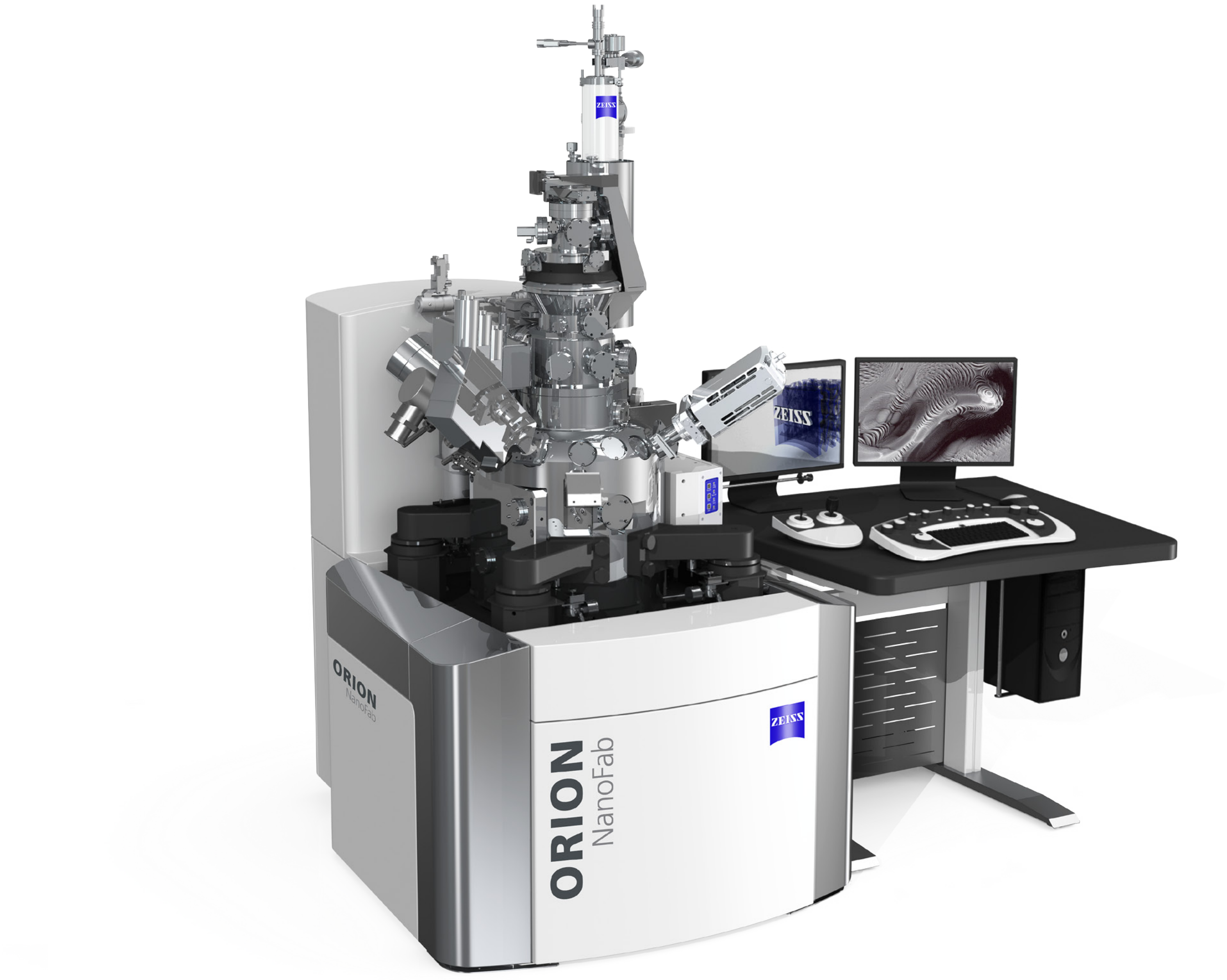
White Paper



Advancing Oil and Gas Exploration
with ORION NanoFab

We make it visible.

Advancing Oil and Gas Exploration with ORION NanoFab

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Shale gas methane is gaining increased interest as an energy source. The fuel gases of interest are resident inside networks of pores inside the shale, however, both the storage capacity of the material and the ability to extract the gases economically depends on the morphology of the pore network. A variety of techniques are applied to determine properties of these geological materials to extract structure/property relationships. Several non-imaging techniques are applied to this problem, and the data suggest that micro- to nano-scale pores exist within shale samples. The application of imaging techniques to this analysis helps to complete the evaluation of this economically important material.

The Challenge

As shale contains pores down to 2 nm and even smaller, very high resolution imaging methods must be applied to this problem. A commonly applied method has been scanning electron microscopy (SEM). This allows for high resolution imaging with wide field of view of inhomogeneous surfaces. While this is good for high throughput characterization, the lower beam energy required for sufficient surface sensitivity – and for charging samples – leads to a trade-off in resolution. Sample coating to eliminate charging is not desirable, as this process obscures the smallest pores which are the aim of the investigation. Ga based focused ion beam (FIB) systems have also been used for obtaining 3D pore data from shale. Images to date have not produced results showing pores less than 5 nm. While this may be a result of either Ga implantation damage or insufficient resolution of the electron beam is yet to be determined, nonetheless, FIB introduces sample preparation concerns and the same imaging concerns as the SEM. Atomic Force Microscopy (AFM) is highly surface sensitive and can readily image non-conductive materials. For this to be carried out, the surface must be relatively flat in order to effectively resolve nano-scale features. Obtaining such a surface from a geological material generally requires microtomy which is, unfortunately, a tedious and time-consuming sample preparation process which ulti-mately yields a surface that is typically only a few square millimeters in size. Transmission Electron Microscopy/Scanning Transmission Electron Microscopy (TEM/STEM) are also capable of observing nanoscale features, but have their own sample preparation limitations. Material must be milled from the bulk, providing only a small area for analysis. Fields of view are also much reduced when imaging with a TEM compared to SEM.

ORION NanoFab Solution

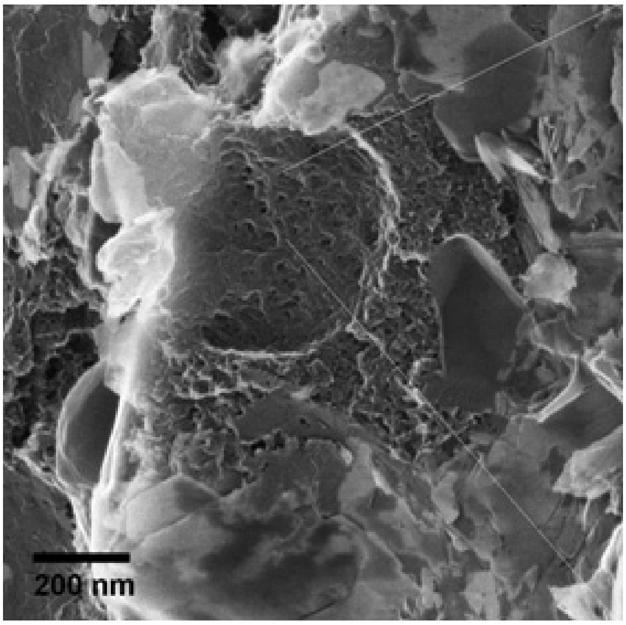
Helium Ion Microscopy (HIM) provides the capability to meet all the requirements for analyzing pore networks, especially at the lower size limits. We describe in this note the functionality for imaging large, inhomogeneous samples with essentially no preparation. Both conductive and charging samples can be imaged with high edge and surface resolution. In fact, sub-nanometer resolution is demonstrated, with the ability to observe pores down to 2.3 nm in size. For the imaging here, the HIM beam energy was set to 35 keV, with a beam current of 0.4 pA. The image was formed from ion-induced secondary electrons. As HIM provides high surface sensitivity at all beam energies (very few backscatter events generating Type-II secondary electrons), there is no need to decrease the beam energy to highlight nanometer-range surface details in the sample. Image magnification reported is according to a 4” x 5” (Polaroid) reference.

Sample preparation was conducted by breaking the shale rock using a hammer followed by mounting it on a stub. No further preparation techniques were required. Fracturing by this method preserves the native pore structure and prevents the risk of artifacts introduced by other imaging techniques. The ability to obtain high resolution imaging with minimal sample preparation is seen in Figure 1. In this case, Middle Otter Park Shale from the Horn River Basin was studied. This shale contains, in addition to the porous organic material, 47% quartz and 33% clay, along with secondary minerals. At low magnification several different phases can be distinguished, with the spongy organic material in the center of the image. The long depth of field in HIM imaging provides a clear three-dimensional view of the exposed surface. High magnification (572 kX) of the center region reveals detail about the arrangement of the pores. The arrows in the figure point out areas where the smallest pores are seen opening into the throat of larger voids. This provides a three dimensional view that is challenging in SEM imaging (below) unless one resorts to serial FIB sectioning and numerical reconstructions, which has not demonstrated pore size on the scale as we report using HIM.

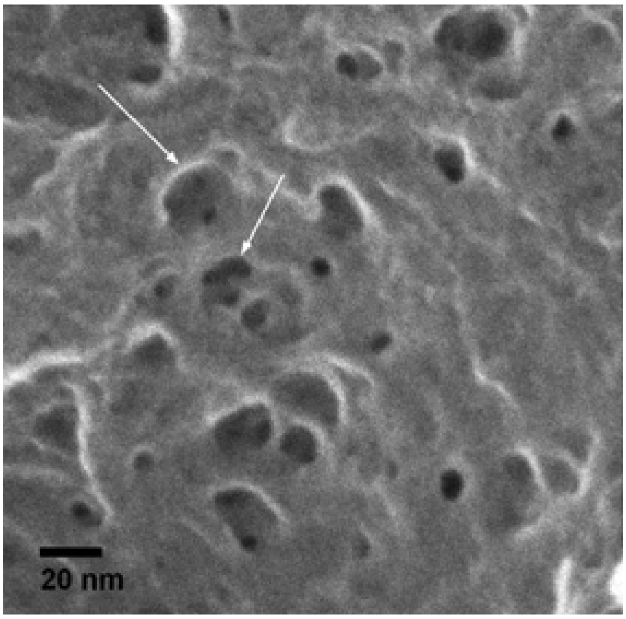
A more quantitative analysis of pore sizes can also be carried out. Figure 2 shows the result of pore size measurement done with the popular image analysis program ImageJ. A high magnification image (572kX, 0.2 nm/pixel) was processed with a 4-pixel bandpass filter as a first step to eliminate false measurements due to noise. A Triangle threshold filter was then applied to create the binary map that was then subjected to particle size measurement. To be conservative, all results below 2 nm^2 area were also rejected. Without carrying out a full process to eliminate false large readings, we can concentrate on the pores in the circled area. The smallest pore detected corresponds to an elliptical shape model with major and minor axes of 2.3 and 1.6 nm, respectively. The Feret diameter of this object is 2.5 nm.

Figure 1

HIM of Middle Otter Park Shale from Horn River Basin.



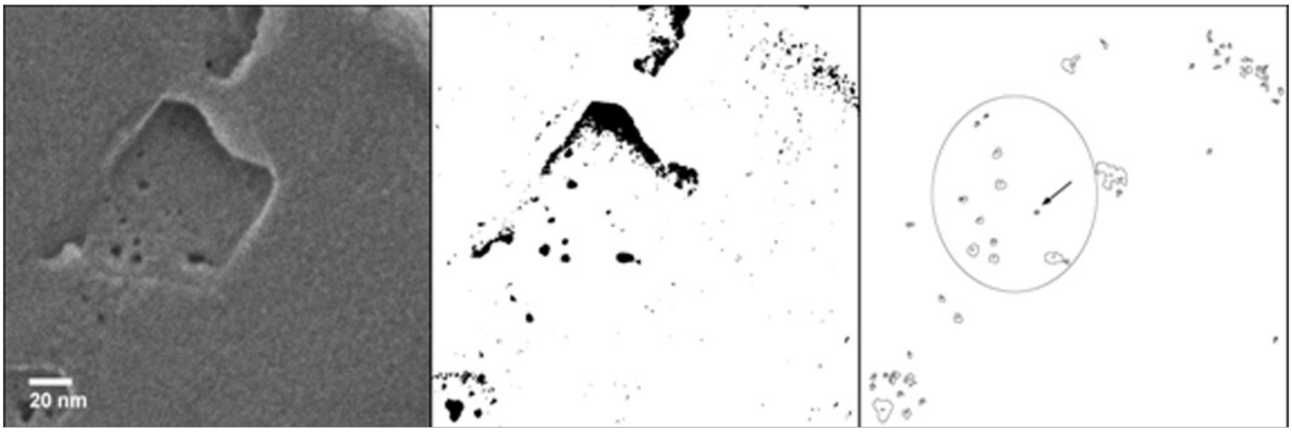
88kX image



572kX image of porous organic phase. No charge neutralization required.

Figure 2

Pore size measurement. Left: HIM image of area (572kX); Center: detected objects in ImageJ; Right: further filtering by minimum size, to highlight pores seen in center of image.

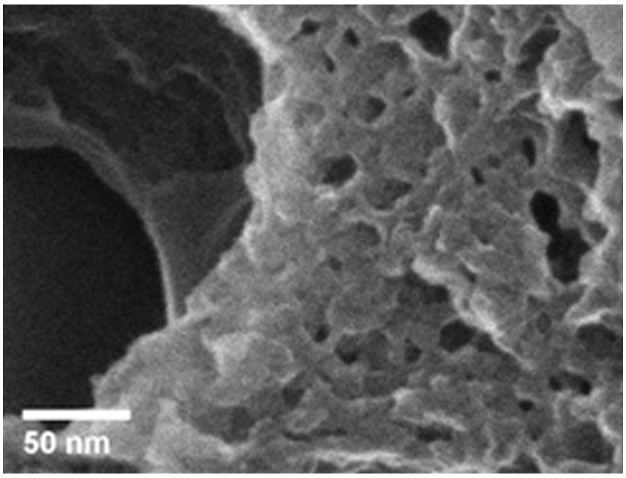


One can get a clearer understanding of the difference in imaging compared to SEM from Figure 3. These are both images taken of the same sample, at 380 kX. This particular sample at high magnification challenges the limitations of surface imaging for materials of low atomic weight materials using SEM. Even at a low 1 keV beam landing energy, the SEM imaging does not capture surface detail and the pores have lower contrast and softer edges than the HIM image. The latter provides an enormous amount of topological information. Quantifying what is observed by eye, edge resolution measurements (25%-75% rise distance) on these images indicate a HIM resolution of 0.80 nm, as compared to 2.0 nm for the FE-SEM.

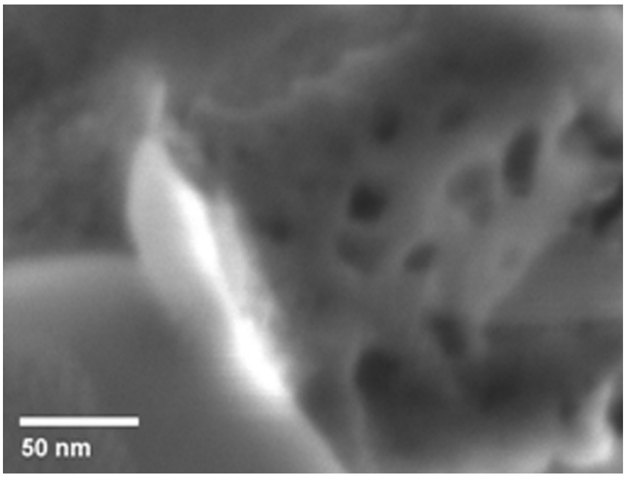
Lastly, we discuss the imaging of insulating shale samples. Porosity typically decreases with depth in sedimentary rocks due to compaction and cementation. Recently, a combination of advanced imaging techniques (high-resolution secondary electron, backscattered electron, and transmission electron microscopy) revealed that quartz cementation is inhibited when a nanofilm of amorphous silica and a layer of chalcedony forms between the surface of detrital quartz grains and the microquartz coating. This inhibiting action maintains the porosity. Observation of this nanofilm is desirable but is made more difficult by the highly insulating na-ture of the quartz. An immature shale sample, containing microquartz, was imaged in HIM using the integrated low energy electron flood gun to neutralize charge build-up. Figure 4 is a 229 kX image of a surface of one quartz facet exhibiting a nanofilm surface. The contrast between the quartz substrate and the film is strong, and the topology of the film is quite evident.

Figure 3

Comparison imaging between HIM and low voltage FE-SEM.



HIM image

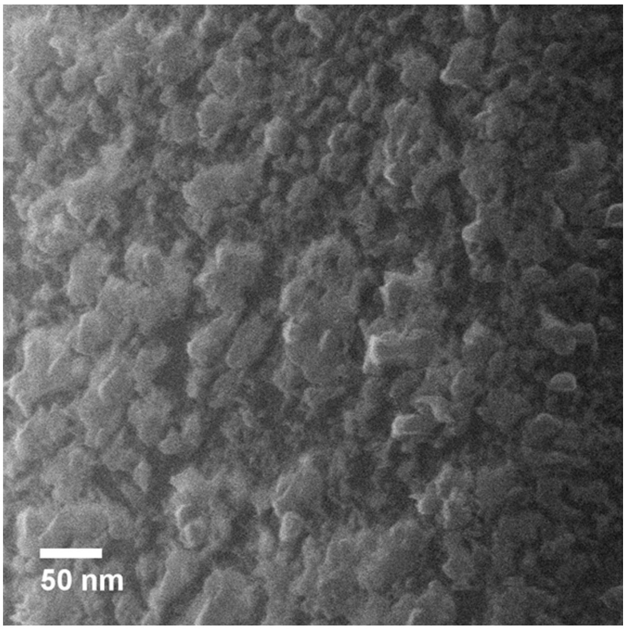


FE-SEM image

In conclusion, we see that helium ion microscopy by ORION NanoFab provide images of organic porosity in shales with resolution surpassing that of FE-SEM. A great level of 3D surface detail is provided, due to the extremely high surface sensitivity and depth of field in HIM. Minimum sample preparation by fracture allows the closest representation of the true microstructure. Quantitative pore size measurements below 3 nm are possible. In addition, this performance can be preserved even on highly insulating samples such as microquartz, immature shales, or other geological materials.

Figure 4

Surface of a facet of microquartz, imaged in HIM using charge neutralization.



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