Microstructural imaging and characterization of oil shale before and after pyrolysis

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HIGHLIGHTS

- Green River (Mahogany Zone) oil shale is visualized and quantified in 2-D and 3-D.
- The impact of temperature on oil shale pore growth is studied from 300 to 500 °C.
- 3-D visualization of the pore space in organic-rich and organic-lean regions.
- Quantified the representative sample size at which porosity remains constant.

GRAPHICAL ABSTRACT

3-D representation of the pore space following pyrolysis of oil shale.

ABSTRACT

The microstructural evaluation of oil shale is challenging which demands the use of several complementary methods. In particular, an improved insight into the pore network structure and connectivity before, during, and after oil shale pyrolysis is critical to understanding hydrocarbon flow behavior and enhancing recovery. In this experimental study, bulk analyses are combined with traditional and advanced imaging methods to comprehensively characterize the internal microstructure and chemical composition of the world’s richest oil shale deposit, the Green River Formation (Mahogany Zone). Image analysis in two dimensions (2-D) using optical and scanning electron microscopy (SEM), and in three dimensions (3-D) using X-ray microtomography (μCT) reveals a complex and variable fine-grained microstructure dominated by organic-rich parallel laminations of the order of 10 μm thick which are tightly bound in a highly calcareous and heterogeneous mineral matrix. We also report the results of a detailed μCT study of the Mahogany oil shale with increasing pyrolysis temperature (300–500 °C) at 12 μm and 2 μm voxel sizes. The physical transformation of the internal microstructure and evolution of pore space during the thermal conversion of kerogen in oil shale to produce hydrocarbon products was characterized. The 3-D volumes of pyrolyzed oil shale were reconstructed and image processed to visualize and quantify the volume and connectivity of the pore space. The results show a significant increase in anisotropic porosity associated with pyrolysis between 400 and 500 °C with the formation of micro-scale connected pore channels developing principally along the kerogen-rich lamellar structures. Given the complexity and heterogeneity of oil shale, we also characterize the representative size at which porosity remains constant. Our results provide a direct observation of pore and microfracture development during oil shale pyrolysis.
1. Introduction

The increasing global demand for liquid fuels has driven unconventional petroleum resources to play an important role in the world’s energy portfolio [1]. Oil shale, an organic-rich fine grained impermeable sedimentary rock represents a large and mostly untapped unconventional hydrocarbon resource with many known deposits across the world [2–4]. The lacustrine Eocene Green River Formation, located in Colorado, Utah, and Wyoming, is the largest known oil shale deposit in the world with an estimated 4.3 trillion barrels of oil originally in place [5]. In the context of petroleum systems, organic-rich rocks have traditionally been considered as non-reservoirs, often fulfilling the critical role as source rocks for hydrocarbon accumulations. However, the potential for oil shale as a direct hydrocarbon resource has been realized, creating an emphasis on effectively releasing this fuel [6–9]. Oil shale consists of highly cross-linked macromolecular organic material in the form of kerogen, a complex structure of carbon, hydrogen, and oxygen with lesser amounts of sulfur and nitrogen that is essentially insoluble in organic solvents or aqueous solutions [10,11]. To convert kerogen that has not thermally matured beyond the diagenesis stage into shale oil and combustible gas, it must be heated, in the absence of oxygen (pyrolysis), to high temperatures 300–500 °C where chemical bonds are broken yielding lighter hydrocarbon molecules [7,12]. Oil shale can either be mined and retorted under anaerobic conditions in large processing facilities at temperatures near 500 °C for times on the order of an hour, or processed in place using downhole heaters at 300–350 °C from days to months [13–17].

Oil shale pyrolysis process involves complex physical and chemical reactions [18–21]. Many experimental studies have been conducted on oil shale pyrolysis to better understand the effect of fundamental parameters on shale oil yield and quality to enhance the reaction conditions. This includes composition of source material [22,23], pyrolysis temperature [24–26], heating rate [25–28], residence time for pyrolysis reaction [29,30], particle size [31–33], mineral matrix [34,35] and composition of pyrolysis atmosphere [36,37]. Pyrolysis under vacuum conditions has been shown to improve both oil yield and quality compared to pyrolysis under atmospheric pressure [38–41]. Vacuum pressures accelerate the transport of pyrolysis products by providing faster escape of primary oil from the reaction zone, therefore reducing the occurrence of secondary cracking reactions [39,41].

As our understanding of the physical and microstructural properties of oil shale rocks continues to be enriched, it has become clear that these rocks comprise compositional and structural heterogeneity; especially at small length scales. These heterogeneities include variations in mineralogy, organic matter distribution, and pore properties, which makes the characterization of physical parameters of oil shale challenging. In particular, there are key questions related to the structure and connectivity of the pore space during oil shale pyrolysis which directly impact hydrocarbon flow behavior through the pore channels and ultimate recovery. Therefore, it is important to comprehensively explore and quantify the evolution of the pore space with increasing pyrolysis temperature. Previous experimental studies have used nitrogen adsorption-desorption isotherms to estimate the pore properties of Green River (Western USA) [42], New Albany (Eastern US) [43] and Huadian (China) oil shales [44–47].

A broad range of imaging methods can also be used to quantify pore structure. Traditional optical and scanning electron microscopy (SEM) can only reveal the surface or two dimensional (2-D) morphology, rather than internal microstructures [48–53]. The development of pores and microfractures during the process of oil shale pyrolysis needs to be assessed in three dimensions (3-D) due to the heterogeneous internal architecture. There are several techniques available for quantitatively characterizing the 3-D microstructure of oil shales including serial sectioning which involves obtaining a series of scanning electron or optical micrographs and then computationally assembling these digital images [54,55]. Although such a method enables the measurement of connectivity and other structural properties such as pore volume and surface area, once sectioned, this destructive process means that the sample is no longer available for other static or dynamic analyses. In addition to being destructive, this technique is time-consuming and may damage the sample during preparation.

X-ray micro-computed tomography (μCT) has emerged as a powerful tool for the visualization and quantification of the internal structure of geological materials, in particular being effective at studying complex pore-scale processes [56–68]. μCT offers several advantages: it is non-destructive, provides 3-D imaging, achieves high spatial resolutions at scales down to the micron level, gives good contrast between phases, and is adaptable to many types of experimental procedures. In the case of oil shales, a 3-D approach allows us to obtain important information on the spatial distribution of organic matter and inorganic minerals to monitor the evolution of the pore space during pyrolysis. Quantitative analysis can provide useful insights into the mechanical and transport behaviors during the oil shale pyrolysis process by characterizing component volume fractions and fundamental pore space geometric attributes, including pore size, shape, tortuosity and connectivity. μCT has been applied to characterize oil shale samples from the United States [69], China [70] and Australia (Queensland) [71]. Tiwari et al. [69] characterized pore structures before and after pyrolysis based on 42 μm voxel size scans reporting pores as large as 500 μm after pyrolysis. More recently, dynamic imaging of oil shale pyrolysis using a synchrotron X-ray tomography was conducted on a Green River (Mahogany Zone) oil shale sample presenting a direct visualization of the temporal evolution of the pore space during pyrolysis [72]. This paper reported microscale disconnected pores at 390 °C; with porosity increasing dramatically between 390 °C and 400 °C where the vast majority of the pore space became connected.

In this study, we complement our previous work [72] by initially characterizing the bulk properties of the Mahogany oil shale followed by an evaluation of the microstructure in 2-D using optical and SEM methods and in 3-D using static μCT to reveal the compositional and structural heterogeneity. We then apply vacuum pyrolysis conditions to visualize and quantify the pore structure development using μCT at 12 μm and 2 μm voxel sizes at temperatures representative of surface retorting technologies (300–500 °C). The representative sample size was also characterized using porosity as the target parameter.

2. Sample characterization

2.1. Oil shale samples

Oil shale samples were obtained from an outcrop of the organic-rich Mahogany zone of the Green River Formation (Uinta Basin,
The stratigraphy, geochemistry, mineralogy and hydrocarbon potential of the Green River Formation has been extensively studied [4,5,73–78]. The richest oil shale horizon is the Mahogany zone (R-7) which is a primary target for shale oil production due to its high oil yield which can exceed 250 L per tonne of rock recovered as liquid fuel by pyrolysis [79]. To initially characterize the Mahogany oil shale, samples were prepared and analyzed to characterize bulk properties including mineralogy (XRD), total organic carbon (TOC), thermal maturity (Rock-Eval and Source Rock Analyzer (SRA)), elemental analysis (CHNOS) and oil yield (Modified Fischer Assay (MFA)). However, given the complexity and heterogeneity of oil shale, samples were also cut and prepared for petrographic analysis, SEM-EDX and μCT image characterization. These imaging techniques offer local information on the spatial distribution of organic material, mineral phases and pore structures. With these bulk analytical techniques and imaging methods, a full characterization of oil shales can be achieved to better understand the internal microstructure and chemical composition which allows for improved modeling and prediction of fluid flow during oil shale pyrolysis.

2.2. Oil shale composition analysis

2.2.1. X-ray diffraction (XRD)

X-ray diffraction (XRD) is a laboratory-based analytical technique for identifying minerals and other crystalline phases in a wide range of materials, including oil shale samples [80–82]. In this work, the oil shale rock sample was first disaggregated gently using a pestle and mortar. A 2 g split of this material was then micronized using a McCrone Micronizing Mill to obtain a powder with a mean particle diameter of between 5 and 10 μm. The fine powder was then backpacked into an aluminum cavity mount producing a randomly orientated sample suitable for XRD. Samples were analyzed using a Bruker D8 Advance X-ray diffractometer with scattering angles, 2θ, between 5° and 75° with a step size of 0.05°/s using CuKα radiation (λ = 1.54 Å) at a tube voltage of 35 kV and a current of 30 mA. Quantitative identification of the minerals in the oil shale sample was achieved using the full pattern analysis technique known as the Rietveld method [83] using the Inorganic Crystal Structure Database (ICSD) [84].

XRD analysis of oil shale from the Green River Formation (Mahogany Zone) reveals a complex mineral signature. The dominant mineral phases were dolomite, calcite, quartz, and feldspars with small amounts of illite, analcime and pyrite (Fig. 1 and Table 1). Although kerogen is the most important component of oil shale, it cannot be detected by direct XRD analysis. However, XRD results provide valuable information in characterizing bulk oil shale mineralogy with previous studies establishing that minerals in oil shale can have both catalytic and inhibitory effects on pyrolysis reactions [34,35].

![Fig. 1. XRD pattern (diffractogram) for the Green River oil shale sample (Mahogany Zone) with characteristic mineral peaks identified.](image-url)

Table 1

| Mineralogy by XRD         |            |
|---------------------------|------------|
| Dolomite (wt%)            | 39.0       |
| Calcite (wt%)             | 18.0       |
| Quartz (wt%)              | 14.2       |
| Plagioclase (wt%)         | 13.6       |
| Illite (wt%)              | 10.7       |
| K-Feldspar (wt%)          | 2.7        |
| Analcime (wt%)            | 1.8        |
| Pyrite (wt%)              | 1.2        |

| LECO Carbon Analyzer     |            |
|--------------------------|------------|
| TOC (wt%)                | 30.15      |

| Rock-Eval SRA            |            |
|--------------------------|------------|
| S1 (mg HC/g rock)        | 6.09       |
| S2 (mg HC/g rock)        | 210.27     |
| S3 (mg HC/g rock)        | 1.44       |
| Tmax (°C)                | 437        |
| HI (mg HC/g rock)        | 697.41     |
| OI (mg HC/g rock)        | 4.78       |
| PI (mg HC/g rock)        | 0.03       |

| Elemental Analysis (Kerogen Isolate) | |
|--------------------------------------|---------|
| Carbon (wt%)                        | 65.22   |
| Hydrogen (wt%)                      | 8.79    |
| Nitrogen (wt%)                      | 2.33    |
| Oxygen (wt%)                        | 19.86   |
| Iron (wt%)                          | 0.12    |
| Sulfur_total (wt%)                  | 0.87    |
| Sulfur_organic (wt%)                | 0.73    |
| Sulfur_pyrite (wt%)                 | 0.14    |
| H/C (molar)                         | 1.62    |
| O/C (molar)                         | 0.23    |

![Fig. 2. Modified Fisher Assay (MFA) results for the Green River oil shale sample (Mahogany Zone) including mineral decomposition and organic products, oil density, and oil yield.](image-url)

Fig. 2. Modified Fisher Assay (MFA) results for the Green River oil shale sample (Mahogany Zone) including mineral decomposition and organic products, oil density, and oil yield. The clean oil density represents the density of the oil recovered as liquid in the receiver following the test. The oil yield represents the amount of potentially extractable shale oil present in the sample as determined the MFA method.
2.3. Total organic carbon (TOC)

The oil shale sample was ground, homogenized and sieved to 60 mesh (<250 μm). 100 mg of the crushed sample was then treated for two hours with concentrated hydrochloric acid to remove carbonate minerals. The acid was removed from the sample with a filtration apparatus fitted with a glass microfiber filter paper. The filter was placed in a LECO crucible and dried at 110 °C for one hour. After drying, the sample was analyzed with a LECO 744 Carbon Analyzer with detection limits to 0.01 wt%. The result reveals a TOC of 30.15% for the Mahogany zone oil shale indicating an organic-rich sedimentary rock.

2.4. Programmed pyrolysis (Rock-Eval, Source Rock Analyzer)

Programmed pyrolysis (Rock-Eval II and SRA) was performed to assess source rock quality and thermal maturity. A 100 mg crushed rock sample was heated in an inert environment to obtain the parameters S1, S2, S3, T_max, hydrogen index (HI), oxygen index (OI) and production index (PI). Sample heating at 300 °C for 3 min produced the S1 peak by vaporizing the free (unbound) hydrocarbons. The temperature was then increased by 25 °C/minute to 600 °C and the S2 and S3 peaks were measured from the pyrolytic degradation of the kerogen in the sample. The S2 peak is proportional to the amount of hydrogen-rich kerogen in the oil shale rock, and the S3 peak measures the amount of carbon dioxide released (to 390 °C) providing an assessment of the oxygen content of the rock. The temperature at which the S2 peak reaches a maximum, T_max, is a measure of the source rock maturity. The pyrolysis data indicates a type I kerogen and the results obtained from the Rock-Eval II instrument showed good agreement with the results obtained from the SRA method.

2.5. Elemental analysis

Kerogen was isolated from the raw oil shale using a standard hydrochloric and hydrofluoric acid treatment which is effective in removing carbonate and silicate minerals. The remaining material contained primarily kerogen as well as pyrite (FeS₂) which is
particularly resistant to these methods. Carbon, hydrogen and nitrogen were determined using a Flash EA 1112 Series Analyzer according to ASTM D5291. Oxygen was determined using a Leco RO-478 Oxygen Analyzer with the method described in ASTM D5622. Sulfur and iron contents were determined by analysis on a Perkin Elmer DV 5300 ICP-AES following a modified EPA 200.7 method for ICP-AES analysis. Iron in isolated kerogen is considered to exist entirely as pyrite and the pyrite sulfur content can be determined given the stoichiometric relationship between the sulfur and iron contents of pyrite ($S_{\text{pyrite}}/Fe_{\text{pyrite}} = 1.148$). The organic sulfur content is then calculated by subtracting the pyrite sulfur from the total sulfur (Table 1).

### 2.6. Modified Fisher Assay (MFA)

A Modified Fischer Assay (MFA) method was used to measure the potential oil yield from the Mahogany oil shale sample outlined in ASTMD3904. A 100 g of 8 mesh (<2.38 mm) oil shale was heated in an aluminum retort to 500 °C at 12 °C/min and held at this temperature for 40 min. The evolved hydrocarbons were passed...
through a condenser system and analyzed. The quantity of oil was measured directly and the gas fraction was analyzed by gas chromatography. The MFA results are summarized in Fig. 2.

### 3. Visualization using optical microscopy

Petrographic analyses provide a starting point to digitally characterize the mineral composition, texture and the fine-grained structure of shale rocks. In this study, geological thin sections from Green River Formation were prepared perpendicular to the laminations. The oil shale samples were air dried followed by epoxy vacuum impregnation. The samples were then hand lapped and polished using progressively finer alumina suspension (1 μm, 0.3 μm and 0.05 μm) alongside a high-purity hydrocarbon lubricant. Thin sections of 20 μm thickness were optically examined using a Zeiss SteREO Discovery.V12 microscope with accompanying AxioVision LE64 software (Carl Zeiss, Germany) using plane-polarized light (PPL). A mosaic photomicrograph was created by the automated stitching of 1152 individual images at 100× magnification (Fig. 3).

Green River Mahogany Zone oil shale thin sections examined by optical microscopy reveal a fabric that is well-defined by micro-laminations, Fig. 4. The laminations are due to an alternation of layers rich and lean in organic matter. The organic rich layers appear as dark brown under transmitted light whilst the organic lean regions appear lighter and are dominated by inorganic minerals. The organic-rich laminae, primarily in the form of kerogen, are of the order of 10 μm thick, alternating with thicker layers of predominantly carbonate minerals in the form of dolomite and calcite. The fine kerogen laminae are both continuous and discontinuous laterally with the occasional presence of wavy laminations. This bipartite rhythmic structure, referred to as varves, is related to the seasonal changes in organic productivity and is one of the characteristic features of lacustrine sediments [74,85–87]. With optical microscopy, a useful initial visualization of the microstructure can be acquired to examine and explore minerals and microscopic features in 2-D. However, with traditional optical petrography, the resolution is limited to approximately 0.23 μm (diffraction barrier of visible light) which prevents the fine grain characteristics and nano-scale pores of oil shales from being characterized.

| Table 2 | Oil shale μCT acquisition settings. |
|---------|------------------------------------|
|         | μ-CT scan at 10 μm voxel size | μ-CT scan at 2 μm voxel size |
| X-ray source Energy (keV) | 80 | 60 |
| Power (W) | 7 | 5 |
| Optical Magnification | 0.4× | 4× |
| Number of Projections | 1601 | 2001 |

Fig. 7. (A) Raw 2-D gray scale image at a 2 μm voxel size, (B) Non-local means filtered 2D gray scale image, (C) Segmented image with pore space shown in blue (D) 3-D volume rendered image the pore space shown in blue and the matrix in gray, (E) Histogram of the tomography data showing the number of voxels with a particular gray value. A clear separation is observed in the histogram peaks corresponding to the pore space and the rest of the solid phase.
4. Visualization using scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was performed on the Mahogany oil shale samples to obtain 2-D high resolution images down to several nanometers and to achieve better contrast between the pore and solid phases. SEM coupled with Energy-dispersive X-ray spectroscopy (EDX) was also used to acquire a localized chemical analysis. SEM-EDX data was collected using a Zeiss EVO MA 10 with a Bruker XFlash Silicon Drift Detector. Images were captured under a backscattered electron detection mode (BSE) with an accelerating voltage of 20 kV and working distances of 10–11 mm. The samples were imaged at a range of magnifications to characterize the morphology of the oil shale rock fabric and the distribution of minerals and organic material. BSE imaging allows for compositional contrast to be recorded as BSE intensity which is a function of the mean atomic number of the specimen volume that interacts with the electron beam. Compounds with a low mean atomic number such as organic matter appears dark (black), and minerals with a high mean atomic number such as pyrite appear light (white) in standard grayscale digital images. Although the BSE intensity of organic matter is very low, void spaces, such as pores and fractures, exhibit even lower BSE intensity, allowing for pore identification in BSE images of shales.

Backscattered scanning electron microscopy (BSE) of the Mahogany Zone oil shale sample reveals the structure and distribution of organic matter, inorganic minerals and porosity at the micron to nano-scale. The sample is characterized by alternating horizontal organic-rich layers and inorganic minerals (Fig. 5A, B and F). The image contrast (grayscale variation) reflects compositional variations (mean atomic number) of the sample. Domains of darker gray

![Figure 8](image.png)

Fig. 8. 2-D gray scale images following reconstruction of the μCT 12 μm voxel size dataset for (a) raw oil shale, (b) pyrolyzed oil shale at 500 °C, (c) Segmented image with pore space shown in white. (d) The porosity profile per slice. The gray scale level indicates variations in the X-ray attenuation coefficients which depend on the density and atomic number of the material within each voxel. Pores and microfractures are observed in the kerogen-rich laminations.
levels represent organic matter (verified by EDS analysis), primarily as kerogen with a predominantly amorphous structure. The brighter gray level reflects higher density carbonate phases, and the brightest gray level represents pyrite. Microgranular dolomite and calcite are the predominant minerals in the oil shale samples, mostly with characteristic rhombohedral structures and relatively equidimensional grains ranging in diameter from about 1 μm up to 30 μm (Fig. 5C and D). Authigenic clay minerals in the form of illite-mica are commonly present as a matrix constituent between the kerogen laminations and inorganic minerals, occurring as exceedingly fine-grained lathlike flakes. The high resolution BSE images reveal isolated nano-scale pores which are not accessible by mercury porosimetry even at high pressures (Fig. 5E). Pores identified in raw Mahogany oil shale include: intra-organic pores, referring to organic matter bounded pores; organic interface pores, referring to pores at the interface of organic matter and minerals; intra-mineral pores, referring to pores fully bounded within mineral grains, and inter-mineral pores, referring to pores lying between inorganic minerals. Although substantial information on the 2-D microstructure and chemical composition of oil shale can be acquired using SEM-EDX, a complementary imaging method to examine the nature of the 3-D microstructure is required to better predict oil shale pyrolysis processes.

5. Visualization and quantification using X-ray microtomography

5.1. Pyrolysis of oil shale samples

Core samples of size 10 mm diameter by 70 mm length and 2 mm by 2 mm were selected from the same bulk Mahogany oil...
Shale rock. The samples were loaded into borosilicate glass tubes allowing for vertical and radial expansion and placed under vacuum pressure at 0.1 kPa absolute. Isothermal experiments at 300, 350, 400, 450 and 500 °C were conducted using a heating rate of 10 °C/min to achieve the reaction temperature, where the cores were held for one hour. A thermocouple measured sample temperature and a proportional integral differential (PID) controller regulated the temperature to ±1 °C. Following pyrolysis at each temperature stage, the samples were cooled to ambient temperature, removed from the furnace and subjected to micro-CT analysis. Photographs of the raw oil shale and pyrolyzed samples from isothermal pyrolysis are shown in Fig. 6.

5.2. X-ray microtomography

A Zeiss Versa XRM-500 X-ray Microscope was used to image the Mahogany oil shale samples. The samples were mounted on a rotary stage, irradiated by a micro-focus polychromatic X-ray source and imaged in transmission onto a detector. The X-rays transmitted through the sample hit the scintillator crystals to give off visible light, which is then focused by the optical objective lens and converted into a digital image by the visible light charge-coupled device (CCD). A series of images (projections) are taken at incrementally spaced angles over 360° as the sample is rotated. The μCT acquisition settings at 12 μm and 2 μm voxel sizes are shown in Table 2.

5.3. Image visualization and processing

The tomograms were reconstructed using proprietary software provided by Zeiss and image processed using the Avizo 9.0 program (FEI, Visualization Sciences Group) and MATLAB (MathWorks). Multiple tomograms recorded at different locations along the vertical axis were reconstructed separately and the volumes stitched together. The total image size for the 12 μm and 2 μm scans was 727 × 754 × 7212 voxels and 1080 × 1131 × 5736 voxels respectively. The images (16-bit unsigned) were represented using unsigned gray scale value integers in the range 0–65,535. The gray scale values for each voxel correspond to X-ray attenuation, which varies as a function of density and atomic number. The less dense organic-rich material is shown as the darker colored regions, while the denser mineral-rich matrix appears lighter. The images were processed using a non-local means edge preserving filter [88,89] and segmented to generate a binarized representation of the pore space. In this study we used Otsu’s thresholding method [90], where the between-class variance (BCV) is defined, and the gray level at the BCV maximum determines the optimal threshold. It is an attractive method due to its simplicity in computation for bilevel thresholding. For this dataset, Otsu’s method is applicable as upon pyrolysis the pore space in the oil shale sample can be separated from the rest of the solid phase as observed by the distinct peaks in the histogram of gray scale values (Fig. 7E).

5.4. 12 μm 3-D μCT analysis

Fig. 8A displays a 2-D image of a 3-D reconstructed gray scale image acquired at a 12 μm voxel size, with the gray scale values for each pixel corresponding to X-ray attenuation which varies as a function of density and atomic number. The less dense kerogen-rich layers are displayed as the darker colored regions, while the denser mineral-rich layers appear lighter. The μCT image...
acquired reveals the spatial variation in organic content and the compositional and structural heterogeneity in oil shale of the Green River Formation. These results further validate results obtained from optical microscopy, which showed different minerals distributed in very thin and parallel laminae (Figs. 4 and 5). Fig. 8B reveals the pore space that evolved following pyrolysis at 500 °C with Fig. 8C depicting the spatial distribution of porosity (white) within the sample in the remaining solid phase (black) following binary segmentation. Micro-fracture networks developed during the pyrolysis process are evident and can be well defined. Large anisotropic micro-fractures are developed inside the kerogen-rich lamellar structures.

The computed porosity per slice is shown in Fig. 8D revealing a significant variation in porosity across the sample. These increased porosities constitute essentially the combined spaces represented predominantly by the loss of the organic matter. The internal vapor pressure of isolated pores increases to an extent that the mechanical strength of the sample is exceeded. From 20 °C to 500 °C the oil shale sample experienced thermal expansion. Before pyrolysis, the distance between the top and bottom surfaces of the core was 5947 voxels or 71.36 mm. After pyrolysis, the distance between the top and bottom surfaces increased to 7212 voxels or 86.54 mm due to the development of pores during pyrolysis. This increase of 15.18 mm corresponds to a 21.27% increase in length. The expansion observed is due to the transformation of kerogen to oil and gas where during oil shale pyrolysis, the oil vaporizes and along with the gas supplies the driving force for structural expansion. The increase corresponds well with a previous study onto the linear expansion of oil shale cores by Duvall et al. in which they achieved an increase of nearly 20% for their richest sample [91].

Quantifying the representative sample size is essential for up-scaling the image analysis results to larger scales. We examined the representative elementary volume (REV), defined here as the minimum averaging volume over which porosity remains constant. For examining laterally laminated oil shale samples, the REV is principally dependent on the vertical thickness where there is variation in organic material and mineral matter distribution. We therefore, in this study, restrict the concept of the REV to a representative elementary thickness (RET). RET analysis was conducted on the segmented 3-D image (Fig. 9A) for vertical thicknesses of 0.01, 1, 2.5, 5, 7.5, 10, 20 and 50 mm using porosity as the parameter of interest due its implication on hydrocarbon flow during oil shale pyrolysis. The analysis involved taking a sampling volume x thickness, moving up by 1 slice up to slice n, with each slice representing one voxel of 12 μm and computing the moving average porosity for each volume. From the porosity profile plot in Fig. 9C, it can be deduced that for thickness values of 0.01 – 5 mm there is significant fluctuation in porosity with the moving sampling volume. We observe a relatively constant porosity profile at a minimum RET of 10 mm. In addition, towards the bottom of the sample we observe an increase in porosity.

5.5. 2 μm 3-D μCT analysis

Following the determination of a minimum RET of 10 mm, a sample of 2 mm (diameter) by 10 mm (length) was imaged at 2 μm voxel size in 3-D using μCT before and pyrolysis at 300–500 °C. The 2D gray scale images with corresponding plots of porosity per slice are shown in Fig. 10. Between 20 °C and 350 °C
no change in porosity was identified in the oil shale sample at the 2 µm voxel size. At 400 °C the first microscale pores are detected parallel to the kerogen-rich laminations resulting in an average sample porosity of 8.6% with a maximum slice porosity of 34.9%. A further increase in temperature to 450 °C resulted in a further increase in average porosity to 20.8% and a maximum slice porosity of 54.3%. At 500 °C a smaller increase in average porosity is computed to 21.9% and a maximum porosity of 57.3%. Fig. 11, shows a 3-D rendering of the connectivity of the pore space following pyrolysis at 500 °C where pores of the same color are connected. To quantify connectivity, the image was cropped from 1080 x 1131 x 5736 voxels to 750 x 750 x 5736 voxels. Horizontally, 85.4% of the pore space is connected whilst vertically no connectivity was detectable at the 2 µm voxel size. The results obtained in this study were compared with those obtained in [72], where dynamic imaging of oil shale pyrolysis using a synchrotron X-ray source with a 2 µm voxel size was conducted on a 2 mm length Green River (Mahogany Zone) sample with a mixed composition of organic-rich and organic-lean laminations (Fig. 12). The comparison reveals a similar trend in the evolution of porosity with temperature, with a resolvable change in porosity taking place between 390 and 400 °C.

To assess the porosity range that results following pyrolysis at 500 °C we selected 10 samples at random from the bulk oil shale specimen. The samples were imaged, reconstructed, filtered and segmented to compute the porosity. Fig. 13 shows the porosity results obtained with the highest value obtained as 37.9%, the lowest 12.8% and an average porosity of 23.1% for the 10 samples. The 3-D volume rendering of organic-rich, lean and mixed samples are shown in Fig. 13 E-G. These results further validate that the final oil shale porosity values after pyrolysis are directly related to the organic matter content.

**6. Conclusions**

Fluid flow through porous structures is a crucial aspect of hydrocarbon recovery during oil shale pyrolysis. The quantification of effective material properties is of paramount importance. This study extended our knowledge of the internal microstructure of the organic-rich Green River Formation (Mahogany Zone) and captured the changes in porosity and connectivity during oil shale pyrolysis. We initially characterized the Mahogany oil shale, by determining bulk properties including mineralogy (XRD), total organic carbon (TOC), thermal maturity (Rock-Eval and Source Rock Analyzer (SRA)), elemental analysis (CHNOS) and oil yield (Modified Fischer Assay (MFA)). However, given the complexity and heterogeneity of oil shale, samples were also characterized using optical microscopy, SEM-EDX and µCT. These imaging techniques provided local information on the spatial distribution of organic material, mineral phases and pore structures.

These techniques are complementary: by combining bulk analytical techniques with traditional (2-D) and advanced (3-D) imaging methods, we presented a full characterization of this important oil shale, which subsequently allows for improved modeling and prediction of fluid flow during oil shale pyrolysis. In addition, the experimental determination of petrophysical properties for oil shale can be uncertain, often producing inconsistent results. In this paper we proposed that multiple random 3-D images are required to perform a statistically representative analysis for oil shale rocks. We also characterized the representative size for the Mahogany oil shale by analyzing the sample size over which porosity remains constant, recommending 10 mm as the minimum representative elementary thickness.

The experimental data presented on oil shale before, during and after pyrolysis, serve as valuable input parameters to effectively...
model oil shale pyrolysis processes and permit a more knowledgeable appraisal of engineering problems associated with both ex situ and in situ operations. Future work will apply the methods used in this paper to explore physical changes during pyrolysis for sulfur poor vs sulfur-rich oil shales, carbonate vs clay-rich matrices and type II vs type I kerogens matrices. Further analysis into the nano-scale pore structure development at the early stages of oil shale pyrolysis is also required to complement the micro-scale pore structure and connectivity analyses presented in this study.

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