Clay characterisation from nanoscopic to microscopic resolution

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BIB-SEM of Representative Area Clay Structures: Insights and Challenges

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Abstract

BIB polishing in combination with SEM imaging is used to study the pore microstructures and -fabrics in clay-rich host-rocks on 2D mm² flat and undamaged CS with resolutions down to a few nanometers in REA. BIB-SEM approach allows both qualitative and quantitative investigations of porosity and targeting for nano-FIB tomography. These results in the characterization of porosity-homogeneous and -predictable islands, which form the elementary components of an alternative concept of porosity/permeability model based on pore microstructures.

Introduction

A major contribution to understanding the sealing capacity, coupled flow, capillary processes and associated deformation in clay-rich geomaterials is based on detailed investigation of the rock microstructures. However, the direct characterization of pores in REA and below µm-scale resolution remains challenging. To investigate directly the mm- to nm-scale porosity, SEM is certainly the most direct approach, but it is limited by the poor quality of the investigated surfaces. The recent development of ion milling tools (BIB and FIB; Desbois et al, 2009, 2011-a; Heath et al., 2011; Keller et al., 2011) and cryo-SEM allows respectively producing exceptional high quality polished cross-sections suitable for high resolution porosity SEM-imaging at nm-scale and investigating samples under wet conditions by cryogenic stabilization. This contribution focuses mainly on the SEM description of pore microstructures in 2D BIB-polished CSs of Boom (Mol site, Belgium) and Opalinus (Mont Terri, Switzerland) clays down to the SEM resolution. Pores detected in images are statistically analyzed to perform porosity quantification in REA. On the one hand, BIB-SEM results allow retrieving MIP measurements obtained from larger sample volumes. On the other hand, the BIB-SEM approach allows characterizing porosity-homogeneous and -predictable islands, which form the elementary components of an alternative concept of porosity/permeability model based on pore microstructures.

Samples

Authors are interested in pore-related microstructures in all types of low porous and low permeable host-rocks: rocksalts (Desbois et al., 2008, 2011-b), clays from reference sites for research (BC-clay, OP-Clay-ShF, OP-Clay-SaF and To-Clay, Desbois et al., 2009; Houben et al., submit.), tight gas reservoir sandstones (Desbois et al., 2011-a), organics-rich shale, coal, mortar and cements. Samples OP-Clay-ShF (Gallery 98-BCS-2), BC-Clay-HADES (EZE55, Core 77c122, Bed 90), BC-Clay-CG
(EZE52, Core 48c, Bed 114) and EZE54 and BC-Clay-FG (Core 65c, Bed 100) are extensively presented in this contribution but pictures from To-Clay (CN4-STD-05-600) and organic-rich shale are also shown.

**Methods**

**Sample preparation**

Core samples, originally stored in Al barrier foil, are slowly dried in air at room temperature. Sub-samples (ca. < 0.5 cm$^3$) are cut dry with very low-speed diamond saw and glued on BIB sample holders. The quality of BIB-CS is optimized by pre-polishing using carbide paper (down to grit size 1200) which reduces the surface roughness to ca. 20 µm. The BIB (JEOL-SM 09010, 6 kV, 8hrs) removes a slice of 100 µm, which eliminates the damage from the pre-polishing, and produces high quality surface. The CS is coated with carbon or gold.

**Ion beam techniques for surface preparation and SEM**

BIB-FIB-SEM are powerful combination to prepare 2D flat undamaged CS (curtaining less than 5 nm deep, Figure 1). Two main types of ion sources are available. (1) A BIB (few mA, Ar-source) is suitable to produce large polished CS area of few mm$^2$ (Figure 1.a). BIB cross sectioners are available as standalone machines able to produce single polished CS. (2) FIB are based on Ga-ion sources (1pA - >50nA) to produce typical CS of a few µm$^2$. FIB sources are commercially embedded into SEM to allow serial sectioning for 3D tomography. BIB has two main advantages: (1) it is potentially less damaging since it is based on noble gas source and (2) it produces CS which fits better to the typical length scale range of microstructures and REA.

![Figure 1. The principle of BIB and FIB sectioning and overviews of produced CS. (a) the ion beam irradiates the edge of a sample un-masked by the shielding plate to create high quality polished CS suitable for SEM imaging. (b) The FIB scans the region of interest to be milled.](image)

Cryo methods can be coupled to SEM in order to track in situ fluids in pore space. This approach is based on the fast freezing of the samples to very low temperatures, which effectively quenches the fluid-filled pores, followed by high resolution electron microscopy at cryostatic temperatures. Cryo-SEM is now commercially combined with a FIB milling (Holzer et al., 2010; Desbois et al., 2008, 2009). A BIB-cryo-SEM is actually in development at RWTH-Aachen University (Desbois et al., 2011-b) to combine all advantages.

**Microstructures and fabrics imaging, and image processing**

The SEM used is a Zeiss Supra 55 equipped with SE2, SE-inlens, BSE and EDX detectors. Typically, SE imaging is performed at <10KV while BSE and EDX imaging at 20-25 kV, both at WD < 10 mm. The point counting method based on the mineralogy with different square box sizes determines the REA for the pores present in a BIB-CS. In order to image the REA with sufficient pore resolution, SE micrographs are combined into one high-resolution image (>100 million pixels) using Autopano giga.
Qualitative investigations of pore space from mm$^3$ scale area down to pore scale

Overviews of BIB-SEM performed on BC-Clay-HADES, OP-Clay-ShF, To-Clay and organic-rich shale (Figure 2) show characteristic fabrics. BC-Clay-HADES is mainly made of highly porous CM with few embedded non-clay, poorly porous minerals. OP-Clay-ShF is built with numerous non-clay minerals with significant intra-grain porosity (fossils and pyrite frambooid) embedded in CM less porous than BC-Clay-HADES. Porous fossils and pyrite frambooid are also common in To-Clay but much more dispersed in very tight CM. Shale fabric is similar to OP-Clay-ShF but with very tight CM.

Resolution of SE-mosaics (Figure 2), allows zooming in to detect single pores close to the SEM resolution (ca. 5 nm) in the CM of BC-Clay-HADES (Figure 3) and OP-Clay-ShF (Figure 4), and typical single pores found in fossil (Figure 4a), in siderite (Figure 4b) in pyrite frambooid (Figure 4d) phases as well as in fractures (Figure 4c) from OP-Clay-ShF.

Figure 2. Overviews of pore fabrics in four different types of clay-rich host-rocks.

Figure 3. Single pores from CM in BC-Clay-HADES, at high resolution.

Figure 4. Diversity of single pore morphologies in different mineral phases of OP-Clay-ShF
In OP-Clay-ShF (Figure 4), five different porous phases were found: (1) *Siderite grains* are parallelogram-shaped with elongated to circular pores with jagged edges non-connected to each other and to the CM; (2) *Fossils* are usually half-moon shaped with angular pores of 500 nm in diameter connected to each other’s and with the CM; (3) *Quartz* are rounded grains with a diameter up to 30 µm and can contain rare round pores, with smooth edges; (4) *Pyrite framboïd* – are up about 5 µm in diameter and made of sub-µm single pyrite grains with between pores of about 500 nm in size; (5) *CM* consists of grains of size < 2 µm with three kinds of pore: Type I - the elongated pores between similarly oriented clay sheets, Type II - crescent shaped pores in saddle reefs of folded sheets of clay and Type III - large jagged pores surrounding clastic grains. In BC-Clay-HADES (Figure 3), only the CM is significantly porous and pore types are the same than those found in OP-Clay-ShF. In addition for both samples, within the CM, cracks are also present and oriented along the bedding.

In OP-Clay-ShF, REA is measured to be about 100 x 100 µm²; about 70 x 70 µm² in BC-Clay-HADES and BC-Clay-FG; and 140 x 140 µm² in BC-Clay-CG. The REA is interpreted as the minimum area to be investigated to describe representative pore microstructures and fabrics. Coupling the information from quantitative (EDX) and qualitative (BSE) chemical composition measurements with single pores detection in REA, maps of porosity are drawn to describe the 2D distribution of pore space as a function of the nature and the distribution of mineralogy (Figure 5).

Figure 5. 2D map of porosity in OP-Clay-ShF vs. mineralogy.

Figure 6. Fluid-filled pores in BC-Clay-HADES (a.) and OP-Clay-ShF (b.) by FIB-cryo-SEM.
Figure 6 shows in situ fluids in the clay matrix pores of type III in sample prepared by FIB-cryo-SEM. Imaging frozen fluids in pore type I and II is more difficult since at higher magnification the energy of the e⁻-beam sublimes the fluids before an image can be recorded. Tracking in-situ fluid-filled pores should offer new insights for the study of fluid-rock interaction. Cryo-stabilization should also be considered as an alternative method to stabilize the pore microstructures without damage.

Quantitative investigations of pore space

Pores visible in SE-micrographs are statistically analyzed in REA. Due to the complexity of pore morphologies (Figure 3a), usual algorithms for object detection do not provide efficient segmentation. Therefore, pores are manually segmented. This is time consuming but allows accurate description of the spatial and size distributions, morphologies and orientation of the pores. Moreover, these data are also used to develop alternative automatic pore detection as benchmark data. For example, a REA of studied OP-Clay-ShF (Figure 5) contains more than 50,000 detected pores corresponding to 3% of visible porosity at the resolution of SEM.

Porosity from BIB-SEM in OP-Clay-ShF vs. MIP

From BIB-SEM data, pores in clay-matrix are power law distributed with $D = 2.3$ (Figure 7a). Assuming that pores, which are not visible at the SEM resolution, are also distributed following the same power law, the extrapolation of this down to 3-4 nm pore diameter gives an estimated total porosity of 17-23% born by the CM (Figure 7b). BIB-SEM shows fossils and pyrite framboïds as well as cracks are directly connected to the CM adding about 1.5-4% of porosity. Therefore, based on BIB-SEM and assuming that pores in CM are connected, the total connected porosity is estimated in the range of 18.5-27%. This matches quite well the porosity measured on similar samples by MIP (Figure 7d). Based on MIP measurement, connected pore follow also a power law distribution with $D = 2.2$ (Figure 7c), which fits quite well the value inferred from BIB-SEM. Thus, this suggests that the CM mainly controls the connectivity of the OP-Clay-ShF. These analogies show also that BIB-SEM investigations can be up-scaled to bulk porosity based on larger sample volume (MIP).

Figure 7. Pore size distribution and total porosity data from BIB-SEM (respectively a. and b.) and MIP (respectively c. and d.) in OP-Clay-ShF.
**Porosity vs. grain size in clay-rich islands from BC-Clay**

At first look, the overall fabrics of BC-Clay-HADES, BC-Clay-FG and BC-Clay-CG (Figure 8.a, b, c respectively) look different for similar areas of investigation. However, at scale of CM regions, statistics for pores < 300 nm in size have same pore size distribution (Figure 8d), same D = 1.7 (Figure 8e), same pore orientation (// to the bedding), same pore types and same pore morphologies, independently of the grain size. Pore of > 300 nm in size are preferentially located surrounding the clastic grains (Figure 8a). This is confirmed by plotting, for each grain, the pore area as a function of distance from the grain (Figure 8f). This suggests that the biggest pores are constrained by the clastic grains. Further work is still needed to check if the mineralogy and the size of single clastic grains play a role.

![Figure 8](image)

Figure 8. (a., b. and c.) Pore fabric overview in BC-Clay-CG, BC-Clay-Hades and BC-Clay-FG, respectively. (d) Contribution to porosity as a function of pore radius. (e.) Pore size distribution. (f) Pore area vs. distance from single grain.

**The concept: pore fabric based on porosity-homogeneous and -predictable islands**

Surprising is that BIB-SEM observations give clear evidences that the non-clay minerals and CM form distinct islands with homogeneous and predictable pore space characteristics in the same BIB-CS. All kinds of islands are considered as “elementary components”, which form the overall fabric of the claystones when combined all together (Figure 9).

For example, the overall fabric of OP-Clay-ShF, defined by a REA of 100 x 100 µm², results then in grains of non-clay minerals (pyrite, mica, quartz, calcite, fossils, pyrite) embedded in CM and randomly distributed along the bedding planes. In terms of connectivity and at the scale of SEM, different kind of islands can be classified into 3 classes: (1) the CM, (2) the porous regions connected to the CM (fossils, pyrite, cracks), and (3) others non-porous islands (quartz, organics, mica, calcite) and porous regions but not connected to the CM (siderite). Thus, from a microstructural point of view, the heterogeneous OP-Clay-ShF can be seen as the combination and juxtaposition of homogeneous and predictable porous islands: regions of high and highly connected porosity (fossils, pyrite, cracks) and non porous (or non connected) regions are isolated and embedded within the low permeable and low porosity CM. Islands with high and highly connected porosity are connected to each other via the low permeable and low porous CM. Following this, the flow properties of OP-Clay-ShF should be mainly controlled by the porosity and permeability of the CM.
Conclusions and outlooks

BIB-SEM approach enables: (1) imaging the porosity in 2D flat and undamaged REA down to the SEM resolution; (2) investigating pore morphologies; (3) classifying pore types as a function of mineralogy and fabrics when BSE and EDX tools are used; (4) quantifying the porosity from digitized pores which results in prediction of pore characteristics for each porous phases; (5) linking pore microstructures to conventional MIP based on larger sample volumes. From these, emerges an alternative concept of porosity/permeability model based on pore microstructures, where the BIB-SEM approach allows characterizing porosity-homogeneous and -predictable islands. BIB-SEM combination appears then as necessary to bridge the µ-CT to nano FIB tomography methods.

To continue the deeper understanding of pore microstructures in natural clay-rich host-rocks, further work is still needed: (1) BIB-SEM approach should be used complementary to µ-CT to describe 3D-mineral fabrics at larger scale and to FIB-SEM to build natural 3D pore network as basic for permeability calculation of local islands. (2) How does the pore distribution in clay-rich islands evolve as a function of depth or local tectonics? (3) Then, may the power law exponent of pore distribution in clay-rich islands define the origin of clay? (4) Can other conventional porosimetry measurements be retrieved from BIB-SEM studies? (5) Image analysis algorithms need to be especially designed for automatic pore segmentation from BIB-CS to speed up the interpretation of images. (6) Because, pore throats are typically below 10 nm (Keller et al., 2011): do we need to include TEM methods in microstructural studies or/and perform Wood’s metal intrusion combined with BIB-SEM to evaluate directly the intrusion process? (7) Tracking the in-situ fluid-filled pores and drying effect by using cryo-SEM approaches.
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References


