Physics and Chemistry of the Earth 36 (2011) 1539–1544

Contents lists available at SciVerse ScienceDirect

Physics and Chemistry of the Earth

journal homepage: www.elsevier.com/locate/pce

On the application of focused ion beam nanotomography in characterizing the 3D pore space geometry of Opalinus clay

Lukas M. Keller [a,*], Lorenz Holzer [a], Roger Wepf [b], Philippe Gasser [b], Beat Münch [a], Paul Marschall [c]

[a] *EMPA, Materials Science and Technology, Laboratory for High Performance Ceramics, CH-8400 Dübendorf, Switzerland*
[b] *ETHZ, Swiss Federal Institute of Technology, EMEZ, Centre for Imaging Science and Technology, 8093 Zürich, Switzerland*
[c] *NAGRA, Hardstrasse 73, CH-5430 Wettingen, Switzerland*

ARTICLE INFO

Article history:
Available online 3 August 2011

Keywords:
Argillaceous rocks
3D pore structure
Gas transport
Focused ion beam technique

ABSTRACT

The evaluation and optimization of radioactive disposal systems requires a comprehensive understanding of mass transport processes. Among others, mass transport in porous geomaterials depends crucially on the topology and geometry of the pore space. Thus, understanding the mechanism of mass transport processes ultimately requires a 3D characterization of the pore structure.

Here, we demonstrate the potential of focused ion beam nanotomography (FIB-nT) in characterizing the 3D geometry of pore space in clay rocks, i.e. Opalinus clay. In order to preserve the microstructure and to reduce sample preparation artefacts we used high pressure freezing and subsequent freeze drying to prepare the samples. Resolution limitations placed the lower limit in pore radii that can be analyzed by FIB-nT to about 10–15 nm. Image analysis and the calculation of pore size distribution revealed that pores with radii larger than 15 nm are related to a porosity of about 3 vol.%. To validate the method, we compared the pores size distribution obtained by FIB-nT with the one obtained by N_2 adsorption analysis. The latter yielded a porosity of about 13 vol.%. This means that FIB-nT can describe around 20–30% of the total pore space. For pore radii larger than 15 nm the pore size distribution obtained by FIB-nT and N_2 adsorption analysis were in good agreement. This suggests that FIB-nT can provide representative data on the spatial distribution of pores for pore sizes in the range of about 10–100 nm. Based on the spatial analysis of 3D data we extracted information on the spatial distribution of pore space geometrical properties.

1. Introduction

Low-permeability rock formations such as clay rocks are proposed as potential host rocks for the disposal of radioactive waste (Andra, 2005; Nagra, 2002, 2004). A validation the disposal system requires a comprehensive understanding of the mass transport mechanism and processes in the host rock as well as in the engineered barriers (i.e. canister, bentonite buffer, etc.). The transport properties of low-permeability rocks are fundamentally controlled by the structure of the available pathways for transport. Clay rocks contains a network of micro to macropores with pores sizes ranging between 1–100 nm which most likely dominates the flow and transport properties in the rock (e.g. Marschall et al., 2005). Furthermore, clay rocks are anisotropic because of preferred orientation (or texture) of clay minerals attained during sedimentation and compaction (e.g. Lash and Blood, 2004; Wenk et al., 2008). It is very well possible that the pore space geometry is linked to the surrounding frame of clay minerals. Thus, a pore space anisotropy can reasonably be expected. In the case of Opalinus clay, experiments indicated anisotropic diffusion of solute species with fast diffusion parallel and slow diffusion perpendicular to the bedding plane (e.g. Van Loon et al., 2004). Anisotropic diffusion is suggested to be related to an anisotropy in pore path tortuosity (Van Loon et al., 2004).

Profound understanding of well-known anisotropic transport phenomena requires knowledge of the 3D topology of pore space. The spatial distribution of transport relevant geometrical properties is ubiquitous when discussing anisotropic transport. Concerning gas transport, the geometry of those pores that corresponds to comparable larger pores (i.e. >10 nm) may control potential gas flow. Thus, information on larger pore connectivity, geometry and distribution is crucial. The transport of gas along the pore network is a key issue regarding the safety of the geological repository (e.g. Horseman et al., 1996; FORGE, 2010; Senger et al., 2008; Ortiz et al., 2002).

With a few exceptions (e.g. Fredrich et al., 1995; Lindquist and Venkatarangan, 1999; Nakashima et al., 2004; Zabler et al., 2008) 3D characterizations of the pore space in geomaterials and in clay rocks in particular are largely absent. The resolution of the used methods was not sufficient to characterize the pore space of consolidated clay rich sediments of which pore sizes range in the nano

---

* Corresponding author. Tel.: +41 44 823 4824.
E-mail address: Lukas.Keller@empa.ch (L.M. Keller).

1474-7065/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.pce.2011.07.010

scale. Therefore, investigations applying new high-resolution analytical techniques to porous geomaterials are urgently needed. Here, we contribute to the nano scale description of clay rocks by presenting results which were obtained in the course of a feasibility study. We tested the viability of FIB-nT (Holzer et al., 2004, 2010; Holzer and Cantoni, in press) in exploring the pore space of naturally compacted clay rocks (i.e. Opalinus clay) in 3D and on the nano scale. To date FIB-nT was successfully applied to bentonite (Holzer et al., 2010). In addition, the method was validated by comparing pore size distributions which were obtained by N_2 adsorption analytics and numerical calculations based on 3D imaging (i.e. FIB-nT). Given that FIB-nT can analyze only very small sample volumes such a comparison allows to evaluate its "representability" in characterizing the properties of geomaterials. In addition, we outline the potential of the obtained 3D data in extracting information on material properties.

2. Methodology

2.1. Samples

The rock sample (i.e. sample BHG A.2/2) was collected from the Opalinus clay rock unit at the Mont Terri rock laboratory in northwest Switzerland (Canton Jura, Switzerland; Bossart and Thury, 2008). This laboratory is located in the security gallery of the Mont Terri motorway tunnel. Sedimentation of Opalinus clay occurred around 180 my ago in a shallow marine basin. After sedimentation the rock unit underwent to two stages of burial with a maximum burial depth of about 1350 m. Folding of the mountain belt occurred between 10.5 and 3 my ago. The Opalinus clay can be subdivided into three main facies: shaly facies, sandy facies and carbonate rich sandy facies. The sample was taken form the sandy facies about 250 m below the surface.

2.2. Sample preparation

Electron microscopy (FIB/SEM) and N_2 adsorption analysis requires drying of the samples prior to analysis. Conventional drying and/or freeze drying of moist clay may cause preparation artifacts such as drying shrinkage (conventional drying), ice formation during freeze drying or surface roughness during mechanical polishing. Special methods such as high pressure freezing and subsequent freeze drying were used in order to avoid these artifacts.

The sample preparation includes the following steps: Clay slaps with a thickness of 200–300 μm and a diameter of 5–6 mm were cut with a diamond wire saw parallel to the bedding plane. Then the slaps were frozen under high pressure (2100 bar) and within milliseconds by using a HPM 010 apparatus. This treatment prevents the formation of ice-crystals and thus preserves the delicate framework of the pore space. Then the vitrified water was sublimated under high vacuum by using a BAF 400 apparatus (see also Holzer et al., 2010). Details of high-pressure freezing techniques and its application for cryofixation are given by Bachmann and Mayer (1987).

2.3. Direct pore space analyzes using FIB-nT

FIB-nT is done with of FIB–SEM instruments in which an ion beam and an electron beam focus and intersect at a point on the sample surface known as the coincident point. The electron beam is vertical and the ion beam is off vertical by about 50° (Fig. 1). The sample is tilted normal to the ion beam, ion milling creates a cross sectional surface that can be immediately imaged at high resolution by the electron beam without moving the sample. 3D information with a FIB–SEM instrument can be obtained by a technique, known as "slice and view", consists of acquiring a sequence of cross sectional images spaced evenly through a region of a bulk specimen, and reconstructing those two-dimensional images into a three-dimensional representation of the sampled volume (Holzer et al., 2004). The slice and view process begins by the milling of a wedge shaped trench in the sample. One wall of the trench is vertical (i.e., normal to the specimen surface) and becomes the initial cross section imaged by the electron beam. After imaging, the ion beam is used to remove a uniform layer of material from this wall, advancing the cross section a predetermined distance through the sample volume. Another electron image is collected and the milling/imaging process iterates until the cross section advances through the targeted volume. For the present image stack SE and BSE images were collected simultaneously. The sequence of images acquired at each step is then combined to construct a three dimensional representation of the sectioned volume. The presented image stack consists of 575 images with a pixel resolution of 2048 × 1536, the voxel size is 15 × 15 × 15 nm and the overall analyzed volume is 2.66e-15 m^3.

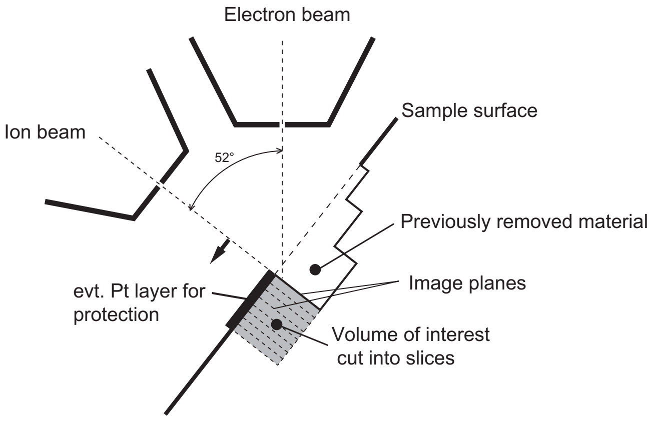

Fig. 1. Schematic representation of the FIB–SEM instrument setup.

2.4. Image processing and analyzes

Regarding image processing and analysis we largely followed the approach outlined by Keller et al. (2011). SE and BSE image stacks were aligned and the maximal overlapping area was cropped from the images. Then we applied a sequence of images filters: (i) a destriping filter eliminated vertical stripes in the images which is an artifact of ion milling (i.e. the so-called waterfall effect), (ii) 3D background correction reduced systematic large-scale intensity variations which are caused by shadowing effects related to the oblique imaging angle and to the subsidence of the image plane into the milled trench. Analyzes of the pore space and the construction of a 3D pore model require a segmentation of the images, i.e. the pores and mineral grains have to be located in the images. The pores were segmented from the SE images which show a higher gray level contrast between pores and surrounding material when compared to the BSE images. We applied multi-level thresholding based on so-called Otsu thresholding (Otsu, 1979) to segment the pores from the SE images. Some mineral grains (e.g. carbonates) have high brightness intensity when compared to the surrounding clay matrix and thus were segmented from the BSE images using gray level thresholding of the Avizo software. Thus, the simultaneous acquisition of BSE and SE images allowed for a more detailed segmentation when compared to a segmentation which is based on a sole BSE or SE image stack.