# Complementary approaches for porous network determination of a limestone by imaging techniques

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## Abstract

The pore size distribution of a material impacts their chromatographic and mechanic properties, and is closely related to the material's transport properties. As such, the pore size distribution is a key property in soil sciences, materials science and civil engineering. As the pore sizes in both natural and man-made materials can easily cover multiple orders of magnitude, characterizing the full pore size distribution with a single instrument is often impossible. X-ray micro-tomography (µCT) provides three-dimensional (3D) datasets that can be used to determine pore sizes ranging from a few microns to a few millimetres or more. Conventional electron microscopy allows to increase in resolution to explore pore classes down to a few tens nanometers. However, in contrast to X-ray tomography, it is a surface technique providing two-dimensional images. Advances in sample preparation in electron microscopy make it possible to generate 3D information by image reconstruction. Emerging technique is available and called Serial Block Face Scanning Electron Microscopy (SBF-SEM); Where an ultramicrotome liberates a surface, which is subsequently imaged by SEM. Thousands of perfectly aligned slices can be imaged in rapid succession and constitute a 3D stack from which a pore size distribution is extracted and analysed. Results by coupling X-ray tomography (pore classes >few µm) with SBF-SEM/X-EDS (pore classes >few nm) in the case of a sedimentary rock with a large pore size distribution are presented. Data obtained provide 3D quantification of pores (fractal dimension, shape and size) and their connectivity. Coupling these techniques is of a high potential due to their complementary and can lead to novel insights in various application domains (catalysis, energy storage, resource extraction, etc.).

## INTRODUCTION

To characterize the morphology of porous media the scientific community can make use of physical techniques and imaging methods. The most popular physical techniques are mercury porosimetry, BET and pycnometry. Imaging methods are based on visualisation using photons (classical or confocal microscopy) and electrons (SEM & TEM) [1]. They concern and cover a large range of pore sizes. Typically, Hg mercury is well adapted for characterizing pores between 4 nm up to 800 µm. The pore size distribution is obtained by monitoring the volume of intruded mercury into the pores as a function of applied pressure to produce a porosimetry curve. As a result, it is particularly suitable for wide pore distribution materials (mainly

macroporous materials). BET is based on gas adsorption/desorption cycles using argon, nitrogen, CO2, or krypton for low porous materials [2, 3]. The volumetric technique provides an isotherm from which BET surface, porous volume, pore size and distribution can be determined. The range of pore size distribution is between 2 – 500nm. Helium gas pycnometry is based on the Boyle–Mariotte law of the volume–pressure relationship and allows determination of the pore size distribution between 10 – 1000nm. A synthetic view, provided in Table 1, summarizes general aspects of the most frequent techniques for the characterisation of the total porosity and the pore size distribution. We do not mention AFM and SAX techniques which could also be used for porosity characterization. For AFM the upper limit to the region of interest ROI conflicts with requirements of representativity for many materials. SAX and consorts are less widely available [4]. Recent developments provide promising techniques like X-ray micro-tomography (µCT) and Serial-Block-Face (SBF) SEM which allow acquiring 3D images and extracting information such as the pore size distribution or the pore connectivity by means of image analysis. Therefore, µCT and SBF-SEM [6] appear to be complementary techniques for pore system characterization over a wide range of length scales.

We illustrate the promising nature of the combination of these two techniques on a natural Savonnieres limestone, an oolitic limestone of the upper Jurassic era and Portlandien floor [7].

Oolitic limestone is composed of ooids and a carbonate cement. Ooids are spheroidal grains with a nucleus and an accreted mineral cortex (aragonite) around it. The sphericity increases with distance from the nucleus. The nucleus is generally either a mineral grain or a biogenic fragment. The nucleus can be conserved or not. The porosity of such limestone is complex (Fig.1), with a large range of pore sizes [8]. While µCT is frequently used for the morphological characterisation of rocks and building stones, SBF-SEM is typically used to analyse soft materials (cell, tissues, vegetal, animal organs, etc.). The resolution of µCT ranges from slightly below 1µm up to a few 100 µm, depending on the sample size and composition. In contrast, SBF-SEM covers features from 1 nm up to a few µm. Often cited advantages of µCT are that it is a non-destructive technique, requiring limited to no sample preparation and providing 3D morphological information (grain size, shape, poral distribution, phase contrast between light and high Z element number). It allows a fast data acquisition on a large volume (several $cm^3$). The SBF-SEM needs a delicate sample preparation (stack of hundred thin slices to reveal a representative volume of the material, stable under an electron beam and high vacuum. Images are typically generated by detecting Back Scattered Electrons (BSE). Time is also an important parameter and if µCT needs minutes to hours (depending of the resolution expected), SBF-SEM could hours or days (function of the number of thin slices and resolution expected). Parameters applied for the 2 techniques are provided in Table 2. The workflow (Fig. 2) induced by SBF-SEM is not a complex one but requires careful sample preparation. In this study we used Napary software for alignment of the acquired data and the processing of the 3D images [9]; Amira 6.4 was used for segmentation [10] and Imaris for image analysis [11]. As will be shown, the association of SBF-SEM with µCT provides complementary information about the porous network of a rock like a limestone of complex porosity.

## RESULTS

µCT provides in few hours a full 3D image of a large volume of the limestone with a resolution of 7µm (Fig.3). The image reveals contrasted zone dense areas (white to grey contrast) and voids (black). They correspond to the limestone with matrix of carbonate calcium ($CaCO_3$) matrix (red arrow) and oolites (blue arrows). Black areas correspond to voids revealing a complex porosity. In fact, porosity can be classified between internal and intergranular ones. Internal porosity corresponds to empty oolites (orange arrow) and intergranular ones to porous network, developing by sedimentary mechanisms during diagenesis. The full volume (around 4 $cm^3$), in 4 hours, was investigated. Dynamic 3D view is available and can be explored slice by slice to calculate limestone porosity. µCT provides an estimation of the porosity range which corresponds to classes (3,4): between 200 µm and few mm.

SBF-SEM generates, after image reconstruction, a 3D images at a resolution of 10 nm (Fig.3). Due to SBF, a reduce volume is required (Tab.2) and time induced by the workflow becomes consequent. From sample preparation to SEM stack images steps approximatively 36hrs have been required. The figure 4 corresponds to the result obtained by SBF-SEM where image stacks (432 slice of 5 nm thickness each). The volume explored, in this example, is around 4 $\mu m^3$. Dynamic contrasted 3D views are generated and reveal porosity (white area) and carbonate matrix (black) of the full volume or by 2D sections (x,z) or ( y,z) planes, illustrated in figure 4; Or along (x,y) plane (not illustrated). By image analysis it is possible to extract quantitative data about porous network. The range size available belongs to the (1,2) classes (fig.1) typically between 10 nm up to few hundred µm.

## CONCLUSION

Demands, relative to 3D poral network texture at different scales (shape, size, type, continuum and connectivity of material, become a key point. If there is lot of techniques able to precise the pore size, and pore distribution; 3D images at nm scale up to mm are required especially to full characterize the poral network texture. For example, to inform about shape (spherical or not), homogeneity or heterogeneity (size or shape gradient), connectivity along the three directions are essential data for modelling transport, catalysis, energy storage, resource extraction, etc. By combining µCT and SBF-SEM, this exploring study confirms their great complementary. They reveal the full poral network of a test limestone by 3D static and dynamic images at different scale, from class 1 (nm) up to 4 (mm) in the case of a reference limestone. By Image analysis, quantitative data have been obtained (not presented) and have to be confirm by another essays. Yet, the authors are fully confident that µCT and/or SBF-SEM will become appropriate methods for poral network characterization, by new technical developments, in a close future.

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Figures and Tables

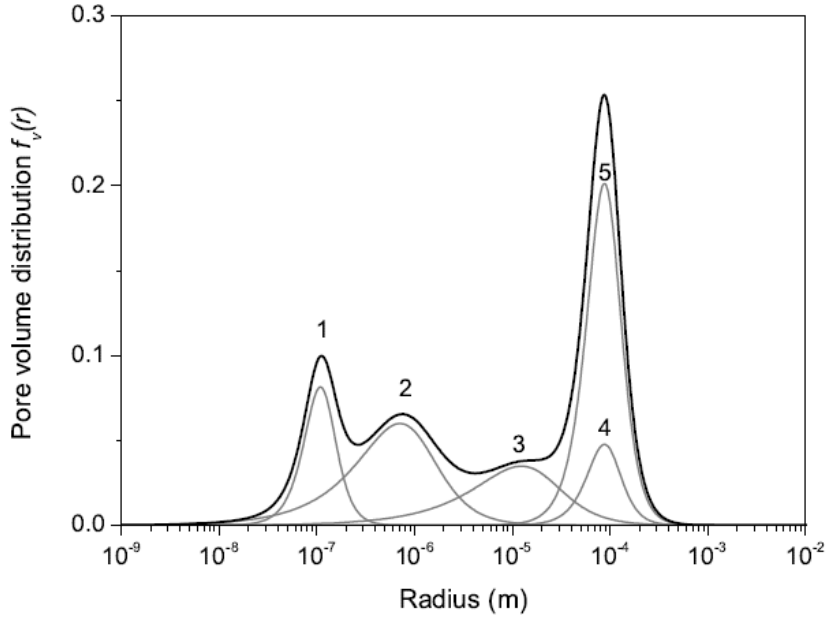


Figure 1 : Pore size distribution of Savonnière limestone (reproduced from H. Derluyn, dissertation, ETH Zurich, 2012).

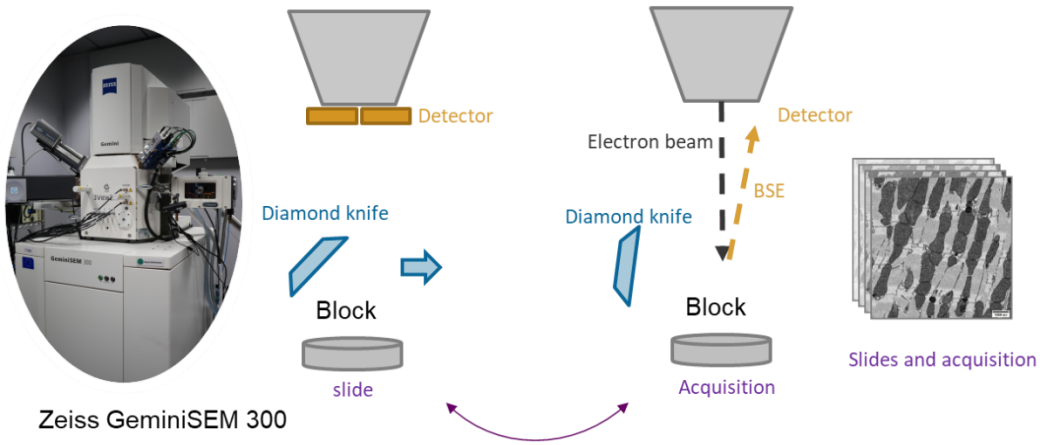


Figure 2: Workflow of SBF-SEM

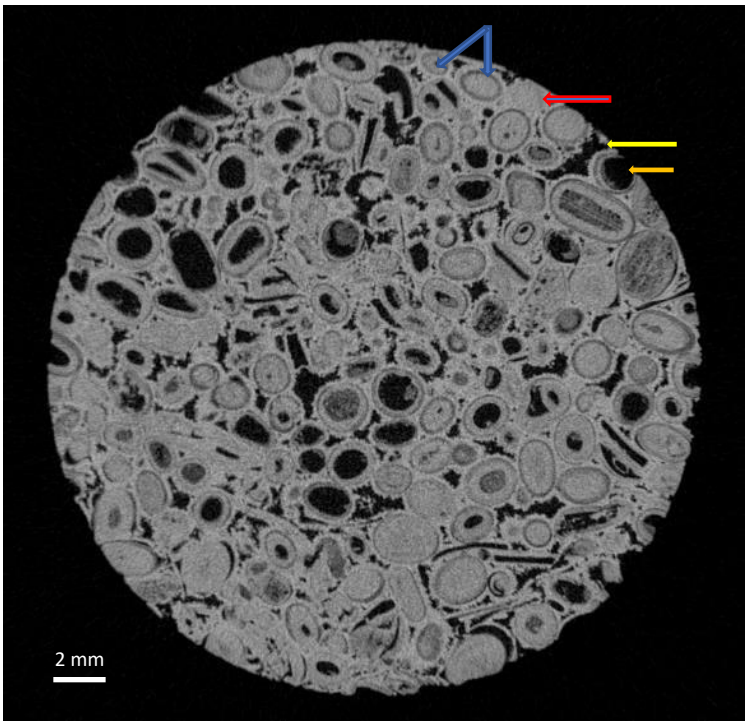


Figure 3: A representative slice extracted from the 3D dataset obtained by µCT. Black corresponds to voids while the different shades of grey all correspond to the $CaCO_3$ matrix with various mass densities.

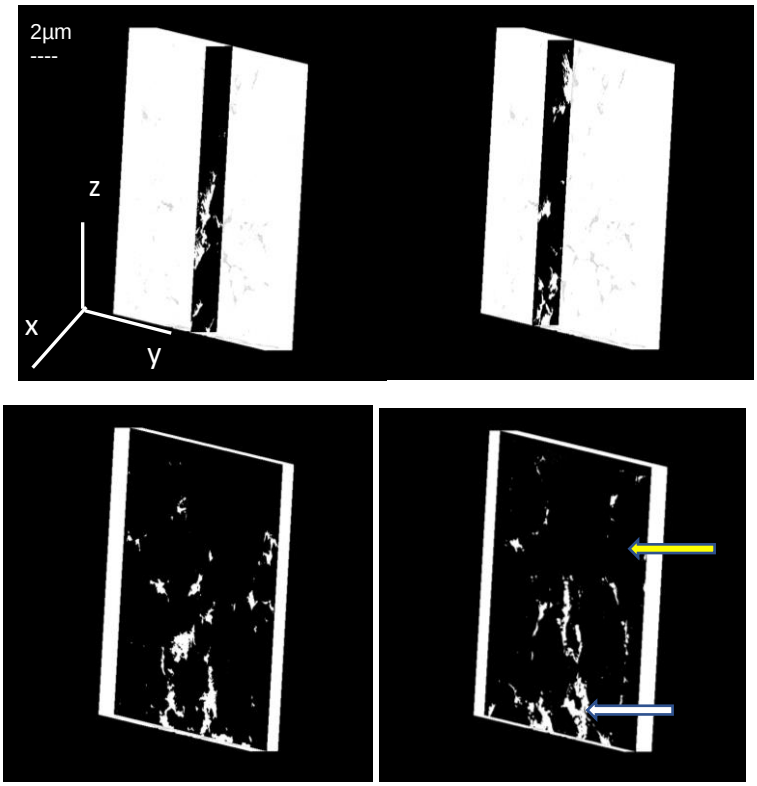


Figure 4: From dynamic video, slice image extraction along (x,z) upper images and (y,z) lower images. Each section corresponds to a slice thickness of 5 nm. In the section, voids appear white (white arrow), while limestone matrix appear in black (yellow arrow).

| Type | Method | Results | Pore Range (nm) | Limit |
|---|---|---|---|---|
| Physical | Hg Porosimetry | pore size distribution, pore diameter | 4 - 80000 | dry hard materials, not adapted for low porous material, Au element, CD (Hg contamination), time |
| | He Pycnometry | pore size distribution, pore diameter | 0.1 - 1000 | dry hard & soft materials, CND, time$^{+}$ |
| | BET | specific surface, pore size distribution | 0.1 - 10 | hard materials, > 0.3 nm$^2$, accuracy ≤ 10%, CND, time$^{+}$ |
| | OM-COM/IA | pore size distribution, pore diameter | > 500 | hard & soft materials, sample preparation, accuracy, large pores,2D-3D, time$^{++}$ |
| Imaging | SEM/IA | pore size distribution, pore diameter | > 1 | hard & soft materials, ROI limited, sample preparation2D, time$^{+++}$ |
| | TEM/IA | pore size distribution, pore diameter | > 0.1 | hard & soft materials, ROI limited, sample preparation, CD,2D-3D, time$^{++}$ |
| | µCT | pore size distribution, pore diameter | > 2000 | hard materials, no sample preparation, CND, 3D, time$^{-}$ |

Table 1: most frequent methods for porosity characterization (CD: Control Destructive; CND: Control Non-Destructive; ROI: Region of Interest; IA: Image Analysis).

| | SBF-SEM | µCT |
|---|---|---|
| Sample preparation | resin embedded, vacuum, Ag glue on a pin of limestone | no |
| Operating parameters | BSE mode, Mag. <15k | absorption contrast |
| Volume analyzed | 4 µm$^3$ (431 slides of 5 nm thickness, surface of 2 mm) | > few cm$^3$ |
| Time | > 32hrs | < 8 hrs |

Table 2: Operating parameters of the 2 techniques