

MACRO TO NANO: CORRELATIVE X-RAY AND ELECTRON MICROSCOPY FOR MULTI-LENGTH SCALE CHARACTERIZATION OF GEOMATERIALS

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ABSTRACT

It is well established that rocks contain a hierarchically-porous microstructure, with transport phenomena occurring over a range of length scales. Equally, it has been demonstrated that there is no single technique capable of capturing a representative volume for a single rock type, or, more appropriately, of a single formation. Here, we demonstrate the union of XRM and FIB-SEM for a comprehensive 3D dataset, representing a porous rock microstructure as viewed across multiple length scales. Further, we show how this information is complementary to traditional laboratory analysis which can provide detailed chemical, mineral, and pore size information, but with spatial averaging over relevant length scales. Using both sets of information gives a more complete understanding of one formation, representing a new paradigm in digital rock analysis.

INTRODUCTION

One of the classic challenges facing the characterization of hierarchical materials is that of length scale. In the digital analysis of rocks, the variations in features of interest span the length scales from kilometers to nanometers, and linking each length scale is critical for characterization of a particular well site [1-2]. This upscaling technique is supported by careful characterization at each of these length scales, but the linkage between them has been a challenge. In order to reduce upscaling uncertainties and properly characterize a hierarchical material, modern researchers are turning toward correlative microscopy to support the analysis. Using a suite of tools, from traditional approaches (e.g., X-ray diffraction, Fourier-transform infrared spectrometry, nuclear magnetic resonance, and gas-intrusion porosimetry) to novel techniques (e.g., X-ray microscopy, focused ion beam tomography, and scanning electron microscopy), a suitable degree of overlap may be introduced, to reduce the uncertainty at each step while simultaneously providing an appropriate range of length scales for sufficient characterization precision. In the

experiments presented here, an investigation is performed to understand the overlapping information achieved using each technique, and the unique strengths of each step are discussed in the context of digital rock physics (DRP) analysis.

MATERIALS & METHODS

In this study, a sample from the Pelplin Green Claystones Formation (Wenlock) [3] from Central Europe was examined. This sample is a mudstone dominated by carbonate-quartz heterolites with thickness up to 0.2 mm. Analysis of thin sections clearly shows detritic grains (mainly quartz, feldspars, plagioclase, carboniferous). Clay material, in which organic matter is dispersed, mainly consists of illite impregnated by iron oxides and iron hydroxides. Cements are represented by clay minerals and early diagenetic dolomite and calcite.

Dynamic porosity was calculated from the measurement performed on an AutoPore IV mercury porosimeter. The samples have been analyzed by an argon adsorption analysis method in a Micromeritic Tristar 3020 pore space analyzer. Moreover, to verify mineral composition of the samples used in XRM and FIB-SEM, ICP and FTIR methods were applied, and the results were correlated with X-ray diffraction measurements. The mid infrared FTIR spectra in a range of 580 - 4000 cm^{-1} were recorded on a Thermo Nicolet 6700 FTIR spectrometer equipped with DLaTGS detector and XT-KBr beam splitter. The measurements were performed on a diamond ZeSe Specac ATR accessory. The sample was carefully ground in an agate mortar for 3min before the measurement, and 128 scans were recorded at a resolution of 4 cm^{-1} . The measurement was independently repeated three times to verify the results. Quantitative XRD analysis was conducted with the use of the internal standard method according to the procedure designed for clay-bearing rocks, using Zinc oxide ZnO as a standard. Results were calculated with the use of the Siroquant programme, based on the Rietveld method. Quantitative measurements were carried out using a Panalytical X'Pert Pro diffractometer with a modern ultra fast detector (real time ultra strip X'Celerator). A voltage of 40 kV, current of 40 mA, and step-width 0.02° 2 θ were applied, and samples were scanned from 5° to 65° in 2 θ . In order to determine main elemental composition, ICP-MS and ICP-OES were performed, preceded by a preparation step, which included dissolving the sample with four acids: HNO₃, HCl, HF, and HClO₄.

X-ray microscopy (XRM) was performed using a Zeiss Xradia 520 Versa system, capable of providing down to 700 nm 3D spatial resolution [4]. The XRM measurements were performed across several length scales: 5 μm , 2 μm , and 700 nm voxel sizes were obtained, in order to capture a large survey volumes, while also providing high resolution microstructure characterization to scout for volumes of interest to be measured by FIB-SEM. Focused ion beam, scanning electron microscopy (FIB-SEM) tomography was performed on a Zeiss Crossbeam 540 instrument equipped with the ATLAS-3D software, using a 20 nm pixel size in all 3-dimensions. High resolution mineralogy maps were obtained using a Zeiss Sigma VP SEM equipped with Mineralogic Reservoir software to

convert quantified EDS spectroscopy into accurately quantified mineral image maps at 1 μm resolution.

RESULTS & DISCUSSION

The results from the 3D XRM and FIB datasets are shown below in Figure 1. XRM shows the bulk mineralogy and some large cracks, but does not capture some of the small pores that are typical of mud rocks. The FIB data, on the other hand, captures the small pores, but is highly localized – that is, the FIB data does not capture the large-scale heterogeneity of this sample. From XRD and FTIR analysis, the bulk chemical composition of the sample is observed, from which the bulk mineralogy may be quantitatively determined. This bulk mineralogy may be spatially localized using XRM, as shown in Figure 2a, to see where the different minerals are located within the sample volume. The FIB-SEM tomography (Figure 2b) further localizes into the 3D dataset, showing the distribution of organics and empty pores.

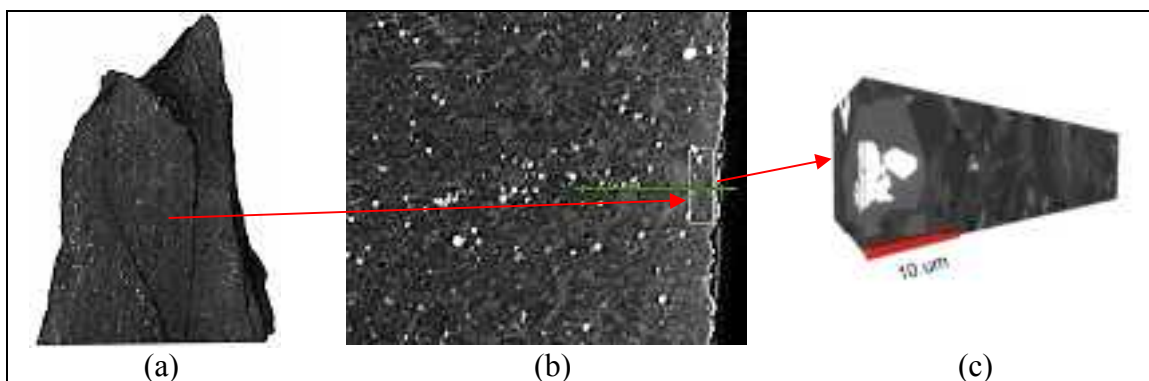


Figure 1 (a) XRM data collected with 5 μm voxel size, (b) virtual slice from the XRM data (0.7 μm voxel size) showing the FIB-SEM tomography region embedded, (c) results of FIB-SEM tomography over a 65 μm x 25 μm x 22.5 μm volume at 20 nm voxel resolution.

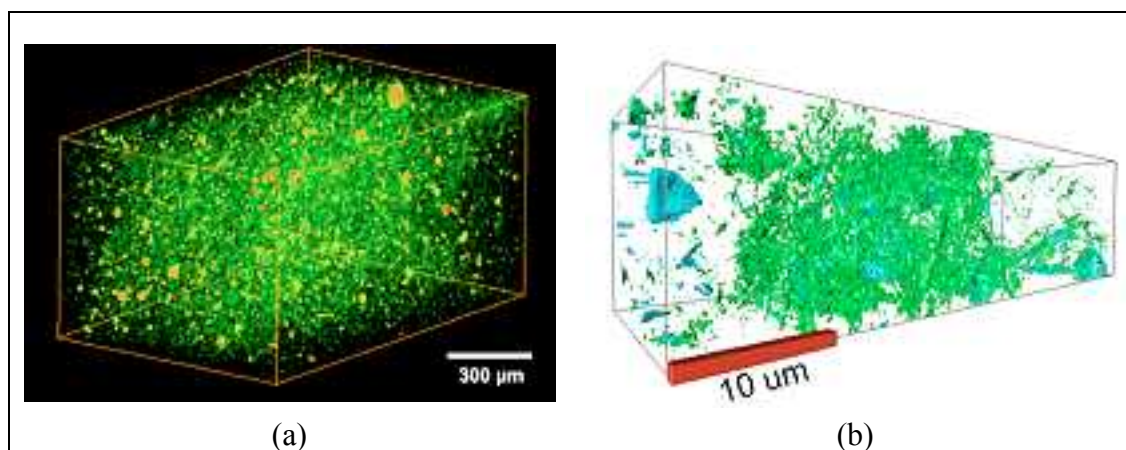


Figure 2 (a) XRM results with minerals isolated and coloured by relative optical density (red = most dense, green = least dense). (b) Segmented FIB-SEM data showing organics (green) and empty pores (blue).

From the XRD results (Table 1), the specimen is primarily composed of clay minerals, with some quartz and a smaller amount of carbonates. This mineralogy is confirmed by ICP (

Table 2), which provides further elemental speciation in terms of weight percentage. The XRM results confirm this observation, showing ~11 at% carbonates and higher-Z materials, with the rest of the mineralogy composed of lower-Z materials, such as silicon-rich minerals. XRM further provides the unique strength of determining the spatial distribution of these minerals (Figure 3), to understand where they are located within the rock microstructure.

Table 1 Results from the XRD analysis reveal a small carbonaceous composition, with the bulk material composed of quartz and clay minerals.

Quartz [%]	Carbonates [%]	Σ Clay minerals [%]	Σ Others [%]
23.7	11.5	50.1	14.7

Table 2 Results from the ICP analysis combined with FTIR (Fig. 2b) confirm the observations with XRD, providing higher elemental sensitivity and, consequently, more details about the mineralogy of this specimen.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Cr ₂ O ₃	V ₂ O ₅	LOI	Sum
55.4	13.7	5.88	4.1	4.71	1.1	3.4	0.68	0.09	0.06	0.01	0.02	8.44	97.5



Figure 3 (a) Histogram of the mineralogy measured by XRM; (b) XRM data segmented into higher-Z (red) and lower-Z (blue) minerals, displayed with their 3D positions. The higher Z materials are determined to occupy ~11% of the mineral volume, with the rest of the minerals in the lower-Z regime (e.g., Si- and Al-rich materials).

While the XRD, ICP, FTIR, and XRM results provide a very thorough description of the sample composition, both in terms of chemical speciation (XRD, FTIR, ICP) and spatial localization of minerals (XRM), they do little to elucidate the nm-scale pore networks in this particular specimen. Through 3D correlative microscopy analysis between XRM and FIB-SEM tomography, the same region was investigated to see the finer details of the specimen pore network and organic content, as shown in the correlated volumes of Figure 4 [5]. This volume of interest was selected based on the large field-of-view XRM data as containing high organic matter and associated porosity. In this way, the XRM data is used to create a sampling strategy for the higher resolution FIB-SEM tomography.

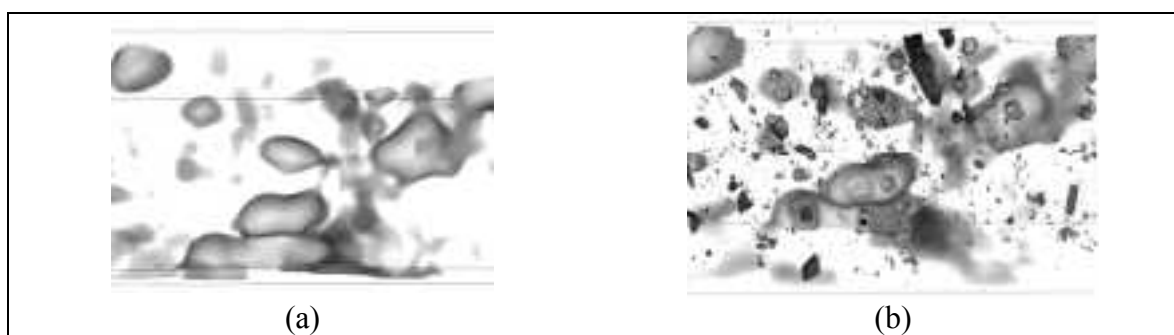


Figure 4 (a) 700nm resolution 3D XRM rendering of a volume-of-interest rich in pyrite framboids. (b) 3D FIB-SEM tomography partial data rendering co-embedded in the same region, showing enhanced detail of the matching pyrite framboids at 20nm voxel resolution.

Analysis of the FIB-SEM tomography data reveals that most of the pores are well below the 100 nm length scale (Figure 6a), and these porosity results are confirmed by the nitrogen isotherm adsorption analysis, validating the FIB technique for subsequent analysis (Figure 5b).

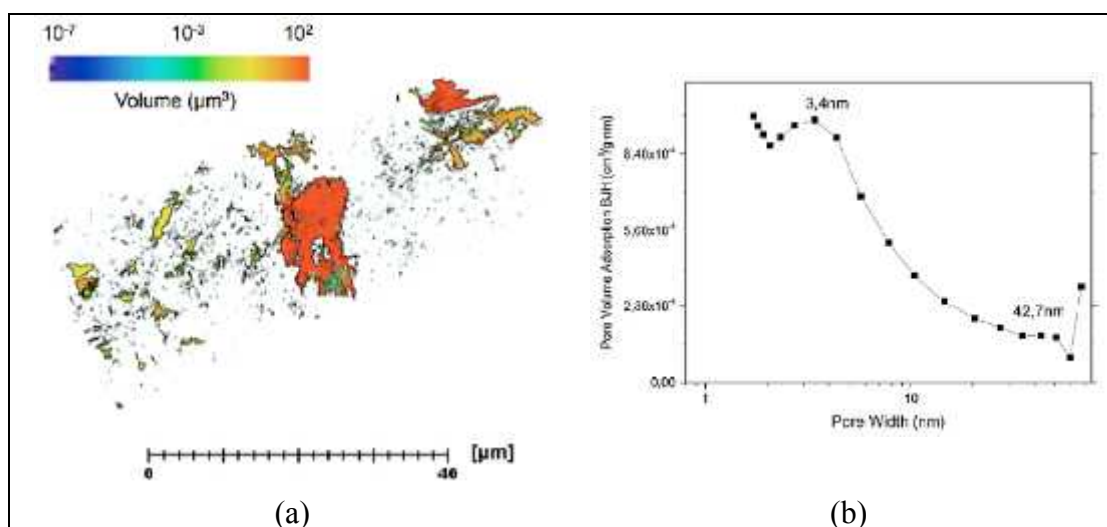
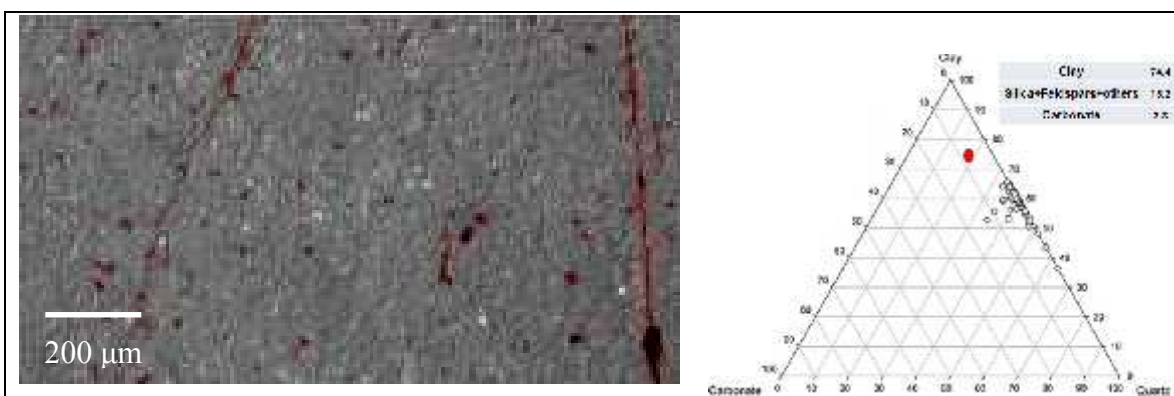
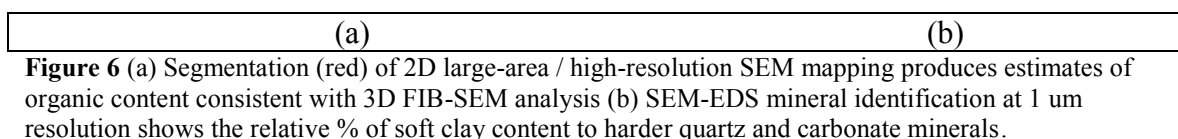


Figure 5 (a) Pore volume from the FIB-SEM tomography displayed in 3D, colored by size. (b) N₂ isotherm adsorption PSD analysis method of the same sample confirms the nm-scale of the pore distribution.





Finally, 2D imaging by SEM at 20 nm resolution was recorded of the entire unpolished 400 mm² rock face under study. This data was segmented (Figure 6a), which produced an estimated total organic content (TOC) of 2.4%, consistent with the more spatially-localized 1.8% TOC calculated from FIB-SEM tomography. An uncoated, polished surface was scanned by fully quantified SEM-EDS results yielding accurate mineralogy maps at $\sim 1 \mu\text{m}$ resolution that could be correlated with XRM and FIB-SEM data. This permitted determination of the local rock brittleness as seen in Figure 6b, shown by placement on a ternary diagram of Clay-Quartz-Carbonate %. This information is important for understanding the local susceptibility of mudrock to varying methods of stimulation, such as hydraulic fracturing. The higher total clay content shown in Figure 6b (74%) compared with the 50% found by XRD (Table 1) is consistent with local clay variation expected given that the area selected for SEM-EDS mineral analysis was an area of higher organic content, of the type shown by the large-area optical thin-section micrograph (Figure 7 – region indicated by red oval). The mineral table (Figure 7b) shows the complete mineral determination produced by SEM-EDS mineralogy, and other rock properties such as grain size and pore size and orientation are possible using this software approach.

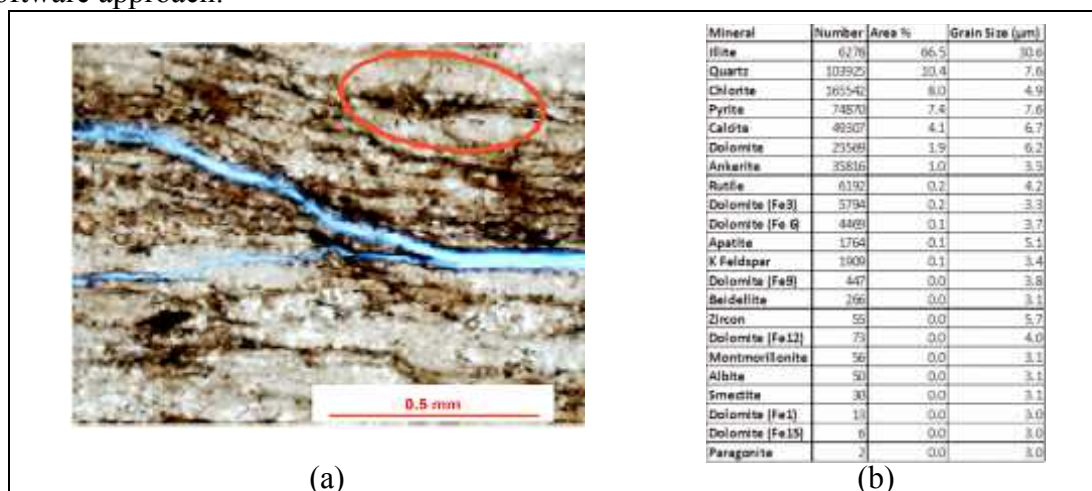


Figure 7 (a) Optical thin-section micrograph showing (red oval) region of higher organic content (b) Detailed mineral determination by SEM-EDS mineralogy including mineral % and grain size.

CONCLUSION

Here, a correlative study of a mudrock sample has revealed the unique strengths of different instruments used in digital rock physics analysis. While bulk mineralogy may be captured using XRD and further refined with FTIR, using XRM allows the minerals to be spatially-located to determine their distribution in 3D throughout the rock microstructure. Using FIB-SEM tomography, the organics and porosity and their 3D distribution may be

determined. Combining all of these results together provides a comprehensive description of the rock, which may be used as a precise input for digital rock physics modelling routines.

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