

and electronic transitions. The potential of MES-MED, will be shown taking spin-crossover [4] materials as an example.

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Non-destructive determination of minerals and their locations within chalk

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Determination, by conventional methods, of mineral type, crystal orientation and spatial position of micrometer sized crystals that are embedded in a rock or porous material has been challenging. Traditionally, individual grains must be picked out and analysed separately. Disintegrating a sample annihilates any possibility for gathering information about the mineral assemblage or the textural relationships within the material. A new method, using three-dimensional X-ray diffraction (3DXRD) microscopy, which was pioneered by H. F. Poulsen and coworkers, [1] to study the dynamic changes in microstructure during e.g. tensile strength tests or recrystallization in a bulk material, has the potential to also be applied successfully to rocks, soils and sediments. We used a combination of X-ray microtomography (XMT) and 3DXRD to examine samples of very fine-grained chalk and the minerals present in fractures. This study is the first application of 3DXRD on a natural, porous, multiphase material.

XMT allows three-dimensional imaging of particles and pore structure at high resolution on samples less than 500 µm in diameter. We used data with voxel size (volume pixel) of 350 nm. The contrast in XMT images is derived from the variation in linear absorption coefficients for the constituting materials. For complex materials, containing unknown phases, the data can be difficult to interpret. For our studies of the flow properties in chalk, it was important to know if the minerals found in the fractures were original, or introduced by drilling. With standard powder X-ray diffraction (XRD) and Mössbauer spectroscopy, we could identify some of the minor phases, but these samples are large compared to the tomography sample and they do not offer spatial information, i.e. it is not possible to tell whether these phases are present in the fractures or elsewhere in the sample. To determine the minor crystalline phases and their position within the sample we employed the method 3DXRD microscopy. [1]

The chalk fragment we investigated is composed of nanoscale calcite crystals with a random orientation. In our 3DXRD experiment, these produced powder rings without texture. Superimposed on this pattern, Bragg diffraction peaks resulting from the other crystalline phases could be observed. From these peaks, we could identify crystals of barite and a bit of pyrite. Magnetite, celestite and siderite, other

minerals that might have been present, were not observed. Aside from these dense minerals in the fractures, we also identified calcite and quartz crystals and defined their positions with reasonable precision. This allowed us to interpret that the fractures were original in these tiny samples. They were not induced by drilling and filled with drilling mud. The identification of the mineral phases provided information that allowed us to interpret the tomography data more precisely and helped the interpretation of chalk's diagenetic history.

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Combining µ-XRD² and DTA: deeper insights in temperature-dependent processes

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Coupling time- and temperature-resolved 2-dimensional X-ray diffraction (XRD²) with differential thermal analysis (DTA) is a promising tool for a more detailed understanding of many temperature-dependent processes like phase transitions, recrystallization phenomena and decomposition reactions with or without structural changes. In our study we used the combination of a in house designed DTA-system with a commercially available micro-diffractometer. Equipped with a 140 mm diameter active area the used 2-dimensional detector covers 40° in 2θ- and psi simultaneously in one measurement shot (µ-XRD²).

Replacing the commonly used pinhole collimator system by a polycapillary lens optic providing a spot size of 200 µm the setup allows short measurement times of only ten seconds per XRD-pattern. The typically used heating and cooling-rates of 10 K/min for DTA-experiments can be realized by these short XRD measurement times as shown in [1].

With this setup we examined the behavior of different organic and inorganic substances in the temperature range from room temperature up to app. 600°C. During the experiments solid-solid phase transitions, decomposition reactions and finally the melting of the substances could be observed by both XRD and DTA. Hence it was possible to combine the structural information from XRD directly with the thermal information from DTA. As a supplementary advantage additional insights into changes of the sample's texture and crystallinity were provided simultaneously by the large 2-dimensional detector. Crystallite ripening processes were monitored in real-time during the heating process as well as recrystallization of the molten sample with just induced cooling. The gained all-embracing information permits to assess the triggering factors for the sample's behavior under thermal treatment. This includes information about changes in structure and crystallinity as well as knowledge about reaction enthalpies and reaction kinetics.

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