FIB/SEM AND SEM/EDX: A NEW DAWN FOR THE SEM IN THE CORE LAB?

Lemmens, H.J. [1], Butcher, A.R. [2], Botha, P.W.S.K.[3]
1) FEI, Netherlands, 2) FEI, Australia

This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Halifax, Nova Scotia, Canada, 4-7 October, 2010

ABSTRACT

Increased interest in shale and tight gas reservoir characterization has led to the adoption of FIB/SEM technology as the next step in resolution to visualize the pore network. The high resolution of a Scanning Electron Microscope (SEM) combined with the precise cutting capability of a Focused Ion Beam (FIB) enables 3D reconstructions with resolution of a few nanometers. The FIB is capable of removing a controlled amount of material to create a subsequent 2D section parallel and aligned with the previous one, with inter-section spacing of the order of 10nm, and having resolution of a few nanometers in the section plane. In this way, after careful combination of the subsequent slices, a 3D model with nanometers resolution in the XY direction and 10nm in the z-direction is obtained. Examples of shale reservoir rock reconstructions are discussed in this paper.

Curtaining is the most common artifact caused by inhomogeneities in the material under study. Shale samples are especially prone to this with the combination of porosity, organic phases, clay particles and pyrite inclusions all having a different milling rate with respect to the ion beam. Curtaining creates vertical lines in the images with a grey level that can be comparable to another, real phase. Improper segmentation can classify curtaining lines as real phases creating for instance non-existing pore throats leading to an overestimation of permeability.

Another emerging application of the SEM is automated mineral identification and textural mapping of cores and cuttings. The electron beam of the SEM does not only generate secondary (SEI) and backscatter electrons (BSE) that create the familiar high resolution black and white photomicrographs, but also secondary X-rays that are characteristic of the phase under the beam. By taking the energy dispersive X-ray (EDX) spectrum, comparing it with a library of phases, and combining this with the BSE and SEI signals, it is possible to create false-colored digital phase and texture maps of cores. This allows cores to be quantitatively lithotyped, especially in terms of how detrital mineral grains, authigenic overgrowths, and pore structures are associated. This in turn leads to a better understanding of pore-matrix interactions, including pore surfaces. Examples of mineral maps generated by automated SEM/EDX analysis of cores and cuttings are presented to illustrate how these data can be integrated with FIB/SEM data to provide a holistic petrographic approach.

INTRODUCTION

Estimating reservoir quality in gas shale requires a thorough understanding of pore structure and pore connectivity. MicroCT is a proven technique to resolve pore parameters with a resolution in the order of 1 micrometer. NanoCT technology has resolution down to 200nm but even that may not be enough for gas shale. Gas shales are known to contain finely-dispersed porous organic matter within an inorganic matrix. The porosity within the organic phase has pore and pore throat dimensions typically below 100nanometers and even down to just a few nanometers. For direct visualization of the pore network, FIBSEM is the only technology with nanometer resolution in 3 dimensions.

Not only is porosity and permeability important for reservoir characterization. Mineralogy and lithotype are also key parameters too and a technology known as Automated Mineralogy allows the creation of mineral and texture maps in a robust, objective, scalable and automated way. Lithotype(s) can be established and quantified based on a sample's mineralogy, mineral distribution and textural attributes such as grain size, cement type, degree of alteration, and heavy mineral content. Most mineral-mineral and mineral-pore associations can be derived from digital images, and pores can be treated as phases too, thus allowing them to be digitally sorted into categories based on size, shape and associations.

FIB/SEM

In a SEM, electrons are accelerated and focused onto the sample surface to produce high resolution images [1]. The major difference with a focused ion beam system is the use of a different particle to create the primary beam that interacts with the sample. As the name FIB indicates, ions are used instead of electrons and this has major consequences for the interactions that occur at the sample surface. For the same energy, the momentum of the ion is about 370 times larger. When the ion hits an atom, its mass is comparable to the mass of the sample atom and as a consequence it will transfer a large amount of its momentum, enough to remove it from its matrix. The removal of atoms from their matrix is a phenomenon known as milling. The milling efficiency is typically a few micrometer^3/nanoCoulomb of beam current and is higher for some materials and lower for others. The actual rate will depend on the mass of the target atom, its binding energy to the matrix and matrix orientation with respect to the incident direction of the beam.

The most important consequence of the properties listed above is that ion beams will remove atoms from the substrate and because the beam position, dwell time and size are so well controlled it can be applied to remove material locally in a highly controlled manner, down to the nanometer scale. The milling rate (μm3/s) is (linear) proportional to the beam current and high amounts of material are removed with high beam currents. In addition, precise control is possible by the use of smaller spot sizes and hence smaller currents. For milling of larger amounts of material, a rectangular area of 10 x 5 x 3 micrometers can take around 10 minutes for complete removal. For a FIB/SEM run however, where hundreds of 10 nm thick slices are required, the milling typically takes 1

minute per slice to expose a 10 micron by 10 micron area for SEM imaging. As the ion beam position is well controlled, milling can be used to create a simple structure such as a square or round hole in the material, but also complex structures are possible. Not only the lateral position, but also the local depth can be controlled. In this way milling is different from etching with a mask on the sample.

3D reconstructions are made by alternating SEM imaging with FIB milling. This technique is hence destructive and leaves a milled cavity in the sample. Consecutive slices are aligned and combined into a 3D model. Beam stability and thermal and mechanical vibrations need to be very well controlled to make sure perfectly parallel cuts with the desired distance between them are obtained. Alignment of the image is further aided by image recognition techniques, focusing on a fixed marking next to where the FIB milling takes place. Figure 1 shows the electron beam and ion beam operating under an angle and alternating between SEM imaging and FIB milling.

Segmentation is further complicated by artifacts of which curtaining is the most common. Curtains (vertical lines in the SEM image) are formed by the ion beam milling through phases with different densities. Figure 2 illustrates the start of a curtain, indicated with an arrow, where the beam has gone through a low density phase at the outer edge of a pyrite framboid in a shale sample. Curtaining is almost always present in FIB milled SEM images but can usually be well controlled by an experienced user that knows both the instrument and the material under study well.

Charging of a non-conductive sample can also complicate the SEM imaging. For regular SEM imaging, carbon coating is commonly used but this is no solution in the case of a FIB/SEM experiment. FIB milling creates a fresh surface, without coating and hence other strategies have to be used to avoid charging. The sample can be flooded with a positive ion-beam, neutralizing the negatively charged electrons at the surface, but this can come at the expense of image quality. Imaging at low accelerating voltages is another option or the use of very short dwell times and averaging. In many cases the solution is a combination of the above measures, tailored to the sample and the kind of data needed.

FIB/SEM on Shale

FIB/SEM generates a 3D model with down to 1nm (order of magnitude) resolution in the XY direction and down to 10nm in the z-direction. The raw data is then a 3D data cube of grey levels with the grey level proportional to the average atomic number of the phase under the electron beam, in the case of backscatter electrons forming the SEM image. Heavy phases, such as framboidal pyrites, show up as bright phases while organics are much darker. Figure 3 shows consecutive SEM images of shale with slice thicknesses, i.e. the distance between the images, of 100 nanometers and 10 nanometers. Proper segmentation is the key to generate 3D porosity and kerogen networks. Segmentation is done by assigning a name to a specific range of grey levels in the image and rendering the images into a 3D cube. This is not straightforward as organic (kerogen) phases and pores can have similar grey levels. Figure 4 shows the 3D reconstruction of 130 slices.

Mineral phases are rendered yellow and bright yellow, depending on the grey level intensity with the brightest phase in the BSE image bright yellow. Porosity and organics are black and grey respectively.

The recent work of Sondergeld et al. [2] and Ambrose et al. [3] illustrates where FIB/SEM provides additional information to characterize pore structures and permeability in shale samples.

SEM/EDX AUTOMATED MINERALOGY

Samples of core (or cuttings) are generally presented to the Automated Mineralogy analyzer as polished flat or diamond saw-cut surfaces. The technique is non-destructive, thus allowing valuable core samples to be preserved for archiving, or for further analysis.

Customized holders allow the cores to be held such that the flat surface is maintained normal to the electron beam at all time. A high precision motorized stage is used to allow the core to be scanned frame-by-frame. Within each frame, an image is automatically collected which contains both mineral and textural information. Numerical petrographic data can be extracted from the images using off line image analysis software.

One of the main advantages that Automated Mineralogy has over conventional petrographic methods (optical or SEM), is the range of scales of observations that can be captured, from cm-mm-um. Digital images can be used to reveal the locations of minerals of specific interest, such as clays or detrital grains, in relation to micro-meso or macro-sedimentary structures and features, such as laminae, bedding, bioturbation, alteration and fracturing [4].

Case Study: Mancos Shale, USA
A collaborative project has been undertaken with the USGS to establish if Automated Mineralogy is an efficient method to quantify the mineralogy of a large number of mudstone core samples. The sequence chosen is through the Graneros Shale Member, into the Bridge Creek and Fairport Limestone Members, and into the Smokey Hill Member.

A total of 27 samples were analyzed, which are a subset of 207 samples obtained from 2¼ inch diameter drill core. The subset was selected to represent a range between inhomogeneous and relatively homogenous material taken from quarter sections of 1 to 3 inch long intervals of core. A thin-section blank was cut from the sample and the remainder was powdered and used for chemical and X-ray diffraction analyses. Part of the thin-section blank was used for a polished thin section and the remainder for Automated Mineralogy analysis.

Preliminary results already reported by Grauch et al [5] suggest modal analyses derived from Automated Mineralogy compare well with RockJock X-ray diffraction values [6], and offer a precise, rapid, and potentially accurate method for determining quantitative mineralogy of fine-grained sedimentary rocks (Figure 5).

In the present paper, we demonstrate the use of quantitative modal analysis of the Bridge Creek Member–Fairport Member sequence to re-construct a mineralogic/stratigraphic sequence. The lithologic breaks clearly evident in Figure 6, and marked by dashed lines, are in general agreement with USGS's megascopic core logging of this sequence. Sequences begin with a significant volcanic ash event, now represented by clay-rich bands, represented by samples 538.67 ft & 528.81 ft.

This method of constructing a stratigraphic sequence from Automated Mineralogy data can be used to objectively place boundaries, help calibrate mapping of cores at the macro-scale, and provide quantification of the mineralogy of each unit.

CONCLUSION
FIBSEM is a promising technique for analyzing pore networks in gas shales. It remains to be seen how data representative for the reservoir can be inferred from FIBSEM results. Preliminary results, however, indicate that valuable data on pore sizes and geometry can be obtained, not possible with other technologies.

Automated Mineralogy is a reliable technique to characterize mineralogy and lithology, both on core and cuttings samples. The high throughput allows analysis of a statistically relevant number of samples, in a robust way, reducing human errors in mineral and rock identification.

ACKNOWLEDGEMENTS

The authors would like to thank Richard I. Grauch and Dennis D. Eberl of the USGS for permission to publish the Mancos Shale results and Mark Knackstedt and Munish Kumar at Digital Core for 3D interpretations of the FIBSEM data.

REFERENCES

1. Giannuzzi, L.A., F.A. Stevie, *Introduction to Focused Ion Beams*, Springer, NY, (2005).

2. Sondergeld, C.H., R.J. Ambrose, C.S. Rai, J. Moncrieff, "Micro-Structural Studies of Gas Shales", SPE 131771, *Proceedings of SPE Unconventional Gas Conference*, Pittsburgh, Pennsylvania, USA, 23–25 February 2010.

3. Ambrose, R.J., R.C. Hartman, M. Diaz-Campos, I.Y. Akkutlu, C.H. Sondergeld, "New Pore-scale Considerations for Shale Gas in Place Calculations", SPE 131772, *Proceedings of SPE Unconventional Gas Conference*, Pittsburgh, Pennsylvania, USA, 23–25 February 2010.

4. Armitage, P.J., R.H. Worden, D.R. Faulkner, A.C. Aplin, A.R. Butcher, J. Iliffe, "Diagenetic and sedimentary controls on porosity in lower carboniferous fine-grained litholgies, Krechba field, Algeria: A petrological study of a caprock to a carbon capture site", *Marine and Petroleum Geology,* (2010), in press.

5. Grauch, R.I., D.D. Eberl, A.R. Butcher, P.W.S.K. Botha, "Quantitative Mineralogy of Fine-grained Sedimentary Rocks: A Preliminary Look at QEMSCAN." *Proceedings of Microscopy and Microanalysis*, Alburquerque, New Mexico, USA, 3-7 August 2008.

6. Eberl, D.D., *U.S. Geological Survey Open-File Report* 03-78 (2003).

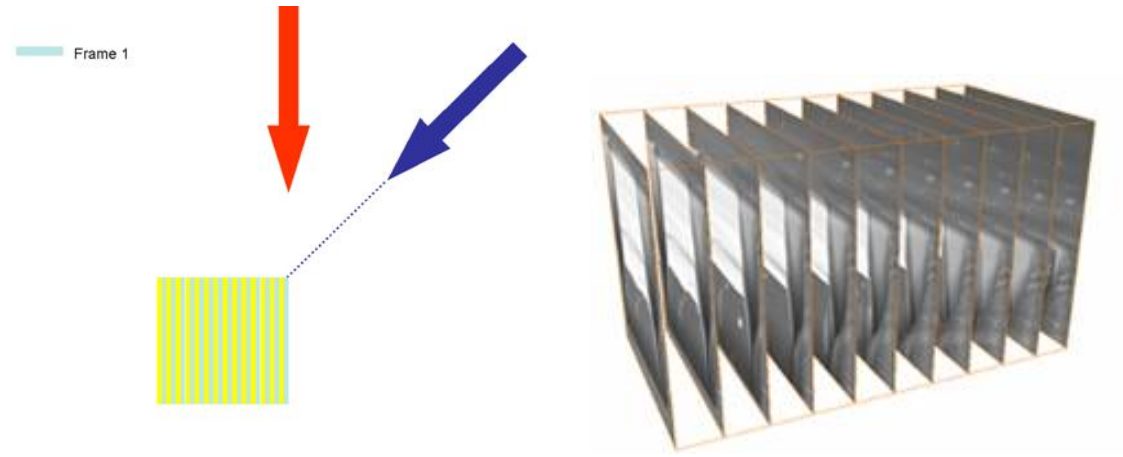

Figure 1. The electron beam (blue) generates a 2D high resolution images of a slice. The ion beam (red) removes the first slice by milling and creates a second slice parallel and aligned with the first slice after which imaging with the electron beam takes place and so on.

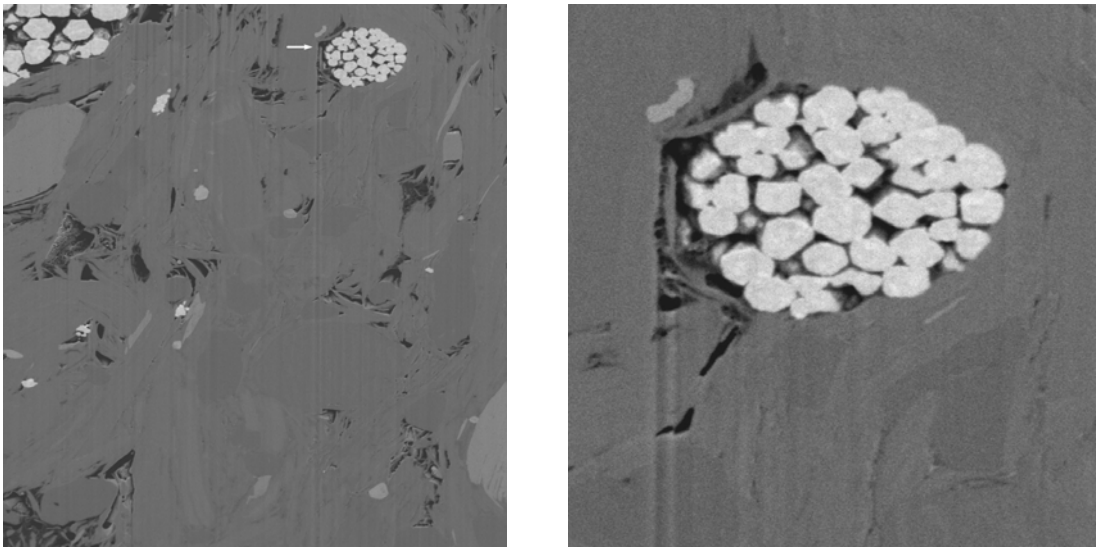

Figure 2: Curtaining as a common artifact in FIB-milled BSE images of gas shale (3nm resolution). The left image shows vertical lines commonly known as curtains, caused by differences in milling rate due to density changes. Full horizontal width of the left image is 10 micrometer. The right image zooms in at the area next to the arrow in the left image, at the small pyrite framboid. The Focused Ion beams mills from top to bottom. The most prominent curtain in the right image can be seen to start where the ion beam went through a low density phase around the framboid.

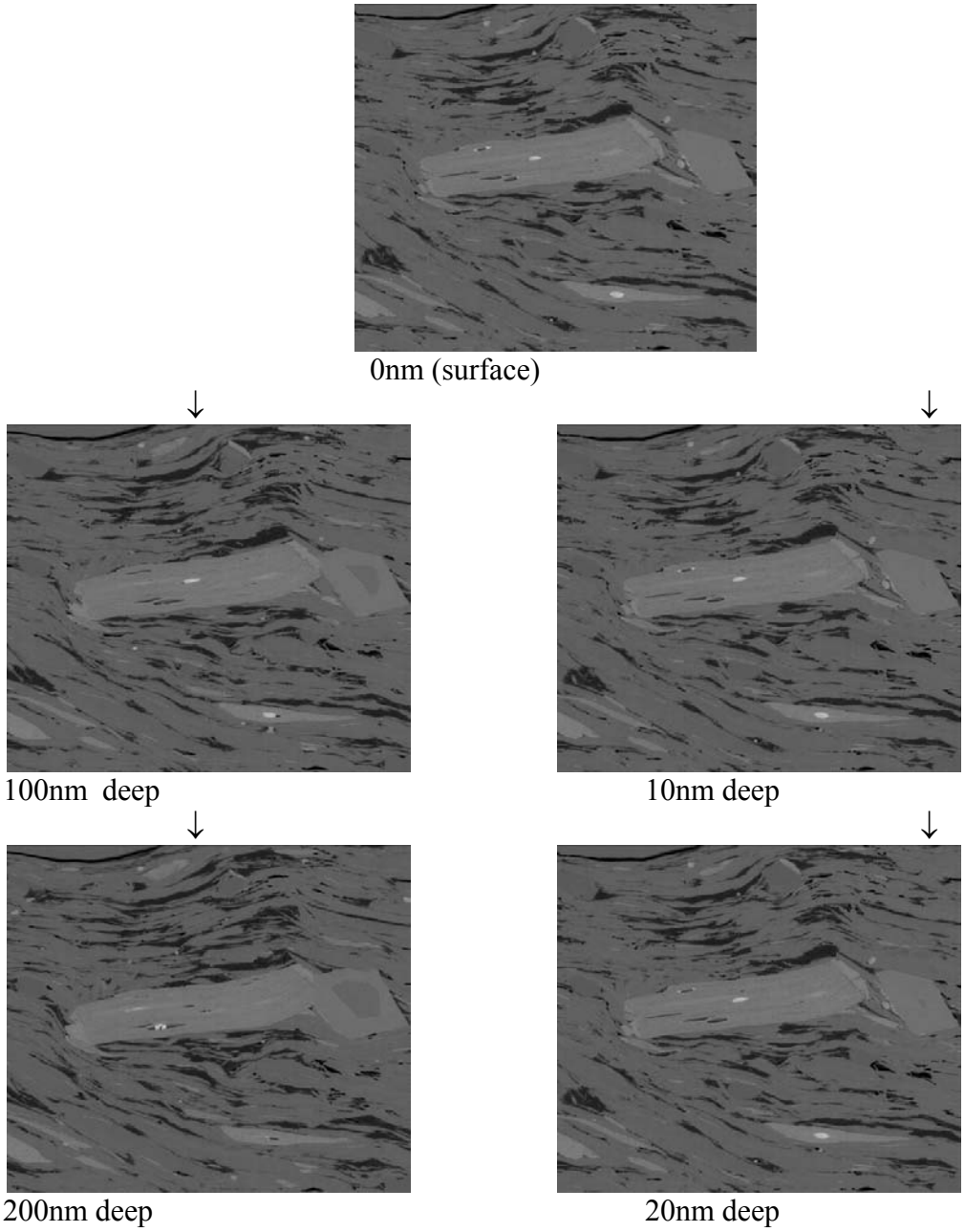

Figure 3: Demonstration of consecutive slices in a FIB/SEM run. The top slice is the surface. The images below are taken with steps of 100nm into the material (left) and 10 nm into the material. BSE images taken at 3nm resolution; horizontal field width is 15 microns.

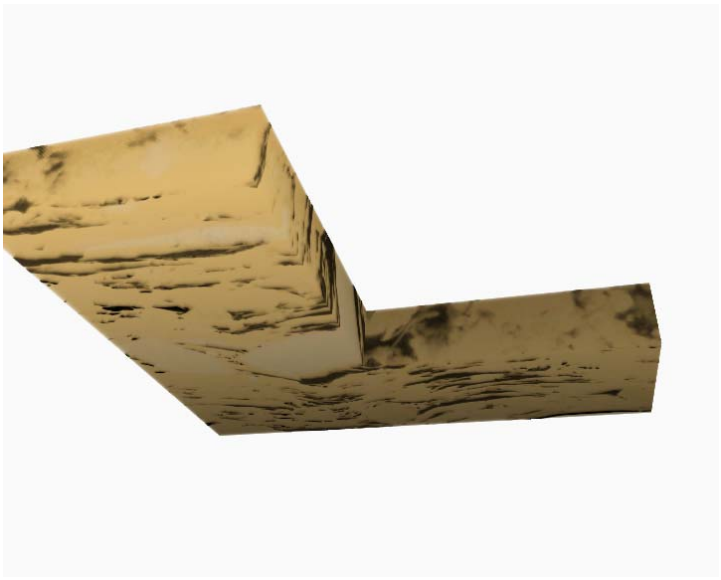

Figure 4. 3D view of the image series shown in Figure 3. The FIB/SEM run consisted of 130 images, with 10 nm slice thickness.

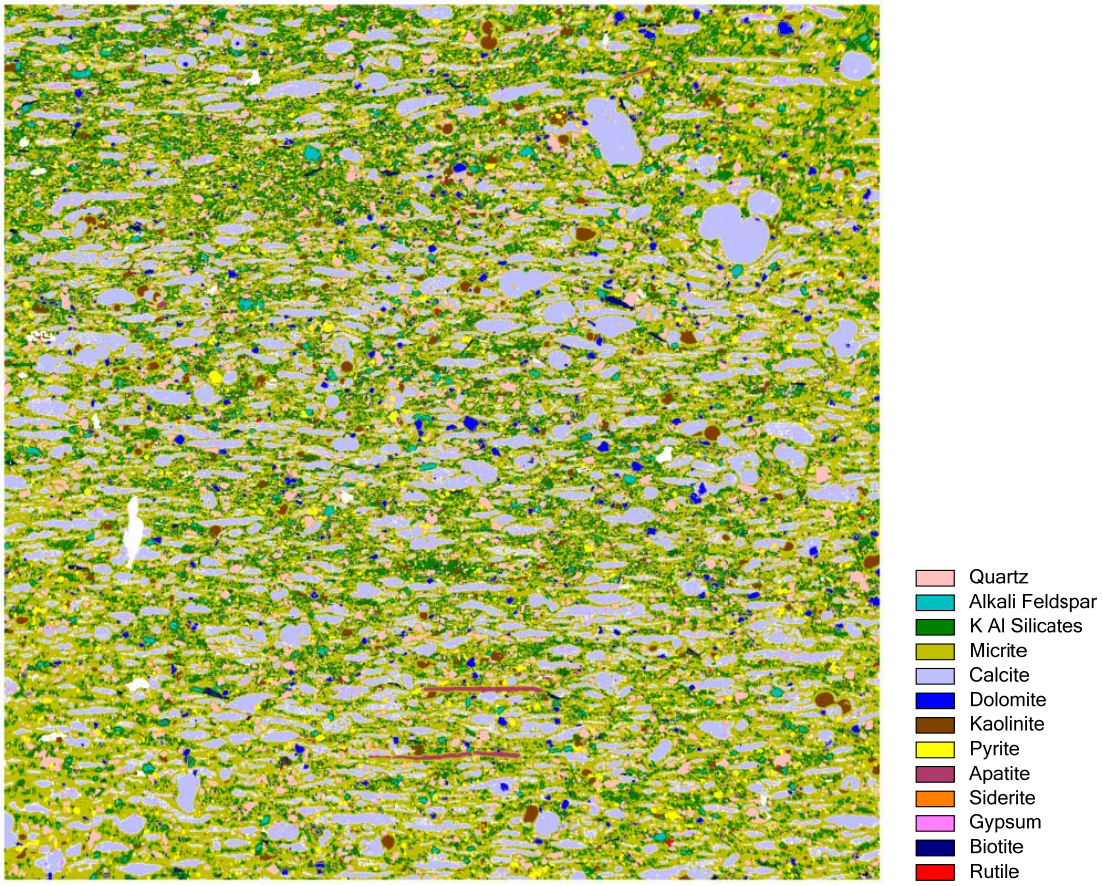

Figure 5: QEMSCAN® mineral and texture map of a representative area from Shale Sample CL—37.9, reported by Grauch et al [5], illustrating the complex mineralogy and textures present. Pixel spacing (electron beam stepping interval) 1.5 microns. Field width 3 mm. Smoky Hills Member. Data by kind permission of the USGS.

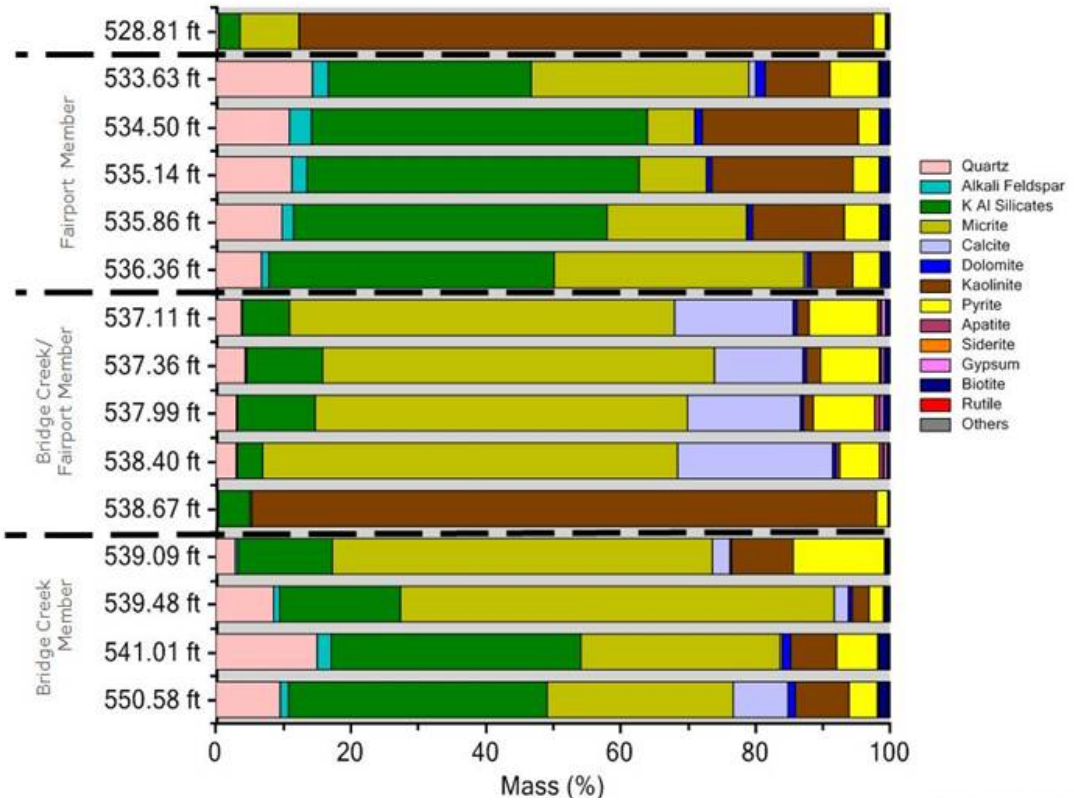

Figure 6: Quantitative modal data from Automated Mineralogical analysis of the Bridge Creek and Fairport Limestone Members allows for a stratigraphic sequence to be derived (data by kind permission of the USGS). Each bar represents the averaged modal proportions derived from the QEMSCAN analysis of an individual core trim. Example digital images, from which these data have been derived, are provided in Figure 7.

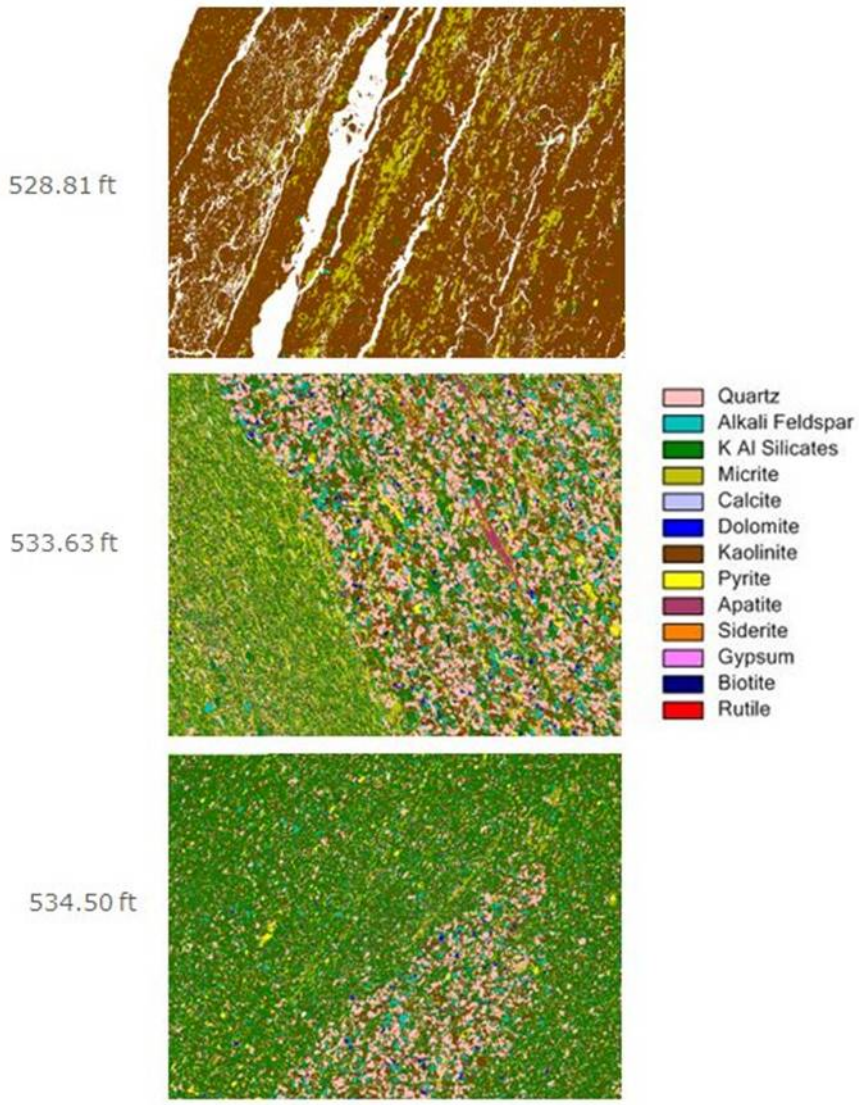

Figure 7: Examples of false-colored digital phase and texture maps illustrating the variation in lithology and structure demonstrated by the Fairport Limestone Member, at the uppermost part of the sequence studied (data by kind permission of the USGS). They represent only a small extract from much larger areas used to quantify the mineralogy of each sample (Figure 6) using iDiscover™ image analysis software. Images were created using a 5 micron electron beam stepping interval. Field width 3mm.