VARIABILITY OF NANOPORE SYSTEMS IN THE LINCOLN LIMESTONE, DENVER-JULESBURG BASIN, COLORADO, USA

Ву

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ABSTRACT:

With a shift to exploiting unconventional petroleum plays in the United States to support energy consumption, understanding the nanopore systems in those unconventional resources becomes important for future exploitation. The goal of this study is to characterize the pore systems of the Cretaceous Lincoln Limestone found in the Denver-Julesburg (DJ) Basin in order to test the hypothesis that lithologic variability has a control on pore characteristics and total porosity. The Lincoln Limestone represents a possible reservoir interval in close proximity to a source interval, the Hartland Shale, which directly overlies it, thus making it a potentially profitable future exploration target. Pore networks in the Lincoln were characterized using AR-milled rock surfaces run through a scanning electron microscope (SEM) for image capture, image analysis with Avizio 9 software, and mineralogical characterization by X-Ray fluorescence (XRF).

Seven samples were chosen for analysis from a single core taken from one well in the DJ basin. Five of the samples span the roughly 70-90 ft thick Lincoln Limestone and the other two come from right above and right below the Lincoln. The seven samples span the range of lithologic and porosity variability in the Lincoln Limestone. They have normalized volumes of carbonate that range from 6.0% to 70.6% (mostly as calcite); clay content ranges from 14.8% to 55.2%. The samples are thus marls (n=5), marly shale (n=1) and shale (n=1). Total organic carbon (TOC) contents range from 1.5% to 7.8% and porosity ranges from 5.0% to 10.4%. Pores that were present prior to hydrocarbon maturation are now generally infilled with migrated hydrocarbons.

Total imaged porosity of the pre-migration pore system ranges from 5.1% to 7.8% in the seven samples. In individual samples, median equivalent circular diameters of those pores range from 64.2 nm to 91.5 nm, median pore elongations (anisotropy) range from .77 to .81, and median pore width ranges from 51.0 nm to 71.3 nm. The data show that median pore width and median pore size increases with increasing volume of carbonate and decreases with increasing volume of clay, although the trends are not strong. Pores associated with calcite are bigger and less elongated because they occur between relatively equidimensional rhombs of calcite. Where calcite is not present, pores are shorter and more elongate because they are associated with clay minerals.

Total imaged porosity also increases with increasing volume of carbonate, and decreases with increasing volume of clay. These trends with total imaged porosity, however, may be misleading. Calcite occurs in two basic habits. One is as compacted but still porous peloids of cocolith and pelagic foraminifera debris and the other is as nonporous, whole pelagic foraminifera shells whose original internal void space is completely cemented, often with calcite. In the latter case, there is calcite, but no pores. Imaged areas were chosen to avoid concentrations of calcite-cemented, non-porous foraminifera in order to document the actual pore systems. But doing so may have biased the amount of imaged porosity with respect to calcite content.

A major implication of this work is that the Lincoln Limestone's pore system is not analogous to the overlying Niobrara Formation. Attributes of the Niobrara's pore system is more strongly related to

total calcite because most of that calcite is found in microporous peloids (Ball, 2015). In contrast peloids are relatively rare in the lower half of the Lincoln, and are not particularly common until near the contact with the overlying Hartland Shale.

Contents:

- I: Introduction
- II: Geologic Setting
- III: Methods
- IV: Sample Characterization
- V: Results
- VI: Discussion
- VII: Conclusion
- VIII: References

Introduction:

With the introduction of horizontal drilling paired with multi-stage hydraulic fracturing the difficulty with producing gas and oil from low permeability rock formations has largely been overcome. This has allowed formations formerly thought to be un-producible to become viable exploration targets. In the United State alone shale and other tight reservoir sources are estimated to hold around 58 billion barrels of liquids with another 567 tcf (trillion cubic feet) of wet natural gas. These figures are roughly 26% and 27% of the total recoverable oil and gas globally, respectively (http://www.eia.gov/analysis/studies/worldshalegas/pdf/overview.pdf). In recent years this newly accessible energy has allowed the United States to become natural gas independent, and to witness reduced imports of oil (Jarvie, 2010). Beyond this, natural gas, being a cleaner burning fuel, has led to a decrease in US CO2 emissions by around 10.4% since 2005 (http://www.eia.gov/environment/emissions/carbon).

The pore systems of these low permeability formations has been a research focus in academia and industry for some time in an attempt to better understand the storage and production capacity of these resources (Loucks et al., 2009; Driskill et al., 2013). These studies have documented the dominance of pores at the micro- to nanometer scale in these formations. Analysis of these pore systems can be done through a combination of SEM imaging of Ar-milled surfaces, and subsequent image analysis. Siliciclastic mudstone units (i.e., shales) are largely the most targeted formations using these techniques and their pore systems are becoming increasingly well understood (Loucks et al., 2009, 2010; Milliken et al., 2010, 2012). Carbonate rich unconventionals have been less heavily studied leaving knowledge on these formations wanting compared to siliciclastic ones. This has resulted in questions about the impacts of carbonate mineral content variations in carbonate-rich unconventionals unanswered. Characterization of the pore size, shape and orientation are some of the first steps that need be taken in order to get a better understanding of how varying carbonate minerology impacts hydrocarbon storage and mobility in these systems.

The Colorado region hosts multiple basins known for oil and gas production out of shales, mudstones, sandstones and carbonate reservoirs (Nelson and Santus, 2011). The DJ Basin (Figure 1) has become one of these important basins holding within it one of the most active petroleum plays in the United States, the Niobrara Formation (Kaiser and Sonnenberg, 2013). Due to its production capabilities the Niobrara's pore systems have been characterized and studied in recent years (Michael, 2014; Burt, 2014; Ball, 2015) but other potential organic-rich mudstone/shale plays in the basin have been ignored with very little research directed towards them. This study seeks to understand the relationship between lithologic heterogeneity and pore systems in one of those units, the Lincoln Limestone.





Figure 1: Map of Colorado with oil and gas basins in light blue. (<u>http://dnrwebmapgdev.state.co.us/mg2012app/</u>). The solid red outline outlines the DJ Basin. The red dashed lines outlines the general area of most unconventional exploration and development activity.

There has been hope that underlying rock in the Greenhorn Formation may be analogous to the Niobrara and could become as valuable an unconventional resource as the Niobrara has been (Kaiser and Sonnenberg, 2013). A key aspect of the Niobrara is that it contains lithologic oscillations between chalk and marl layers. The marls contain the petroleum sources and the chalks are easily fractured and become the target of the horizontal drilling. Similar lithologic variations occur in the Greenhorn Formation with the marls of the Lincoln Limestone being the calcite-rich equivalent to the Niobrara's chalk zones. This study seeks to assess if the lithologic oscillations in the Lincoln means its pore systems are similar to the Niobrara. Beyond this, this study seeks to categorize both the pre-migration and post-migration pore systems associated with the variations in lithology.

II: GEOLOGIC SETTING

The Lincoln Limestone here was deposited during the Cretaceous period when large parts of the western US were overlaid by the Western Interior Seaway (WIS). The WIS was a large asymmetric north-south orientated foreland basin that stretched from the Gulf of Mexico to the Artic and was around 1600km at its widest. It was formed over thick continental crust and was bordered on the west by a fold-thrust belt and on the east by the North American craton (Weimer, 1983). The basin evolved between the Late Jurassic to the Cretaceous time in response to accelerated plate convergence, subduction, and spreading along the western plate boundaries of North America (Kauffman, 1985). Sedimentation in the WIS basin halted with the onset of the Laramide Orogeny (71-75 MA) while Laramide deformation broke the larger WIS into the now present Rocky Mountain intermountain basins (Weimer, 1960). One of these basins is the DJ Basins.

The DJ Basin is found on the eastern section of what was the WIS. The DJ Basin extends below northeastern Colorado, southeastern Wyoming, southwestern Nebraska, and western Kansas (Figure 1). The Lincoln Limestone was deposited in the eastern WIS (e.g, Colorado) during the Late Cretaceous. The Late Cretaceous was characterized by multiple transgressive-regressive sequences related to global sea-level rises and falls. Hallam (1977) showed that what is now North American was roughly 35-38% submerged during those transgressions. The Greenhorn transgressive sequence includes largely terrigenous mud overlain by largely marine pelagic carbonate known as the Lincoln Limestone (Sageman and Johnson, 1985).

Siliciclastic sediments came into the WIS from the western Cordilleran mobile belt (Weimer, 1970; Pollastro and Scholle, 1986). In the eastern portion of the WIS, however, high concentrations of calcite in the transgressive deposits suggest a different depositional environment from those influenced by sediments from the Cordilleran Orogenic Belt. The carbonate sediment is pelagic in origin and consist of cocolithophore debris and foraminifera, all deposited on broad, flat areas far from sources of terrigenous mud (Hattin, 1975). Much of the cocolith debris is in the forms of peloids (fecal pellets) formed by predators that ate the cocolithophores in the oceanic water column. Thickness patterns and facies patterns suggest a relatively deep-water model for the calcite-rich units (Weimer et al., 1986). This environment is interpreted to be a nearly featureless expanse of sea floor at depths around 100m (Hattin, 1975).

III: Industrial Interests:

With the importance of the Niobrara and its being one of the largest unconventional plays in the country the hope has been that the Greenhorn Formations, and specifically its Lincoln Limestone member, could be similar to the Niobrara in terms of production potential. When compared to the Niobrara the Lincoln has seen gas to surface in less than 30 minutes as well as recovery of gassy or muddy oil to surface in around 1 hour (Kaiser and Sonnenberg, 2013). The Lincoln thus does hold promise, but that promise is still unproven.

IV: Methods:

Twelve core samples were obtained from one core drilled through the Lincoln Limestone. Samples were chosen that were felt to best represent the lithologic heterogeneity exhibited in the core through photographs of the whole core that surrounded provided sample. Care was taken to avoid bentonite layers that were present and macroscopic beds of cross-laminated foraminifera layers (pure calcite) with the exception of one sample so that image analysis wouldn't be biased to this one type of calcite-rich accumulation. Seven of the 12 original samples were high-graded for pore imaging. The seven were chosen to represent a range of normalized volume of carbonate, TOC, and porosity values. Of these 7 samples, 5 were from the Lincoln and the other 2 where from the formations directly above and directly below the Lincoln. The two samples outside of the Lincoln were chosen so as to collect data directly on or near the contact between the Lincoln and the over/underlying formations. The sample from the overlying Hartland shale was also calcite-rich and may actually be from the Lincoln Limestone if the reported depth of the contact was in error. The other reason for choosing the 2 samples outside of the Lincoln was that they increased the range of lithologic and petrographic attributes sampled.

A petrographic analysis of these thin sections from the 7 high-grade samples was performed using transmitted light microscopy. The sections were categorized for bedding, lamina, sedimentary structures, and microfacies. Based on the petrographic examination, an area of ~1cm² was then selected on each of the seven thin sections that was felt to best represent the entire sample's lithology, grain size and sedimentary structures. Care was again taken to avoid areas that might be completely foraminiferal calcite. This was done because the calcite occurred largely as well-cemented foraminifera in all samples and there was no reason for multiple examinations of such material in the SEM.

After the 1 cm² areas were chosen on each thin section, the corresponding locations on the core stubs left over from thin sectioning were identified and trimmed into 1x1x1 cubes. The cubes were then Ar milled at the USGS in Denver, Colorado. After milling the samples were then imaged at a magnification of 10,000x using a JOEL 5800LV SEM equipped with secondary and backscattered election detectors (http://usgsprobe.cr.usgs.gov/sem.html). Two photomosaics each consisting of 25 images (5x5) were collected for six of the samples and the seventh sample was imaged for a 6x6 photomosaic. Figure 2 below shows an example of a 5x5 mosaic. Both backscattered electron (BSE) and secondary electron (SE) images were collected of each field of view. The BSE images respond to elemental density and are best for distinguishing pores, organic matter, and mineral matrix across the entire mosaic. The SE images capture microtopography across the imaged area and were useful for distinguishing the exact boundaries of pores due to their negative relief.



Figure 2: BSE photomosaic based on 25 individual images.

The individual BSE images of each photomosaic were initially processed in Adobe Photoshop CS4 for pre-analysis editing. In Photoshop, the images were first stitched together with the Photomerge function, a process that's typically used to create panoramas. The rows were then imported into Adobe Illustrator CS4 and manually merged into one single mosaic. Each row was aligned based on noticeable features common to each row due to the SEM images having a certain amount of vertical overlap.

After the BSE photomosaics were created, they were reimported into Photoshop for additional editing. Each mosaic was run through a custom "action" process in Photoshop where various image editing processes can be recorded and then reapplied to multiple images in a batch. This subjected each mosaic to sharpening, contrasting and overall brightening. This process allowed greater contract between organic matter (OM) and the matrix material (Figure 3). In the raw SEM images, those materials sometimes bled into one another, which made it difficult to properly segment the two materials in many samples. To elaborate further, it was common that accurately estimating the boundary between organic matter (OM) and matrix in one part of a sample meant that, in other sections

of the same sample, OM would be segmented as matrix or matrix segmented as OM material. This issue arose due to the fact that OM greyscale values were not uniform across the photomosaic of an individual sample. As a result attempting to auto segment all OM by a single greyscale meant that other OM samples would not be included. Given that OM, in individual mosaics often numbered into the thousands of objects, hand segmentation of each OM objects would be inefficient. This Photoshop "Action" process helped to standardize the greyscale ranges of OM and matrix material so that faster automatic segmentation in Avizio 9 could be done, thus saving time while also accurately capturing the OM-matrix boundary.

This same process also helped to standardize the OM-pore or matrix-pore boundary greyscale values so that these components in each image could also be more rapidly segmented by Avizio 9. The matrix-pore boundary was less of an issue given that pores typically have a significantly lower greyscale value than matrix material, but the "action" process did aid in reveling pores by exaggerating small greyscale differences. To check if the pores that emerged were truly pores, the SE images were compared to the BSE images in the mosaics because the SE images often showed pores more effectively than the BSE images. The OM-pore boundary proved slightly trickier given that greyscale differences between OM and pores is not nearly as great as greyscale differences between matrix and pores. However this "action" process did aid in defining the more obvious pores by increasing the greyscale differences between these two materials. The process, however, did have the tendency to over exaggerate some pore boundaries and make the pores artificially bigger. To remedy this, segmentation of the pore-OM boundary was done manually with the aid of the SE images. In summary, the presegmentation "action" in Photoshop helped to define the OM-matrix boundary more clearly, and though it created issues with the OM-pore boundaries, hand segmentation of the latter took significantly less time than hand segmenting the OM-matrix boundary would have given that pores were not as common as OM in the samples.



Figure 3: BSE image (left) and the same image (right) after the Photoshop "action" processing. The red circle highlights the editing process' ability to sharpen the OM-matrix boundary.

Image Analysis

After all processing and editing, each mosaics were then uploaded into Avizio 9 software for final processing and segmentation. Images were first subjected to a non-local means filter to smooth gray-scale variations and remove imaging artifacts. Then each mosaic was segmented to identify: detrital OM, migrated OM, matrix, pores in detrital OM, and pores in migrated OM. Detrital OM, which is OM present upon deposition, was identified by shape (typically long elongated masses or large blocky masses) and a lack of matrix crystal terminations into the OM object (Figure 4). Migrated OM was identified based on position (inside of grains, between clay sheets, and inside of fractures) and the presence of crystal terminations protruding in the OM object (Figure 5). The last of these indicates that pore space was present upon deposition and the surrounding crystals grew into this pore space, followed by liquid OM (hydrocarbons) migrating into and filling the remaining space. Another criteria used to distinguish between detrital and migrated OM was a determination of whether the OM appeared to be supporting grains that would have otherwise collapsed together (Figure 4). If the OM was doing so, it was assumed the OM had to be present between grains before compaction and thus was classified as detrital OM. Pores also occur within both types of OM, and those pores were identified as black voids within the dark gray OM. Matrix was identified and segmented based on its high (light) grayscale relative to all other material. Pores within matrix material were initially grouped with migrated OM given that the latter fills the former.

The work flow to segment all objects began with detrital OM being segmented by hand using the "brush" tool, given it was less common than migrated OM in all samples. Migrated OM was then distinguished using similar greyscale values that were used to segment detrital OM. Given the number of migrated OM objects, the thresholding tool was used for that step. At this point, all material other than detrital and migrated were locked and then pores in both types of OM were segmented using the "brush" too. Next, matrix material was segmented based on a range of grayscale values, the lower end of which was chosen to insure no pores would be included. At this point, much of the image had been classified, thus the "watershed" tool was run to automatically in fill all remaining pixels. That tool takes into account greyscale values of adjacent segmented objects and extrapolates each objects extent based on the grayscale values of the intervening and unclassified pixels.



Figure 4: BSE image showing an example of detrital OM exhibiting an elongate shape and a lack of crystal terminations into it. The OM mass also prevented clay matrix from above collapsing onto the

clay matrix below.



Figure 5: Figure 5: BSE image showing dark gray migrated OM. Inside the red circle calcite crystal terminations indicate a once open pore that is now filled with OM that migrated into the space after the crystals grew. In the blue circle, dark gray OM occurs between clay mineral sheets and thus had to migrate into the pores created between those sheets.

V: Sample Characterization:

Core analysis data were provided by the core's owner for twenty seven samples in and immediately surrounding the Lincoln Limestone. That data included mineralogy from x-ray diffraction analysis, total organic carbon (TOC) values, porosities and permeabilities. Based on those data, 12 samples were collected and 7 of those were high-graded for pore network characterization. Those seven were chosen so as to capture the full range of mineralogies, TOC, and porosities in the larger sample data base. Observations made while sampling the core are given in Table 1.

Sample	Depth below	Core Observations
	datum (ft)	
1	4.4	% CO3 less than below; but ample peloids in thin section
2	13.55	% CO3 less than below
3	22.85	fewer thin CO3 lams than below and slightly less gray, but more CO3 than above & below
4	29.65	cross bedded foramifera grainstone – lowest porosity as forams are well cemented
5	33.15	mix of CO3 laminae and grayish marl laminae – CO3 laminae at greatest abundance
6	41.5	mix of CO3 laminae and grayish marl laminae – CO3 laminae at greatest abundance
7	54.8	thin CO3 laminae in grayish marl
8	67.25	thin CO3 laminae in grayish marl
9	78.8	thin CO3 laminae in grayish marl
10	96.8	dark mudstone, few CO3 laminae
11	112.15	darker mudstone, trace of CO3 laminae
12	116.05	dark mudstone with crushed forams

Table 1: Relative depths of the 12 core samples and general core observations noted during sampling. Green highlights the 7 samples high graded for pore imaging.

Lithologic Characterization:

Figures 6 shows the mineralogical variability of the 12 samples. All 12 samples are mudstones, and based on calcite contents, the 7 samples chosen for analysis consist of 1 marly chalk, 4 marls, 1 marly shale, and 1 shale. These samples represent the entire continuum in lithologic variability exhibited by Lincoln Limestone (Figure 7).

The 12 samples show a range of normalized volumes of clay, carbonate and silicates. Carbonate contents range from 6.0% to 70.6%, framework silicates (quartz and feldspars) range from 14.7% to 39.2%, and clays make up anywhere from 17.1% to 55.2% of the sample (Figure 7). Across the seven samples carbonate volume ranges from 6.0% to 70.6%, clay ranges from 14.8% to 55.2%, and silicates range from 14.7% to 38.8% (Figure 7). Clay content increases downward through the Lincoln Limestone and calcite content reaches a maximum at the top of the unit (Figure 6).



Figure 6: Sample number (increasing sample number synchronizes with increasing depth) displayed with corresponding normalized volumes of carbonate (blue) and clay (red) for each of the 12 original samples. Arrows denote the 7 samples chosen for pore imaging. Top of the Lincoln Limestone is supposedly between samples 2 and 3; base of the Lincoln Limestone is below sample 10.



Figure 7: Ternary plot showing the mineralogical heterogeneity of the 12 Lincoln Limestone samples. Red arrows denote the 7 imaged samples.

In order to understand how the various minerals were distributed within each sample, elemental maps of Ca, Si, and Al were constructed using an electron microprobe. The three sets of maps were merged and converted to RGB images. In those images (Figures 8-15), calcite is blue, quartz is red, and all other silicate minerals (clays and feldspars) are varying shades of green, greenish-yellow or light orange depending on their Al and Si contents. The maps reveal that calcite primarily occurs as foraminifera, calcite cements in foraminifera, and peloids. Kaolinite primarily occurs as cement in foraminifera. Quartz is present as silt-sized grains. Matrix materials, by contrast, were observed to include varying amounts of calcite (particularly in samples 4 and 5), detrital guartz and feldspars, plus detrital and presumably some authigenic clays. Clay and framework silicates constituted up to 75% of the field of view in some samples. Overall, marly shale and shale samples have higher amounts of clay matrix material with calcite limited to relatively rare peloids and foraminifera. In contrast, marly chalk and marl have calcite in the matrix alongside clays and appreciable more foraminfera and/or peloids. One imaged sample (#4 in Table 1; Figure 11) is from a laminae of cross-laminated foram grainstone. It has a high calcite content, but nearly all that calcite is present as forams and calcite cement infills the foraminifera shell. The sample with the least carbonate content comes from the Granerous shale immediately below the Lincoln Limestone, and the sample with the second highest calcite content is from the Hartland shale immediately above the Lincoln Limestone. That sample had the greatest abundance of peloids and it is possible that the top of the Lincoln has been misidentified and that sample is actually from the Lincoln.





Figure 8-14. Elemental maps depicting mineralogical attributes of the 7 samples imaged. Figure 8 is from the Hartland Shale above the Lincoln Limestone; Figures 9-13 are from the Lincoln; Figure 14 is from the Graneros shale below the Lincoln Limestone. Blue is calcite, red is quartz, light green is kaolinite, black is pyrite or large OM masses, and all other greens and yellow-orange colors are clay minerals (primarily illite and mixed illite-smectite). Figures 8 and 9 show ovoid bodies of calcite that are peloids, while also showing the high degree of clay matrix material (green and orange, respectively) common in the calcareous mudstone. Figure 10 shows large circular masses of calcite, which are foraminifera (yellow circles). Interiors of forams are typically calcite-cemented, but some are kaolinite cemented (light green). Large quartz grains (red) are also present in the clay matrix (yellowish- orange). Figures 11-13 depict an increasingly more calcite-rich rocks, with the increase in calcite primarily due to an increase in calcite in the matrix rather than an increase in the abundance of peloids. Figure 14, from the Graneros shale, has some calcitic peloids, but the balance of the rock is composed of some quartz silt (red) and an abundance of clay matrix.

Porosity Characterization:

As seen in Figure 15, there is an increase in porosity determined by core analysis with increasing clay content (R^2 =.5798) and a decrease in porosity with increasing calcite content (R^2 =.2056). The seven samples chosen for pore imaging mimic the trends of the original 12 samples.



Figure 15: Relationships between porosity (core analysis) and abundance of clay (red) and carbonate (blue) minerals. Plot A depicts all 12 samples and B shows the 7 samples used for pore imaging.

VI: Results:

The Ar milling of the Graneros sample (#11) did not adequate smooth the samples' surface, which made segmentation difficult. The irregular surface resulted in more material being segmented in the BSE images as porosity than was apparent in the corresponding SE images. This sample is thus not considered in the results.

Porosity Changes with Lithology:

Most original pores within the samples were observed to be infilled with migrated hydrocarbons (Figure 5). The original, pre-migration pore network was thus reconstructed by summing all objects segmented as migrated OM, pores in migrated OM and the few open pores observed into a single category (original porosity). Imaged original porosity in the Lincoln and lowermost Hartland samples ranged from 5.3% to 7.8%, and those values positively covary with carbonate mineral content (Figure 16) with an R² value of 0.32 indicating a moderate correlation. The same porosity values show only a very weak negative covariance against normalized clay volume (R²=.05).



Figure 16: Covariance of imaged original porosity as a function of normalized volumes of carbonate (blue) and clay (red). Mineralogical data is from core analysis of the footages imaged.

Imaged Original Pore Sizes:

Median equivalent circular diameter (ECD) was used as a proxy for pore size. Median ECD values range from 64 to 92 nm, and they increase with increasing carbonate concentrations (Figure 17), although the trend is weak (R^2 =.16). Median ECD values also decrease with increasing clay content on a slightly weaker trend (R^2 =.13).



Figure 17: Plot showing the median ECD (nm), across the samples, as it changes with normalized volumes of carbonate (blue) and clay (red).

Histograms of imaged original pore size displays trends among the sample suite (Figure 18). Overall, the 50-100 nm size range is the most common across all samples (24%-39.5%) with the exception of sample #8, which has equal amounts of pores in the 0-50 and 50-100 bins. The 0-50 nm bin is the second most common range (20.7-36.7%) for all other samples. Variations based on lithology are small with only the marly shale (#10) displaying a slightly greater proportion of original pores in the smaller ECD bin sizes.



Figure 18: Plot displaying the percentage of objects classed as original porosity from each sample that fall into various ECD (nm) bin sizes. The samples are arranged from shallowest (#1) to the left and deepest (#10) to the right. Histogram is color coated based on lithology with dark blue=marly chalk; light blue = marl; red = shaly marl.

Median pore widths were also examined as a metric of pore size. Median widths range from 32 to 71 nm and show a weak covariance with normalized volume of carbonate R^2 =.11 (Figure 19). With increasing normalized volume of clay, median pore width decreases with a similarly weak trend (R^2 =.12, Figure 20).



Figure 19: Median original pore width versus normalized volume of carbonate.



Figure 20: Median original pore width versus increasing normalized volume of clay.

Original Porosity Pore Shape:

The shape of pores is characterized by anisotropy or the ratio of the shortest vector inside a pore to the longest vector normal to the shortest vector. Objects with a lower anisotropy values are more equant or less elongate than objects with larger values.

The Lincoln samples display similar population distributions for pore shape (Figure 21) as they did for ECD values. The .9-1.0 bin is the most common anisotropy size (20.9%-30.992%) while the .8-.9 is the second most common size (18.4%-22.0%). There are no clear trends as a function of lithology other than that the marly shale (#10) displaying a slightly lesser proportion of original pores in the smaller (more equant) bin sizes.

Median anisotropy values do not change much across changing volumes of mineral phases (Figure 22). Median anisotropy is independent of normalized volume of carbonate (R^2 =.00) and only a very weak (R^2 = 0.08) trend emerges between median anisotropy and normalized volume of clay.



Figure 21: Plot displaying the percentage of objects classed as original porosity from each sample that falls into various ECD (nm) bin sizes. The samples are arranged from shallowest (#1) to the left and deepest (#10) to the right. Histogram is color coated based on lithology with dark blue=marly chalk; light blue = marl; red = shaly marl.



Figure 22: Plot displaying the trends of median anisotropy with increasing normalized volumes of clay (red) and carbonate (blue).

TOC Variations with Mineral Phases:

Imaged TOC (detrital OM + migrated OM) ranges from 5.5% to 9.5% of the photomosaics. Allowing for the lesser density of OM relative to minerals, volume of TOC is generally about two times the weight percent. Thus the amount of TOC imaged is approximately 2.8% to 4.8%, which compares well to the weight percentages reported in the core analyses. Imaged TOC displays a positive covariance with abundance of carbonate (R^2 =.15), but no trend with respect volume of clay (Figure 23). The sample with the lowest TOC value (#4) is the sample of cross-laminated foraminifera grainstone.



Figure 23: Imaged TOC values for the 6 samples in relation to normalized volumes of clay (red) and carbonate (blue).

VI: Discussion:

A limitation of this study is that it characterizes the original 3-D pore network by 2-D image analysis, and as a result, it cannot explain the interconnected nature of the original pore system. Nonetheless, the data do address the research question, namely how does the pore network of the Lincoln Limestone relate to lithology.

Lithologic Impacts on Porosity:

Figure 15 shows that the porosity obtained by lab analysis of the core samples decreases with increasing calcium content, yet Figure 16 indicates the imaged original pore network increases in abundance with increasing carbonate content. One reason behind this reversal of trend likely comes from the overall small scale of this study. A single mosaic analyzed for each sample (about 0.025 mm2) represents only a fraction of the material that would have been analyzed in the core analysis (about 6.5 cm3). As a result, even though the imaged material was chosen based on it representing the entire sample, it's still likely that the chosen field of view was no longer an accurate representation of the entire sample. A second possible factor is foraminifera, which are typical calcite cemented (Figure 30). They thus represent a lot of calcite, but no porosity. This is evidenced in sample 4, which has abundant laminae of foram but with a core porosity of only 5%. This study avoided foraminifera-rich areas when collecting images; rather the effort was to collect images of pores, thus the focus was on the porous calcite, thus the trend of increasing porosity with increasing normalized volume of carbonate. Further mosaic generation and analysis would likely help to alleviate both of the potential reasons for a different trend in imaged porosity relative to percent calcite.

Imaged original porosity values are also systematically less than those measured by core analysis, typically by 2% to 3%. There are a number of possible reasons for this discrepancy. First, the values of imaged original porosity do not include pores within the detrital organic matter, yet those pores would be included in laboratory porosity analysis. Another reason for the difference in imaged and core analysis porosities would be pores that are too small to be resolved at even 10,000X magnification (referred to as sub-nano pores). These pores would be associated with clays and organic matter and would be detectable in laboratory porosity. Their presence might explain why core porosities increase with clay content yet imaged porosity did not.

Pore Size Implications to Fluid Flow:

Pore width for a 2-D image serves as a proxy for 3-D pore throat diameters (Ball, 2015). Hydrocarbons structures can range from .3-.4 nm, in the case of paraffins and asphaltines, and up to 1000 nm for the most complicated structures (aggregated asphaltines, kerogen particles, oil-in-water emulsions and colloidal oil; Momper, 1978). The smaller of these individual molecules could easily fit within the pore sizes captured in this study. However, the larger complex hydrocarbons compounds would not be able to pass through much of the pore system. As hydrocarbon structures grow bigger they require larger pore throats in order to accommodate movement. Given the trends observed for pore width against normalized volume of carbonate and clay (Figure 19 and Figure 20, respectfully) it should be expected that more clay rich layers in the Lincoln should expect less hydrocarbon flow. This is not to say that clay sample should expect overall less porosity but rather that it should expect less hydrocarbon flow through original porosity structures given that these pore widths (throats) are observed to decrease with increasing clay content. The opposite is true for the more carbonate rich layers in the Lincoln. Given the increasing median pore width more calcite rich layers should expect to see greater hydrocarbon flow.

Crystalline Effects on Pore Attributes:

The relationship between pore morphologies - pore shapes and sizes – and the crystal form of the minerals associated with the pores could be a possible reason for the pore width, size, and anisotropy trends observed. The original pores associated with clays can be classed into three distinct morphologies: "sheets" associated with compacted and aligned clays (Figure 24), a "lacy" structure associated with diagenetic illite and/or mixed layer illite-smectite filling originally larger pores within the clay matrices (Figure 25), and "booklets" associated with kaolinite cements within foraminifera shells (Figure 26). Pore morphologies associated with calcite minerals all relate to how rhombic crystals of calcite pack. They form a spectrum ranging from an open network of polyhedral pores where calcite crystals begin to fuse together (Figure 5, red circle), to isolated small tetrahedral pores where calcite crystals have become an interlocking mass (Figure 28). In the latter case, the calcite masses have only isolated pores within them that display very narrow pore widths and are typically isolated from other original porosity objects. In the extreme case, calcite cement crystals can completely grow into each other and interlock, leaving no pore space. This is the typical case within whole foraminifera (Figure 30) that this study opted to avoid.

The clay-related pore morphologies were rarely observed to connect during image analysis. The booklet and sheet morphologies in particular were isolated. With increasing clay content numerous original porosity objects would be created and as a result higher overall porosity with increasing clay content would seem logical. However, given the small pore size associated with these morphologies it logical that as more of them appear, with increasing clay content, pore widths and ECD values would decrease in comparisons to more carbonate-rich samples.

In contrast, the polyhedral and tetrahedral pores related to calcite crystals were common in most samples, particularly characterizing the peloids composed of 100% calcite (e.g., Figures 8, 9, 11, and 12). Unlike the clay structures, these calcite-related pore morphologies exhibit large pore widths and sizes, and less anisotropy. The nature of these morphologies may also help explain the decreasing porosity with increasing carbonate trend found in core analysis. This trend might be the result of large polyhedral pores being uncommon as they tended to be associated with crushed foraminifera. Intact and cement-infilled foraminifera are much more common but tend to be associated with few pores that are largely isolated from the overall pore network (Figure 29). The core analysis would then show a decrease in porosity with increasing calcite content if increasing calcite content is a result of increasing foraminifera. Imaged data would be biased by the focus on peloid and crushed foraminifera pores and this would result in the increasing porosity with increasing calcite content observed.



Figure 24: Sheet structure example. Blue circle highlights the extact location within the image of the sheet structures.



Figure 25: "Lacy" pore structure (blue circle) produced by diagenetic illite or mixed-layer illite-smectite filling larger original pore spaces. The morphology of the clays – ribbon-like flakes is inferred to indicate illite, rather than smectite.



Figure 26: Booklet pore structure formed within masses of diagenetic kaolinite cement formed with the shell of a foraminifera.



Figure 27: Large polyhedral pores (arrows) within a peloid dominated by a crushed formaninfera, but also containing calcite rhombs probably related to cocolith debris.



Figure 28: Isolated, small, and unconnected tetrahedral pores (blue circles) associated with a fused calcite mass. Note also lacy and sheet pores in lower left associated with clay minerals and clays in a tetrahedral pore (arrow) creating a mixed pore morphology.



Figure 29: Foraminifera grain whose original intrashell pore where the animal lived is completely infilled with calcite cement. There is no porosity associated with any of this large amount of calcite.

None of the Lincoln Limestone samples, however, are composed exclusively of the clay-related or calcite-related pore morphologies. All samples are mixtures of all types of morphologies (e.g., Figure 28). For this reason median ECD and widths show only weak trends with mineralogical content graphed as similar to clay widths is the result of the other carbonate structure calcite chunks.

Lincoln-Niobrara Analogue:

The Niobrara's carbonate content is related only to calcite-rich peloids that support increasing porosity as calcium (i.e., peloid) content increases (Ball, 2015). The Lincoln is the opposite of this with lower porosity associated with increasing carbonate content due to calcite-cemented foraminifera which support few and mostly isolated pores. The Lincoln does contain both peloids and foraminifera but the relative proportion of foraminifera relative to peloids is much higher in the Lincoln than in the Niobrara Formation.

Published images of clay-related pores in the Niobrara also are dominantly of a sheetmorphology. The Lincoln, however, also includes clay-related pores with lacy and booklet morphologies; pores formed by authigenic clays. The presence of these authigenic clay-related morphologies may explain favorable porosities in more clay rich intervals in the Lincoln, but the pore network in those intervals would still be largely isolated and with narrow widths as clay volume increases.

VII: Conclusions:

The pore network of the Lincoln Limestone, a member of the Greenhorn Formation in the Denver-Julesburg Basin, was imaged and analyzed at the nanometer scale using Ar-milled surfaces and scanning electron microscopy. This effort was to expand upon our understanding of the role lithology plays in the original pore system of the Lincoln Limestone. The findings of this study are summed up in five points:

1: Total original porosity has a slightly increasing trend with increased volume of carbonate and a slightly decreasing trend with increased volume of clay. This is opposite of what core analysis data suggests and is likely the result of a sampling strategy designed to limit over analysis of foraminifera in order to characterize the pore system in the Lincoln Limestone. This strategy, however, resulted in an unrepresentative analysis of calcite-rich areas as porous because the non-porous calcite associated with foraminifera was undersampled. That in turn yield artificially high porosity values in the imaged data and the trend stated earlier.

2: Pore widths, which act as a proxy for pore throats, decrease with increasing volume of clay and increase with increasing volume of calcite. This comes from clay pores being small and largely isolated due to the morphology of pores associated with clays. Pore sizes and widths increase with increasing volume of carbonate largely due to carbonate crystals yielding well connected polyhedral and tetrahedral pores that are morphologically larger than the sheet, lacy, and bookletpore morphologies associated with clays.

3: Equivalent circular diameters (ECD) and anisotropy of pores correlate, with varying significance to volumes of carbonate and clay. Median ECD decreased with increasing volume of clay and increased with increasing volume of carbonate. This is due to the fact that pore morphologies associated with clay minerals are in fact smaller than morphologies associated with calcite. Median anisotropy had no trend with increasing volume of carbonate, but a weak covariance with increasing volume of clay. The anisotropy trend with respect to clay probably reflects compaction and the formation of sheet pores, but the trend is weak since sheet pores are not the only type of clay-related pores. The lack of an anisotropy trend with respect to calcite probably reflects the fact that calcite crystals grow and form polyhedral and tetrahedral pores with no directional preference. That process is not influenced by compaction.

4: The pore networks in the Lincoln Limestone are not similar unit to the Niobrara Formation. The carbonate in the Lincoln occurs in association with both peloids and foraminifera but more commonly in low porosity, calcite-cemented, foraminifera that produces poor pore networks in high calcite zones. Clay in the Niobrara is dominated by sheet-morphology while the Lincoln includes this same morphology in addition to lacy and booklet morphologies formed by authigenic clays. These autigenic morphologies provide favorable porosities but produce isolated pores through the Lincoln.

5: The best pore networks in the Lincoln Limestone would likely be in footages with moderate clay and carbonate volumes so as to avoid the small pore throat sizes associated with high clay volumes and the poorer pore networks associated with high carbonate (high foraminifera) zones. The top of the unit and lowermost part of the Hartland shale, where porous peloids become more common, might be the best reservoir zone. This inference suggests further analysis of the overlying Hartland Shale is warranted. If it is peloid-rich as the the two samples analyzed in this study suggest, its pore systems may be more analogous to the Niobrara Formation.

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