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Preparation of clay mineral samples for high resolution x-ray imaging

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Abstract. In the development of optimum ceramic materials for plastic forming, it is of fundamental importance to gain insight into the compositions of the clay minerals. Whereas spectroscopic methods are adequate for determining the elemental composition of a given sample, a knowledge of the spatial composition, together with the shape and size of the particles leads to further, valuable insight. This requires an imaging technique such as high resolution X-ray microscopy. In addition, fluorescence spectroscopy provides a viable element mapping technique. Since the fine particle fraction of the materials has a major effect on physical properties like plasticity, the analysis is focused mainly on the smallest particles. To separate these from the bigger agglomerates, the raw material has to pass through several procedures like centrifugation and filtering. After that, one has to deposit a layer of appropriate thickness on to a suitable substrate. These preparative techniques are described here, starting from the clay mineral raw materials and proceeding through to samples that are ready to analyze. First results using high resolution x-ray imaging are shown.

1. Introduction

Insight into the finely particulate nature of plastic clay materials is of fundamental importance for the development of optimum materials for the plastic forming of ceramics. This would provide the basic information required, for example, for the development of special binders to control the degree of agglomeration of the fine particles in an aqueous environment. It would thereby open the door to increasing the sustainable use of natural resources, which would otherwise find no direct economic use. In order to gain this insight, it is necessary to develop a good method for preparing the plastic clay materials.

2. Sample preparation

2.1. Particle size

Depending on which properties of the clay minerals are of interest, it may be necessary to separate the raw materials into several particle size fractions. This can be carried out either with the aid of different filters or by using a centrifuge.

Larger particles and other contaminations of the raw materials are removed by a 32 µm sieve. After liquifying with water, sodium pyrophosphate or ethanol followed by sonication using an ultrasound bath, the sample is centrifuged and then divided into several fractions. For a even better separation, this procedure is repeated a few times with the single fractions, until the desired particle size distribution is reached. These distributions of particle sizes have been measured with a laser particle analyzer, in order to determine influence of the rotational speed and time of the centrifuge.

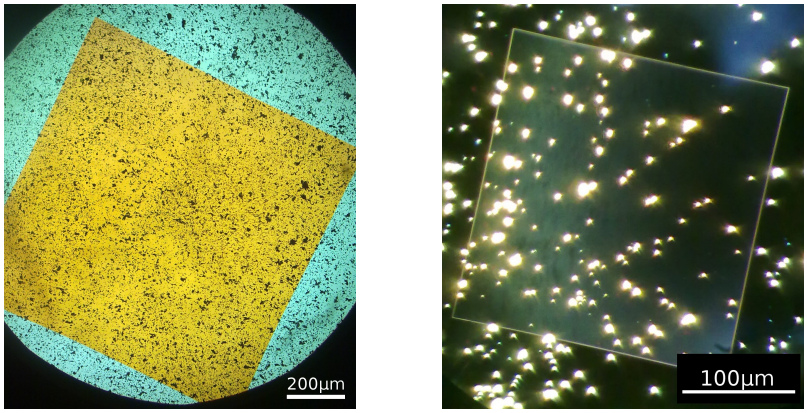
If, alternatively, the filter-based method of separation is used, and only a few µl of the sample are needed, a syringe filter is a suitable way to achieve this separation. For the comparability of future measurements though, it is important to have more than just a few µl of sample. This points to the superiority of the centrifuge method.

2.2. Sample deposit

After selecting the desired particle size fraction, the sample must be deposited on to a suitable substrate, in this case a silicon nitride membrane with a thickness of 100 nm. This process can be carried out either with the sample in a fluid or in a solid state.

2.2.1. Fluid state For the fluid sample the most obvious way is the application as a droplet with a pipette. After the fluid has evaporated, only the sample particles adhere to the membrane. Owing to the surface tension of the fluid, the particles will not be uniformly arranged but concentrated at the border of the droplet. This leads to a higher layer thickness, which is undesirable because of higher x-ray absorption. By using the technique of spin-coating and hydrophilic membranes, the layer thickness can be decreased, but the non-uniform distribution remains.

2.2.2. Solid state Preparing the sample as a non-fluid has been found to be an appropriate way to deposit it on to the substrate. For this, the sample first has to be dried after the filtering. At this time, the sample is in the state of a fine powder. By poking the box containing this powder, dust is dispersed. Mounting a stage holding the silicon nitride window above this cloud of dust leads to particles adhering to the membrane. Some results of this treatment, which have



(a) Bright field image (b) Dark field image

Figure 1: Silicon nitride membranes with sputtered clay minerals imaged by a microscope with visible light

been imaged in a light microscope are shown in Fig. 1. In this case, the thickness of the sample depends only on the thickness of the agglomerates. So, in order to obtain a thin sample, the agglomerates have to be split into smaller ones. This can be achieved with dispersants and a sonicator.

3. Results

The sputtered samples have been imaged on the laboratory transmission X-ray microscope (LTXM) at BLiX [2] with an energy of 500 eV (see Fig. 2). The resolution reached down to 30 nm. It can be seen that there are single agglomerates, which can be analyzed independently. However, to visualize the fine clay materials, whose expected shape is that of plates, one has to break up the agglomerates in even smaller particles.

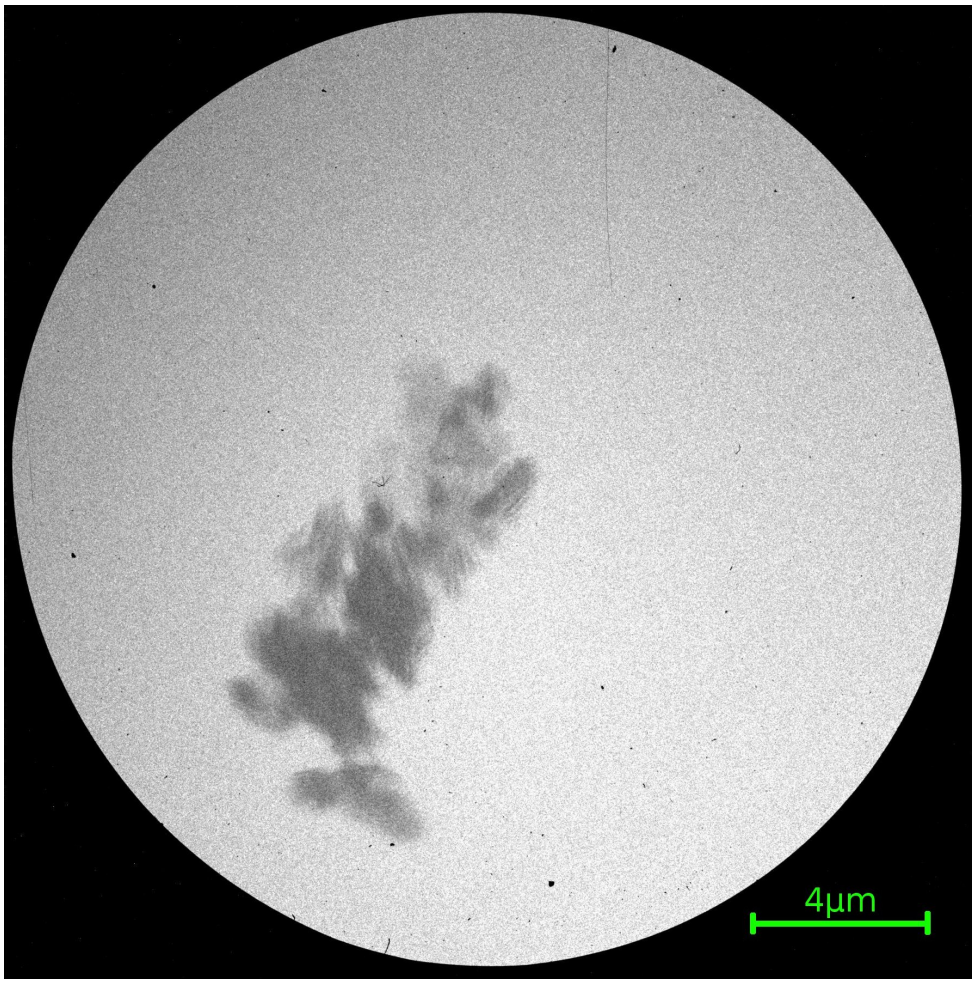
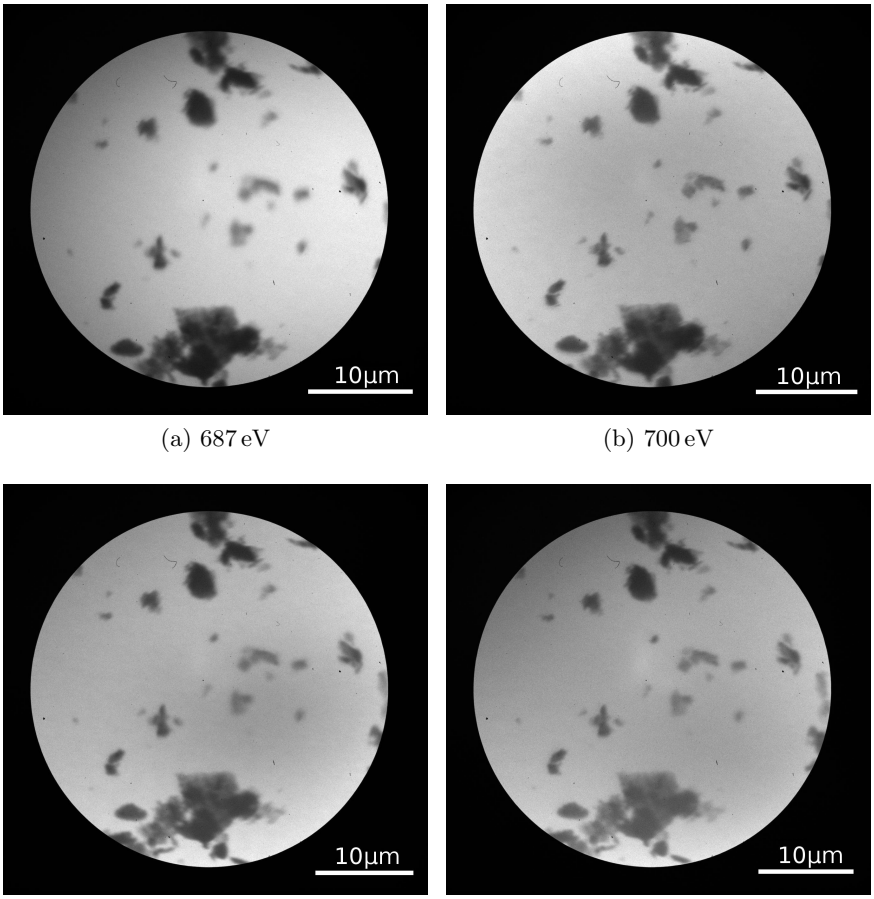


Figure 2: Sputtered clay minerals imaged with the LTXM at BLiX at 500 eV

Further measurements with the purpose of mapping Fe in clay minerals were made at the P04 beamline at PETRA III, DESY. Some results are shown in Fig. 3. For further information about the TXM used for this images, please refer to the proceeding of Philipp Wessels for this conference [3].

These first results show that the mentioned preparation steps can lead to satisfying images. Even more, these separation and filtering steps are essential for visualizing distinct particles.



(a) 687 eV (b) 700 eV

(c) 712 eV (d) 727 eV

Figure 3: Images of a clay mineral sample near the L-edge of *Fe* (706,8 eV) taken at the soft x-ray beamline P04 at PETRA III, DESY

4. Future Work

The separation of different particle sizes with the centrifuge will be further improved to narrow the size-ranges even more and to increase the accuracy. Furthermore, the use of membrane filters will be investigated as an alternative way of separation.

Further measurements will be done both on the imaging of the fine particles and on element mapping of iron and other elements of which they are composed, e.g. titanium.

Finally, the behaviour of plastic clay materials in an aqueous environment will be analyzed. Therefore a suitable wet cell has to be constructed. A merging of all these techniques using the methods of microtomography will allow the composition of plastic clays to be visualized in three dimensions.

References

[1] Thomas N W 2008 *cfi/Ber. DKG* **85** E29–E40
[2] Legall H et al 2012 *Opt. Express* **20** 18362-18369
[3] Wessels P et al 2012 *J. Phys.: Conf. Series* (see proceedings of this conference)