FIB-SEM Tomography of Porous Geological Materials

A State-of-the-Art 3D Characterization Technique

Focused Ion Beam (FIB) milling capabilities incorporated into a traditional Scanning Electron Microscope (SEM) constitutes a powerful tool for the observation of internal structures at high resolution in biological and materials science, as well as in industry. In recent years its use has been extended to geological samples [1–5], enabling 3D volume analysis with nano-scale resolution providing Earth scientists with unparalleled insights into the complex internal structural and chemical variations that govern the physical properties of geological materials. This short article introduces the application of FIB-SEM into the study of porous geological materials.

Introduction

Unravelling the reactivity of geological materials to changes in temperature, pressure and fluid infiltration depends on a thorough understanding of the internal chemical and structural variations within these materials. Particularly processes that are governed by the presence or formation of porosity require high spatial specificity for sample site selection as well as high resolution images as pore sizes vary from micrometers to nanometers. In addition, 2D imaging of porous materials provides very limited information about the overall structure of any pore networks present. Modern focused ion beam-scanning electron microscopy (FIB-SEM) instruments offer a solution to these challenges, providing high spatial selectivity in analysis allowing geoscientists to look directly at reaction interfaces, the frozen-in traces of system reactivity pathways, as well as providing high resolution images of internal structures at a specified spacing that later can be combined to produce a 3D reconstruction of the target volume. Modern instruments are also often fitted with tools such as energy dispersive X-ray spectroscopy (EDX) providing both structural and chemical information about the material of interest.

FIB-SEM and Tomography

As a showcase, we discuss FIB-SEM tomography on a sample of natural diatomite rock from the Tripoli diatomite formation (Sicily, Italy), which was analyzed on a
This instrument is a double column system, which combines a conventional SEM and a second column containing an ion source of Gallium. By combining high resolution imaging using electrons and material removal by an ion beam, such a system can provide a greater variety of applications than when the two sources are used separately, including tomographic acquisition, site specific sample preparation and material manipulation. As the word tomography implies, 3D volumes of the material are imaged as individual slices before being reconstructed during data processing. The procedure for applying FIB-SEM tomography to geological samples, e.g. porous minerals, is very similar to FIB-SEM tomography in other scientific disciplines [6,7]. However, some geological materials show high beam sensitivity. In these cases the sample is brought to cryogenic conditions that are retained for the entire tomography work, significantly reducing the damage by imaging and thus providing more representative images of the true, internal structure of the geological sample. The diatomite material is composed predominantly of siliceous material and did not require cryogenic conditions.

Diatomite is composed of the fossilized remains of thousands to millions of micron-sized marine algae called diatoms [8]. Its large number of pores and their connectivity make this material interesting for a range of applications. As can be seen from the surface image of the diatomite sample (fig. 1), these pores range from tens of nanometers to micrometers, making FIB-SEM tomography the best choice for quantifying the pores, rather than X-ray or TEM tomography. Not only does the FIB-SEM provide an imaging resolution that is adequate for these sizes of pore structures, but it also provides the ability to analyze a large representative volume to study the pore network. In order to perform a tomographic acquisition once an area of interest is selected on the sample using the electron beam imaging, the stage is tilted to 52° allowing the ion beam to arrive perpendicular to the
sample surface. The top surface of the area of interest is first coated with Platinum to protect it during milling. Then a ‘U’ shape cavity is prepared around the area of interest to expose the slice face, which lies parallel to the FIB, for electron beam imaging and to limit curtaining effects. This also isolates the sample volume to be analyzed. Next the front cross section is milled away layer by layer by the FIB, and electron images are successively taken from each freshly milled surface. The electron images are subsequently realigned during data processing to reproduce the original volume of ablated matter. FIB-SEM tomography has almost no volume restriction because the length in the slicing direction is limited mainly by the sample size, however, larger samples require longer isolated zones to be prepared and take longer to mill [9]. Due to the large variation of pore size a volume of 2500 µm$^3$ was chosen to be a representative volume for the diatomite structure. The pore size, our parameter of interest, also dictates the step size used, where in our example material a series of 376 slices was chosen with a thickness of 20 nm with a pixel size in the electron beam images of 12.5 nm. Realignment of the images was conducted in Fiji [10] and produced a cropped frame of 1677 x 1260 pixels. These images were then processed and segmented using Avizo 9. Analysis of the porosity indicates that the total porosity is approximately 35.4%, with a connectivity along the slicing direction of 35.1% (see video1). A wealth of information can be gained from this simple tomography experiment including surface area, estimated to be $2.28 \times 10^{10}$ nm$^2$. Permeability within the pore space can also be modelled using surface meshing. In our example a subvolume of 200x200x200 voxels along the slicing direction was examined, as shown in figure 2 along with the corresponding calculated velocity field along a sampled plane. The calculations were performed in the CFD software OpenFoam [11].

**Further Applications of FIB-SEM**

The example shown demonstrates the viability of using FIB-SEM tomography to acquire a large representative volume from porous minerals in order to obtain information on the physical properties, such as porosity, surface area, and other knowledge required as input parameters for simulations and calculations. With a resolution from micrometer to nanometer, it also fills the gap between X-ray tomography and TEM tomography. However, tomography is not the only application of FIB-SEM to geological materials. Its high spatial selectivity make it an ideal tool for the preparation of thin foils for (Scanning) Transmission Electron Microscopy ((S)TEM) (see video2) [12,13] and more recently for the preparation of 100 nm long tips for atom probe tomography (APT) [14–16]. This provides the geoscience community with unparalleled extraction capabilities allowing them to explore small scale changes that contribute to large scale phenomena without having to destroy an entire sample. Thus FIB-SEM provides the ideal link between the centimeter-
scale, i.e., mineral grain-scale, and the nanoscale changes in chemistry and structure examined using TEM. In addition, as for conventional SEMs, FIB-SEMs can be equipped with a range of accessories including EDX and cathodoluminescence (CL) systems to provide chemical maps of samples as well as electron backscatter diffraction detectors to generate crystallographic orientation maps.

References


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