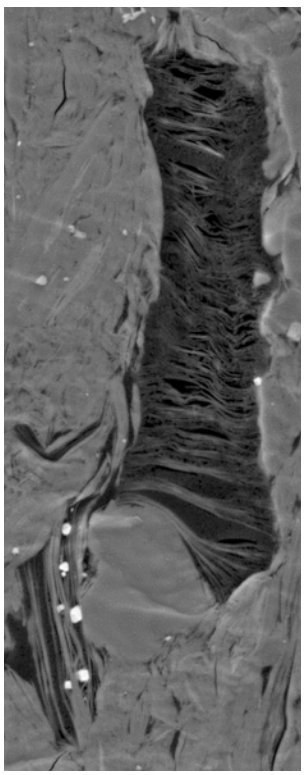
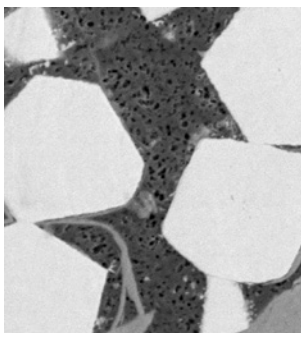
Application Note





# Multiscale imaging of shale samples in the Scanning Electron Microscope

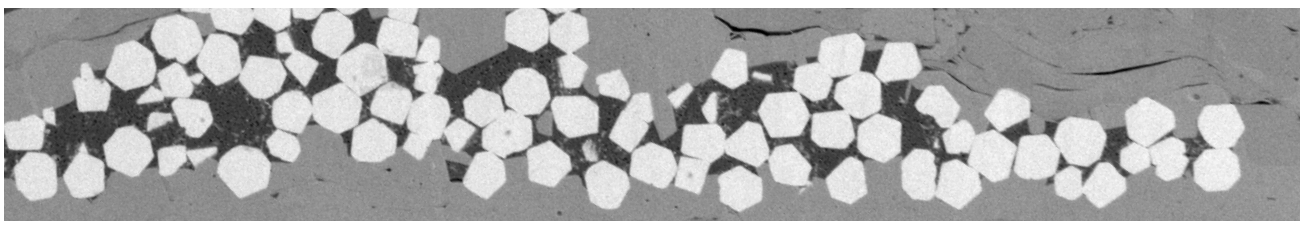
## Introduction

Unconventional reservoirs are also largely unknown reservoirs. Every time the first high resolution SEM images of the newest shale play get to the interpreting scientist, there is a wave of excitement. Each shale play seems to exhibit another intriguing network of clays, organic matter and porosity. Typical for shales is the occurrence of porosity at the nanoscale and very fine features in the clays, requiring high imaging magnifications. FIB/SEM (DualBeam™) takes this even one step further by providing a 3D dataset composed of hundreds of such high resolution SEM images. A typical DualBeam dataset has a spatial resolution of 10 nm for a volume of 10 x 10 x 10 micrometer.

A most relevant question is how representative those small volume DualBeam datasets are. Industry-standard approaches are to take about 10 SEM images and decide from those images what the relevant and representative features are. For a 1 inch core sample, this still means that less than 1% of the sample surface is actually imaged at a resolution able to resolve the porosity before deciding where to perform a DualBeam experiment.

The risk associated with the much higher resolution characterization of shale core sample material with high resolution SEM and DualBeam is that the structural association with fabric is lost. Yet fabric heterogeneity is equally important for the characterization of shale samples, and the association of nanoscale pore structures with fabric domains may provide important information to permeability and fluid flow on the scale of the core.

FEI developed MAPS Tiling & Stitching software to enable pore scale resolution over the full core surface in one image. This allows simultaneously retrieving fabric and pore level information without losing correlation. Furthermore, it allows choosing the DualBeam locations in a more representative way.



## The Pore-Fabric Paradox

Gas shale samples typically contain pores as small as 10 nanometers. Resolving those pores requires a pixel size in the order of 3 nanometers. A common SEM image is 4096 pixels wide. This results in a field of view of about 12 micrometers. Figure 1 shows such a high resolution image of a shale sample with the porosity in the kerogen clearly visible.

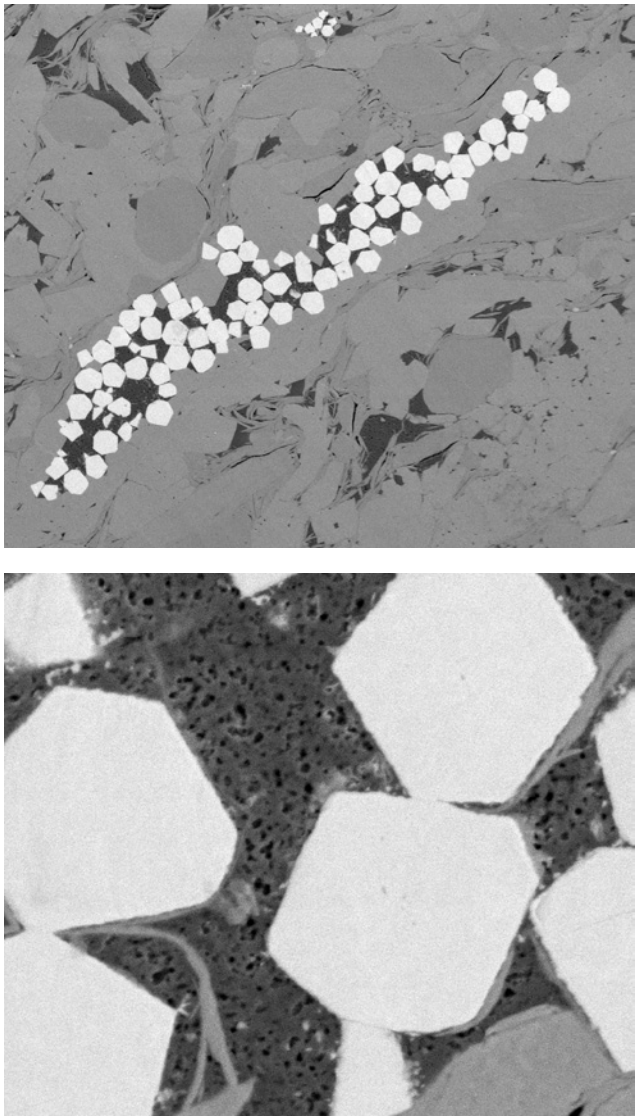


Figure 1. Top image shows a high resolution SEM image of a gas shale sample. Horizontal field of view is 13.4 micrometer; effectively isolating this image from the sample fabric. The bottom image zooms in on the porous matter between the pyrite crystals and clearly shows the porosity in the organic matter. Field of View is 1.5 micrometer.

**MAPS software enables visualization of pore+fabric in one image**

This image shows pyrite crystals in a porous kerogen matrix but the small area imaged makes it impossible to judge whether this particular microstructure is representative for this sample or not. This can only be answered by studying a larger surface at the resolution required to resolve the pore space. The FEI MAPS Tiling & Stitching software creates image mosaics of hundreds to thousands of high resolution SEM images; spanning 6 orders of magnitude in feature size. Figure 2 shows a mosaic consisting of 12.800 SEM images, totaling 394,815 by 394,807 pixels. The high resolution in this mosaic is clear from the submicron porosity in the organic matter.

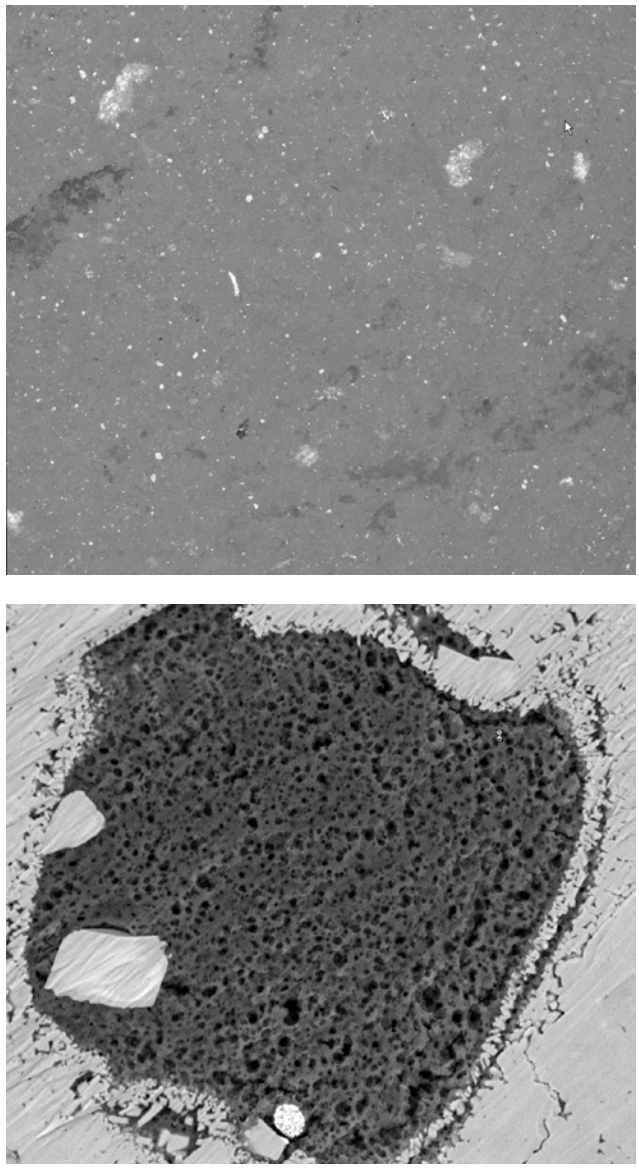


Figure 2. Overview image of a 12 mm wide shale sample consisting of 12,800 individual high resolution SEM images, totaling 156 gigapixels. The bottom image shows the pore scale resolution obtained over this large surface (field of view is 10 µm).

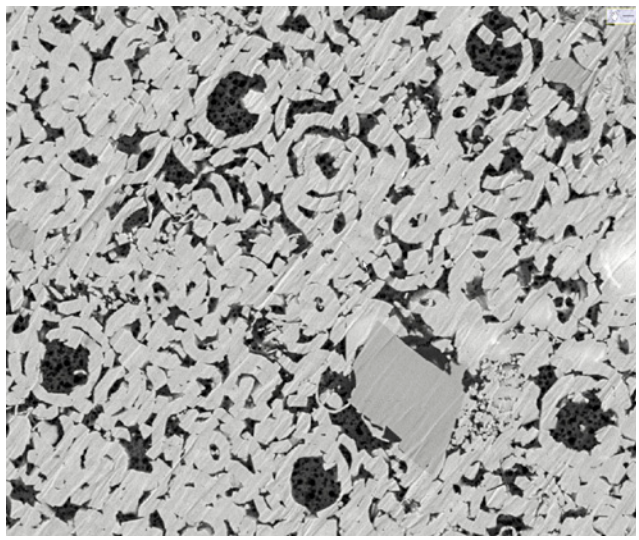


Figure 3. Two regions of the same sample, with solid and porous organic matter, spaced 6 millimeters apart. Field of view is 30 micrometer.

## Sample Preparation

Mechanical polishing is not suitable for shale samples as this technique tends to destroy the fine structure of the pore network. A non-contact polishing technique using Ar Ions is used to obtain a smooth surface. The traditional approach to preparing shale samples in the oil and gas petrology laboratory with the Argon ion mill uses a mask to create a cross section, but in that case the result is a parabola shaped flat section; limited to about 1x1mm. Larger-scale MAPS images provide ample evidence of fabric differences on length scales larger than 1 mm.

Figure 3 shows two images from a 12 x 12 mm section, displaying two very different types of organic matter; spaced more than 6 miillimeters apart. A 1 x 1 mm section would have missed at least one of these two types of kerogen.

For the samples discussed in this article, the Fischione 1060 SEM Mill was used. Samples are attached to a 25 mm diameter pin–type stub using carbon tape, and loaded into the 1060 SEM Mill. 5 kV ions under a 5˚ incident angle and 360˚ sample rotation produce a polished surface after 1.5 hours. Figure 4 shows the setup of the two argon ion beams polishing the sample.

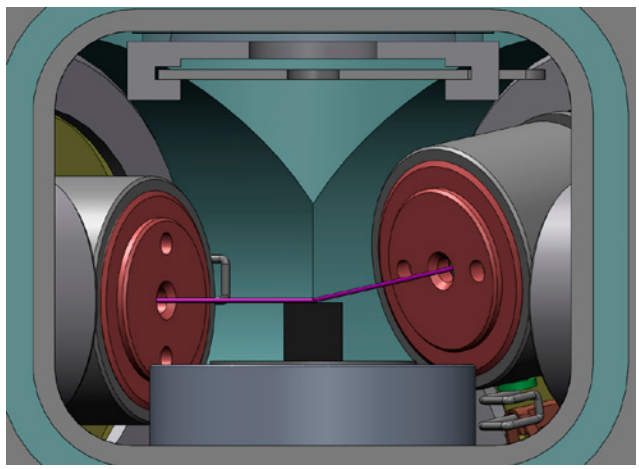
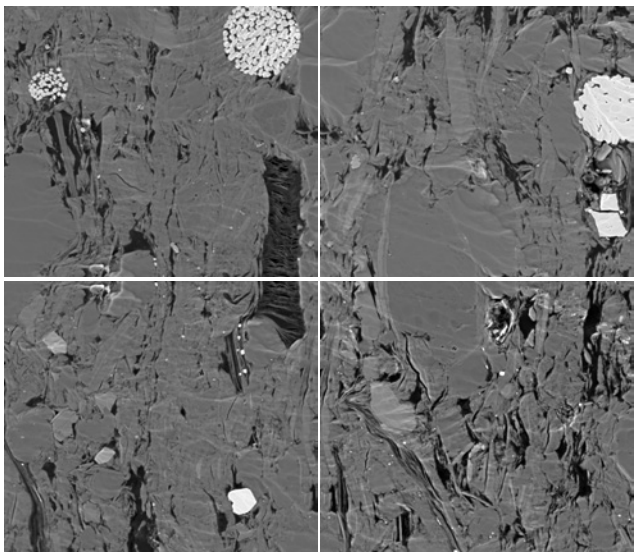


Figure 4. Schematic of the Argon Ion Mill



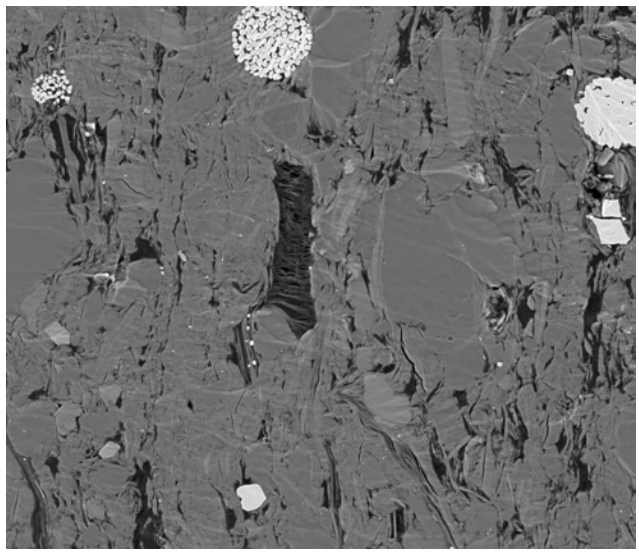


Figure 5. A 2 x 2 set of high resolution images; before and after stitching. The high accuracy piezo-electric stage of the Helios DualBeam, requires only 5% frame overlap.

## Explanation of imaging Methods

### Large Scale Imaging

Large Scale Imaging with the FEI MAPS Tiling & Stitching software uses tiling and stitching to create a high resolution image mosaic where the size is limited only by time constraints. Auto-imaging controls (focus, brightness, contrast) contribute to an image that is truly seamless; even when it is composed of many thousands of individual SEM images. Figure 5 shows a set of 2 x 2 individual tiles and the resulting seamless mosaic. Overlap between the images could be kept to a minimum because of the superior accuracy provided by piezo-electric stages deployed on FEI's high resolution SEMs and DualBeams. Stage accuracy also facilitates retrieving nanometer sized particles by navigating on the mosaic image. Large scale high resolution MAPS images are taken on the FEI Helios 650 DualBeam.

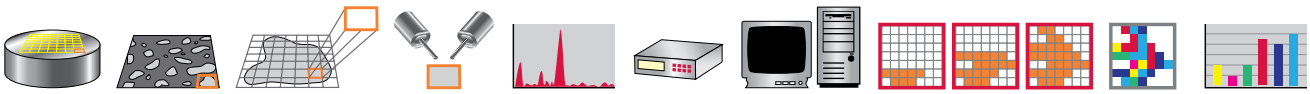
**MAPS uses stitching algorithms optimized for O&G samples**

**Helios piezo stage provides high accuracy for sample navigation and limits frame overlap**

### Automated Petrography

The traditional method for fabric characterization is optical petrography on thin sections. Optical petrography generates mineralogical and textural information in a single image, however with severe resolution limitations on fine-grained shale samples. SEM-based Automated Petrography (QEMSCAN®) provides a high resolution alternative to optical petrography. QEMSCAN uses Backscatter Electron Imaging and Energy Dispersive X-ray analysis (EDX) to obtain the elemental composition of the phase under the electron beam. Coupled to a library of mineral phases, Automated Petrography allows fast, reliable and unattended mineral characterization along a finely spaced grid of measurement points (Figure 6). In addition to mineral identification, textures such as laminations and grain size variations are revealed. While this technology was originally developed for the mining industry, it is now commonly used in the Oil & Gas industry. Clay standards from the Clay Society were used to validate a specific clay mineral library (Figure 7). Automated Petrography measurements were performed on an FEI QEMSCAN 650F instrument with two EDX detectors.

**The QEMSCAN® clay library has been calibrated on clay standards from the Clay Minerals Society.**



Scan block frame-by-frame

Use BSE to differentiate particles from mounting media

Scan particles on a grid basis

Each analysis point examined by EDS x-ray detectors

Spectrum acquired

Species Identification Protocol (SIP)

Phase classification

Pixel assigned composition

Pixels progressively measured

Image created as mineral and texture map

Data interpreted and quantified off-line

FIG 6: Schematic of the QEMSCAN® Automated Petrography analysis routine. From the backscatter electron image grey level, the particles are separated from the resin in case of cuttings samples. For core samples the full surface is mapped with Energy Dispersive X-ray analysis, with a user-defined pixel spacing. The EDX spectrum is matched to a spectrum from an O&G specific mineral database.

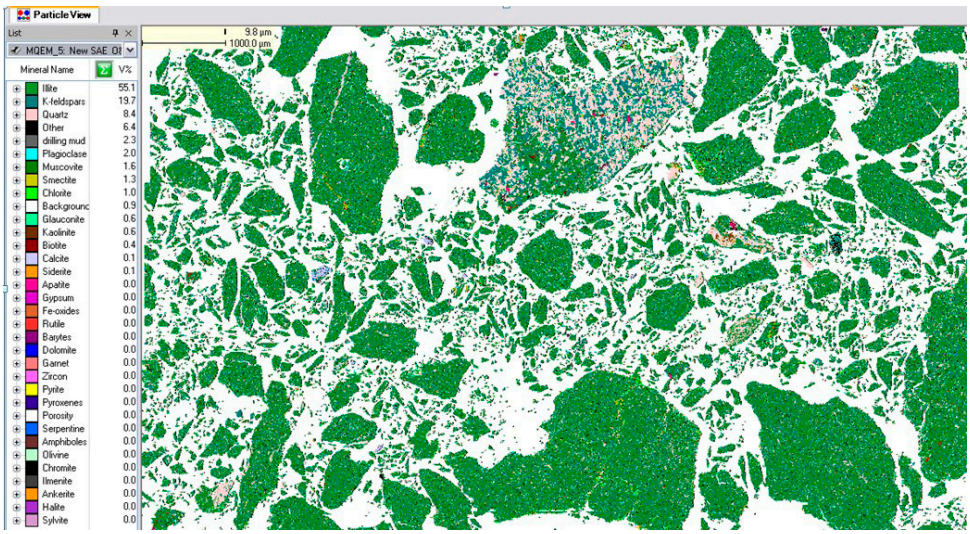
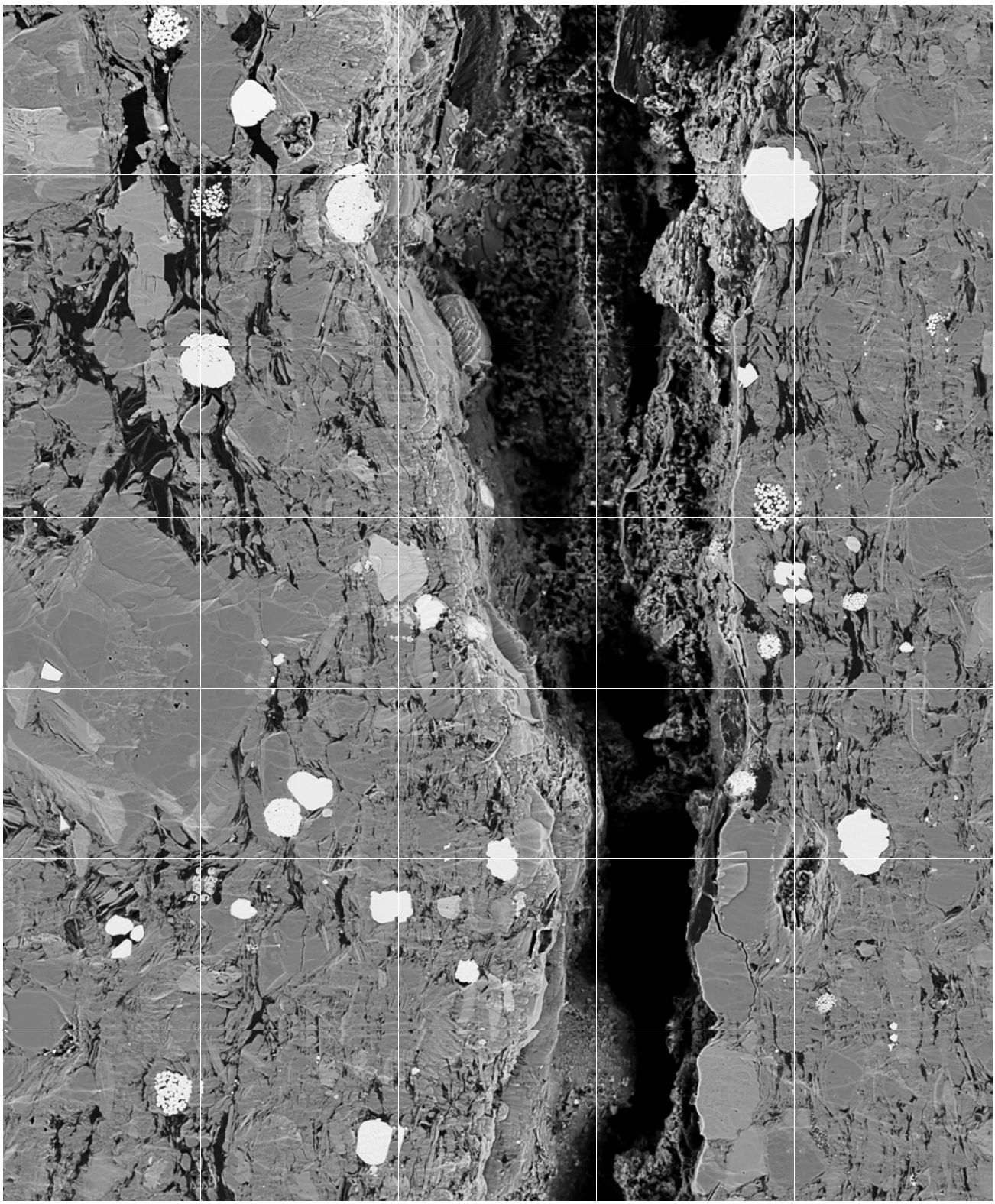
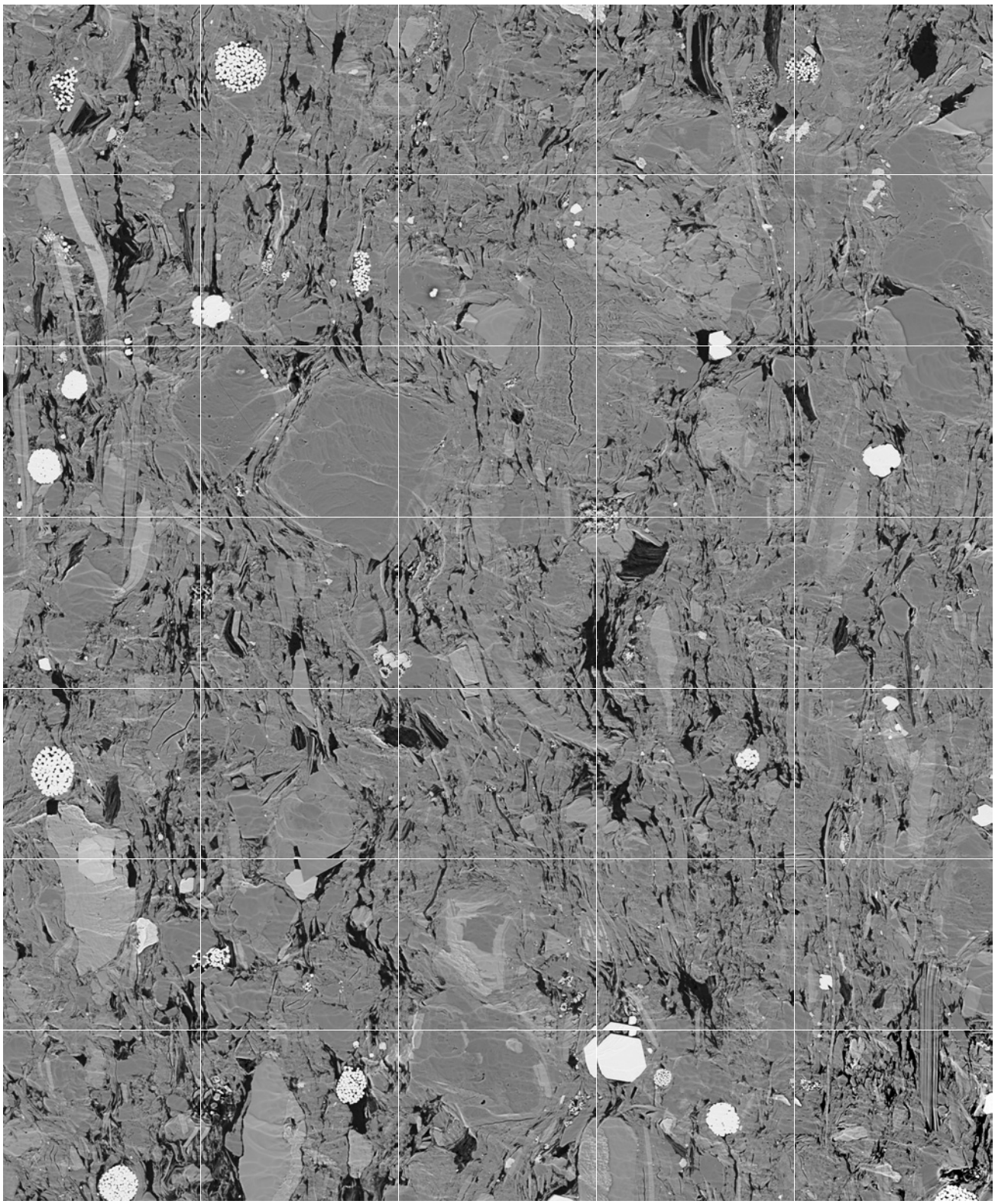


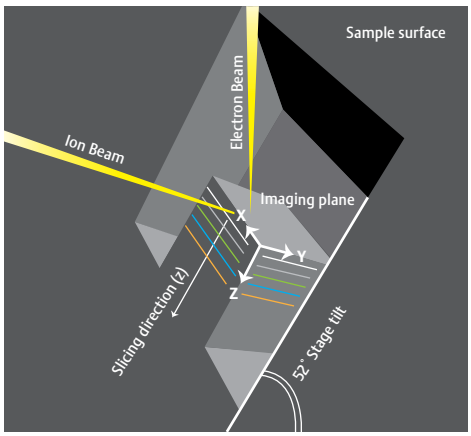

Figure 7. QEMSCAN® analysis of clay standard "IR6 IMt-1 Illite" obtained from the Clay Minerals Society. The majority phase identified correctly is illite (green) with quartz, calcite and K-feldspars also present.



10 x 7 high resolution MAPS mosaic, showing some of the individual tiles (5% overlap) used to create Figure 11.



10 x 7 high resolution MAPS mosaic



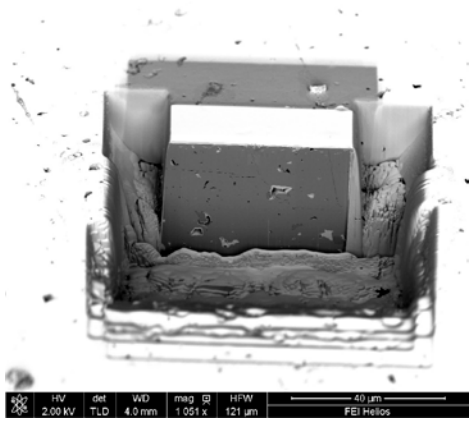




Figure 8. Sample setup in a typical DualBeam™ experiment. First, a trench is milled around the cube that will be analysed. Then, FIB milling and SEM imaging are used sequentially to generate a 3D dataset of parallel, high resolution images.

**DualBeam**

DualBeam uses a Focused Ion Beam (FIB) to cut parallel, evenly-spaced slices in combination with SEM imaging to obtain a high resolution 3D dataset (Figure 8). Slice thickness can be as low as 3 nanometers, though a thickness of 10 nanometers seems to be the standard developed for shale samples. Between slices, recognition marks are used for alignment of the individual slices and quality control on the slice thickness (Figure 9).

The result is a set of aligned SEM images that are turned into a 3D volume by dedicated reconstruction software. Grey level segmentation is used to analyse spatial distributions of e.g. pores.

A common issue with DualBeam imaging is preferential milling causing an artifact called curtaining. Shale samples are heterogeneous with phases that have very different material removal rates under the ion beam. This creates laminations in the cross section, shown as vertical bands in the SEM image, that may lead to segmentation errors. To reduce this effect without compromising milling speed and hence sample throughput, an ion beam with excellent beam profile at high beam currents is preferred, which is a particular strength of the ion beam used on FEI's Helios 650 DualBeam system.

Shale samples typically charge heavily under the electron beam; creating artifacts in the image. The Helios 650 DualBeam uses low accelerating voltages to prevent charge buildup; without compromising resolution or contrast.

**Strict process control accounts for high quality data alignment**

**The Helios has a semiconductor grade FIB column for ultimate performance over a wide range of milling energies**

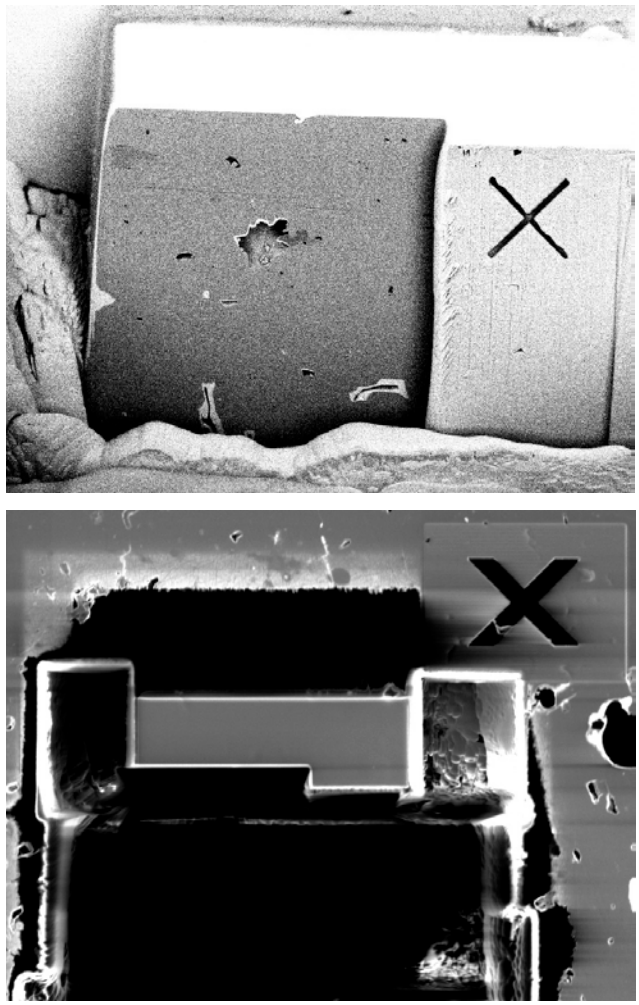


Figure 9. After the area of interest has been defined, the alignment between slices is guaranteed by calibrating on two recognition marks (two FIB milled crosses), one for the ion beam (bottom) and one for the electron beam (top).

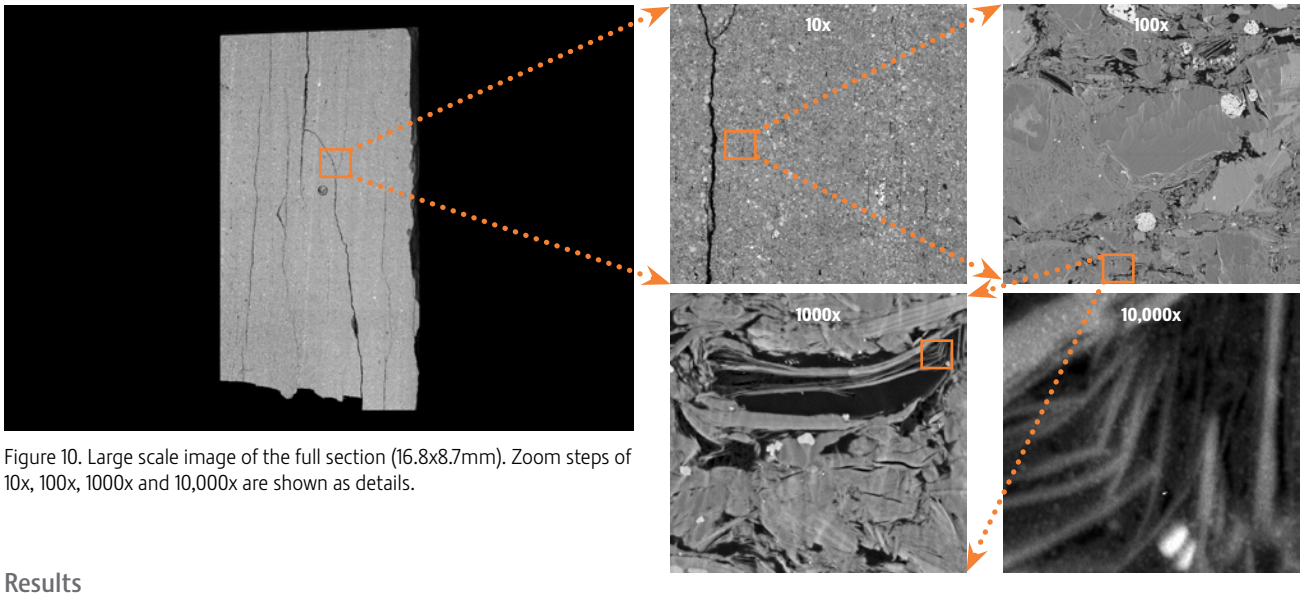



Figure 10. Large scale image of the full section (16.8x8.7mm). Zoom steps of 10x, 100x, 1000x and 10,000x are shown as details.

## Results

### Large Scale Imaging

An overview mosaic of the full section, with 4 zoom steps, is presented in Figure 10. Longitudinal cracks (black) and pyrite-rich laminations (white) are clearly visible from the backscatter electron image contrast, with no apparent evident fabric variations.

The Correlative Petrography software allows easy navigation and unlimited zoom-in capability over the entire mosaic. This was used to subsequently focus on a specific area that is considered representative, suggested also by the Automated Petrography results presented further on.

A high resolution image mosaic of the specific selection is shown in Figure 11. Two organic-filled cracks in the top-left portion of the image, connected to the central open crack, are a dominant feature. Organic matter in these two veins can be seen to exist both as porous and non-porous particles of arbitrary shape. The high resolution mosaic consists of 300 SEM images, with 20 micron Field of View per individual tile. The stitched image is a 3.2 gigabyte tiff file.

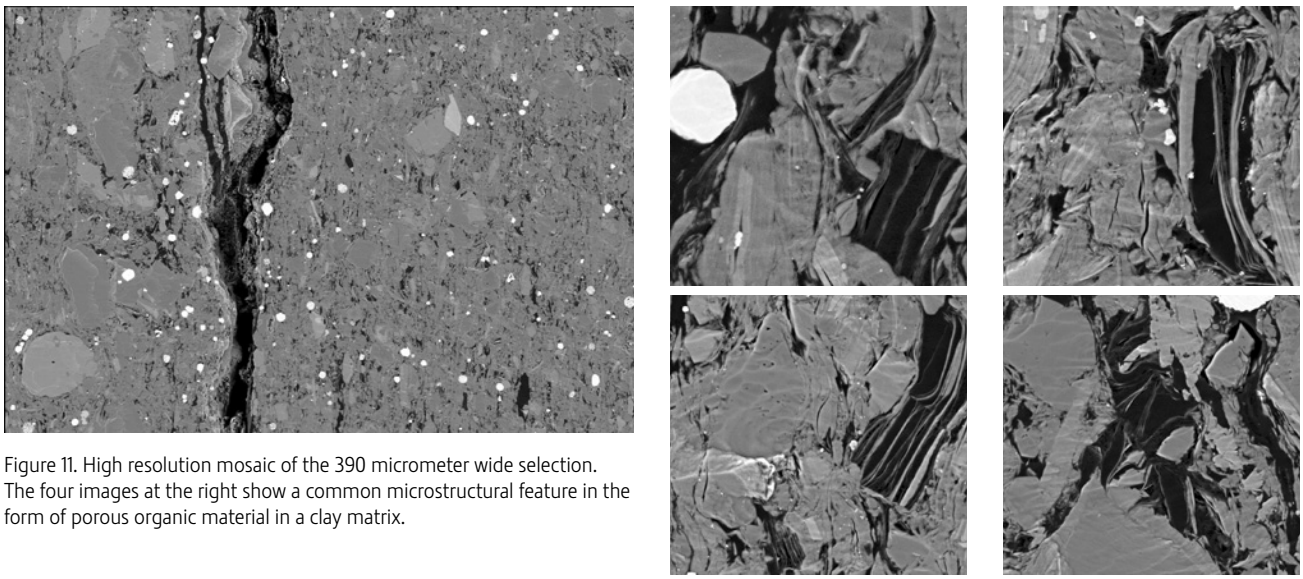


Figure 11. High resolution mosaic of the 390 micrometer wide selection. The four images at the right show a common microstructural feature in the form of porous organic material in a clay matrix.

### Automated Petrography

Two mineral maps were obtained, with respectively 5 micrometer and 0.5 micrometer pixel spacing for the EDX measurements (Figures 12 and 13). The 5 micrometer spacing results were obtained on the full surface (16.8 x 8.7mm). In total 7,096,623 spectra were measured, analyzed and attributed to different mineral phases in 11 hours and 23 minutes.

The higher density mineral map was taken over an area of 500 micrometer wide and yielded 1,040,701 EDX spectral analyses in 55 minutes. This area overlaps with the mosaic in Figure 11. Both petrography images clearly reveal grain size variations across horizontal bands in the sample. The modal mineralogy differences between the full surface and the smaller section appear only minor (Fig. 14). The slightly higher organic content in the smaller section is attributed to the two veins of solid organic matter originating from the crack. It is information like this that facilitates thorough investigations of fabric differences as well, and for that reason has to become an integral part of fabric to pore ("core to pore") shale investigations.

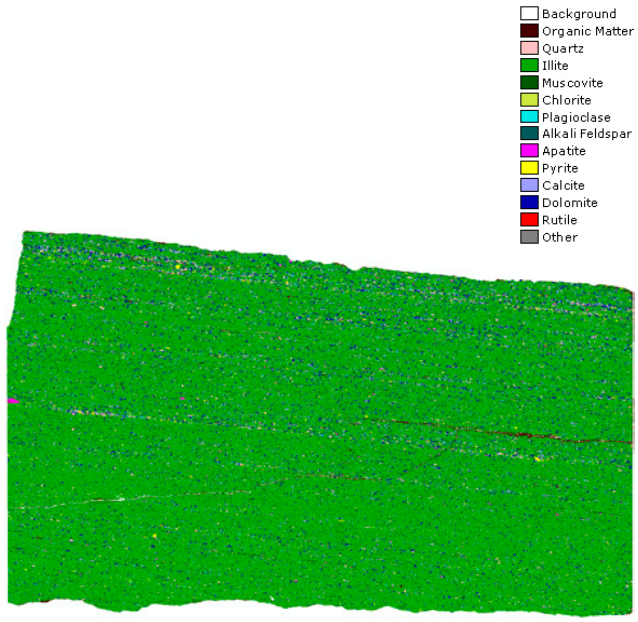



Figure 12. Petrographic image of the full section (16.8 x 8.7mm). More than 7 million EDX spectra were recorded in less than 12 hours.

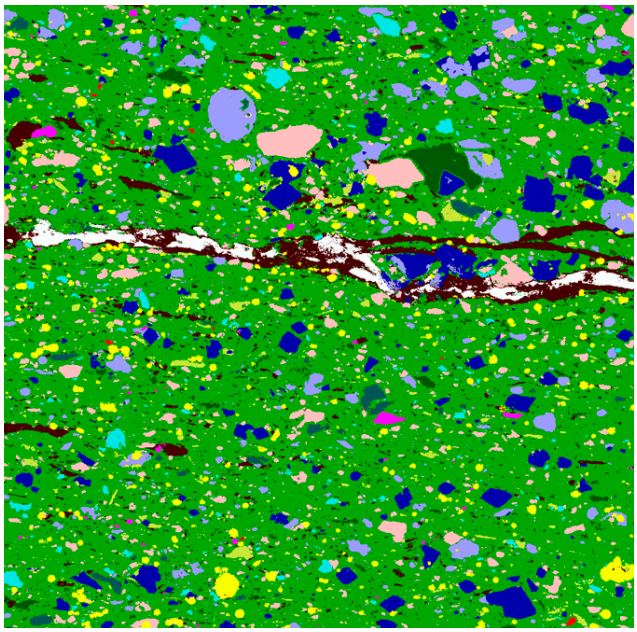


Figure 13. Petrographic image of a smaller section (500 micrometer wide). Over 1 million EDX spectra were collected in less than 1 hour. Note the grain size variation at either side of the fracture.

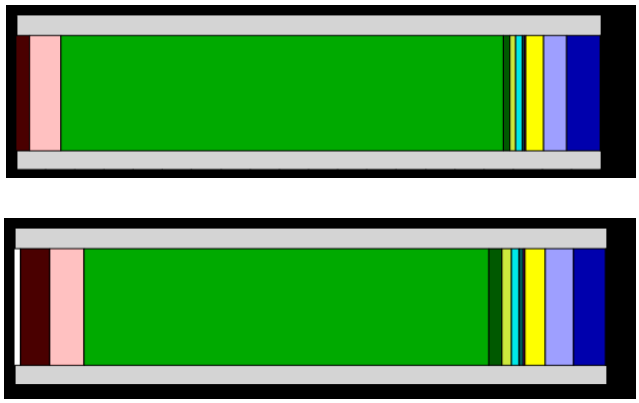


Figure 14. Modal mineralogy comparison between full surface (top) and smaller section (bottom), revealing only minor modal mineralogy differences.

**Mineral texture is readily revealed by QEMSCAN® measurements**

**High throughput measurements account for solid statistics**

### DualBeam

Based on the Large Scale Imaging and QEMSCAN results, it became clear that a prime candidate for DualBeam imaging is the porous organic matter associated with a clay platelet structure. 300 slices with 10 nm pixel resolution in the slices and 10 nm slice spacing were recorded. Figure 15 shows the first slice of this sequence and a grey level segmented reconstruction. Organic matter can be seen between clay platelets. Grey level segmentation is performed and the organic phases are colored red and the porosity is black. Some of the organic phases can be seen to be connected by cracks or spaces between clay platelets.

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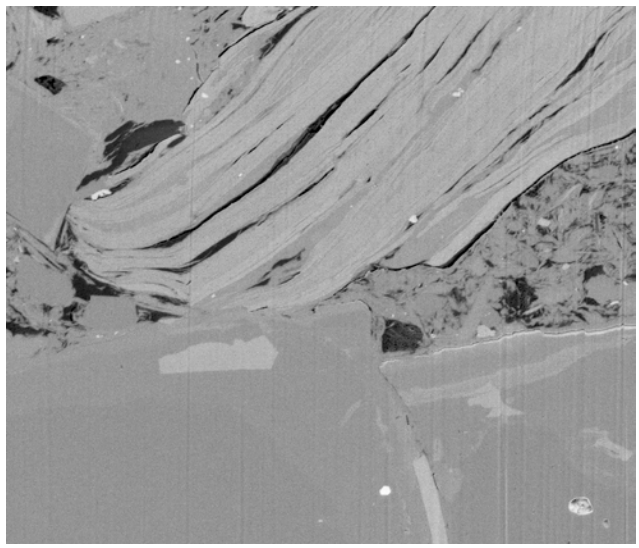


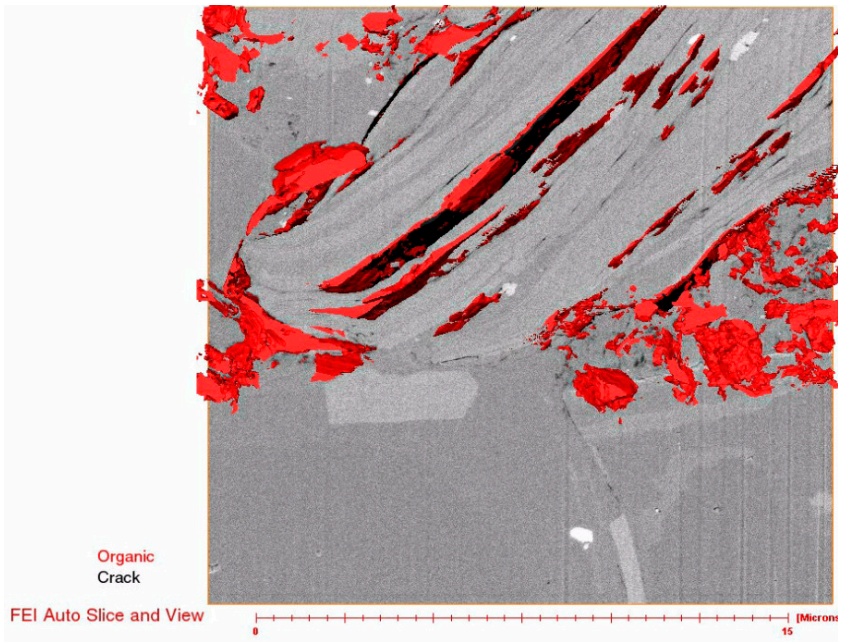



Figure 15. The first slice of the DualBeam™ dataset. Horizontal width is 20 micrometer. The reconstruction shows organic matter connected by pore space between the clay platelets.

**The Helios 650 DualBeam™ keeps the 1nm resolution spec down to 1kV imaging**

## Acknowledgments

Hu Dong and Sven Roth at iRock Technologies are gratefully acknowledged for providing the sample and insightful discussions on the experimental results.

The authors appreciate the support from Paul Fischione and Rocco Cerchiara at Fischione Instruments for polishing the sample with the Argon Ion Mill. We thank Aukje Benedictus at FEI Australia for the QEMSCAN Automated Petrography measurements and Anthony Burgess, David Wall and Michael Janus at FEI Netherlands for the MAPS Image Mosaics and the DualBeam work.

## The Lab

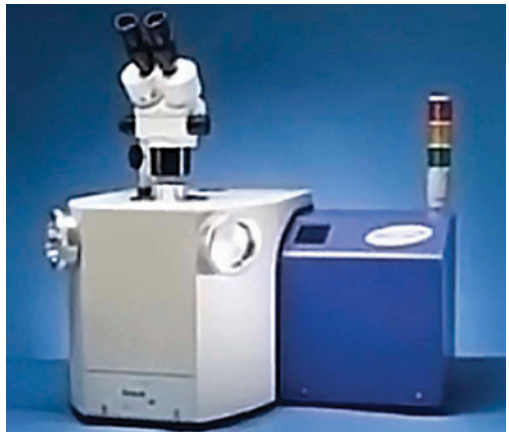
Sample preparation was done in the Fischione 1060 SEM Mill. Mineral and textural analysis was carried out on the QEMSCAN 650F. Large scale imaging and 3D imaging were performed on the Helios 650 DualBeam with Slice&View and MAPS software.

## About the authors

**Dr Herman J. Lemmens** is a solid state physicist with a background in electron imaging of microstructures in minerals and ceramics. His focus is on integrating imaging techniques at different length scales to enable upscaling of observations at the nanoscale. Lemmens is a Society of Petrophysicists and Well Log Analysts 2011 distinguished speaker on multiscale imaging, and co-recipient of the 2011 American Association of Petroleum Geologists' Al Levorsen Memorial Award in recognition of a paper on the shale diagenesis of the Marcellus in northeastern Pennsylvania.

QEMSCAN® 650F

Helios 650 DualBeam™



Fischione 1060 SEM Mill



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