Originally published as:

Kanitpanyacharoen, W., Kets, F. B., Wenk, H.-R., Wirth, R. (2012): Preferred mineral orientation and microstructure in the posidonia shale in relation to different degrees of thermal maturity. - Clays and Clay Minerals, 60, 3, 315-329,

DOI: 10.1346/CCMN.2012.0600308

PREFERRED ORIENTATION OF MINERALS AND MICROSTRUCTURES IN POSIDONIA SHALES OF THE HILS-SYNCLINE WITH VARIABLE MATURITIES

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Abstract---Thermal maturity of Posidonia shales collected in the Hils Syncline, Northern Germany varies strongly as a function of location, indicating differences in local temperature history. Synchrotron X-ray diffraction was used to document composition and preferred orientation of four Posidonia shales with different maturity (0.68-1.45% R_o) to determine possible effects on diagenesis and preferred orientation pattern. Overall, the degree of preferred orientation of clay minerals (illite-smectite, illite-mica, and kaolinite) in all samples is similar, with (001) pole figure maxima ranging from 3.6 to 6.1 multiples of a random distribution (m.r.d.). Also calcite displayed weak preferred orientation, with *c*-axes perpendicular to the bedding plane (1.1-1.3 m.r.d.). Other constituent phases such as quartz, feldspars, and pyrite had a random orientation distribution. The difference in thermal history, which causes significant changes in the maturity of organic matter, at most marginally influenced the preferred orientation of clays as most of the alignment seems to have evolved early in history. Synchrotron X-ray microtomography was used to characterize the three-dimensional microstructure of a high maturity sample. More porous features, including micropores, fractures, and kerogen were observed to be anisotropic and aligned parallel to the bedding plane and estimated to be

approximately 7 vol%, consistent with previous petrophysical measurements of porosity of 8-10 vol%. Transmission Electron Microscopy (TEM) analysis of two different maturity samples (0.74% R_o and 1.45% R_o) was used to document microstructures at nanoscale as well as the presence of kerogen. In the high maturity sample, pores were less abundant while minerals were more deformed as evidenced by fractured calcite as well as kinked and folded illite-clays. Part of the porosity aligns with clay platelets.

Key words---Clays; Microstructure; Porosity; Posidonia shale; Preferred orientation.

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INTRODUCTION

Shales are here defined as fine-grained sedimentary rocks, containing high volume fractions of clay minerals. Due to their sheet-like structure, these minerals preferentially align with (001) lattice planes parallel to the bedding plane, during compaction and diagenesis (Ho *et al.*, 1999). In particular, compaction and recrystallization processes lead to a reorientation of clay platelets, increased elastic and seismic anisotropy, an increase of clay packing density, and a loss of porosity and permeability (*e.g.* Baker *et al.*, 1993; Hornby, 1994; Sayers, 1994; Johansen *et al.*, 2004; Draege *et al.*, 2006; Bachrach, 2011). Recently, shales have been recognized to have potential for natural gas production as unconventional reservoirs (shale-gas), which consequently have increased interest in studying their physical and chemical characteristics (*e.g.* Curtis, 2010; Loucks *et al.*, 2009; Jenkins and Boyer II, 2008; Martini *et al.*, 2003; Schulz *et al.*, 2010; Bernard *et al.*, 2010).

The mineralogical composition and microstructure of shales have been extensively studied; however, preferred orientation (or fabric) of clay minerals in these shales is much less

discussed. The fabric and anisotropic pore space are important contributors to elastic and seismic anisotropy (Vernik and Nur, 1992; Hornby, 1994; Kanitpanyacharoen *et al.*, 2011) and studies by Vernik (1993, 1994) suggest that the intrinsic anisotropy of organic-rich shales is further enhanced by bedding-parallel microfractures that were created during hydrocarbon generation. Due to the complex structure and poor crystallinity of clay minerals, preferred orientation quantification is challenging. Several studies, which rely on traditional X-ray pole figure goniometry (*e.g.* Curtis *et al.*, 1980; Sintubin, 1994; Ho *et al.*, 1995; Ho *et al.*, 1999; Aplin *et al.*, 2006; Valcke *et al.*, 2006; Day-Stirrat *et al.*, 2008a,b) and on synchrotron X-ray diffraction techniques (*e.g.* Lonardelli *et al.*, 2007; Wenk *et al.*, 2008; Voltolini *et al.*, 2009; Wenk *et al.*, 2010; Kanitpanyacharoen *et al.*, 2011), have supplied evidence that the preferred orientation of clay minerals increases with increasing clay content, burial, and diagenesis. Given the diversity of shales and the dependence of preferred orientation on provenance, clay mineralogy, and bioturbation, fabric changes cannot be attributed to a single factor.

In this study, shales of a single formation but with a different thermal history were measured to investigate whether the difference in thermal history has affected the preferred orientation patterns of constituent clay minerals. A synchrotron X-ray diffraction technique was used to characterize composition, preferred orientation, and microstructure of four Lower Jurassic Toarcian Posidonia shales retrieved from the Hils Syncline in northern Germany (Figure 1). The samples vary in vitrinite reflectance (R_o) from 0.68% in the SE to 1.45% in the NW (Littke and Rullkötter, 1987; Littke *et al.*, 1988). The variation indicates differences in local temperature history due to either a local igneous intrusion or a complex burial history (*e.g.* Leythaeuser *et al.*, 1980; Rullkötter *et al.*, 1988; Petmecky *et al.*, 1999). The three-dimensional (3D) distribution of porosity and constituent phases was investigated by synchrotron X-ray

microtomography and a comparison was made to the porosity previously obtained by other techniques (Mann *et al.*, 1986; Mann, 1987). Microstructures at the nanoscale were also studied by transmission electron microscopy (TEM).

SAMPLES

The Lower Jurassic Toarcian Posidonia shales are the main hydrocarbon source rocks in the North Sea offshore Netherlands and in northern Germany (Rullkötter *et al.*, 1988; Littke *et al.* 1991, 1997, Doornenbal and Stevenson, 2010 and references therein). Posidonia shales are generally dark grey, laminated, and bituminous, and were deposited in a low energy and oxygen-depleted environment. The shales represent peak transgression during a sea-level highstand and correspond to a global oceanic anoxic event, dating back approximately 176 Ma (Doornenbal and Stevenson, 2010).

In the Hils Syncline of Northern Germany (Figure 1), properties of the Posidonia vary considerably depending on the burial depth, compaction, and temperature history (Littke and Rullkötter, 1987; Littke *et al.*, 1988). The low energy environment rocks from the same sedimentary sequence are laterally continuous, with main variability caused by organic content as a function of depth and stratigraphy (Littke *et al.*, 1991). Significant lateral variation in maturity of the organic content of Posidonia shales retrieved at the Hils Syncline has been observed and is due to local temperature history of the Lower Saxony Basin (Rullkötter *et al.*, 1988). Lateral differences in thermal maturity are believed to be caused by deep Cretaceous igneous intrusions (e.g. the Vlotho and Bramsche plutons, inferred from geophysical observations, Deutloff *et al.*, 1980; Leythaeuser *et al.*, 1980; Rullkötter *et al.*, 1988), or, as was demonstrated for structures slightly west of the area of interest, by a combination of deep burial,

substantial subsidence, and intense uplift processes of individual structures (Petmecky *et al.*, 1999; Muñoz *et al.*, 2007). The cause of the thermal anomalies is still under discussion (Kus *et al.*, 2005; Bilgili *et al.*, 2009).

We analyzed Posidonia shales retrieved from four different wells about 10-20 km apart (Mann, 1987) at the rim of the Hils syncline (Figure 1). The samples were obtained from approximately 40 m thick Toarcian formation at a depth of approximately 50 – 60 m. No evidence has been found for significant variation in depositional environment over the sampled area (Littke *et al.*, 1988), but faulting has been diagnosed at the location of S4, leading to a locally higher porosity (Mann, 1987). The maturity of the organic matter, defined by vitrinite reflectance (R_o) (Tissot and Welte, 1984), ranges from 0.68% R_o to 1.45% R_o (Littke and Rullkötter, 1987; Littke *et al.* 1988; Bernard *et al.*, 2011). As inferred from mercury injection (MICP), the porosity of shales with similar thermal maturity obtained from the same set of wells is generally low, ranging from 4% to 10% (Mann, 1987), with porosity decreasing as a function of maturity.

EXPERIMENTAL METHODS

Scanning Electron microscopy (SEM)

A polished slice of sample S4 was coated with carbon and examined with a Zeiss Evo MA10 low vacuum SEM, equipped with an EDAX Energy-Dispersive Spectroscopy (EDS) system. The SEM was operated with an accelerating voltage of 30 kV and a probe current of 20 nA to collect images. The brightness variation of backscattered (BE)-SEM images (Figure 2a,b), ranging from low (black) to high (white) is due to the contrast in atomic number, with high atomic numbers giving white. EDAX Genesis Imaging/Mapping software was used to collect

compositional maps for Al, Si, O, Fe, Mg, and K as displayed in Figure 3, indicating an abundance of pyrite (FeS₂) and Fe- and Mg-containing illite.

Synchrotron X-ray Diffraction

Four shale samples were first embedded in low-temperature hardening epoxy resin in plastic containers to produce epoxy cylinders, approximately 2 cm in diameter. The shale-containing cylinders were then cut and polished into 2 mm slices. A monochromatic synchrotron X-ray beam, with a size of 1mm in diameter and a wavelength of 0.10779 Å, was used to collect diffraction patterns at the BESSRC 11-ID-C beamline of the Advance Photon Source (APS) at Argonne National Laboratory. Detailed information of the experiment setup is described elsewhere (*e.g.* Wenk *et al.* 2008). The sample was mounted on a goniometer, translated parallel to the goniometer-axis over 5 different spots in 2 mm increments to obtain a representative sample volume. The sample slab was then tilted around the goniometer-axis from -45° to 45° in 15° increments to obtain a significant pole figure coverage. Diffraction patterns were recorded for 60s with a Mar345 image plate detector (3450 x 3450 pixels), positioned at about 2 m from the sample. The 2θ angles range from 0° to 4.6° in each diffraction pattern.

The instrument geometry (wavelength, sample-detector distance, beam center, and image plate tilt) was first calibrated with a CeO₂ powder standard. The diffraction images with Debye rings were then “unrolled” by integrating from 0° to 360° azimuth over 10° intervals to produce 36 spectra, which represent distinctively oriented lattice planes. A stack of these spectra for the 0° tilt image of S4 clearly indicated peak intensity variations with azimuth (Figure 4a, bottom: Exp). The spectra are expressed as function of $Q=2\pi/d$ rather than d (lattice spacing), where everything becomes compressed towards small lattice spacings. A Q range of 0.37-3.70 Å⁻¹ (d -

spacing 1.80-16.98 Å) was used. The diffraction spectra were further processed with the MAUD (Material Analysis Using Diffraction) software (Lutterotti *et al.*, 1997). The software relies on Rietveld refinement (Rietveld, 1969), which is a least-squares approach to minimize the difference between experimental diffraction data (Figure 4a, bottom: Exp.) and a calculated diffraction model (Figure 4a, top: Calc.). The calculated model is defined by several factors such as instrumental parameters, scattering background, crystal structure, microstructure, volume fraction of each phase, and its preferred orientation. Seven major minerals were recognized in the Posidonia shales (Figure 4b, bottom).

Crystallographic structures of clays were obtained from the American Mineralogist Database (Downs and Wallace, 2003; specifically triclinic kaolinite from Bish, 1993, monoclinic illite-mica from Gualtieri, 2000, and monoclinic illite-smectite, based on a muscovite-phengite composition, from Plançon *et al.* 1985) whereas quartz, calcite, feldspar, pyrite, and dolomite structures were imported from the database contained in MAUD. The spectra were refined with background polynomial functions, scale parameters, phase volume fraction, and lattice parameters, but atomic coordinates were kept constant. The peak shapes and widths were modeled by refining anisotropic crystallite size and microstrain. Preferred orientation was computed by the EWIMV algorithm (Matthies and Vinel, 1982), using 10° resolution for the orientation distribution function (ODF) determination, without imposing sample symmetry.

The ODF, which defines the crystallite orientation relative to sample coordinates, was then exported from MAUD and imported into the BEARTEX software (Wenk *et al.*, 1998) to further process the orientation data. The ODF was smoothed with a 7.5° filter to minimize artifacts from ODF cell structures. The sample was rotated so that pole figures are defined in respect to the bedding plane. The pole densities are expressed as multiples of random distribution

(m.r.d.). The basal plane (001) in clay minerals is most significant, thus the (001) pole figures are displayed, with the bedding plane normal in the center (Figure 5).

X-ray Microtomography

A small cylinder of S4 with 1 mm in diameter and 5 mm long was investigated with X-ray tomography at the TOMCAT (TOmographic Microscopy and Coherent rAdiology experimenTs) beamline of the Swiss Light Source (SLS) at the Paul Scherrer Institute in Villigen, Switzerland. Energy of the X-ray radiation was 16.0 keV, corresponding to a wavelength of 0.775 Å. The sample was scanned with an optical 10x lens. A total of 1,440 projections were recorded with a CCD detector (PCO2000) as the sample was rotated in 0.125° increments about the cylinder axis for 180°. More details about the beamline specifications are described elsewhere (*e.g.* Stampanoni *et al.*, 2006; Marone *et al.*, 2009).

Each projection image represents a 2D X-ray absorption map. Octopus software (Dierick *et al.*, 2004) was used to normalize projections with background images and remove artifacts caused by the X-ray beam fluctuation and defects in the instruments, resulting in filtered images. The normalized data was then reconstructed into 3D images. Reconstructed slices are displayed parallel to the bedding plane or perpendicular to the cylinder axis (Figure 6a). The 3D array consists of cubic cells (voxels), which represent the grayscale values that are given as 16-bit integers and are related to the rate of X-ray absorption per unit length (cm) of a given voxel. For calibration, the average grayscale on images outside the sample was subtracted from all values, resulting in grayscales, ranging between -21.9 and 82.6. The lowest value (-21.9) corresponded to the darkest voxel while the highest value (82.6) indicates the brightest voxel. The zero grayscale value should not be construed as indicating zero absorption (Wang *et al.*, 2001). The

voxel size is $0.74 \times 0.74 \times 0.74 \text{ } \mu\text{m}^3$.

A volume of $1000 \times 1000 \times 300$ voxels ($1.21 \times 10^8 \text{ } \mu\text{m}^3$) inside the cylinder was selected to be analyzed with Avizo software (Visualization Sciences Group). A 3D median filter was first applied to avoid unnecessary blurring. The frequency distribution of grayscale values in logarithmic scale is shown in Figure 6b. A thresholding method on grayscale values was applied to differentiate between low-absorbing (more porous materials, including micropores, fractures, and organic matter or kerogen) and high-absorbing (pyrite) phases by visual inspection of microstructural features in the reconstructed images as shown in Figure 6a. Examples of areas in the reconstructed image (Figure 6a) corresponded to grayscale values in Figure 6b. Area [1] indicated more porous features, including micropores, fractures, and kerogen, area [2] illustrated clays, calcite, feldspars, and quartz, and area [3] displayed pyrite grains. A threshold was set between the minimum grayscale (-21.9, darkest) and the maximum grayscale of the assumed micropores, fractures, and kerogen (7.2). Segmentation for pyrite was done on similar basis with the threshold range between the minimum (21.2) and the maximum grayscale values of pyrite (82.6, brightest). The intermediate gray shades were not segmented into different components (clays, quartz, calcite, and feldspars) as they have very similar absorption characteristics. The 3D representation of more porous features, including micropores, fractures, and kerogen as well as pyrite are illustrated in Figure 7. The volume proportion, the size distribution, and the aspect ratio (length/width) of the components were also extracted from the chosen area (Figure 8).

Transmission Electron Microscopy (TEM)

Thin slices of S2 and S4 samples, $10 \text{ } \mu\text{m} \times 5 \text{ } \mu\text{m} \times 0.15 \text{ } \mu\text{m}$ in size, were prepared by a focused ion beam thinning device (FEI FIB200TEM) and analyzed by a FEI Tecnai G2 X-Twin

TEM at GeoForschungsZentrum (GFZ) of Potsdam, Germany. The instrument is equipped with a Gatan Tridiem energy filter, a Fishione high-angle annular dark-field (HAADF) detector, an EDAX energy dispersive X-ray spectroscopy detector (EDS) for chemical characterization, as well as an electron energy loss spectrometer (EELS).

RESULTS

Backscattered SEM images (Figure 2a,b) show complex microstructures of very fine-grained clays, calcite veins, coarse-grained quartz, and pyrite. Pyrite was observed as euhedral crystals and as fine-grained clusters of small octahedra in a framboid structure ($<5\text{ }\mu\text{m}$) (Figure 2b). Calcite veins filling fractures were clearly aligned with well-developed horizontal bedding planes. Very fine-grained clays were abundant in the matrix, in particular Fe- and Mg-containing detrital illite, which was verified by EDS elemental maps (Figure 3).

A summary of different phase proportions in weight fractions and lattice parameters, based on the Rietveld refinement, is given in Tables 1-2. In general, calcite (31-44 wt%) and the illite-group (24-39 wt%) dominated the composition in all samples. The amount of other phases such as quartz, kaolinite, pyrite, and albite were fairly similar. Dolomite was observed only in high maturity shales *i.e.* S3 (0.88% R_o) and S4 (1.45% R_o). The weight proportions of different phases in this study are consistent with the proportions reported by Mann *et al.* (1986) and Mann (1987). The broad diffuse peak of illite-smectite (inset of Figure 4) indicates a low degree of crystallinity, small crystallite size, and stacking disorder.

The main focus of this investigation was to quantify the preferred orientation of constituent minerals. The refined model diffraction spectra (top: Calc) were compared with experimental spectra (bottom: Exp) in Figure 4a, which show a close similarity, indicative of an

excellent fit, both in intensities as well as position of diffraction peaks. Figure 4b shows the average spectra for the 0° tilt images, with dots for experimental data and a thin solid line giving the calculated fit. Pole figures of preferred orientation analysis are displayed for kaolinite, illite-mica, illite-smectite, and calcite (Figure 5), with pole densities summarized in Table 3. Overall, the degrees of preferred orientation for clay minerals were quite strong (3.6 – 6.1 m.r.d.) whereas orientation of quartz, albite, pyrite, and dolomite were close to random (pole figures are not shown). All pole figures were more or less axially symmetric with the (001) maximum perpendicular to the bedding plane, though no sample symmetry was imposed. Illite-mica, with a sharper (002) diffraction peak at lower *d*-spacing, was generally coarse-grained and had a stronger preferred orientation (4.4 – 6.1 m.r.d.) than fine-grained illite-smectite (3.6 – 4.6 m.r.d.), with some variation between samples. Illite-mica in S3 had the strongest degree of preferred orientation with a (001) maximum perpendicular to the bedding plane of 6.1 m.r.d. Maximum pole densities of kaolinite and illite-smectite were similar in all samples (Figure 5). Calcite grains also oriented their *c*-axes perpendicular to the bedding plane, but had much weaker alignment than clays, ranging between 1.1 to 1.3 m.r.d. The (001) minima of clay phases ranged from 0.1-0.4 m.r.d., suggesting a significant number of randomly oriented crystallites.

The resolution of the microtomography image (Figure 6a) was comparable to that of the backscattered SEM image (Figure 2a), *i.e.* slightly better than 1 µm. The high-absorbing materials were mainly pyrite and the distribution of these particles was scattered and did not appear linked to the bedding plane orientation (Figure 7a). Based on the segmentation with Avizo, the proportion of pyrite in S4 was estimated at 2.7 vol%, which is consistent with the amount obtained from Rietveld analysis (3.0 vol%) as well as the fraction reported by Mann (1987) (3-4 wt% or ~2 vol%). Intermediate gray shades, representing calcite, quartz and clay

minerals, were approximated at 90 vol%. The volume fraction of low-absorbing features, taken to be indicative of more porous materials, including micropores, fractures, and kerogen (Figure 7b), was estimated at 7.3 vol%. The low-absorbing features ranged in size from $500\text{ }\mu\text{m}^3$ to $1\text{ }\mu\text{m}^3$, which is considered to be the limit of the resolution. Small micropores volume ($1\text{-}10\text{ }\mu\text{m}^3$) clearly dominated (Figure 8a), though their contribution to the total volume may not be as significant. Micropores were anisotropic, mostly penny-shaped with high aspect ratios (Figure 8b), and organized mainly parallel to the bedding plane, with little connectivity of the flat porous zones in the direction perpendicular to the bedding plane (Figure 7b). A few horizontal fractures, which are probably a result of pore growth and coalescence or of unloading as a result of uplift, were also observed. Due to the limitation of resolution in microtomography, only pores and fractures in micron-scale and larger can be adequately investigated by this method. Therefore the volume percentage of micropores, fractures, and kerogen did not correspond to the total porosity.

TEM images provide important additional information and insights on the material distribution at micrometer to nanometer scale. TEM investigations were performed on small regions of FIB slices, which may not be representative of the whole sample. The HAADF images of the low maturity sample S2 (0.74% R_o) illustrate an open framework of calcite fragments and some quartz (Figure 9a). The grain size was relatively large for shale material, approximately less than $1\text{ }\mu\text{m}$ in diameter. Clay platelets, mainly illite-smectite with some Mg, occurred as clusters in interstitial pockets and along grain boundaries. The orientation of platelets was variable, but the overall direction was parallel to the bedding plane (vertical direction in Figure 9a). Open pores (black, Po) and kerogen (gray, Ke) were also observed in the HAADF image (Figure 9a). Organic matter does not cause diffraction effects such as Bragg fringes and thus it appears uniformly gray in Figure 9. Porosity was observed as white areas in a TEM bright-field

image (Figure 9b). A number of pores were elongated following the clay platelet structure and hence organized roughly subparallel to the bedding plane (horizontal) while some were more equiaxed or spherical, ranging between 2 nm and 20 nm in diameter (nanopores). The HAADF image (Figure 9a) and EELS map (Figure 10a) display that quartz partially dissolved near the rim. Quartz and calcite showed weak deformation with some dislocations and subgrains. The elemental composition of organic matters was verified by EELS scans of carbon and sulfur. Figure 10a represents an EELS scans on the same area as depicted in Figure 9a. The gray areas of elemental maps (Figure 10b-c) were composed of carbon and some sulfur, which was absent in the surrounding calcite, illite-smectite, and quartz.

The HAADF images of high maturity sample S4 (1.45% R_o) show finer grain size and less porous segment than that in sample S1. A TEM bright-field image (Figure 11b) illustrates high concentrations of dislocations in calcite, with subgrains formation and mechanical twins. Illite-smectite stacks were kinked and bent. Several sets of 11 Å fringes and bending of lattice planes were observed in high resolution images (inset in Figure 11c). Illite-smectite (with some Mg) was interlayered with a carbon-rich phase, presumably kerogen (Figure 11a). Some small crystallites of kaolinite (established by EDS, not shown) were also observed, with moderate preferred orientation. Framboid aggregations of pyrite were commonly found (Figure 11d), corresponding to those imaged by SEM (Figure 2b) and microtomography (Figure 7a).

DISCUSSION

Care must be taken not to over-interpret the differences observed between the four samples in this study, although they were acquired at similar depths, in the same stratigraphic unit, but possibly in slightly different stratigraphic positions. Small samples on the millimeter

and micrometer scale were analyzed thus the sophisticated analytical methods precluded statistical tests about variability.

Mineralogy

Previous studies of Posidonia mineralogy based on bulk- and fine fraction XRD (Mann, 1987; Littke *et al.*, 1988) show no systematic dependence of mineralogy on maturity and exposure to different temperatures. Similarly, based on Rietveld analysis of synchrotron X-ray diffraction images, all samples had similar mineralogical composition, with the illite-group (23-39 wt%) and calcite (31-44 wt%) dominating. No clear evidence for diagenetic transformations of clay minerals was observed. Dolomite was observed only in high maturity samples, which may be indicative of the temperature history. Small amounts of albite were also present in the high maturity samples, but the diagenetic history cannot be fully established solely from this study.

Preferred Orientation

Mann (1987) note a gradual decrease of porosity with maturity, with an exception noted for the well Haddessen, located in a more faulted area (corresponding with S4). The porosity reduction with maturity has been interpreted due to increased cementation and/or an increased depth of burial. Similarly, a trend can be observed as an increase of fabric strength with maturity in illite-mica for low maturity samples (S1: 0.68% R_o , S2: 0.74% R_o , and S3: 0.88% R_o), with a slight reversal trend for a high maturity sample (S4: 1.45% R_o) (Table 3). Illite-mica in S3 had the strongest alignment with a (001) maximum of 6.1 m.r.d. A slight variation in the degree of preferred orientation between illite-smectite and kaolinite was observed in all samples. No trend

as function of maturity can be observed for degree of preferred orientation of illite-smectite and kaolinite, except that S4 had the lowest preferred orientation for both of these minerals. A considerable portion of clay crystallites in all samples was randomly oriented, expressed by (001) minima of 0.1-0.4 m.r.d. for kaolinite, illite-mica and illite-smectite. The orientation distributions of quartz, albite, dolomite, and pyrite were nearly random and close to 1 m.r.d. Interestingly, calcite had a weak but significant preferred orientation, ranging from 1.1-1.3 m.r.d. in (0001) pole figures (Figure 5). Maximum preferred orientation of calcite was observed in sample S4, and the alignment may not be affected by the structural deformation.

The trends observed in preferred orientation of clays, notably the increasing trend of illite-mica, may not be statistically significant, as variability between samples, even taken centimeters apart, can be considerable. The thermal maturity did not seem to be a major effect on the degree of preferred orientation of clays, suggesting that the clay alignment formed early, in line with other observations on other shales.

Microstructures

Continuous layers of calcite such as the veins illustrated in Figure 2a were observed and these may be related to cementation. The SEM image of sample S4 reveal that calcite mostly aligned as horizontal veins parallel to the bedding plane. Higher maturity samples (S3 and S4) were exposed to higher temperatures, which may have reduced the organic content and increased the already high carbonate content (Rullkötter *et al.*, 1988). Carbonates in S3 and S4 had been diagenetically altered to dolomite, possibly due to decomposition of organic matters (Slaughter and Hill, 1991).

Contrary to some other shales, clays did not dominate the microstructure of Posidonia

shale. The TEM images (Figure 9-11) clearly show that calcite was abundant with fragments, which were more closely packed in S4 than in S2. Different generations of calcite were observed: (1) older fragmented calcite appeared to be more pure than (2) second generation crystallites, which were less deformed, and (3) those that occurred in euhedral clusters and were enriched in Sr. The weak calcite alignment in S4 can be attributed to a shape alignment of calcite fragments, which are preferably broken along cleavage planes $r = \{10\bar{1}4\}$, and to alignment of crystals in younger and less deformed veins, which resulted from cementation of fractures. Organic matter was often interlayered with clays (Figure 9a, 10a). Clays occurred as pockets in interstitial space and along calcite grain boundaries. In general, clay platelets tend to align parallel to the bedding plane but a wide dispersion was observed. In some clusters, kaolinite occurred as fine crystallites in pores (Figure 10b), which is quite different from the kaolinite crystallites in Kimmeridge shale that are very strongly oriented (Militzer *et al.* 2011). The high maturity sample (S4: 1.45% R_o), retrieved from a more tectonic active area, was clearly deformed as illustrated by kinked and folded clays, fractured calcite fragments with mechanical twins, and high dislocation densities. The observations imply considerable local stresses, probably associated with compaction of tectonic origin (burial, uplift) or as a result of hydrocarbon expulsion. The strong deformation in S4 may have contributed to a relatively weak preferred orientation. The observation of stress related phenomena in S4, and the presence of late carbonate veins as well as the marginal increase of the fabric intensities of illite-mica in S1-S3 as a function of thermal maturity, are consistent with a scenario in which the Posidonia shales have been buried and uplifted.

Porosity Analysis

Total pore volume, including organic matter, and pore structure anisotropy are relevant for the determination of elastic properties in shales. Less dense features, consisting of micropores, fractures, and kerogen, were investigated by X-ray microtomography and corresponded to approximately 7.3 vol%. The 3D representation (Figure 7b) as well as the distribution of volume and aspect ratio of these features (Figure 8) show that they were mostly dispersed, small ($<10 \mu\text{m}^3$), and flat (aspect ratio 1.5-2.5). Fractures and kerogen were usually aligned parallel to the bedding plane, relatively larger ($>10 \mu\text{m}^3$), and more elongated (aspect ratio >2.5). The aspect ratio of micropores and fractures can play a significant role on the elastic anisotropy of shale.

Based on the segmentation of the 3D voxel array, one can calculate the volume fraction of micropores, fractures, and kerogen, but cannot quantify the total volume of porosity, which includes nanopores. Nanopores are substantially smaller than the voxel size ($\sim 0.41 \mu\text{m}^3$), which is the limit of the microtomography technique used here. Also, multiphase materials correspond to different grayscale peaks, which are often overlapped, in the histogram. Nanopores were observed in SEM and TEM images (Figures 2 and Figure 9-11). Judging from TEM images, the volume fraction of nanopores was approximately 2-5 Vol% (*e.g.* Figure 9b, 11b). While some pores in sample S2 were spherical (*e.g.* at triple junctions of calcite fragments), a majority had a plate-like shape and was approximately parallel to the bedding plane (Figure 10a-b). The platy pores were frequently bounding larger clay crystals. The flat pores imaged by HAADF (Figure 9-11) were found mostly parallel to the bedding plane, possibly due to pore growth and coalescence, or to the unloading of the sample when uplifted to the current shallow depth. The same unloading mechanism may have caused fractures later filled with calcite observed in SEM and X-ray microtomography.

Mann (1987) reports nanopore throat sizes between <2.2 nm and 60 nm, which are comparable with those of sealing shales as documented by Best and Katsube (1995) with mercury injection measurements (MICP). The pore sizes reported in Curtis *et al.* (2010) for gas-shales are approximately between 5 nm and 150 nm on basis of FIB-SEM, NMR, and MICP measurements. Intraparticle organic pores (< 75 microns) and pyrite-framboid intercrystalline pores were also identified by Ar-ion-milling in the SEM (Loucks *et al.*, 2009). Nanoporosity is beyond the resolution of the X-ray microtomography measurements. For nanoscale resolution, 3D mapping methods have been developed for TEM (Midgley *et al.* 2007), FIB etching (Elfallagh and Inkson, 2009; Keller *et al.*, 2011), synchrotron X-ray nanotomography (Heim *et al.* 2009), and scanning transmission X-ray microscopy (Holzner *et al.* 2010; Bernard *et al.* 2010). Further study of nanoporosity and appropriate statistical averaging methods are necessary for understanding macroscopic physical properties, especially elastic anisotropy, of shales in detail.

CONCLUSION

The focus of this study was a quantification of preferred orientation of clays in Posidonia shales from the Hils syncline in Northern Germany, subjected to a different local temperature history. Preferred orientation of kaolinite, illite-mica, illite-smectite, and calcite was quantified by synchrotron X-ray diffraction techniques, followed by Rietveld refinement. The degree of preferred orientation of clays and calcite in all four samples with different maturity history was comparable. Kaolinite and illite-mica generally exhibited stronger preferred orientations than microcrystalline illite-smectite. The difference in temperature history, which causes significant changes in the maturity of organic matter, did not influence the preferred orientation to a large

extent and thus most of the fabric features evolved rather early in history. The pore structure was investigated by synchrotron X-ray microtomography and TEM, suggesting that pores were mostly small ($<10\text{ }\mu\text{m}^3$), platy (aspect ratio >1.5), and layered in the bedding plane but not well-connected. The low porosity of the high maturity sample was due to carbonate cementation and deformation, which is consistent with previous measurements.

ACKNOWLEDGEMENTS

This project is supported by NSF (EAR-0836402) and DOE (DE-FG02-05ER15637). The authors would like to thank Dr. Volker Dieckmann (Shell International Exploration and Production) for providing samples used in this research and Dr. Johannes Wendebourg (Shell) for his permission to use these samples in our work. The material was acquired by Dr. Ulrich Mann (FZ Jülich) and used in earlier studies. The authors acknowledge the access to beamline 11-ID-C at APS as well as assistance from Yang Ren for diffraction experiments and the access to beamline TOMCAT at SLS and assistance from Rajmund Mokso for tomography experiments. The authors greatly appreciate help from Timothy Teague for sample preparation, Luca Lutterotti for updating MAUD software to analyze these complex shales, Dula Parkinson for advices on tomographic data analysis and access to Octopus and Avizo softwares at beamline 8.3.2 at ALS, and Anja Schreiber for kindly preparing the TEM samples. The authors would like to thank Andrew Aplin and Manuel Sintubin for useful comments that helped to improve the manuscript.

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TABLES

Table 1: Quantitative phase proportions in weight% fractions extracted from the Rietveld refinement of S1, S2, S3 and S4 samples.

Sample	Kaolinite	Illite-smec	Illite-mica	Calcite	Quartz	Albite	Pyrite	Dolomite
S1	8.60	13.08	10.35	43.65	15.83	2.57	5.92	-
S2	11.66	19.62	15.60	35.11	15.07	0.99	2.53	-
S3	7.29	24.00	15.22	31.35	14.84	1.94	4.05	1.29
S4	7.76	17.58	12.71	35.87	12.24	5.68	5.50	2.65

Table 2: Lattice parameters of major phases used in the Rietveld refinement. Parameters of quartz, calcite, feldspars, pyrite and dolomite are kept constant throughout the refinement (marked with asterisk). Monoclinic phases are displayed in the second setting system.

Phase	Sample	A (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
Kaolinite	S1	5.18(1)	8.98(1)	7.44(1)	92.13(2)	105.06(2)	89.31(1)
	S2	5.15(1)	8.96(1)	7.41(1)	91.86(1)	104.99(1)	89.91(1)
	S3	5.17(1)	8.98(1)	7.43(1)	92.14(1)	104.06(2)	89.29(1)
	S4	5.16(1)	8.97(1)	7.44(1)	92.57(1)	105.10(1)	89.19(1)
Illite-Smectite	S1	5.11(1)	9.49(1)	11.16(1)	90.00	90.00	90.00
	S2	5.39(2)	8.94(2)	11.16(1)	90.00	95.66(2)10	90.00
	S3	5.11(1)	9.50(1)	11.16(1)	90.00	0.53(2)	90.00
	S4	5.23(1)	8.97(1)	11.16(1)	90.00	100.3(2) 98.33(1)	90.00
Illite-Mica	S1	5.25(1)	9.06(1)	20.34(1)	90.00	95.09(1)	90.00
	S2	5.20(2)	9.00(3)	20.12(2)	90.00	95.87(1)	90.00
	S3	5.25(1)	9.06(1)	20.34(1)	90.00	95.37(1)	90.00
	S4	5.28(2)	9.03(2)	20.44(2)	90.00	95.24(1)	90.00
Calcite*	S1						
	S2						
	S3	4.99	4.99	17.06	90.00	90.00	120.00
	S4						
Quartz*	S1						
	S2						
	S3	4.92	4.92	5.40	90.00	90.00	120.00
	S4						
Feldspars*	S1						
	S2						
	S3	8.14	12.79	7.16	94.33	116.57	87.65
	S4						
Pyrite*	S1						
	S2						
	S3	5.42	5.42	5.42	90.00	90.00	90.00
	S4						
Dolomite*	S1	-	-	-	-	-	-
	S2	-	-	-	-	-	-
	S3	4.81	4.81	16.08	90.00	90.00	120.00
	S4	4.81	4.81	16.08	90.00	90.00	120.00

Table 3: Pole densities for (001) of kaolinite, illite-smectite, illite-mica and calcite pole figures (m.r.d.).

Sample	Kaolinite		Illite-smectite		Illite-mica		Calcite	
	Min	Max	Min	Max	Min	Max	Min	Max
S1	0.32	4.35	0.13	4.58	0.19	4.43	0.92	1.07
S2	0.35	4.83	0.13	4.40	0.35	5.25	0.81	1.09
S3	0.29	4.22	0.14	4.20	0.26	6.12	0.89	1.11
S4	0.32	3.83	0.13	3.64	0.36	5.57	0.78	1.25

FIGURES

Figure 1: A geological map of Posidonia shales used in this study (modified from Littke *et al.*, 1988). Sample locations and different thermal maturity (Ro%) contours (Horsfield *et al.*, 2010) are also displayed.

Figure 2: Backscattered SEM images of sample S4 illustrating a) microstructure of component minerals and b) the presence of pyrite framboid structure.

Figure 3: EDS analysis of sample S4 showing elemental maps of Al, K, Fe, Mg and S, indicating an illite-muscovite grain.

Figure 4: A comparison of (a) “unrolled” diffraction spectra of sample S4 between calculated model (top: Calc.) and experimental data (bottom: Exp.) and (b) diffraction peaks display 8 constituent minerals.

Figure 5: (001) pole figures for clay phases and calcite in all samples. Pole densities are expressed in multiples of random distribution (m.r.d). Different scales are used for clays and calcite.

Figure 6: a) A tomographic slice in XY plane and b) the histogram (in log scale) of grayscale values extracted from the selected area in the 3D reconstructed images of sample S4. Examples of different phases were identified *e.g.* area [1] for micropores, fractures, and kerogen, area [2] for clays, quartz, feldspars, and dolomite, and area [3] for pyrite.

Figure 7: Microtomography images of sample S4 showing the distribution of a) pyrite and b) micropores, fractures, and kerogen.

Figure 8: The histogram plots showing the frequency of a) pore volume and b) pore aspect ratio in the selected area of sample S4. The pore distribution and geometry were extracted from the segmentation data shown in Figure 7b.

Figure 9: Microstructures in low maturity sample S1. (a) HAADF image illustrates microstructure with black pores (Po), gray kerogen (Ke), grains of calcite (Cc) and quartz (Qu) and clusters of illite-smectite (IS), (b) TEM brightfield image illustrating high porosity (light) between phyllosilicate platelets, a large calcite grain with dislocations and its subgrains (center), and a quartz grain (top) with pores.

Figure 10: HAADF image (a) and EELS maps of carbon K α post-edge (b), and sulfur L α post-edge (c) of sample S1, both corrected for extrapolated background. The light regions correspond to kerogen with correlation of high C and S.

Figure 11: Microstructures in high maturity sample S4. (a) HAADF image illustrating kinked illite-smectite and fractured calcite fragments, (b) TEM bright-field image of calcite with dislocations, subgrains and mechanical twins and fluid inclusions, (c) TEM bright-field image showing kinks in illite-smectite and deformed calcite with the inset showing a high resolution

image of illite-smectite with 11 Å (001) stacking showing bending of lattice planes and (d)

HAADF image of framboidal structure of pyrite.