Cryogenic Broad Ion Beam milling (BIB) and Scanning Electron Microscopy (SEM) to image pore morphology and fluid contacts in hydrocarbon reservoir rocks

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Introduction

Cryogenic BIB-SEM allows direct study of the oil-water-mineral system in hydrocarbon-bearing reservoirs, at resolutions of 10 nm. We quenched sandstone reservoir samples, equilibrated with oil and brine, to liquid nitrogen temperature and subsequently sectioned them using BIB-cutting under cryogenic conditions (Desbois et al. 2013). The flat cross-sections with dimensions of 1 mm^2 allow cryo-SEM imaging of oil-brine-mineral interfaces, with high-resolution EDX-mapping for phase identification. 3D-reconstruction of capillary contact angles is done using serial sectioning with a distance of 1 µm.

Materials and Methods

The fluid-filled sample slabs were rapidly frozen in slushy nitrogen, which minimized the Leidenfrost effect and prevented the formation of ice crystals (Bodnar, 1993). Under vacuum conditions the sample was transferred into the cryo-preparation chamber in which it was sputter-coated with Platinum (Pt) to prevent charging effects. From here the sample was directly transferred into the SEM. Both, the preparation chamber’s and the SEM’s sample stage had the controlled temperature of -185 ºC. A cold trap cooled down to -190 ºC was used to minimize condensation of matter on the sample’s surface. Inside the SEM a titanium mask (Ti-mask) was positioned at the region of interest using a 3-axis Cartesian nanomotor. The cross-section was prepared at the coincidence point of BIB, sample, Ti-mask, and electron beam (Figure. 1).

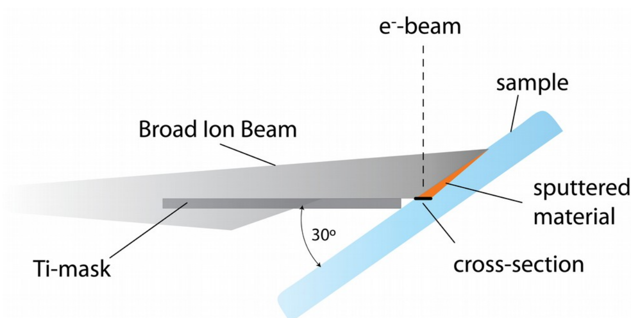

Figure 1. Sketch showing the BIB slope-cut set-up. A Ti-mask, assembled with an angle of 30º and in a distance of a few µm from the sample's surface is used to partly shadow the argon ion beam. The mask 's orientation, and consequently the orientation of the cross-section are perpendicular to the SEM's electron beam. See Desbois et al. (2013) for a detailed description of cryo-BIB-SEM setup.

During milling, the SEM stage oscillated with ±30º to minimize curtaining of the cross-section. Average sputtering rate was 0.1 mm^2/h. The sample was moved back to the preparation chamber to undertake a Pt-coating that allowed investigations at higher acceleration voltage (15-20 kV) using the BSE and EDX-detectors. Realignment of the Ti-mask parallel to the previous section using the 3-axis Cartesian nanomotor allowed preparation of serial surfaces required for 3D information on the material.

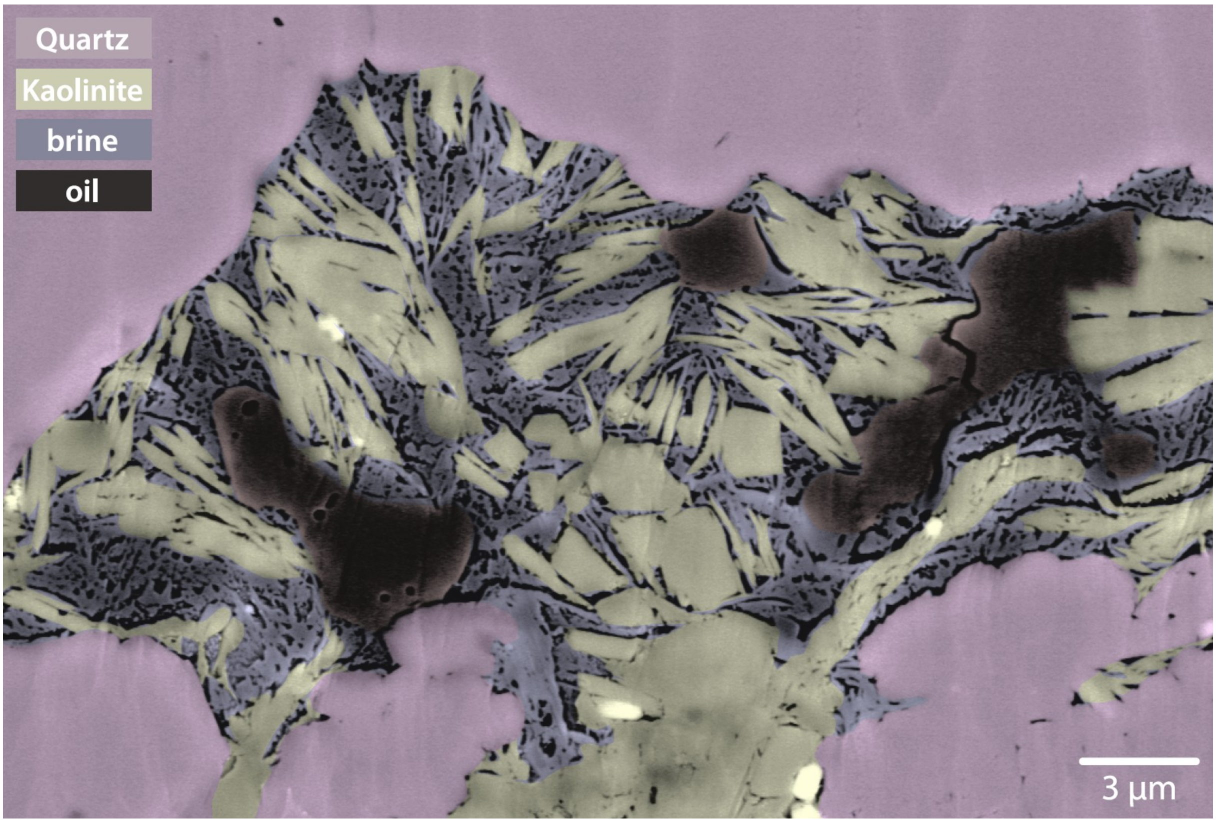

Figure 2. Backscattered electron image with segmented phase overlay showing kaolinite-cemented pore in sandstone filled with brine and oil (see legend for color code). Oil droplets adhere to kaolinite facets and quartz asperities. Image modified from Schmatz et al. 2015.

Results and Discussion

We observed, as expected, the non-wetting oil phase separated from quartz surfaces by a thin brine film, but also direct contacts between oil and rock at asperities and clay aggregates, which act as pinning points and cause discontinuous motion of the oil-water-solid contact line (Figure 2). In pore scale flow of oil in a mixed-wet sandstone the distribution of localized pinning points is inferred to make the motion of the oil-water-solid contact line discontinuous. The mobilization of oil requires the de-pinning of the localized contact points with additional force and time, and hence needs to be added as a separate process to digital rock models (Schmatz et al., 2015).

Edge effects that might influence measurements of phase distribution are the brine's segregation pattern and the formation of destabilization cracks inside the oil. It has been shown in many studies that shock freezing ensures very minor water volume changes during freezing and satisfactorily preserves the initial microstructure of water-saturated soils and rocks (Delage et al., 1982; Schenk et al., 2006; Stokes and Hayles, 2009; Doan et al., 2012). The frozen brine showed the typical segregation pattern of hydrohalite (NaCl x 2 H2O) and ice (Bodnar, 1993) with a segregation cell size of 2 µm (Fig. S2c, Table S1) and is not expected to affect the microstructure (Desbois et al., 2013). Fractures and cracks inside the oil phase could be a possible consequence of slight shrinkage during freezing (Doan et al., 2012) or due to the release of volatile components during high-vacuum investigations (e.g., Egerton and Malac, 2004).

Conclusion

The combination of the cryo-BIB, SEM, and EDX allows the imaging of fluid-fluid-rock contacts at a resolution that permits the testing of predictions on the morphology and dynamics of contact lines.

Our results call for improvements in models of multiphase pore-scale flow in digital rocks. Further anticipated applications of the method are i. a. the investigation of pore-level mechanisms of EOR or aging processes; the investigation of oil-sands, gas-hydrates, and other sensitive or wet materials; or the investigation of in-situ fluid distribution reservoir- sandstones and carbonates.

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