3D imaging of clay minerals inside sandstone – Pushing the spatial resolution limits using ptychographic tomography

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Abstract

Characterization of microporous, clay-sized particles in natural stone is essential for the understanding of their dynamics. These processes are importand in the fields of oil and gas, groundwater, building stone weathering and soil science. Methods such as X-ray micro-computed tomography is an excellent tool to study features larger than or just under 1 µm, but below the 400 nm limit, the technique falls short. Although destructive methods exists (e.g. FIB/SEM), non-destructive imaging at these very high resolutions has been impossible, until recent developments at synchrotron beam lines.

In this study, we use ptychographic tomography at the cSAXS beam line of the PSI in Switzerland, for imaging of clay microstructure at resolutions down to 45 nm, which is the first application of ptychographic tomography for geological samples to our knowledge. During these experiments, relative humidity of the sample's environment was controlled, in order to asses the influence of R.H. on the analyzed clay minerals. Based on these images, quantitative data on mineral content, porosity, connectivity and behavior under changing environmental conditions of clay mineral clusters was acquired.

Introduction and methodology

High resolution X-ray tomography (µ-CT) has proven to be a valuable tool in geosciences (Cnudde and Boone, 2013; Ketcham and Carlson, 2001; Wildenschild and Sheppard, 2013). The development of the method provided new insights on the internal structures of rocks and sediments, adding an extra dimension in comparison with more traditional techniques such as electron and optical microscopy. With µ-CT it is possible to image and analyse samples from the centimeter to the millimeter scale, a key feature for the study of heterogeneous geological materials.

However, the resolution of X-ray tomography is typically limited to a few hundreds of nanometers for standard laboratory setups (Dierick et al., 2014), or just under one hundred nanometer for synchrotron tomography or laboratory systems using optics (Kastner et al., 2010). This leaves an important resolution gap between scanning electron microscopy and µ-CT data. For this reason, the quantitative study of microporous or fine-grained materials is typically not done using µ-CT. We propose the novel application of ptychographic tomography at synchrotron beam lines for geological samples, to quantitatively study porosity and pore network characteristics of fine-grained clay minerals inside two varieties of sandstone (French Vosges sandstone and Indian Kandla Grey sandstone). The behavior of clay minerals is of great importance in the prediction of weathering of building materials, and direct imaging of their structure under changing conditions has been impossible up until now, a problem that has been traditionally solved by indirect measurements on large samples (Van Den Abeele et al., 2002; Wangler et al., 2011).

Ptychography is a coherent diffraction imaging technique in which a coherent, confined X-ray illumination is used to scan the specimen in such a way that the illumination spot overlaps at consecutive scanning positions. Coherent diffraction patterns are recorded in the far field at each position, and iterative phase retrieval algorithms are then used to reconstruct the complex-valued transmissivity of the specimen (Rodenburg and Faulkner, 2004). The resolution of this technique is only limited by the scattering angles at which diffraction intensities can be reliably recorded, and can be as little as 16 nm (Holler *et al.*, 2014), much better than the size of the illumination or the scanning step size. By combining 2D phase projections acquired at different incident angles of the X-ray beam (Fig. 1), quantitative 3D distributions of electron density can be obtained (Diaz et al., 2012; Dierolf et al., 2010). Geological samples are very suited for ptychographic imaging, as they are very stable and do not tend to suffer from radiation damage. This is an important characteristic, as ptychographic tomograms take several hours up to a full day to acquire. However, as in most high-resolution imaging techniques, a drawback is that the samples have to be very small to achieve these extreme resolutions.

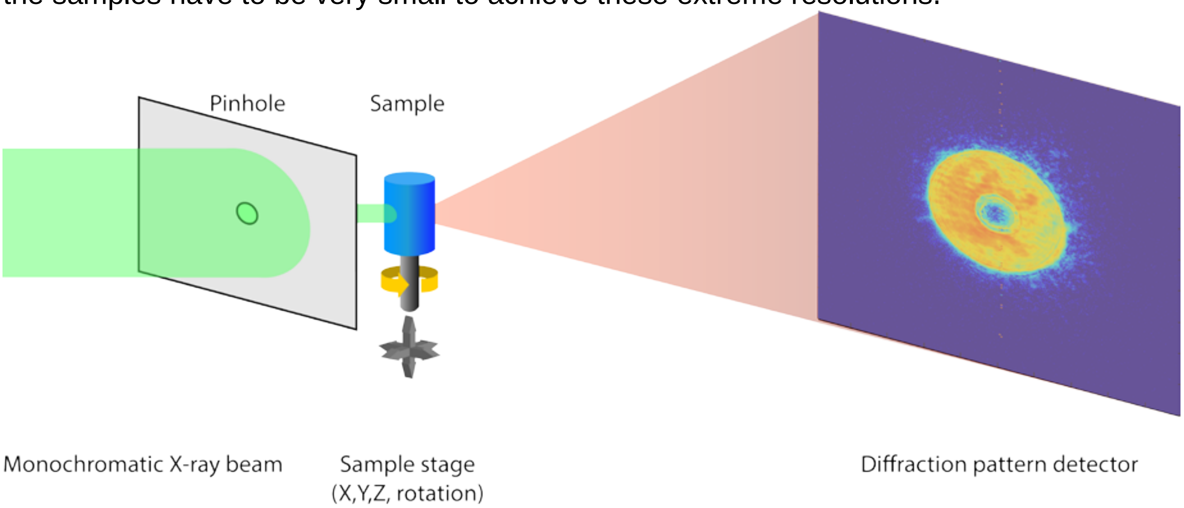

Fig. 1. *Schematic representation of the layout of the cSAXS beam line.*

Clay mineral samples were extracted from the stone, and mounted on a sample pin for analysis. The samples (< 50 µm) where imaged at the cSAXS beam line of the Paul Scherrer Institut in Villigen (www.psi.ch), obtaining a voxel size of 34 nm, and a corresponding spatial resolution of 89 to 136 nm in 3D. During these measurements, we were able to control the relative humitidy of the sample's environment, enabling us to analyze and compare the behavior of extracted clay minerals at high (95 %) and low (5 %) relative humidiy. In following experiments, a 25 µm sized sample was measured using the setup described in Holler et al. (2014), achieving a spatial resolution of 45 nm (voxel size 17 nm) in 3D.

Summary of results

The resulting images show excellent contrast between pores and grains, and different mineral phases were clearly distinguishable. This enabled us to get quantitative results on clay microporosity, connectivity and shape of the pore network, and distribution of different mineral phases in these clay clusters. The nanoporosity inside mica minerals from the Kandla Grey sandstone was visualized, and the preferantial absorption of liquids through these paths was proven (Fig.2). Images recorded during relative humidity control showed a small volume increase from dry to wet state in a sample from the Vosges sandstone. Furthermore, different mineral phases could be identified based on their refracion index, and their distribution of could be visulaized and analyzed. This way, it was possible to see the relative amount of different clay minerals (Fig. 3). At the highest resolution, we could observe how tiny iron oxide particles coat the exterior of larger grains, causing the macroscopical red to pink color of the Vosges sandstone.

The results prove that ptychographic tomography is a novel method that provides outstanding images of geological materials. The possibility of adding peripheral equipment during these measuremen

Ptychographic tomography proves to be a novel method providing outstanding images of geological materials. The possibility of adding peripheral equipment during these measurements, whilst maintaining very high resolutions makes it a unique method, with many possibilities for the entire geoscience community.

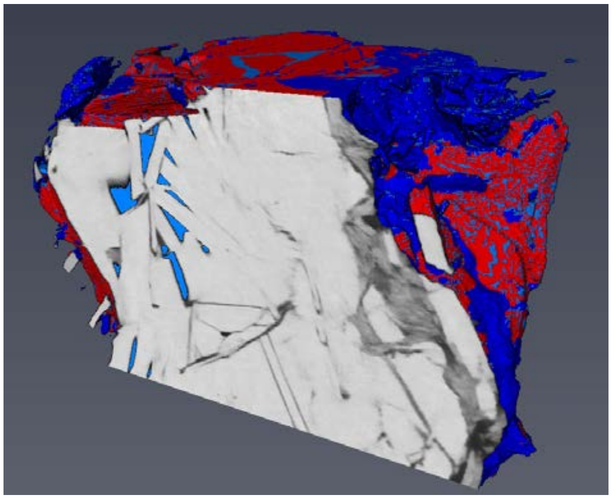

Fig. 2. *3D render of sample K1: A muscovite cluster with narrow cleavage porosity, filled with liquid. Sample size is about 40 µm.*

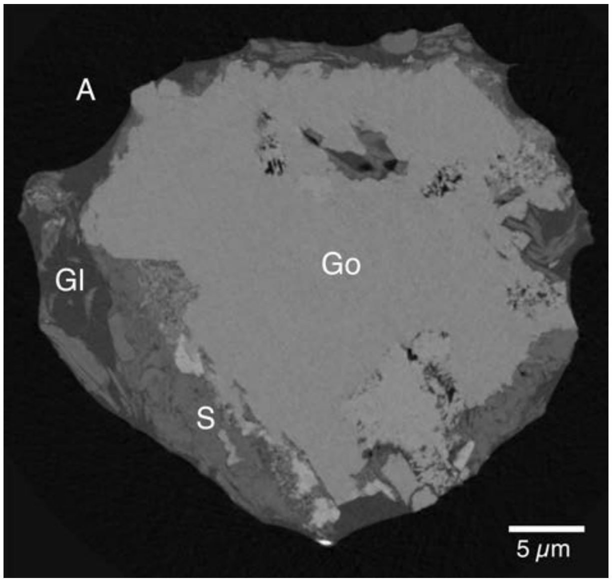

Fig. 3. *Horizontal slice through a sample imaged at a resolution of 106 nm. Different phases inside the sample can be observed: Air (A), glue holding the sample in place (Gl), smectite clay minerals (S) and goethite iron oxide (G).*

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