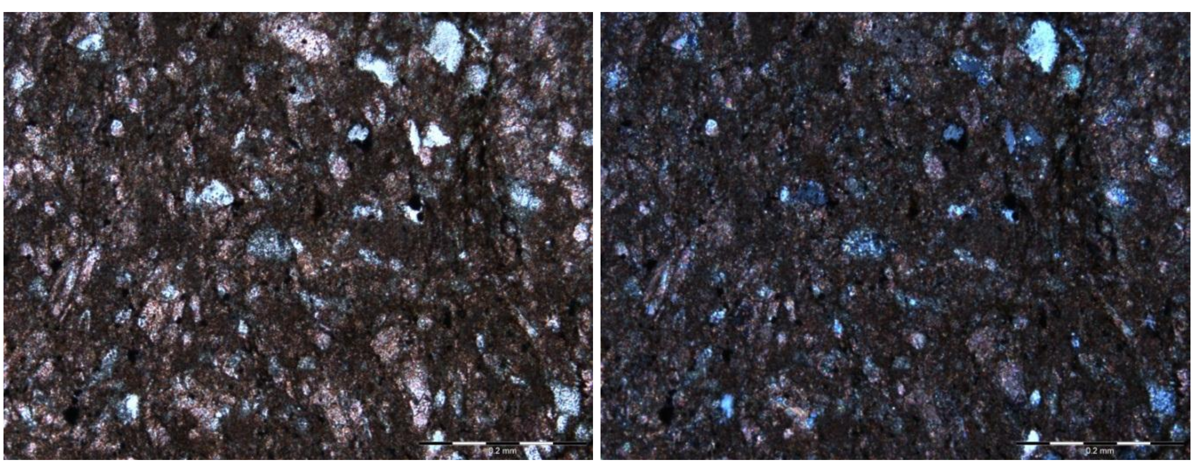
5. Bedded cherty limestone: lithofacies 5 (Figure 18 A) extends from 3752 ft to 3578 ft, and consists of dark grey to grey, slightly to moderately silicified, cherty limestone (Figure 19 B), with sparse and widely distributed fossil fragments, and nodular, elongated to flaser chert nodules. Lithofacies 5 is silty, burrowed, peloidal, and micritic wackestone, with small patches of calcite and chert cements. Fossils fragments are usually replaced by microcrystalline quartz and chalcedony. Calcite is partially replaced by microcrystalline quartz, and cherty zones have a higher percentage of spicules. Laminated pyrites are common at the interface with shaley limestone in the interval from 3711 ft to 3621 ft. Borrowed, mottled textures are common in the upper part of this interval (3752 ft ~ 3578 ft), and burrows are commonly cemented by calcite or microcrystalline quartz. Pyrite is also associated with the burrowed zones. Chert-rich zones have increased vertical fractures, both open and cemented by calcite. Spiculites (Figure 20 A&B) are shown in the cherty intervals, which contain more than 50% spicules in micritic matrix, along with bioclasts including ostracodes and brachiopods, some of which are recrystallized as microcrystalline quartz (Figure 20 C&D).

6. Burrow-mottled cherty limestone: lithofacies 6 (Figure 21 A) occurs from 3578 ft to 3531 ft, and is light gray, moderately to entirely silicified, cherty limestone (Figure 21 B&C) that is stylolitic, and mottled by burrowing. Facies 6 is micritic, peloidal and silty wackestone to wackestone with bioclasts and silt-rich laminae (<5%), as well as patches of silica cement that forms chert nodules. Bioclasts, including spicules, crinoids and brachiopods, are preserved by calcite and partially replaced by microcrystalline quartz. This facies is apparently 10 ~20% peloids, which can be difficult to recognize in the micritic matrix. Patches of chert cement give a nodular appearance in hand specimen. Silty zones contain less matrix and more chert. Micro-fractures are partially cemented or open. Cherty zones are usually brecciated, and contain small white nodules (~0.5 cm). Vertical fractures extend the height of the chert layers and terminate in calcite-rich beds. Horizontal fractures connect vertical ones, creating an orthogonal pattern. Isolated dolomite rhombs also occur in the chert nodules.



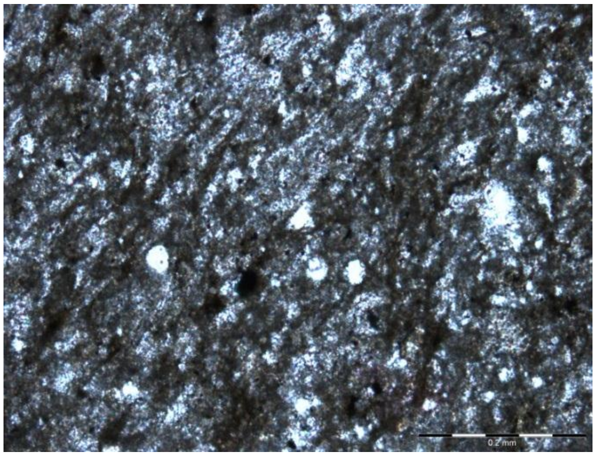
(A) (B)

Figure 13. A: Core photographys of lithofacies 1, grey shaley limestone. Two healed fractures cemented by white calcite and small crinoids (marked by white arrows), and pyrite (marked by red arrow), no chert is evident. Depth: 3775 ft. Core photograph of lithofacies 2, light grey limestone without obvious nodular or bedded chert. The dark and light color liners in the middle are vertical healed fractures. Depth 3767.5 ft.

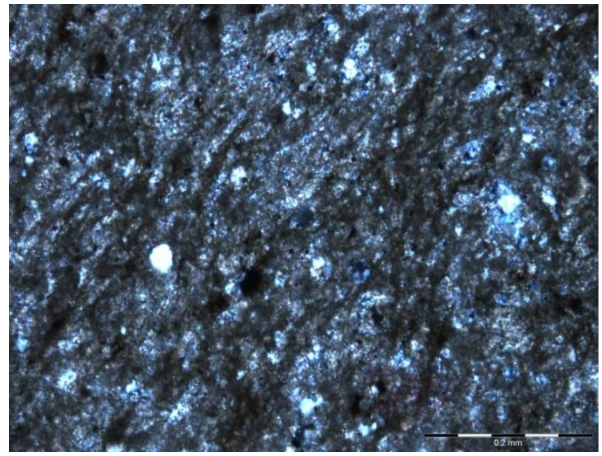


(A) (B)

Figure 14. Thin section photomicrographs of lithofacies 1 grey shaley limestone. A&B: Micritic matrix with spicules and silt-size quartz. A. PPL, B. CPL. Scale bar in lower right of image is 0.2 mm; entire image is approximately 0.7 mm long. Depth 3777.8 ft.

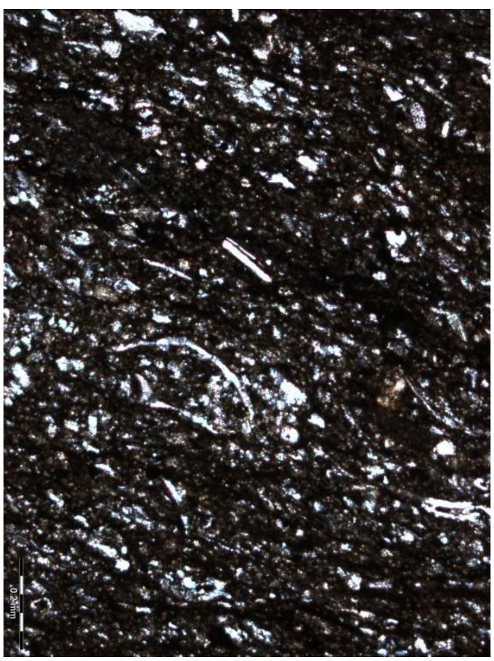


(A)

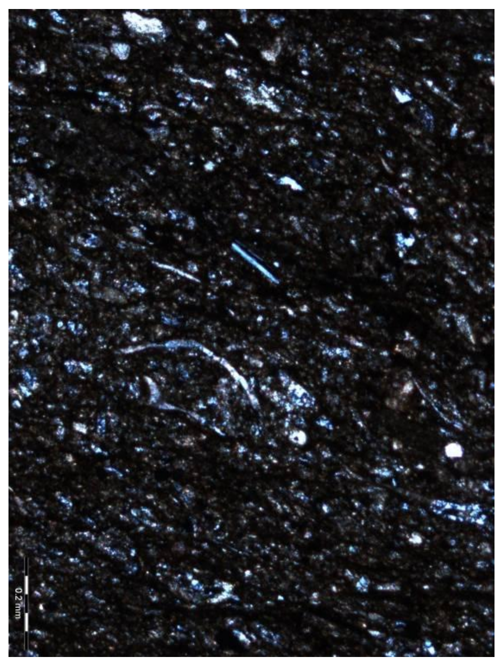


(B)

Figure 15. Thin section photomicrographs of lithofacies 2, light grey limestone. A & B: Micritic matrix with spicules, silt-size quartz and calcite cement. A. PPL, B. CPL. Scale bar is 0.2 mm. Image is approximately 0.7 mm wide.

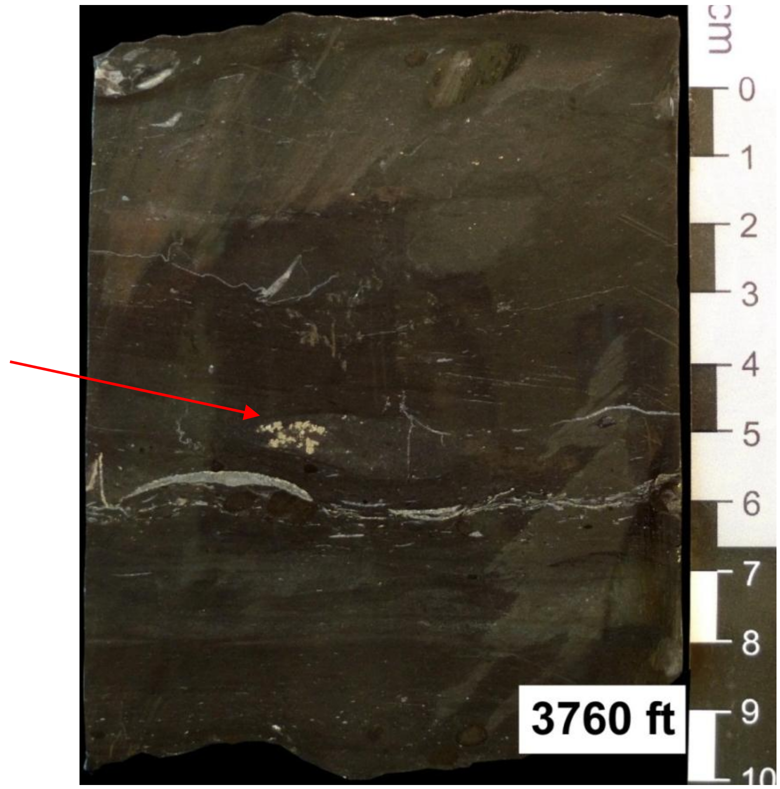


(A)

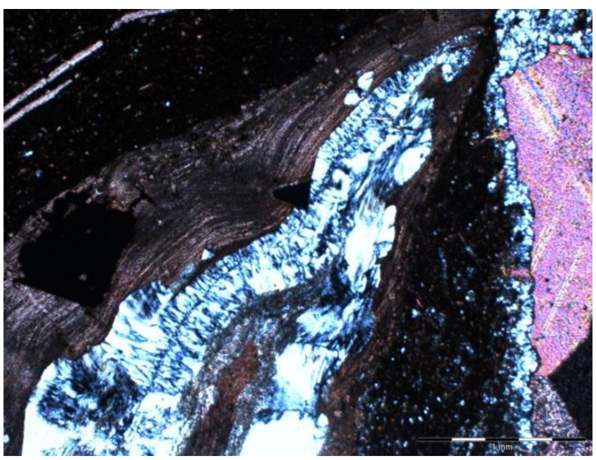


(B)

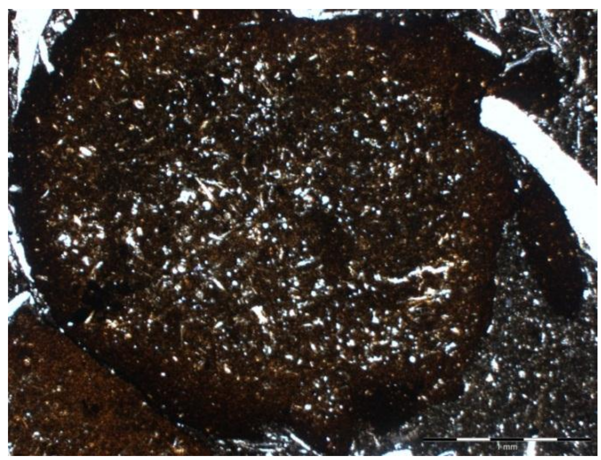
Figure 16. Thin section photomicrographs of lithofacies 3, black calcareous shale. Lithofacies 3 consists of clay-rich matrix with siliceous spicules and silt-size quartz grains. A. PPL, B. CPL. Scale bar is 0.2 mm; image is approximately 1.4 mm tall. Depth 3760.4 ft.



(A)



(B)



(C)

Figure 17. Core photograph and thin section photomicrographs of lithofacies 3. A: Black calcareous shale with large brachiopod fragments and pyrite (arrow). Depth 3760 ft. B: Brachiopod fragment replaced by microcrystalline quartz and chalcedony. CPL. Image is 3.5 mm wide. C: Phosphate of biogenic origin. PPL. Image is approximately 3.5 mm wide. Depth: 3760.4 ft.

(A)

(B)

Figure 18. Core photograph of lithofacies 5, bedded cherty limestone (A), and lithofacies 4, bedded shaley limestone (B). A: Cherty beds with chert nodule (base). Healed fractures are evident in the silica-rich beds. These fractures terminate in the clayed calcite-rich zones. Depth 3670.5 ft. B: Laminated shaley limestone in the upper part with laminated crinoid fragments. Burrow mottled texture in the lower part.

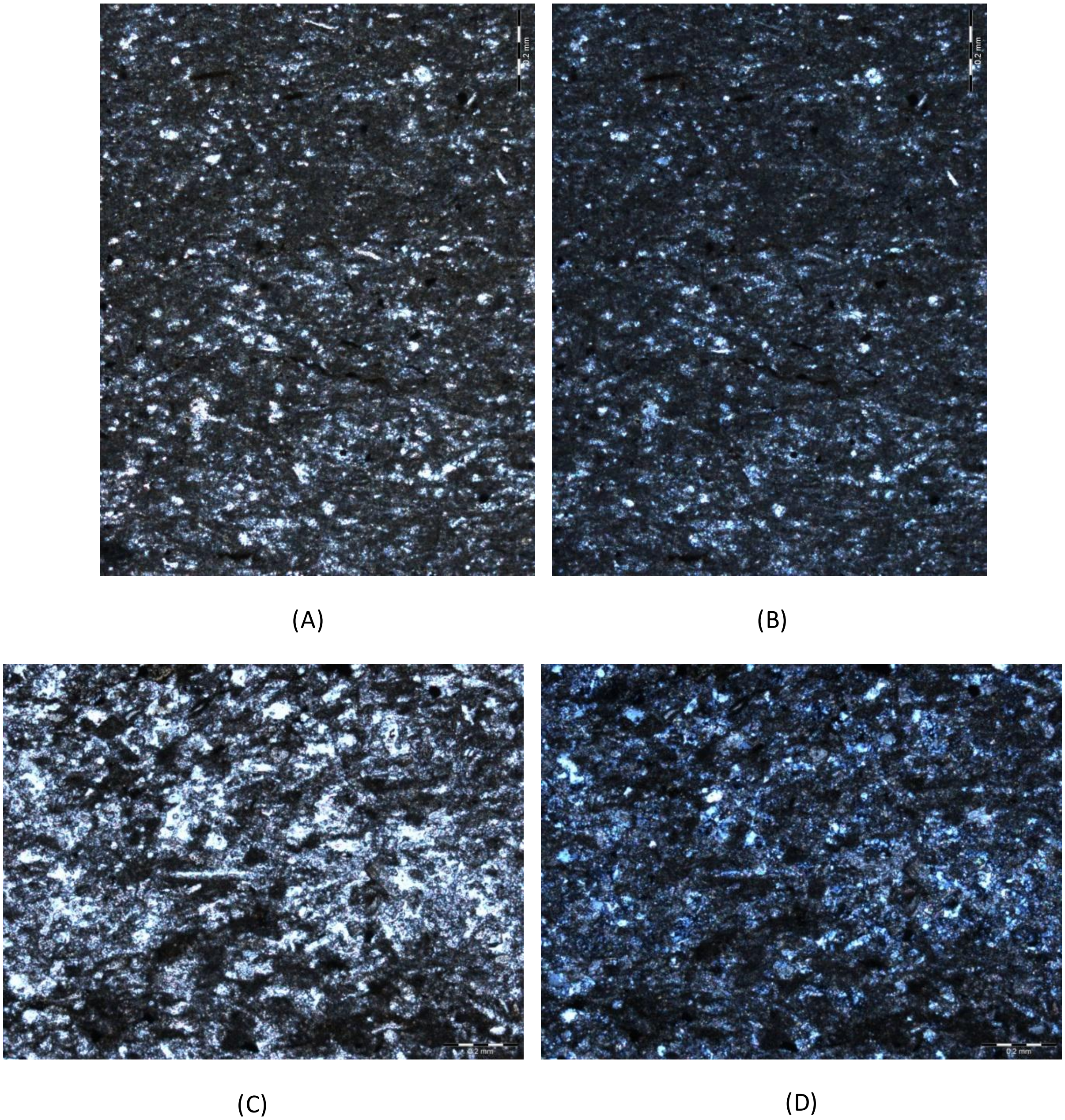


Figure 19. Thin section photomicrographs of lithofacies 4, shaley limestone (A&B), and lithofacies 5, cherty limestone (C&D). A & B: Clay-rich micritic matrix with silt-size quartz grains, and small cherty spicules. A. PPL, B. CPL. Image is 1.4 mm tall. Depth: 3724 ft. C & D: Thin section photomicrographs of cherty zone with higher percentage of spicules and peloids. C. PPL, D. CPL. Image is 1.4 mm tall. Depth 3588.4 ft.

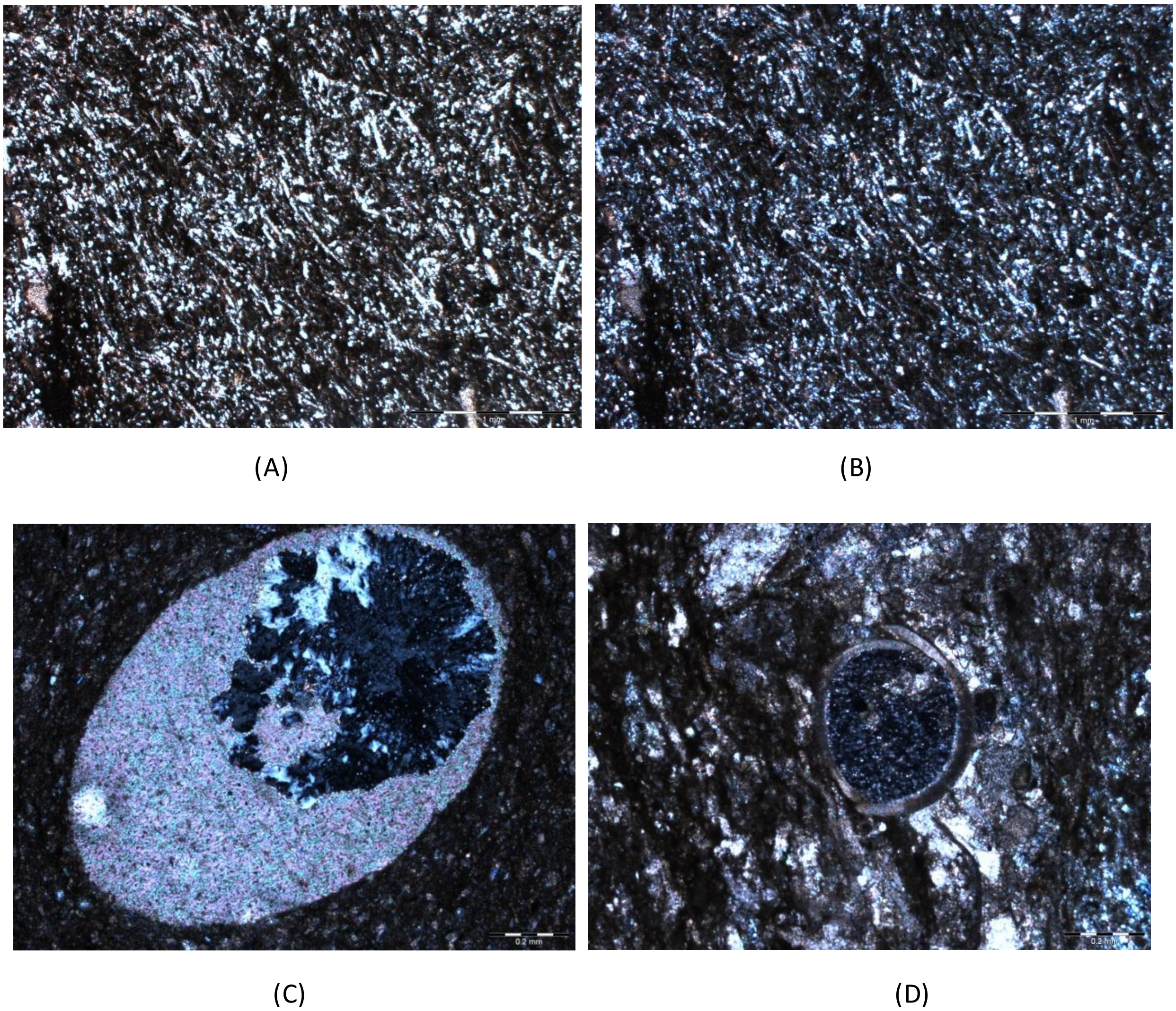


Figure 20. Thin section photomicrographs of spiculites and partially replaced bioclasts. A & B: Spiculites with >50% monaxial chert spicules. A. PPL, B. CPL. Image is 1.4 mm tall. Depth: 3750.8 ft. C: Thin section photomicrographs of crinoid fragments that are partially replaced by chert and chalcedony. CPL. Image is approximately 1.4 mm wide. Depth 3644 ft. D: Ostracode shell preserved by calcite, with interior replaced by microcrystalline quartz. CPL. Image is 3.5 mm tall. Depth 3750.8 ft.

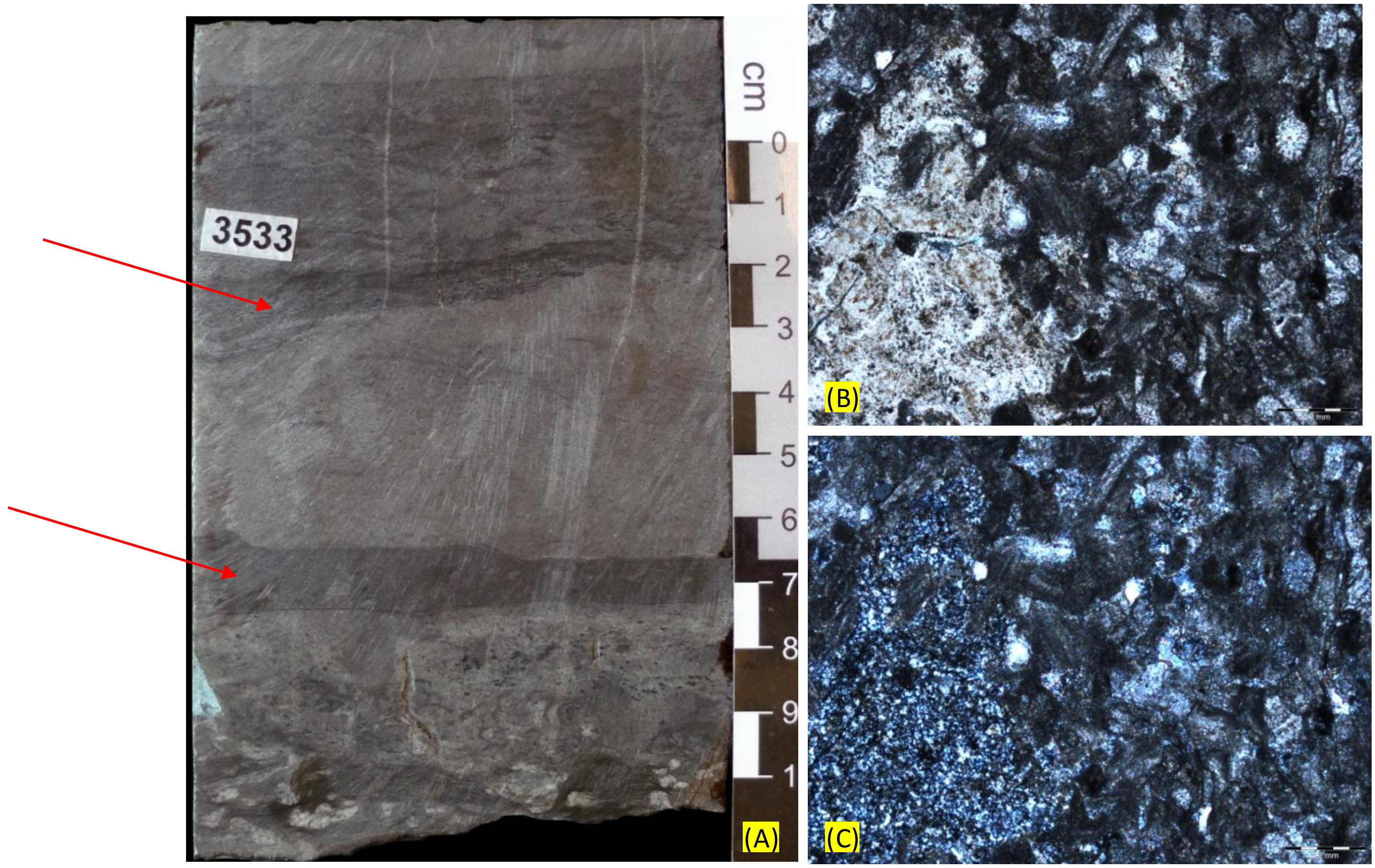


Figure 20. Core photographs and thin section photomicrographs of lithofacies 6, burrow mottled cherty limestone. A: The core is moderately to entirely silicified, with horizontal band of blue-grey chert (arrow) and burrowed zone near the base of the interval. Fractures are evident in chert bed in upper part. Depth 3533 ft. B & C: Thin section photomicrographs of lithofacies 6, burrow mottled cherty limestone. Silts and patch of silica cement with characteristic "chert" birefringence in CPL. B. PPL, C. CPL. Image is 1.4 mm wide.

Comparison between the Mississippian Chert and Mississippian Cherty Limestone

Mississippian chert and Mississippian cherty limestones have similar origins, but exhibit considerably different properties as a result of weathering and erosion during the subaerial exposure. Generally speaking, Mississippian cherty limestone is solid, low porosity, non-to-moderately silicified, peloidal mudstone to wackestone. In contrast, Mississippian chert is light colored, highly weathered, pervasively silicified, spicule-rich, vuggy and fractured, with high porosity.

Compositional difference: The Mississippian chert is generally highly or entirely silicified, and contains minimal amount of calcite and micrite. Tripolitic chert (Figure 22 A) is weathered spiculites containing partially dissolved chert clasts, and no or rare calcite cement or carbonate. Less weathered chert (Figure 22 B) has a peloidal micritic matrix with chert clasts and patches calcite in the matrix or at the interfaces between chert clasts and matrix, as well as occasional dolomite along stylolites. Less weathered chert is somewhat similar to Mississippian cherty limestone (Figure 22 C), but is lighter colored and contains higher porosity as a result of weathering, and more fractures. Mississippian cherty limestone is generally dark colored, peloidal, pyritic, micritic mudstone to wackestone, with patches of calcite and chert cement. The shaley limestone is clay-rich, with silt laminae, less spicules and less volume of chert. The cherty limestone is more similar to less weathered chert, and has a peloidal micritic matrix with chert and patches of calcite. The cherty limestone is unweathered, and contains less chert, spicules, and porosity, and is darker colored than chert.

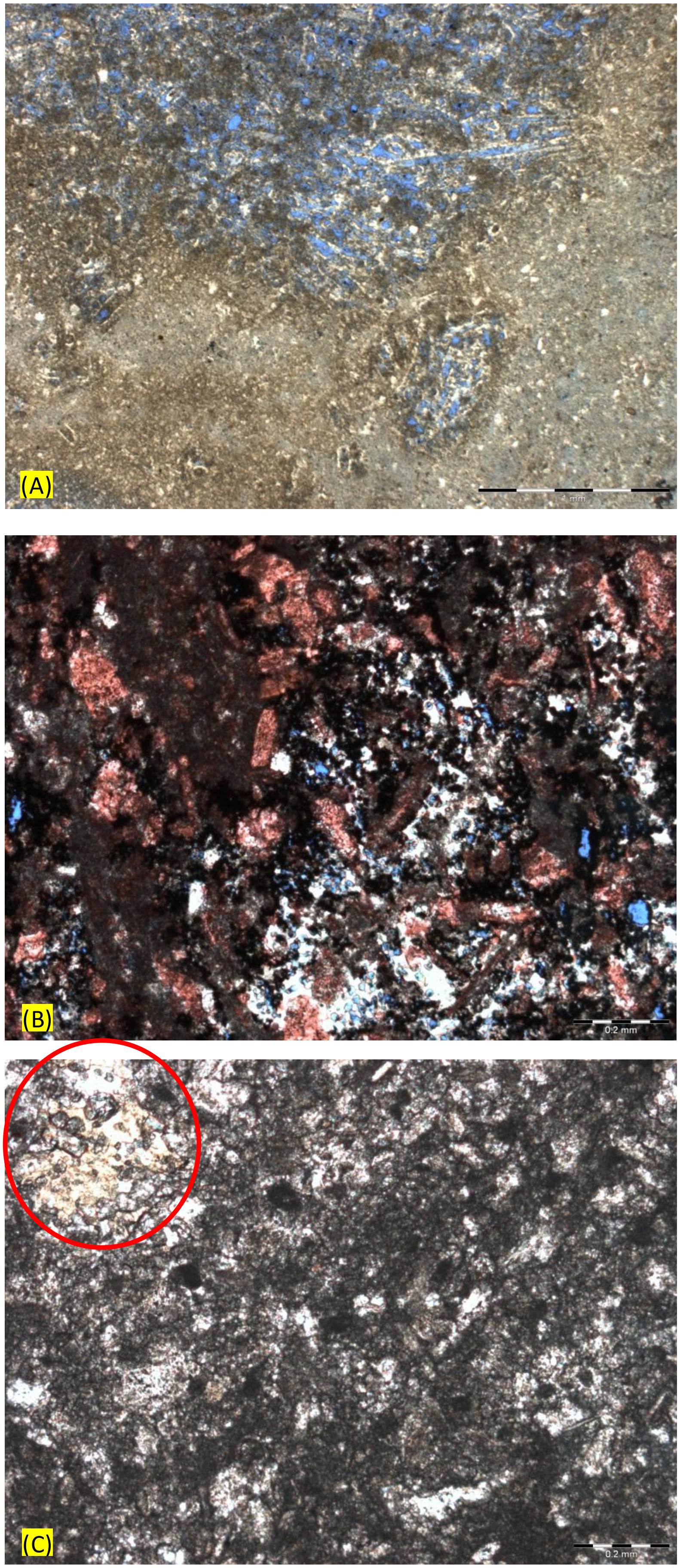


Figure 21. Thin section photomicrographs of the tripolitic chert (A), less weathered chert (B), and cherty limestone(C). Note the changes of texture, composition and porosity. A: Tripolitic chert that is entirely silicified, highly weathered, spicule-rich, with porous matrix and chert clasts. PPL. Depth 2532 ft. B: Less weathered chert that contains chert clasts, some calcite cement, and porosity resulting from weathering. PPL. Depth 2546 ft. C: Cherty limestone that consists of micritic matrix, chert

Dissolution features: Mississippian chert exhibits significant dissolution features. Vugs, micro-vugs and karst features, such as collapse breccia deposits, are very common in the Mississippian chert. Micro-vugs in the matrix are minute and difficult to recognize with low magnification microscopy, whereas large vugs are up to several centimeters in diameter. Dissolution of spicules is preferred in most chert clasts, forming spicular moldic porosity. Stylolites are common in both core samples and thin sections of Mississippian chert. Dissolution features other than stylolites are rare in the Mississippian cherty limestone.

Fractures: Because of the brittle nature of chert, fractures in various sizes are common throughout the Mississippian chert interval (Figure 23 A). Brecciation of chert clasts generated fractures in the spicular matrix and chert clasts. Most of these fractures are orientated near vertical and open, but some are healed by calcite cement and contain bitumen. In the Mississippian cherty limestone, cores with fractures are not common, and generally confined to the chert-rich intervals. Most fractures are healed with calcite cement (Figure 23 C), but some small and micro-size fractures are open in chert bands or nodules, and often terminate in adjacent carbonate-rich or shaley beds. Occasionally these fractures cross carbonate and shaley beds and extend to silicified adjacent beds.

Spicules and other bioclasts: Siliceous sponge spicules form the cherty matrix and chert clasts, marking spiculite or spicular chert a major component of the Mississippian chert (Figure 24 C&D). In less weathered chert, the percentage of sponge spicules is lower than that in tripolitic chert, even though spicules are still widely distributed in the matrix, mixing with micrite and calcite. Besides sponge spicules, other fossil fragments, such as foraminifera and crinoids, are very rarely observed. Sponge spicules are much less abundant and in smaller size in shaley limestone, and usually make up less than 10% of rock volume. Spicules are more abundant in cherty limestone, but generally under 20%. Occasionally, cherty limestone contains thin (centimeter scale) spiculites that have >50% spicules (Figure 24 A&B). Crinoids, ostracodes, and brachiopods (Figure 25) are more common in the Mississippian limestone, especially in shaley limestone, whereas peloids are common in some intervals.

Chert: Chert clasts are abundant in the Mississippian chert, making up 50% to 90% of the rock (Figure 23 A&B). The size of chert clasts varies because of brecciation, but larger clasts are >10cm in diameter. These chert clasts are usually highly deformed by brecciation and dissolution, and occur in irregular and flaser shapes (Figure 23 A&B). In the Mississippian limestone, chert is much less common, and usually nodular, elongated, and bedded in the chert-rich zones (Figure 23 C).

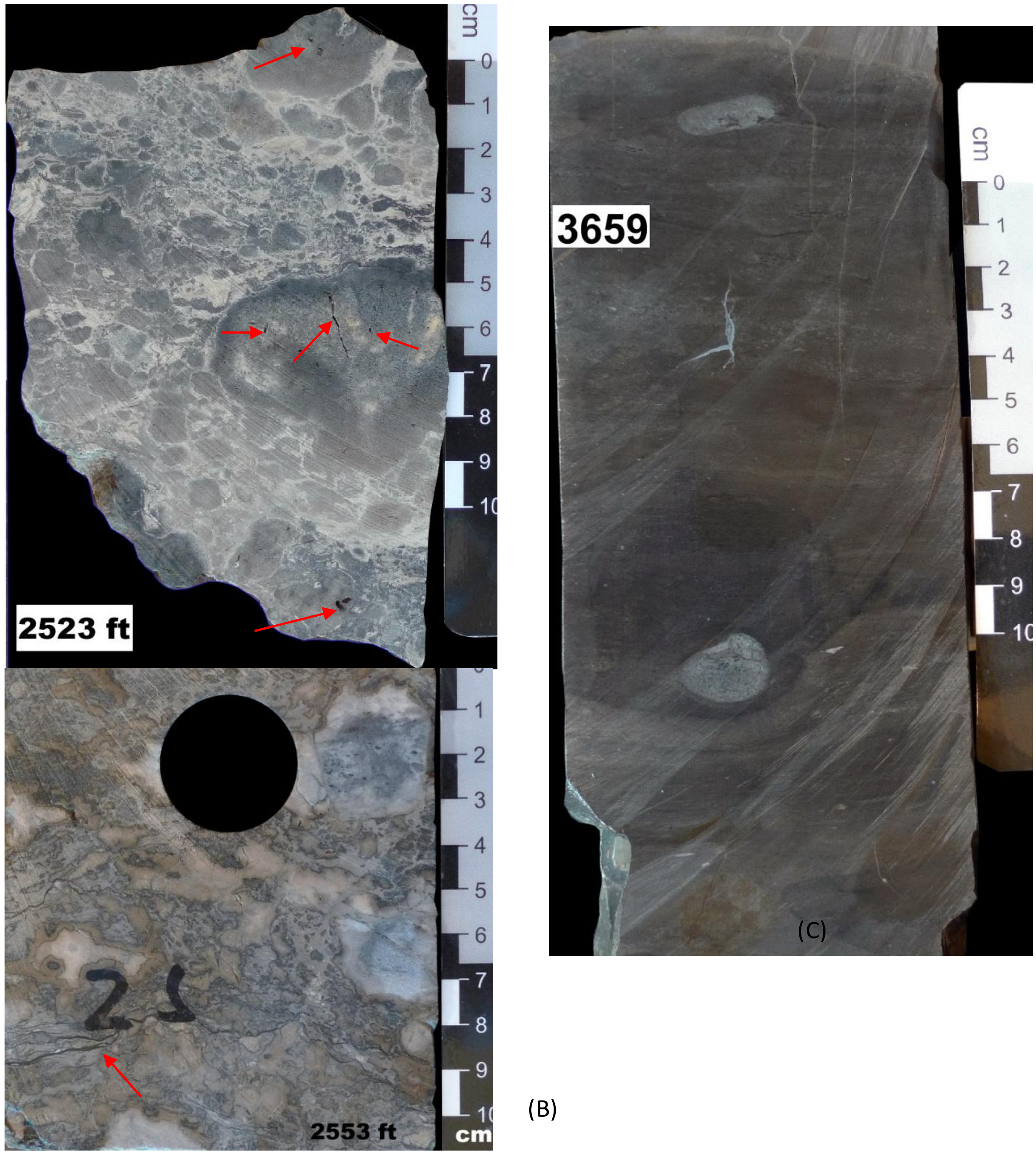
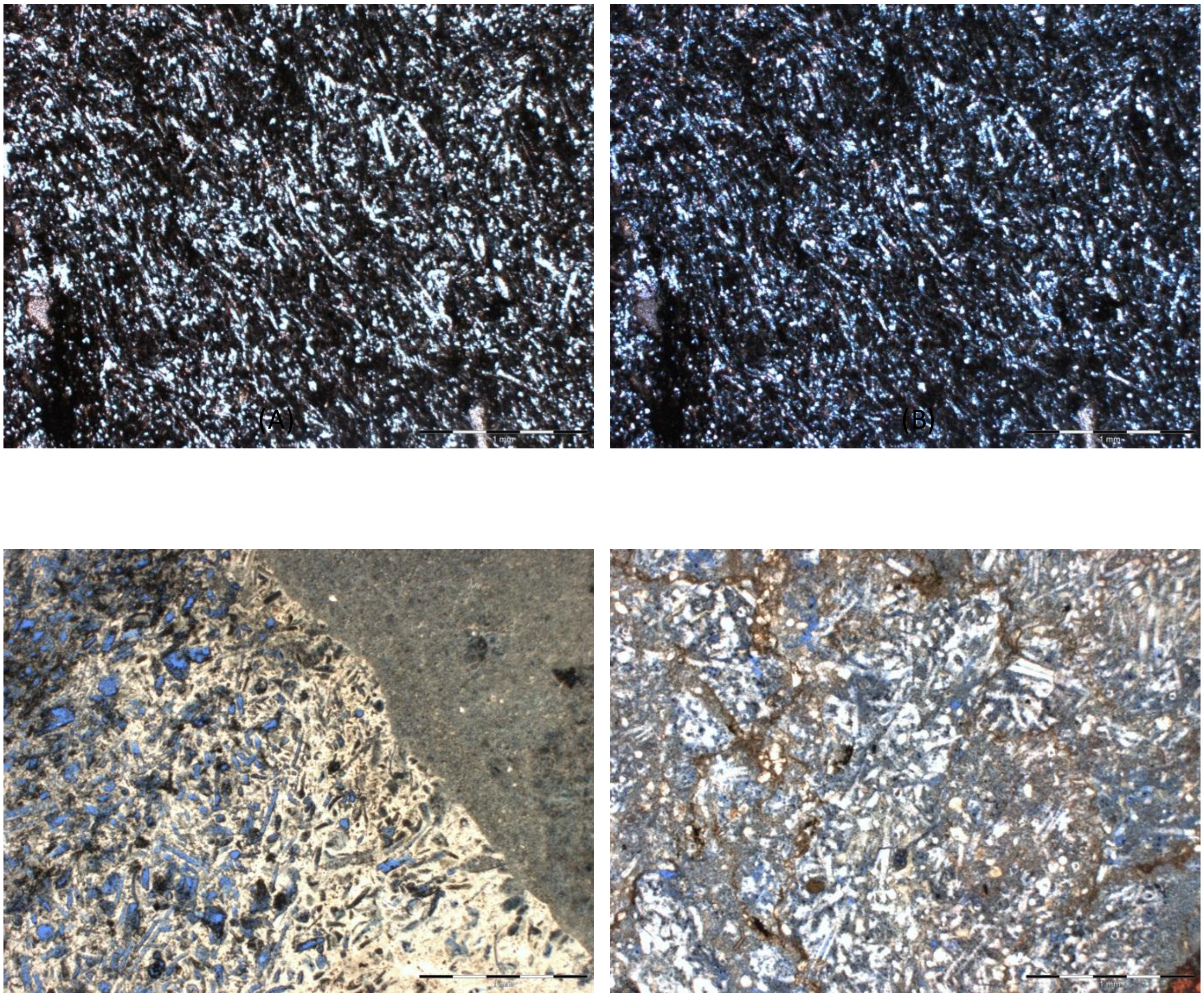
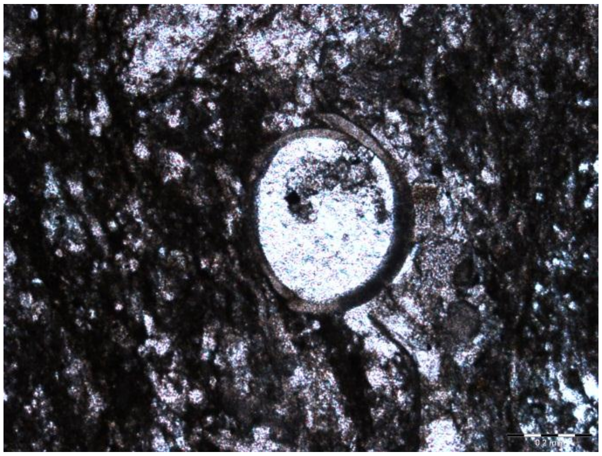


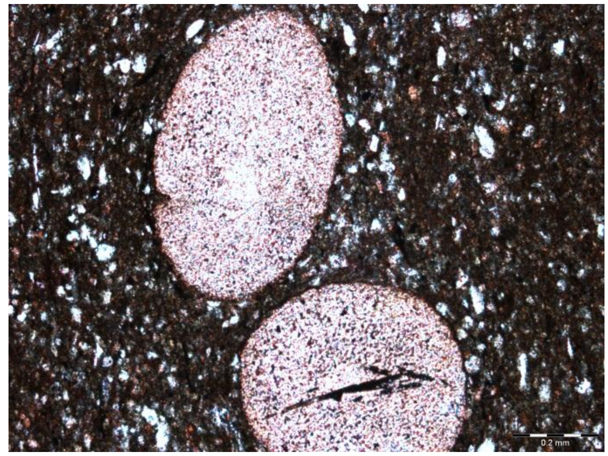
Figure 22. Core photographs of the Mississippian chert and Mississippian cherty limestone. Note the percentages, shapes of the chert, and textures of these three rocks. A: Tripolitic chert that is highly weathered and contains subangular chert clasts, open fractures and vugs (arrow). B: Less weathered chert, with flaser chert and stylolites (arrow), small vugs and micro-fractures. C: Mississippian cherty limestone with nodular cherts, scattered crinoids (white), and vertical fractures, either open or healed.



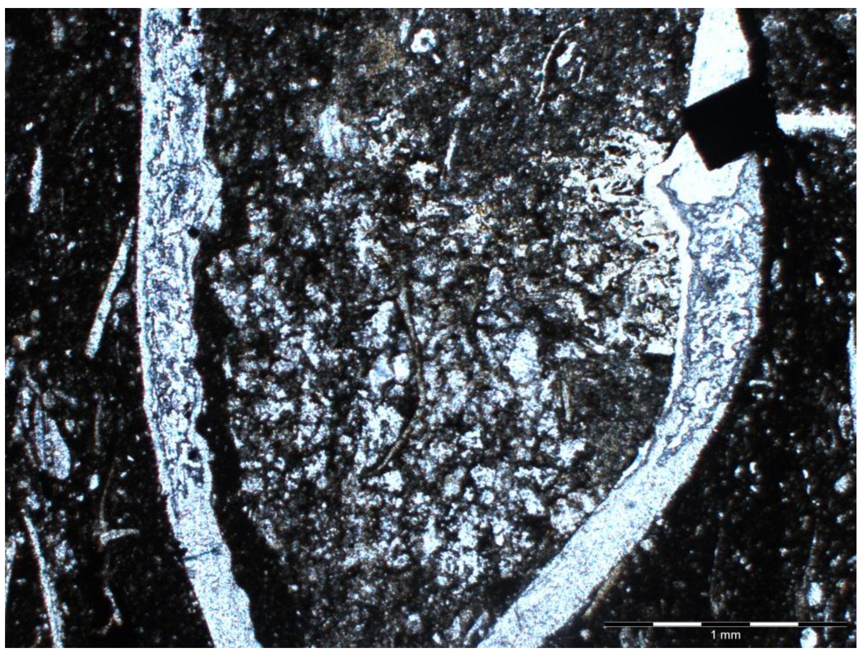
(C) (D)

Figure 23. Thin section photomicrographs of spiculites in Mississippian cherty limestone and the tripolitic chert in the Mississippian chert. A & B: Spiculites with cherty micritic matrix. Lone Star, Anderson #1, Pawnee County, OK. A. PPL, B. CPL. C & D: Tripolitic chert that consists of dissolved, porous spicular matrix (D) and chert clasts (C). Chapman Barnard Ranch #14, Osage County, OK. PPL.





(A) (B)



(C)

Figure 24. Thin section photomicrographs of bioclasts in argillaceous micritic matrix of Mississippian limestone. A: Ostracodes. B: Crinoids. C: Brachiopods. Lone Star, Anderson #1, Pawnee County, OK. PPL.

Pore System

Porosity values determined from point counting thin sections are highly variable, ranging from 0 to 29.8%. The lower and upper tripolitic chert zones have higher porosity, generally from 14% to 20%, with the highest value exceeding 29% at the very top of the zone. Porosity values for the Mississippian cherty limestone are low and all below 5%.

Secondary porosity is dominant in the Mississippian chert, and mainly formed by dissolution and brecciation during weathering. Primary porosity was not recognized. The major types of porosity are molds, micro-porosity in the matrix, vuggy porosity in various sizes, and fractures.

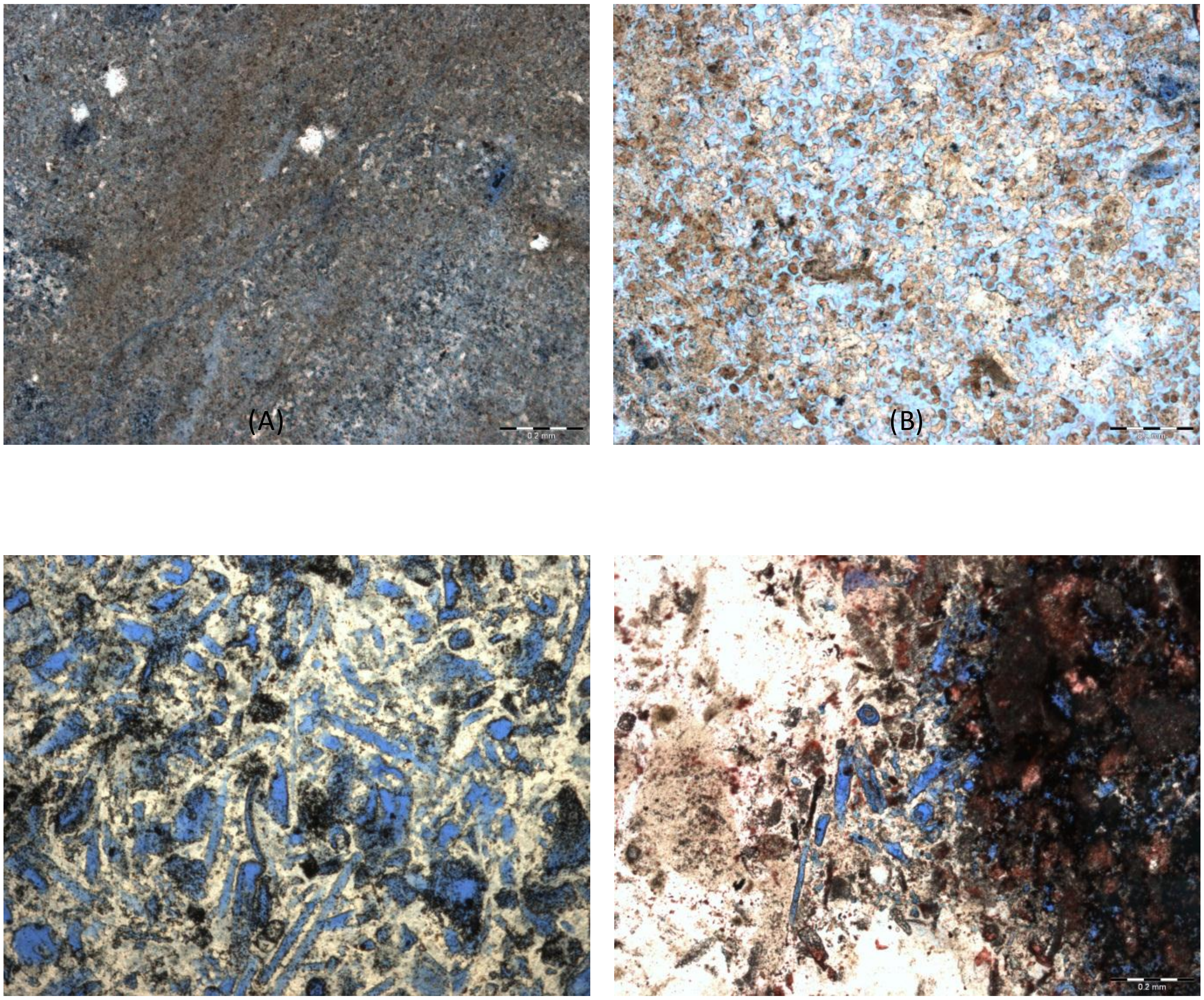
Moldic porosity (Figure 26 C&D) is the easiest to identify, and was formed by the dissolution and leaching of sponge spicules, which results in a needle-like shape. Spicular-moldic porosity occurs throughout the Mississippian chert, and is most pronounced in the uppermost tripolitic chert. It occurs within chert clasts in the highly weathered, porous rocks (Figure 26 C), and at the interfaces between matrix and chert clasts in the less-weathered rocks (Figure 26 D).

The micro-porosity in the matrix (Figure 26 A&B)) was formed by selective removal of silica, and named micro-intercrystalline pores between the micro-size quartz spherules in the chert matrix by Rogers (1996). This type of pore is very small (<<0.01 mm), and difficult to observe and measure using thin-section microscopy, which contribute to porosity values determined by point counting to be less than porosity from core plug measurement and well logs. Micro-porosity is common in the tripolitic chert, where it is enlarged by dissolution to create small vugs.

Vuggy (Figure 27 A&B) porosity is common in the Mississippian chert and formed by weathering and dissolution, as indicated by removal of calcite and/or siliceous cement. It has a large range of sizes from micro-vug porosity (<<0.01 mm) to vugs evident in the core that are several centimeters in diameter.

Fracture porosity (Figure 27 C&D) is evident in most samples. Brecciation of chert clasts creates most fracture porosity, and fractures also occur in the cherty matrix. In the highly weathered tripolitic rocks, fractures are commonly enlarged by dissolution, whereas those in less porous zones are cemented by calcite. Fractures do not make up a large percentage of total porosity, but undoubtedly contribute to permeability.

Porosity determined by thin section is very limited in amount and type in the Mississippian cherty limestone. Intercrystalline and moldic porosity is essentially nonexistent. Fracture porosity was the only type observed. It was more common in the chert rich zones, but still only minimal based on thin section point counting. Fractures in the Mississippian cherty limestone were small (<0.05 mm wide) and often partially to completely cemented. Most fractures evident in hand specimen examination of the core were cemented by calcite (Figure 26 A).



(C) (D)

Figure 25. Thin section photomicrographs of micro and spicular-moldic porosity. A & B: Micro-porosity in the chert matrix. A. PPL, depth 2632 ft. B. PPL, depth 2614 ft. C & D: Moldic porosity formed by dissolution of sponge spicules. C: Spicular-moldic porosity formed by dissolution of sponge spicules. PPL, depth 2519 ft. D: Moldic porosity at the interface between micritic matrix and chert clasts; calcite grains are stained in red; bitumen (black) fills in the pores. PPL, depth, 2536 ft. All thin sections are from the Chapman-Barnard Ranch #14, Osage Co., OK.

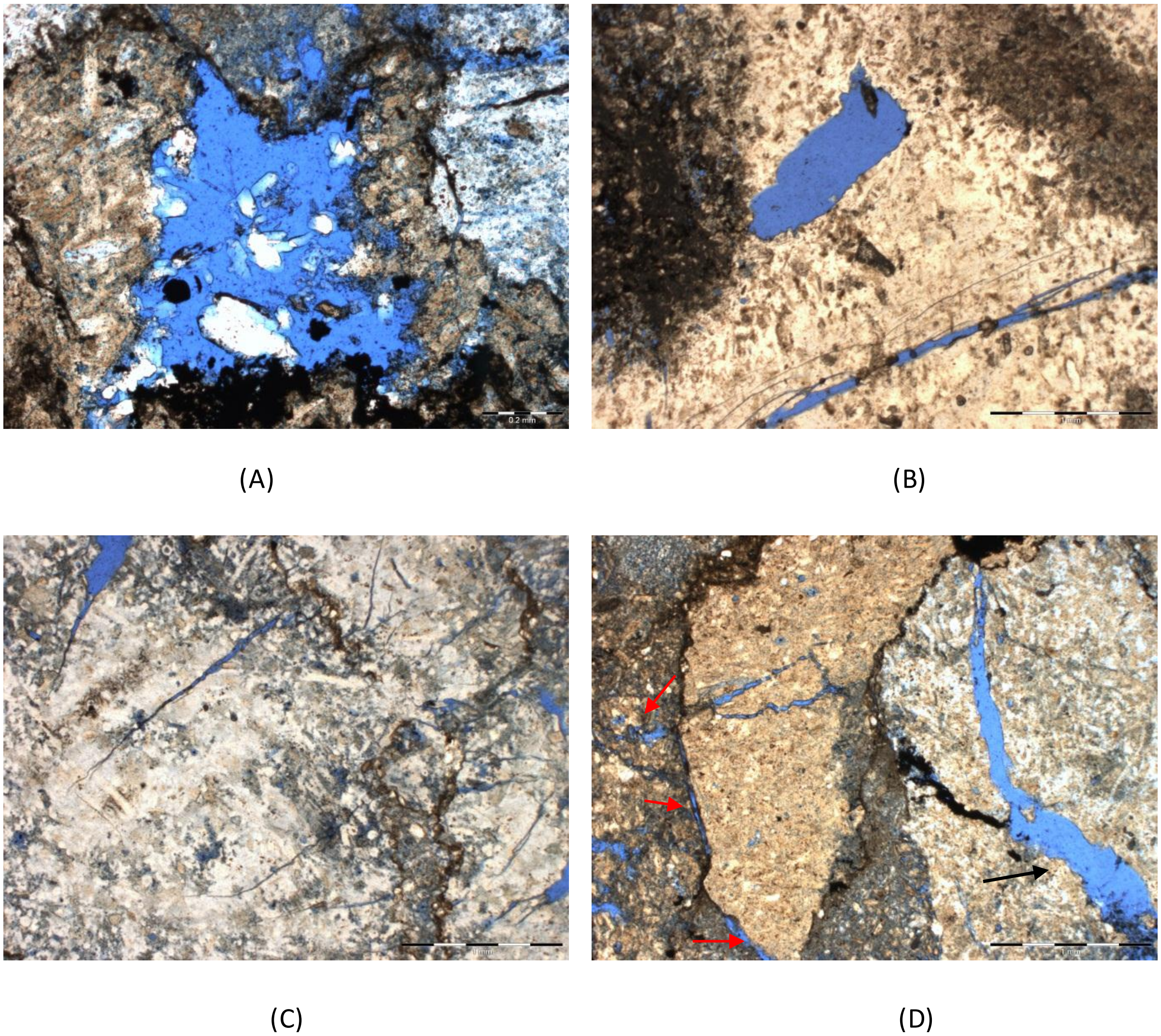


Figure 26. Thin section photomicrographs of major types of vuggy and fracture porosity. A & B: Vuggy porosity. A: Dissolution vug in the spicular matrix with later precipitated quartz (white). PPL, depth 2614 ft. B: Vug and open fractures in the chert clast. PPL, depth 2546 ft. C & D: fracture porosity. C: Fractures in the chert clasts by brecciation, some probably enlarged by dissolution. PPL, depth 2632 ft. D: Fractures in chert clasts and spicular matrix (red arrows), the fracture on the right (black arrow) enlarged by dissolution. PPL, 2614 ft. All thin sections are from the Chapman-Barnard Ranch #14, Osage Co., OK.

CHAPTER IV

PETROPHYSICAL CHARACTERISTICS OF THE MISSISSIPPIAN CHERT

Porosity and Permeability

Fifteen core plugs from selected intervals of the Mississippian chert were tested to determine porosity and permeability (Table I). The one-inch diameter core plugs were drilled and measured using a Core Lab PORG-200 gas porosimeter and Core Lab PERG-200 gas permeameter, at the Devon Energy rock lab in the Boone Pickens School of Geology, Oklahoma State University.

Generally speaking, the tripolitic chert exhibits both high porosity and high permeability. Porosity in the tripolitic chert ranges from 13% to 40%, with a 27% average. Its permeability ranges from 0.4 millidacies (md) to 44.4 md, is generally >1md, averaging 12.2 md. In contrast, Mississippian cherty limestone has low porosity (average=4.6%, range: 1.7 ~ 11.3%) and permeability (average=0.35md, range: 0.3 ~ 0.5 md).

Figure 28 displays the crossplot of porosity versus permeability of sampled core plugs from Venezuelan Sun-Golden Chapman Barnard Ranch #14. Data from the 4 lithofacies are plotted: lower tripolitic chert, LC cherty limestone, less weathered chert and finally highly weathered upper tripolitic chert. The highly weathered tripolitic chert is the most porous and permeable. Its porosity ranges 36% to 40%, and averages 38.1%;

permeability ranges 8.1 md to 44.4 md, and averages 23.7 md. Less weathered chert transitions to the LC cherty limestone. Figure 29 shows that porosity and permeability drop significant from the upper highly weathered tripolitic interval to less weathered chert, and continues to decrease with depth. However, the porosity in the less weathered chert still ranges from 13% to 22%, and averages 17.8%. Permeability of the less weathered chert deviated from tracking the porosity curve and ranges from 0.4 to 2.6 md, and averages 1.4 md. The tripolitic chert in the lower part of the cored interval has better permeability, 7.9 md, based on only one measurement, which coincides with >19% porosity. Cherty limestone is both low porosity and permeability. The porosity is generally below 4%, except for one core plug sampled in the transition zone, and permeability is between 0.3 md and 0.5 md.

TABLE I
POROSITY, PERMEABILITY, AND DENSITY MEASUREMENT FOR THE MISSISSIPPIAN CHERT FROM CORE PLUGS AND THIN SECTIONS, FROM CHAPMAN BARNARD RANCH #14, LOCATED AT N/2 NW Sec.28, T.28N., R.8E., OSAGE COUNTY, OKLAHOMA

Depth (ft)	ϕ (%) from thin section	ϕ (%) from core plug	K (md) from core plug	Density (g/cm^3)	Rock Density (g/cm^3)
2519.5	19.0	38.062	23.8	1.624	2.621
2523	16.7	36.329	28.6	1.531	2.405
2527	N/A	39.256	44.4	1.605	2.643
2530	N/A	38.555	8.1	1.539	2.505
2532.5	18.0	38.315	13.8	1.540	2.497
2538.5	N/A	21.087	2.6	2.126	2.694
2538.8	N/A	16.298	1.5	2.236	2.671
2546.5	3.5	21.577	1.9	2.054	2.619
2553	11.3	15.329	0.7	2.230	2.634
2559	N/A	13.209	0.4	2.338	2.694
2570	0.3	11.281	0.3	2.374	2.676
2576.2	2.8	3.437	0.3	2.531	2.621
2591.3	0.0	1.935	0.5	2.607	2.659
2596.8	N/A	1.647	0.3	2.611	2.655
2612	14.8	N/A	N/A	N/A	N/A
2632.3	29.8	19.318	7.9	2.031	2.517

Porosity determined by core plug analysis is generally much higher than porosity measured by thin section point counting. This is expected as thin-section measured porosity is two dimensional and a very small sample. Furthermore, it is very difficult to measure micro- intercrystalline porosity in the matrix, which is believed to contribute considerably to the total porosity of the Mississippian chert. The one sample from the lower tripolitic chert has higher porosity in the thin section than that measured from the core plug, but this is attributed to sampling bias as the thin section captured fractures and large vugs, whereas the core plug was taken in an area perceived to be fracture free to ensure plug recovery.

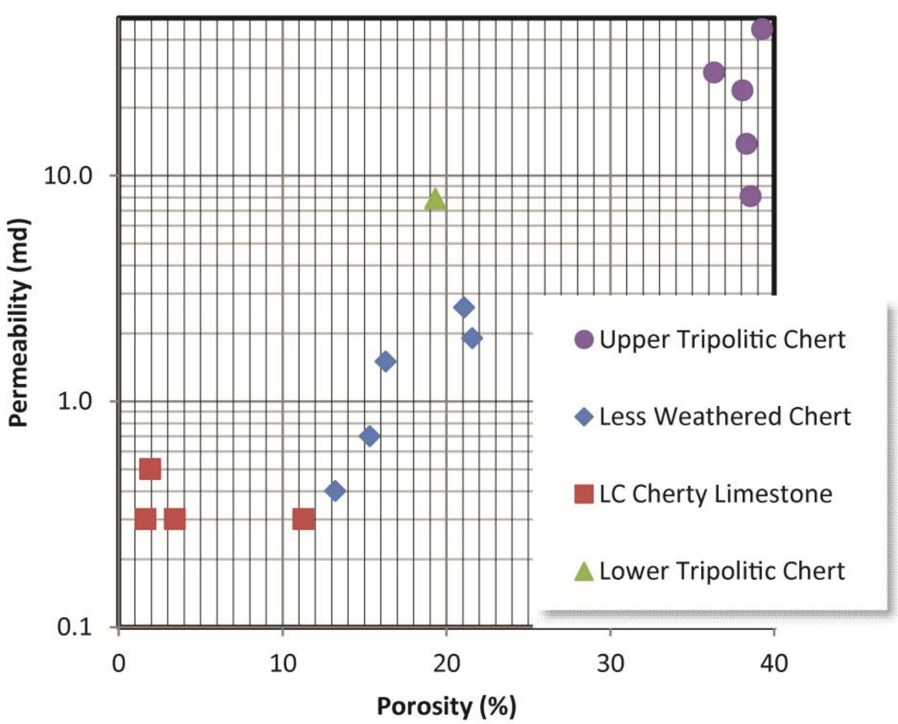


Figure 27. Crossplot of porosity and permeability of Mississippian chert from Chapman Barnard Ranch #14, Osage County, Oklahoma.

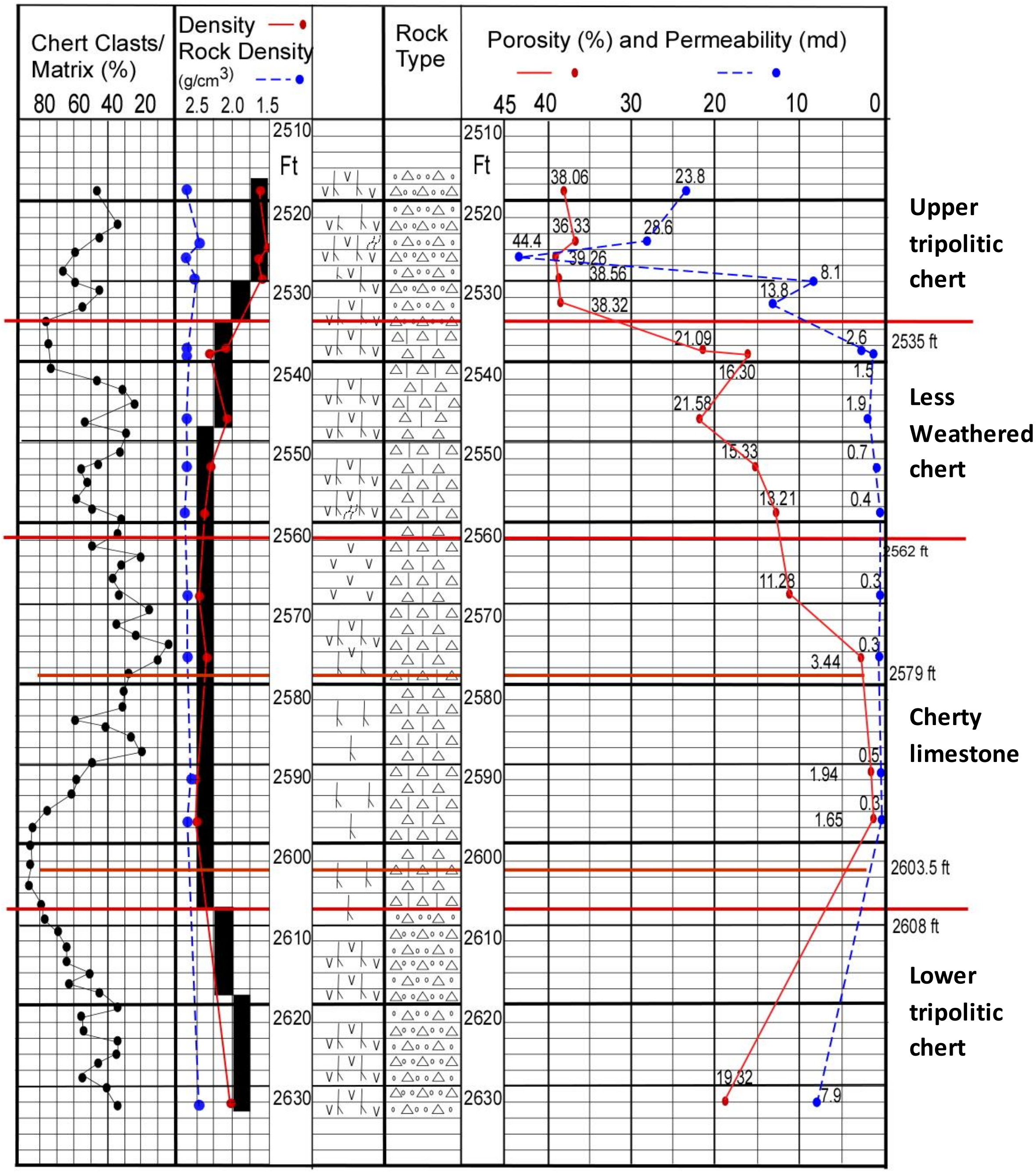


Figure 28. Core measured porosity, permeability, density, rock density and chert clasts/matrix ratio for the Mississippian chert in the Chapman Barnard Ranch #14, Osage County, Oklahoma.

Bulk Density

Total core plug volume and grain volume measured by the Core Lab PORG-200 gas porosimeter were used to calculate bulk density and rock density (Table II). Rock density is determined by dividing the mass of the plug by grain volume. This value reflects the density of the solid rock fabric, and is affected by the composition. In contrast, bulk density is calculated as dividing mass by total volume, and thus is influenced by porosity and fluid types. Bulk density of the Mississippian chert was also acquired from well log and compared to the bulk density value from core, as shown in Figure 30.

TABLE II
BUILK DENSITY, AND ROCK DENSITY OF THE MISSISSIPPIAN CHERT DETERMINED FROM CORE PLUGS, CHAPMAN BARNARD RANCH # 14, OSAGE COUNTY, OKLAHOMA

Depth (ft)	Total volume (cm^3)	Grain Volume (cm^3)	ϕ (%)	Mass(g)	Bulk Density (g/cm^3)	Rock Density (g/cm^3)
2519.5	12.934	8.011	38.062	21	1.624	2.621
2523	16.981	10.812	36.329	26	1.531	2.405
2527	15.572	9.459	39.256	25	1.605	2.643
2530	13.642	8.382	38.555	21	1.539	2.505
2532.5	12.987	8.011	38.315	20	1.540	2.497
2538.5	14.113	11.137	21.087	30	2.126	2.694
2538.8	12.523	10.482	16.298	28	2.236	2.671
2546.5	14.608	11.456	21.577	30	2.054	2.619
2553	13.902	11.771	15.329	31	2.230	2.634
2559	12.832	11.137	13.209	30	2.338	2.694
2570	15.161	13.451	11.281	36	2.374	2.676
2576.2	14.222	13.733	3.437	36	2.531	2.621
2591.3	13.424	13.164	1.935	35	2.607	2.658
2596.8	18.765	18.456	1.647	49	2.611	2.655
2612	13.297	10.728	19.318	27	2.031	2.517

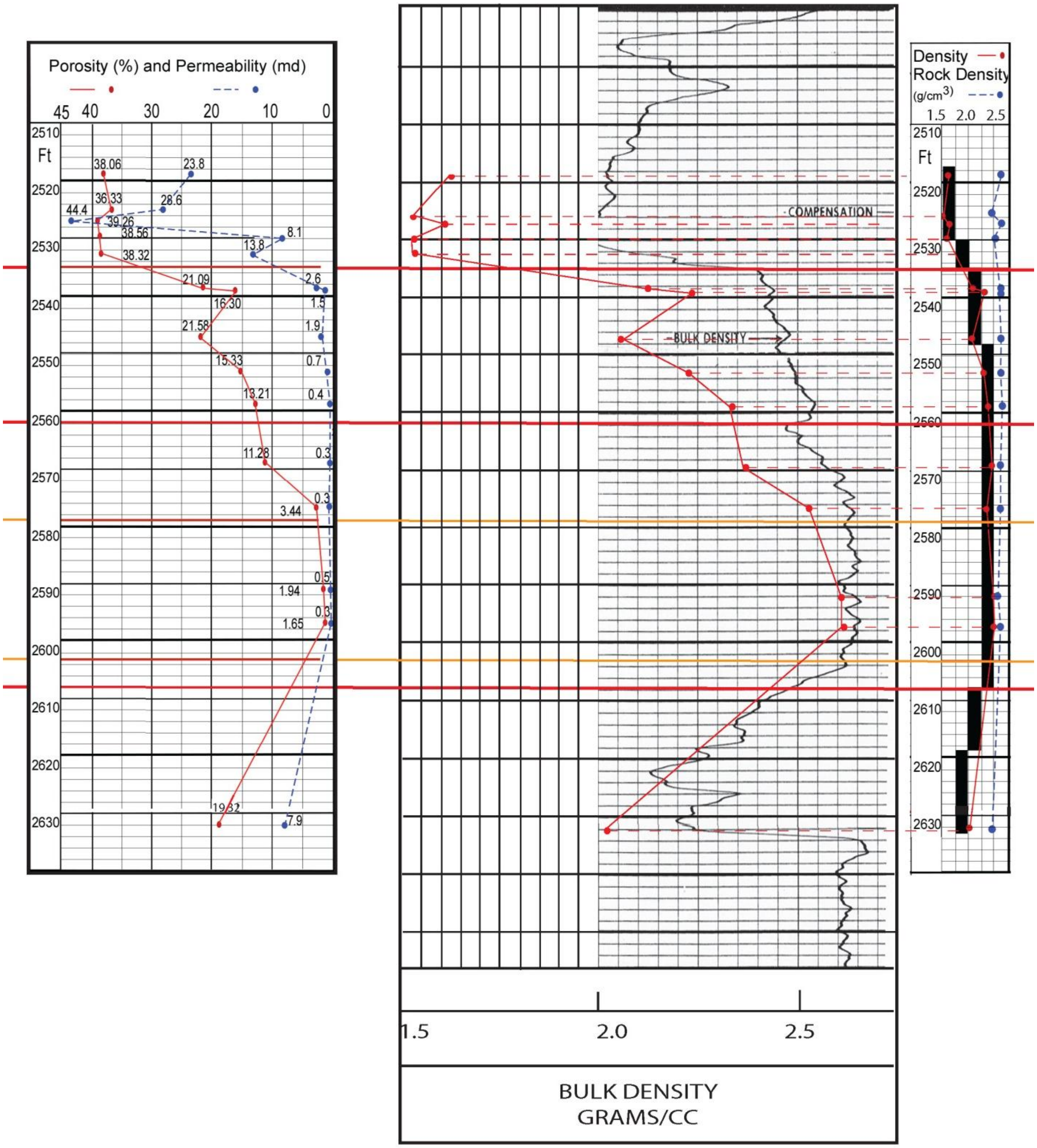


Figure 29. Calculated bulk density and rock density and bulk density from well logs, Chapman Barnard Ranch #14, N/2 NW Sec. 28, T.28N., R.8E., Osage County, Oklahoma.

The measured bulk density from core plugs was plotted along with the bulk density determined by well logs and the porosity curve. Since porosity is an important factor affecting bulk density, bulk density from core plugs and that from log should show similar changing trends with porosity. The separation between the measured bulk density curve and the bulk density log curve shown in Figure 30 may be related to the composition of pore fluids. The discrepancy between log and core porosity measurements is likely the result of sample bias. The higher the rock porosity, the higher the formation fluid content during logging. Since helium was the fluid used in core analysis and oil, gas and brine filled pore during logging, differences in bulk density showed increase in higher porosity intervals. In addition, logging tools average the recorded properties across several feet, whereas core plugs are discrete measurements. However, with these caveats, it is expected that the trends of the values will be similar. The upper tripolitic chert with highest porosity has the lowest bulk density and largest separation between the two bulk density measurements. Bulk density value ranges from 1.539 g/cm^3 to 1.624 g/cm^3 from core, and generally around 2.1 g/cm^3 for the log. The highest bulk density values are for samples of the solid Mississippian cherty limestone. Bulk density is above 2.3 g/cm^3 according to core samples, and ranges from 2.45 g/cm^3 to 2.7 g/cm^3 for the bulk density log. At 2591.3 ft and 2596.8 ft, porosity is less than 2%, bulk density reaches 2.61 g/cm^3, which is very close to the 2.65 g/cm^3, the value from the log. Bulk density of the less weathered chert ranges from 2.05 g/cm^3 to 2.33 g/cm^3 from core, and ranges from 2.4 g/cm^3 to 2.55 g/cm^3 from the log, which supports the contention that separation of bulk value from core and log increases with increasing porosity.

Rock density or matrix density for the Mississippian chert and Mississippian cherty limestone is generally around 2.65 g/cm^3 (Table II), and does not change dramatically with change of lithofacies (Figure 30), as the entire core is highly siliceous. The highly weathered tripolitic chert has a slightly lower rock density than the less weathered chert and Mississippian cherty limestone, because the latter two have higher calcite content (2.71 g/ cm^3).

Well Log Characteristics Associated with Core

Well logs were correlated to the respective Mississippian chert cores. Responses of individual curves were correlated with core attributes to determine if the results were consistent with the interpreted lithologic divisions established for the Mississippian chert (Figure 31). Acquired well log data is too limited to specific log signature to the Lone Star Anderson #1 cherty Mississippian limestone core.

The Chapman Barnard #14 core does not contain the base or top of the Mississippian chert. However, the logs do reflect the abrupt changes in SP, porosity and resistivity associated with the contacts between the more porous Mississippian chert and the lower porous Mississippian LC cherty limestone.

The lower tripolitic chert, from 2633 ft to 2603.5 ft, exhibits gamma-ray readings of about 60 API units, which are consistent with the Mississippian LC cherty limestone above. Abrupt spontaneous potential (SP) deflection of about -40 millivolts with the contact of the overlying and underlying carbonate zones identify fluid or compositional changes. A sharp decrease in resistivity to values less than 1 ohm-m indicates conductive fluid, high porosity or both. The shallow induction curve is separated from medium and deep induction curves, which track each other. The deep and medium resistivity values are around 1 ohm-m, whereas the shallow resistivity readings are from 3 ohm-m to 5 ohm-m. Neutron porosity ranges from 6% to 20%, density porosity ranges from 6% to over 30%.

The LC cherty limestone, from 2603.5 ft to 2562 ft, has a gamma-ray value of about 60 API units, minimal SP deflection (0~20 millivolts), and higher resistivity values from 20 ohm-m to 100 ohm-m. There is little separation between the resistivity curves. Neutron and density porosity measurements are lowest in this interval: 0~2% neutron porosity and 2~4% density porosity. These values do increase in the upper transition zone (depth: 2579 ft ~ 2562 ft).

The less weathered chert, from 2562 ft to 2535 ft, has gamma-ray readings of about 55 API units, and SP deflection to 40 millivolts at the contact with underlying LC cherty limestone. Resistivity values of the less weathered chert are between that of the LC cherty limestone. The deep resistivity is 6 ohm-m, shallow resistivity is about 15 ohm-m with some separation from deep resistivity curve. Porosity values increase upwards: neutron porosity increases from 4% to14%, and density porosity increases from 10 ~ 20%.

The upper tripolitic chert, from 2535 ft to 2518 ft, exhibits similar log responses with the lower tripolitic chert, including low gamma-ray value (~50 API units), large SP deflection (40 millivolts), low resistivity and high porosity values. The deep and medium resistivity values are about1 ohm-m, and shallow resistivity values are 3 ~ 4 ohm-m, showing obvious separation. Neutron porosity ranges 16% to 26%, and density porosity is >30%.

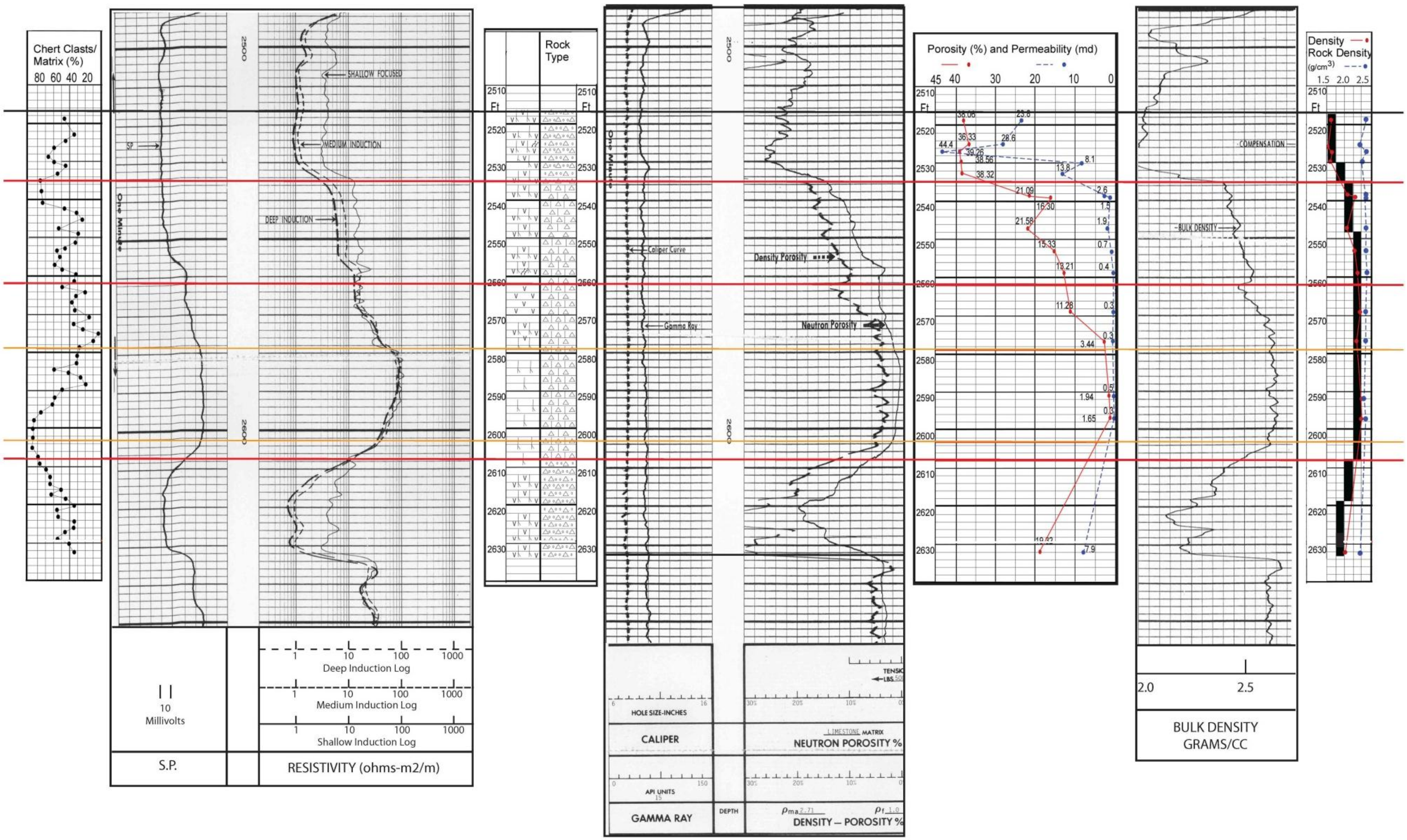


Figure 30. Correlation of well log responses to rock attributes determined by core plug analysis. Sun Venezuelan Chapman Barnard #14, Osage County, OK.

CHAPTER V

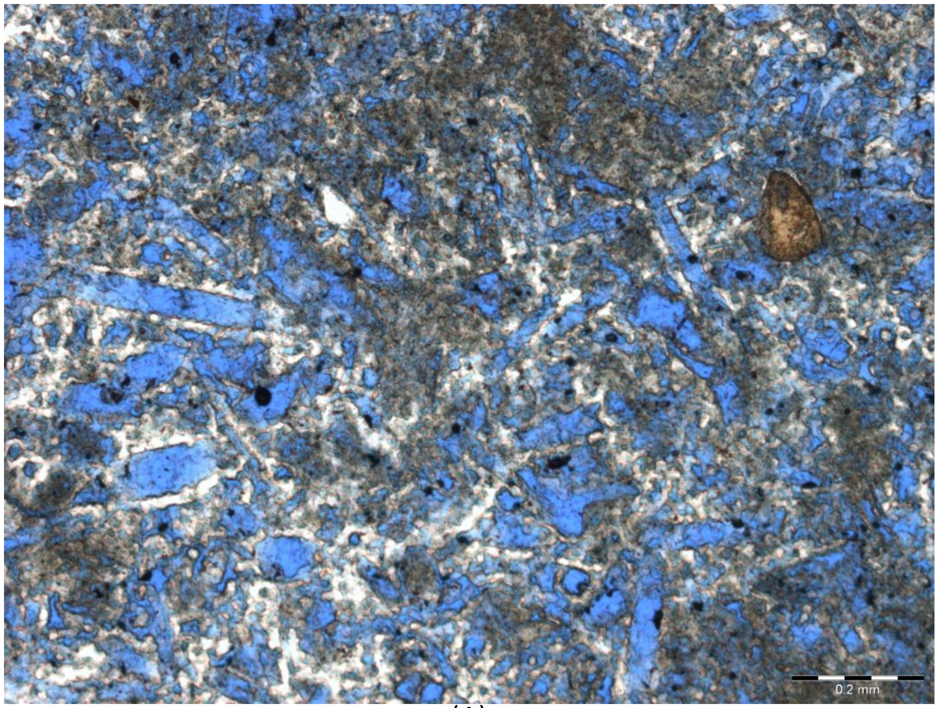
DISCUSSION

Origin of Silica

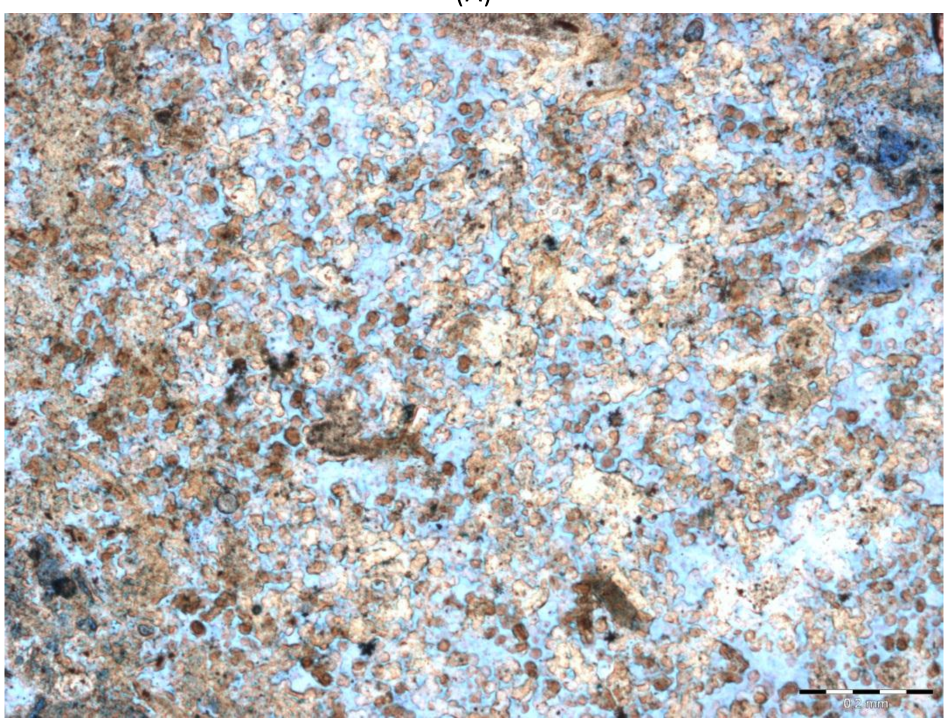
The origin of silica of the Mississippian chert and other equivalent or similar chert-rich rock units is not well understood. Previous studies identify a number of possible sources of silica, including hydrothermal emanations, dissolution of volcanic ash, weathering of silica-rich rocks, and dissolution of biogenic material such as sponge spicules, input from terrigenous sources, eolian dust, dewatering of basin sediments (Rogers, 2001, Mazzullo, 2009, Dolbier, 2010).

The subaerial exposure of cherty Mississippian rocks during late Mississippian to early Pennsylvanian provide enough opportunity for their weathering. Dissolved silica produced during this weathering process or weathering of terrigenous sediments are possible sources of silica for formation of chert (Roger, 2001; Mazzulo, 2009).

Results from acid digestion of cores and thin section analysis confirm that dissolution of sponge spicules is one source of silica in the Mississippian chert. Sponge spicules are major component of the Mississippian cherty limestones, and especially the Mississippian chert. Residues of core digestion are almost entirely sponge spicules with very a small portion of foraminifers, without any conodonts (Boardman, 2011). Absence of conodonts could be the result of the prevalent colonization of demosponges in the ancient Mississippian sea excluding the residence of conodonts. Also, study of thin sections shows prevalence of sponge spicules in both the Mississippian chert and the Mississippian limestone (Figure 33). The analyzed thin sections contain different percentages of sponge spicules, which were more prevalent and larger in the cherty samples, and less abundant and smaller in less-silicified carbonate. Moreover, dissolution and leaching of sponge spicules is evident as spicular-moldic pores (Figure 32). In this case, leaching of abundant siliceous sponge spicules could have been an important source of silica for chert in the Mississippian “chat” and “solid”. This conclusion is consistent with other studies of the Mississippian chert, or similar units (Thomas, 1982; Rogers, 1996; Rogers, 2001; Mazzullo, 2009).

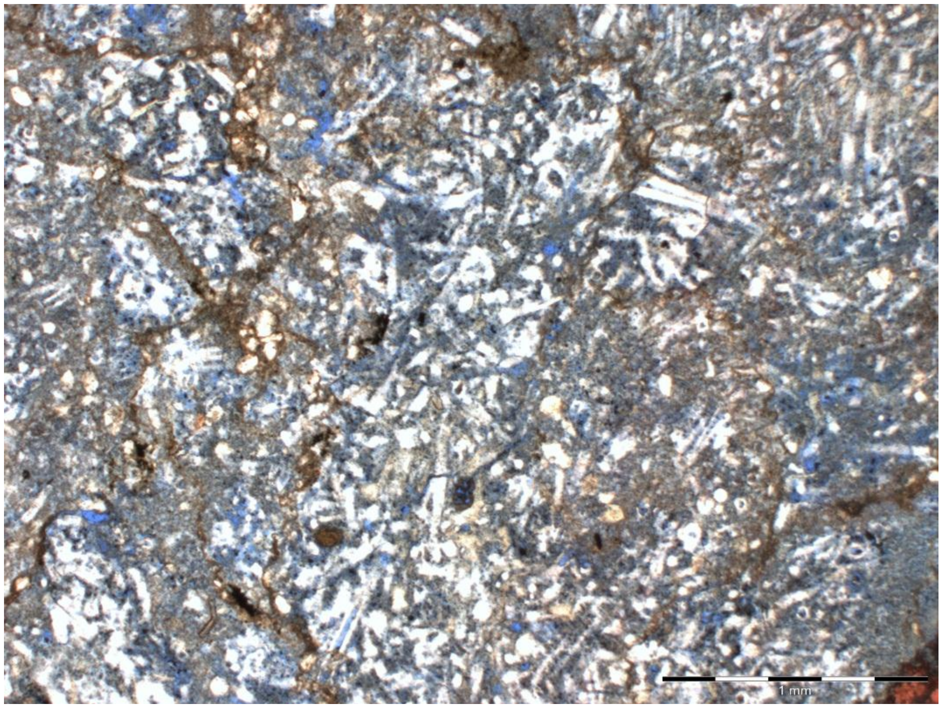


(A)

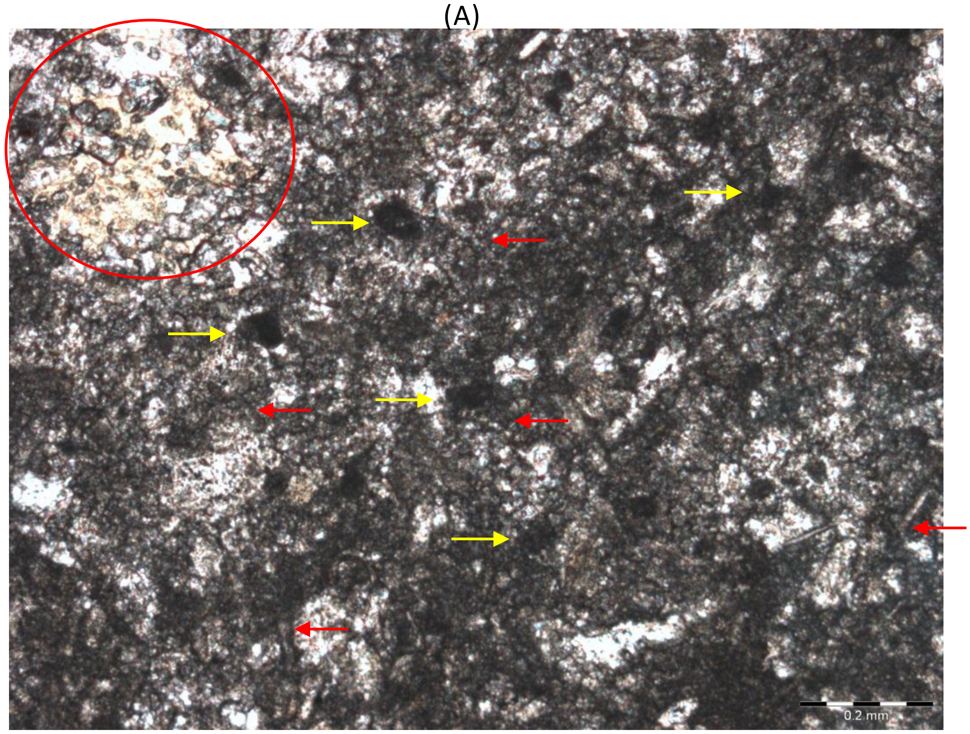


(B)

Figure 31. Thin section photomicrographs showing dissolution of siliceous spicules. A: Spicular-moldic porosity in the chert clasts. PPL, depth 2532 ft. B: Dissolution of cherty spicular matrix by leaching of spicules. PPL, depth 2614 ft. Chapman Barnard #14, Osage County, OK.



(A)



(B)

Figure 32. Thin section photomicrographs showing the abundance and distribution of spicules in the entirely silicified and slightly silicified zones. A: Entirely silicified zone with densely packed spicules that are about 0.5 mm big, 0.1 mm wide. PPL, depth 2632 ft. B: Sparse spicules (red arrows), pellets (yellow arrows) and micritic matrix in a slightly silicified zone. Spicules are 0.1 mm long and 0.01 mm wide. PPL, depth 2576 ft. Chapman Barnard #14, Osage County, OK.

Origin of Silt

The silt-sized quartz grains that are not abundant, but common in the Mississippian chert and cherty limestone are believed to be of eolian origin. These silt grains are randomly distributed, and only occasionally concentrated along bedding planes. The grains are sub-angular to sub-rounded, which supports the interpretation of non-fluvial transport.

Diagenesis

Silicification and dissolution are main diagenetic processes that altered the sediments that ultimately became the Mississippian chert. Pore fluid chemistry is crucial to these processes, since pH and pore water saturation with respect to calcite and silica account for the resulting precipitation or dissolution (Rogers, 2001).

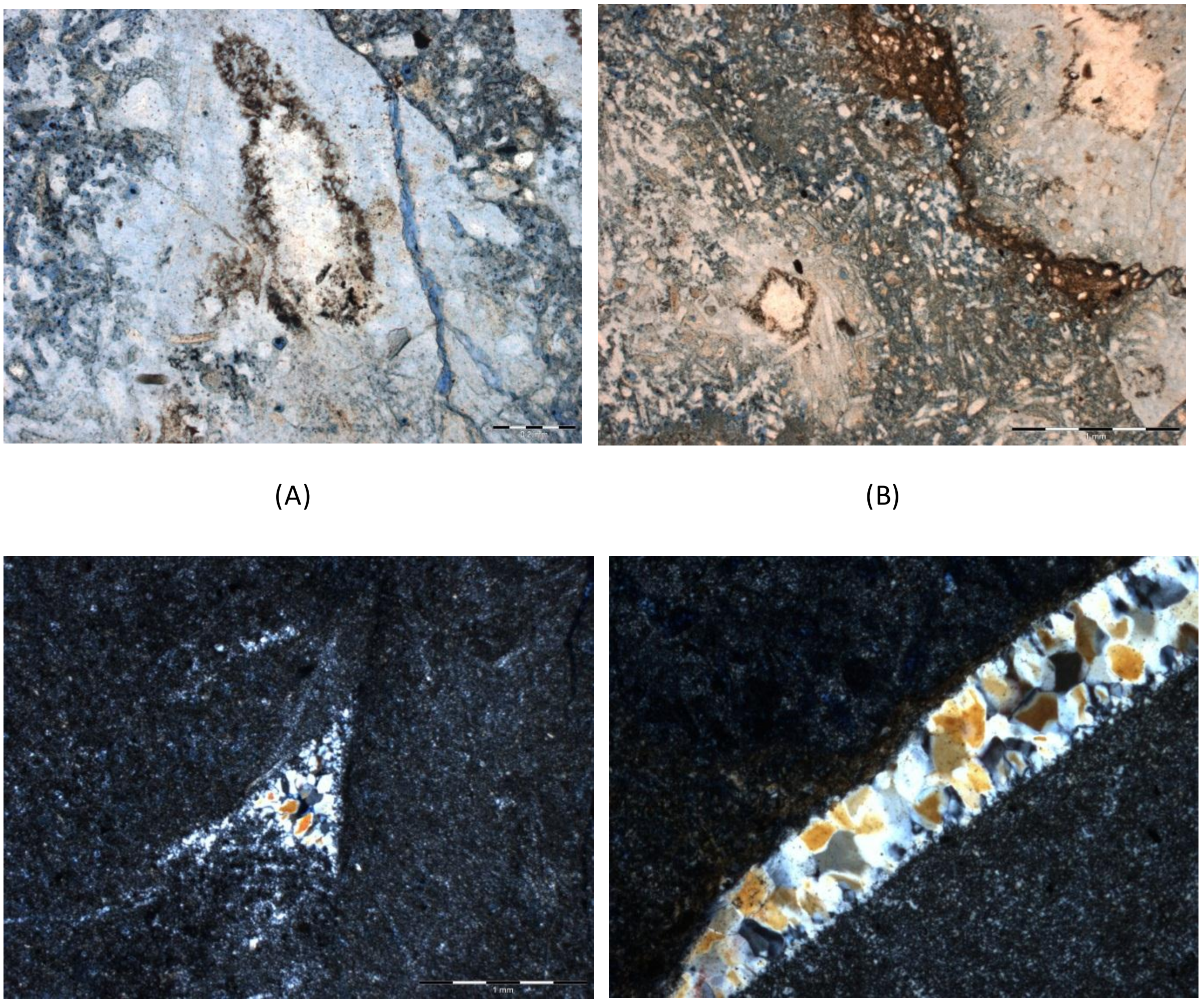
During early diagenesis, siliceous sponge spicules were dissolved and precipitated as microcrystalline quartz that occluded the intraparticle pores within the original hollow sponge spicules (Mazzullo, 2009). Mobilized silica from dissolved spicules replaced the carbonate of the nodular zones, and probably precipitated as the initial nodular chert in zones of highest permeability. These zones experienced carbonate dissolution in response to solubility changes at groundwater interfaces, such as the interfaces between fresh water and marine water, between oxic fluid and anoxic fluids, and/or in response to force of crystallization of growing quartz crystals (Knauh, 1994). Compaction induced fractures within the first generation of cherts, and calcite precipitated in these fractures when the water was saturated with respect to it. Mazzulo (2009) indicated that fracturing occurred before significant burial when the surrounding sediments were mostly uncemented. Thus, the first generation of cherts are interpreted as having formed syndepositionally from modified marine pore fluids within unconsolidated, shallow-buried sediments. This is consistent with Knauh's (1994) opinion about the formation of nodular chert that the replacement occurred in the coastal environments during the conversion of metastable biogenic carbonate into calcite and dolomite.

During subaerial exposure, the Mississippian chert was exposed to a mix of meteoric-marine and meteoric water (Mazzulo, 2009), and multiple periods of alternating silicification and dissolution occurred. A steady decrease in pH could promote dissolution of calcite and silicification, because silica solubility tends to be constant while calcite solubility decreases with decreasing pH (Correns, 1969; Knauth, 1994). Possible reasons for the lowering pH could be oxidation of microbial H_2S during mixing of oxic and anoxic pore fluids (Clayton, 1986). Also, when marine seawater mixes with meteoric water, it is possible that the mixed fluid becomes undersaturated with respect to calcite, even if the seawater was initially saturated with respect to calcite (Knauth 1979). In this model, high concentrations of silica from dissolved spicules began to precipitate chert concurrent with calcite dissolution, promoting silicification (Knauth 1979). The increased pressure exerted by growing quartz crystals could further enhance the dissolution of carbonate (Maliva and Siever, 1988; Knauth, 1979). During this period of silicification, chert nodules from small to large are formed in the chert, as silica precipitated on the first generation cherts, which acted as nuclei for continued coalescent growth. Most nodular cherts in carbonate rocks appear to result from a diagenetic episode in which carbonate was replaced incrementally on a volume-for-volume basis by silica (Knauh, 1994). This coalescent growth of chert nodules is illustrated in the chert by black bitumen rims inside the chert nodules with multiple growth bands (Figure 34 A& B). Occasionally, fibrous and drusy quartz are precipitated in the void space between and within chert clasts where the limestone dissolved (Figure 34 C&D).

Rogers (2001) suggests that replacement of carbonate by silica is on molecule basis, as evidenced well preserved delicate structures of fossil fragments, and that the degree of selective replacement is influenced by the supply and location of spicules and type of fossils. Delicate fossils partially or total replaced by microcrystalline quartz are evident in the Lone Star Anderson #1 core.

Isolated dolomite rhombs precipitated within cherts are common in thin section (Figure 35 B). Knauh (1992) believes these dolomite crystals indicate that preferential silicification of calcite and aragonite occurred after inception of dolomitization but before it could proceed beyond formation of isolated crystals.

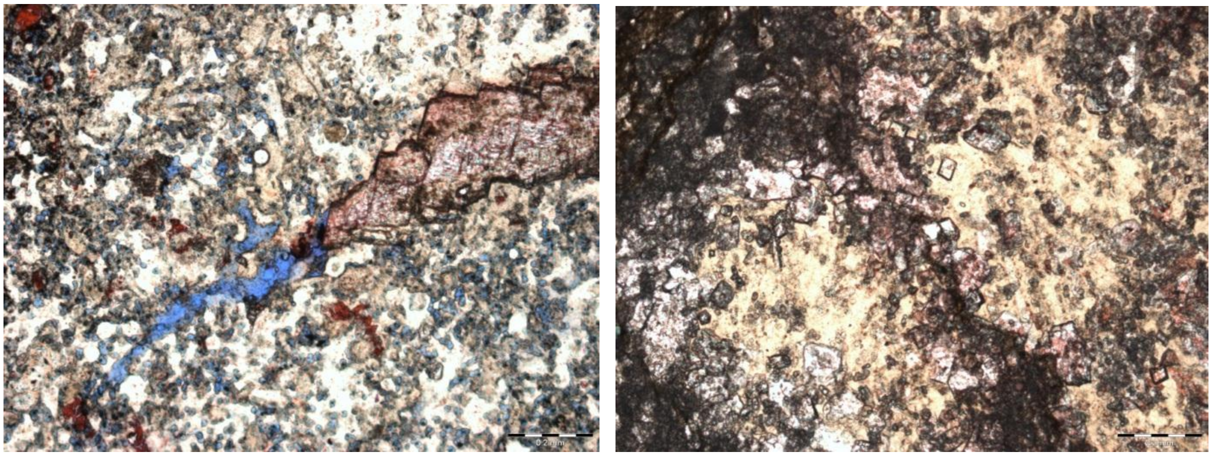
During the later stages of subaerial exposure, changes in pore fluid chemistry occurred as a result of continued uplift and the resulting infiltration of undersaturated meteoric water (Rogers, 2001). At this time, precipitation of new silica terminated, but dissolution continued. Dissolution of calcite opened previously cemented fractures (Figure 35 A), and could have enlarged them. Moreover, leaching of silica also occurred at this stage. The pervasive, extremely fine porosity in the matrix of the tripolitic chert is thought to be associated with dissolution of siliceous matrix material (<= 60um) and sponge spicules, but not with removal of carbonate material (Duren, 1960; Goebel, 1966; Meyers, 1977; Parham and Northcutt, 1993). This is possibly caused by the constant leaching of meteoric water that dilutes the concentration of silica, resulting in pore fluid undersaturated with respect to silica and a slightly increased pH. In the studied core, there are two porous intervals of the Mississippian chert separated by a low porosity LC cherty limestone. The higher interval underwent intense weathering in the vadose zone and was subjected to leaching from surface water (Duren, 1960; Rogers, 2001). Vugs and karst textures are indicated by collapse breccia in the core. The lower interval was probably associated with ground-water dissolution in a subsurface karst environment (Rogers, 2001). This difference may have caused the differing preferential dissolution of chert clasts evident in the chert: in the lower tripolitic chert, dissolution of silica between spicules is common (Figure 36 A), whereas in the uppermost more weathered zone, dissolution of spicules within chert clasts formed pervasive spicular-moldic porosity (Figure 36 B).



(A) (B)

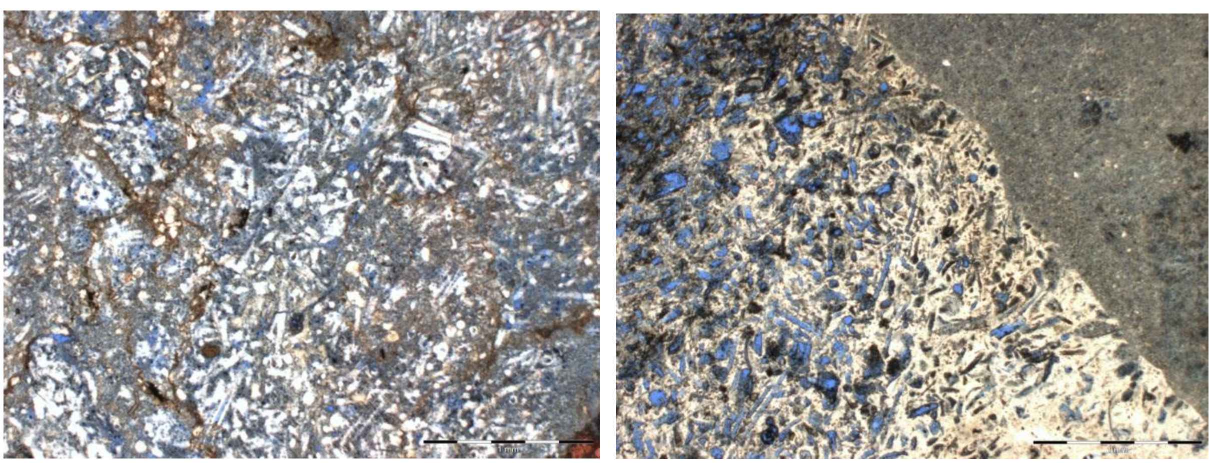
(C) (D)

Figure 33. Thin section photomicrographs of multiple generations of chertification. A & B: Bitumen saturated chert that separates two generations of chert. PPL, A. scale bar represents 0.2 mm, B. scale bar presents 1mm. C & D: Drusy quartz cement filling the void space between chert clasts after carbonates dissolved. PPL, scale bar is 1 mm. Chapman Barnard #14, Osage County, OK.



(A) (B)

Figure 34. Thin section photomicrographs showing carbonate in chert. A: Calcite cement filled fractures are partly dissolved. PPL, scale bar represents 0.2 mm; B: Dolomite rhombs within chert clasts. PPL, scale bar represents 0.2 mm. Chapman Barnard #14, Osage County, OK.



(A) (B)

Figure 35. Thin section photomicrographs showing the selective removal of silica. A: Lower tripolitic chert at base of core. Removal of silica between spicules formed porosity similar to interparticle porosity. B: The tripolitic chert in the upper porous zone. Selective removal of siliceous spicules forms large quantities of spicular-moldic porosity. PPL, scale bar represents 1mm. Chapman Barnard #14, Osage County, OK.

Possible Controls on Petrophysical Properties

The Mississippian chert displays considerable variability in petrophysical properties that are different from the Mississippian cherty limestone, and the Mississippian solid limestone. Table III compares petrophysical attributes between the tripolitic chert and LC cherty limestone, and possible controls. The limestone in this table is the solid LC cherty limestone located between the upper and lower tripolitic chert intervals in the Chapman Barnard #14, and has the same burial and diagenetic history as the subjacent and superjacent porous zones.

TABLE III

COMPARISON OF PETROPHYSICAL PROPERTIES BETWEEN MISSISSIPPIAN CHERT AND LC CHERTY LIMESTONE AND POSSIBLE CONTROLS. POROSITY OF WELL LOGS IS CROSSPLOT POROSITY.

	Tripolitic Chert		LC Cherty limestone		Possible Controls
	Range	Aver.	Range	Aver.	
ϕ (%) Helium	36.33 ~ 39.26	38.10	1.65 ~ 11.28	4.58	Dissolution→ diagenesis→pore water chemistry: pH, saturation state
ϕ (%) log	27.4 ~ 37.3	32	2 ~ 9.5	~ 3.5	
K(md) Helium	8.1~44.4	23.74	0.3 ~ 0.5	0.35	Fractures→ brittleness → composition of rocks
Density (g/cm^3)	1.53 ~ 1.62	1.57	2.37 ~ 2.61	2.53	Composition of rocks, porosity, and fluid
Rt (ohm-m)	0.9 ~ 2.5	~1	10 ~ 90	~45	Content of silica, porosity, and bound water

In Table III, both helium porosity and crossplot porosity from logs display dramatic differences between the Mississippian chert and cherty limestone. Secondary porosity is dominant in chert, including vugs, micro-porosity in the matrix, molds, and fractures. Most of the porosity is the result of dissolution during diagenesis. As discussed in previous section, pH value of the pore fluid, and saturation with respect to calcite and silica mainly control the occurrence of dissolution during diagenesis.

Permeability is enhanced by pervasive fractures of various sizes in the Mississippian chert. Besides stress, which should be the same on the chert and cherty limestone because of their same origin, fractures are mainly determined by brittleness of rocks. Under stress, limestones generally tend to form stylolites, whereas the brittle cherts fracture. Thus, the composition of rocks, or the chertification during diagenesis, affects the difference of permeability between the chert and cherty limestone.

Wireline log resistivity is determined by the composition of the rock, bound water, porosity, and the resistivity of the formation water. The Mississippian chert has a higher silica content, microporosity and porosity, and more bound water than Mississippian cherty limestone. As a result, the chert exhibits much lower resistivity values than the Mississippian LC cherty limestone.

CHAPTER VI

CONCLUSIONS

Based on the results of this research, the following conclusions are proposed concerning the origin of silica, general diagenetic history, petrophysical characteristics and reservoir properties for the Mississippian chert and cherty limestone.

1. Secondary porosity is dominant in the Mississippian chert in the Chapman Barnard# 14 core. Micro-porosity in the matrix is pervasive in the tripolitic chert, but the upper tripolitic chert contains more moldic porosity than the lower tripolitic chert. Porosity of the less weathered, lower porosity chert is mainly isolated vugs and fractures, which are often cemented. The cherty limestone shows minimal porosity in the thin section analysis.
2. Porosity determined by core plug analysis and well logs is generally much higher than porosity measured by thin section point counting. This is expected as thin-section measured porosity is two dimensional, and a very small sample. Furthermore, it is very difficult to measure micro- intercrystalline porosity in the matrix, which is believed to contribute considerably to the total porosity of the Mississippian chert.

3. Bulk density measurements from core plugs and well logs are closest in the tight rock, and most different in the high porosity zone. The deviation between these volumes is related to difference in pore fluids, which is helium in core plugs and formation fluids (water or oil) in the logged rock. In addition, logging tools average the recorded properties across several feet, whereas core plugs are discrete measurements.
4. Rock density measurement is affected by silica (density=2.65 g/cc) and calcite (density=2.71 g/cc) content. The highly silicified chert has a slightly lower rock density than Mississippian cherty limestone, because the latter has higher calcite content.
5. Dissolution of sponge spicules is an important source of silica in the Mississippian chert and the Mississippian cherty limestone.
6. Diagenetic processes that altered the Mississippian chert involved multiple episodes of dissolution and silicification. Multiple episodes of silicification (chert phases) are evident and separated by bitumen. Fractures and inter-chert-clast areas are cemented by calcite and microcrystalline quartz.
7. Favorable hydrocarbon reservoirs have high porosity to store hydrocarbon, and high permeability to allow oil and gas to efficiently transmit to the well. In the Mississippian chert, the tripolitic chert is intensely weathered, which greatly improves its porosity and permeability. The tripolitic chert shows the highest porosity, which is generally well above 30%, and multiple pore systems including micro-porosity and larger dissolution vugs and fractures. Its permeability ranges

from 7.9 md to 44.4 md, and is well enhanced by fractures and micro-fractures within chert clasts and matrix.

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VITA

Min Zhao

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Scope and Method of Study:

The Mississippian chert has been explored and developed for more than 80 years as an important significant oil and gas reservoir. However, the origin of silica is poorly understood, its petrologic and petrophysical characteristics rarely discussed, and the formation of the chert debated.

In this study, cores containing the Mississippian chert and Mississippian cherty limestones were described, sampled and analyzed. Core analysis included determination of grain types and textures, morphology of cherts, ratio of chert to matrix, relative density, and porosity types. Further information regarding petrophysical properties were acquired by analysis of well logs and measurement of porosity, permeability and density on core plugs. In particular, well logs across these intervals were examined to determine variations in gamma ray, spontaneous potential, resistivity, density and neutron porosity, and bulk density. Thin-sections were examined to determine mineral composition, pore types, confirm the possible sources of silica, and determine the relationship between cherts and limestones.

Findings and Conclusions:

The abundance of silica in the Mississippian limestone is closely linked to the abundance of spicules, evidence that the chert is mostly biogenic. Dissolution of sponge spicules is an important source of silica in the Mississippian chert, and the Mississippian cherty limestone. Diagenetic processes that altered the Mississippian chert involved multiple episodes of dissolution and silicification. Secondary porosity is dominant in the Mississippian chert. Porosity is formed by dissolution of chert matrix, clasts and spicules as well as fracturing. The highly silicified chert has a slightly lower rock density than Mississippian cherty limestone, because the latter has higher calcite content. Bulk density measurements from core plugs and well logs are closest in the tight rock, and most different in the high porosity zones. The upper and lower tripolitic chert are most favorable reservoirs, according to their high porosity and permeability. Also, tripolitic chert is very clean and contains abundant microporosity that affects wireline log signature.

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