Preferred orientation and elastic anisotropy in shales

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ABSTRACT

Anisotropy in shales is becoming an important issue in exploration and reservoir geophysics. In this study, the crystallographic preferred orientation of clay platelets that contributes to elastic anisotropy was determined quantitatively by hard monochromatic X-ray synchrotron diffraction in two different shales from drillholes off the coast of Nigeria. To analyze complicated diffraction images with five different phases (illite/smectite, kaolinite, quartz, siderite, feldspar) and many overlapping peaks, we applied a methodology based on the crystallographic Rietveld method. The goal was to describe the intrinsic physical properties of the sample (phase composition, crystallographic preferred orientation, crystal structure, and microstructure) and compute macroscopic elastic properties by averaging single crystal properties over the orientation distribution for each phase. Our results show that elastic anisotropy resulting from crystallographic preferred orientation of the clay particles can be determined quantitatively. This provides a possible way to compare measured seismic anisotropy and texture-derived anisotropy and to estimate the contribution of the low-aspect ratio pores aligned with bedding.

INTRODUCTION

The elastic properties of shales are crucial for understanding seismic field measurements in sedimentary basins. The anisotropy of elasticity mainly depends on preferred orientations of rock-forming minerals, single crystal properties, the fracture and pore distribution, and pressure-temperature conditions (Hornby et al., 1994; Sayers, 1994, 2005). Preferred orientation or texture is caused by slow sedimentation of plate-shaped clay minerals that favors orientation of platelets parallel to the sediment surface. This pattern is modified during compaction and diagenesis (Swan et al., 1989; Schoenberg et al., 1996). A quantitative understanding of the texture, and thus the intrinsic contribution of single crystals and their orientation to anisotropy, may help us to better evaluate the effects of the oriented fracture and pore fabric and porosity by comparing calculated and measured elastic properties.

Clay minerals are fine grained and poorly crystalline. Conventional analysis with X-ray pole figure goniometry gives only limited information. An X-ray transmission technique has been developed to study the orientation distribution of basal planes of sheet silicates and has been successfully applied to slates (e.g., Kaarsberg, 1959; Oertel, 1983; Sintubin, 1994b; Ho et al., 1999). However, so far, no quantitative 3D crystal orientation distributions (ODs) exist for any clay minerals in shales. Knowledge of the OD is necessary to model the polycrystalline elastic properties in a rigorous and quantitative fashion.

Hard X-rays produced at synchrotron sources provide a new method to investigate weakly scattering materials. Advantages are a very intense and highly focused X-ray beam and short wavelength that permit high sample penetration without major absorption. Two-dimensional detectors, either charge-coupled device cameras or image plates, are used to record diffraction images. Shales are polyphase materials with many overlapping reflections. Both quantitative phase and texture analyses are necessary to determine the volume fractions and the ODs for each mineral, respectively. The recently developed Rietveld method with texture capabilities has been applied to illite (Wenk et al., 2007) and biomineralized materials (Lonardelli et al., 2005) and has emerged as a powerful tool to extract reliable texture information.

Our aim was to investigate texture in two shales with different porosity by hard X-ray synchrotron diffraction measurements and to determine 3D ODs with the Rietveld method. From the OD, we obtained the polycrystalline elastic tensor by averaging single-crystal elastic properties. From those compressional and shear-wave velocities and their texture-related component, anisotropy can be calculated.
MATERIAL AND EXPERIMENT

Two different well-preserved wet shales from a drillhole off the Nigerian coast were provided by Chevron. The first one from a higher level is a soft shale with low density ($\rho = 2.21$ g/cm$^3$) and high porosity (26%). The second, from a lower level, is a hard shale, more compacted and lithified, with a higher density ($\rho = 2.51$ g/cm$^3$) and lower porosity (6%). The exact location of these shales is Chevron proprietary information. The microstructure for both (Figure 1) reveals a matrix composed of clay minerals and relatively large inclusions caused by the presence of approximately 15%–20% of silt, particularly in the hard shale.

Slabs of 20 $\times$ 10 $\times$ 1 mm were cut from core plugs with the long dimension more or less parallel to the bedding plane as well as could be determined macroscopically. It was later determined that, in the case of hard shale, the core plug axis was about 20° off the bedding plane. The samples were then mounted on an aluminum holder for stability.

These samples were analyzed on beamline BESSRC 11-ID-C at the Advanced Photon Source (APS) at Argonne National Laboratory on a high-energy beam line with a monochromatic wavelength of 0.107863 Å. Beam size was 1 mm, and sample-to-detector distance was approximately 2 m. The samples were mounted on the metal rod parallel to the vertical axis (y in Figure 2) on a goniometer. Images were recorded using a Mar345 image plate detector (3450 $\times$ 3450 pixels) at seven different omega tilt angles, rotating the samples around the axis perpendicular to the beam (y) in 10° increments. Images collected at $\omega = 30°$ for both soft and hard shales, with the complete coverage used in the analysis, are shown in Figure 3. The intensity variations along the Debye rings immediately reveal the presence of texture. After data collection, images were converted in FIT2D (Hammersley, 1998) to 16-bit tagged image file format (TIFF) and exported for further processing. A lanthanum hexaboride powder standard was used to calibrate the sample to detector distance and refine instrumental parameters.

The TIFF images were entered into the material analysis using diffraction (MAUD) program, a Rietveld code written in Java (Lutterotti et al., 1997). An image manager provides the possibility to interactively set the correct parameters (e.g., sample/detector distance, ranges for integration, center coordinates, number of spectra) to obtain integrated spectra. In this study, the integration was performed over 10° sectors, providing for both samples 36 spectra for each 2D image. Seven images, rotating the sample around $\omega$ in 10° increments from −30° to +30°, provided $7 \times 36 = 252$ spectra that were used simultaneously in the Rietveld refinement. The d-range used for the analysis was from 1 to 12 Å.

First, instrumental parameters such as the center of the ring, the background parameters (three for each spectrum), and the scale parameters (one for each image) were refined. The scale parameters take into account different absorption and volumes with tilt (Heidelbach et al., 1999). The second step was to extract the correct volume fractions for each phase (quantitative phase analysis) and structural–microstructural information concerning lattice parameters and orientations.

Figure 1. Microstructures for (a) hard shale and (b) soft shale. Hard shale is characterized by large grains of silt. SEM micrographs, secondary electron image.

Figure 2. Schematic sketch illustrating a X-ray diffraction experiment in transmission geometry. The sample is rotated around the y-axis ($x$, $y$, $z$ define the sample reference system) to improve pole figure coverage. The diffraction pattern is recorded with a 2D detector.

Figure 3. Diffraction images recorded with an image plate detector. Intensity variations along Debye rings are indicative of texture. (a) Hard shale, (b) soft shale, and (c) pole figures coverage provided by seven images at different rotation angles $\omega$. The reference system for the experiment in transmission geometry is $x$, $y$, and $z$. (Figure 2). An equal area projection.
isotropic crystallite size (Popa, 1998). The refined values are shown in Table 1. In a last step, a modified EWIMV algorithm related to WIMV (Matthies and Vinel, 1982) and implemented in MAUD was used for texture analysis. This algorithm allows us to calculate ODs for irregular and incomplete pole figure coverage. No sample symmetry was imposed.

An example of one selected spectrum from each sample (soft and hard shale) is shown in Figure 4. Notice the extremely complicated profile with numerous overlapping peaks and the good agreement between experimental data (dots) and the recalculated fit (solid line). In the 2D multiplot that stacks all spectra and displays intensities in gray shades (Figure 5), some reflections are indexed. Here, the difference in texture between the two shales is clearly visible. In particular and contrary to hard shale, the kaolinite (001) diffraction peak in soft shale shows no significant variation in relative intensity because of its very weak texture.

Table 1. Density, porosity, anisotropic crystallite size, and quantitative phase information (in weight percent). The error generated during Rietveld refinement (standard deviation) is shown in parentheses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g/cm³)</th>
<th>Porosity (%)</th>
<th>Crystallite size (nm)</th>
<th>Weight fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(100)</td>
<td>(010)</td>
</tr>
<tr>
<td>Hard shale</td>
<td>2.51</td>
<td>6</td>
<td>15.1(7)</td>
<td>16.5(8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>22.4(8)</td>
<td>20.1(9)</td>
</tr>
<tr>
<td>Soft shale</td>
<td>2.21</td>
<td>26</td>
<td>26.4(8)</td>
<td>18.5(12)</td>
</tr>
</tbody>
</table>

Figure 4. Example of spectra from (a) hard shale and (b) soft shale. Dots are experimental data, and the solid line is the Rietveld refinement fit.

Figure 5. Map plots illustrating, with gray shades, intensity variations in 36 spectra from one 2D synchrotron diffraction image. (a) Hard shale and (b) soft shale. Notice that in soft shale the kaolinite line is barely textured. The bottom plot in each image is experimental data, and the top is the Rietveld fit for each sample.
RESULTS

Table 1 shows some information regarding the density and porosity for both shales as well as the volume fractions for each phase obtained with Rietveld refinement. The aim of this work is to quantify texture; thus, illite and smectite are treated as a single mixed-layer phase in both samples (I/S), with a 1:1 ratio (50% illite, 50% smectite) and a Reichweite (R) ordering parameter R1. Each layer is identical and contains an Al-rich and an Al-poor tetrahedral sheet and alternating K-rich and K-poor interlayers (Stixrude et al., 2002). For this phase, we assume a crystal structure of muscovite (Comodi and Zanazzi, 1995) with monoclinic symmetry and space group C2/c (Hermann-Mauguin convention). We are aware of the limitations these assumptions put on interpretations, particularly elastic properties, and we hope this can be refined in the future. For kaolinite, space group P1 was used (Young and Hewat, 1988).

We used MAUD to extract ODs for quartz, feldspar, siderite, I/S, and kaolinite and to export them for further processing in BEART-EX (Wenk et al., 1998). The strength of lattice-preferred orientation (F2, Bunge, 1985), the OD minimum-maximum, and additional texture information are summarized in Table 2. The (001) and (100) pole figures are used for graphic representations (Figures 6-8). For both samples, I/S displays strong preferred orientation (Figure 6a and b). Kaolinite is oriented in hard shale (Figure 7a) but is more or less random in soft shale (Figure 7b). Quartz, feldspar, and siderite are oriented randomly, so pole figures for silt components are not shown.

For hard shale (001), pole figures of I/S display a slightly oblique maximum (Figure 6a) with a concentration of 3.01 multiples of a random distribution (MRD). The apparent tilt of approximately 15°-20° from the center is caused by the core plug not being exactly perpendicular to the foliation plane. The significant (001) minimum (also OD minimum) of approximately 0.37 MRD tells us that a significant portion of crystallites is randomly oriented. The (100) pole figure for I/S displays a broad girdle with no significant concentrations, indicating the mineral tends to align in a fiber texture rotating freely around the (001) normal. Figure 7a shows (001) and (100) pole figures for kaolinite where the maximum is more than 30° displaced from the I/S maximum. The texture is similar to that observed for I/S, with a larger proportion of crystallites randomly oriented (minimum 0.5 MRD). In the hard shale, the strong texture for both clay minerals (kaolinite and I/S) is also easily recognized by looking at the map plot (Figure 5a).

To confirm the tilt of the (001) pole figure maximum relative to I/S, we have extracted the ODs for three additional different regions of the hard shale sample. Figure 8 shows the (001) pole figures for three different spots separated by 3 mm. The results confirm an asymmetric maximum of kaolinite with respect to the foliation plane.

In the soft shale, I/S is more strongly aligned than in the hard shale, with (001) poles perpendicular to the foliation plane and a maximum of 4.9 MRD (Figure 6b). The volume fraction of randomly oriented crystallites is similar (0.33 MRD). Although I/S is more textured than in hard shale, kaolinite is nearly randomly oriented with a (001) maximum of approximately only 1.18 MRD (Figure 7b). This result can be confirmed qualitatively by inspecting the map plot in Figure 5, where the variation in intensity along the (001) kaolinite reflection is minimal compared with hard shale. Just to confirm that this unexpected feature is representative of the sample and not a local aberration, several spots were investigated. Figure 9 compares experimental (001) kaolinite lines on several spots for both soft and hard shale, indicating a consistent pattern.

DISCUSSION

Hard X-ray synchrotron radiation was used to investigate the preferred orientation of two different shale samples collected at different burial depths. Two-dimensional diffraction images were analyzed with the Rietveld method to provide a quantitative texture characterization from full spectra. Both samples show strong alignment of I/S with (001) planes parallel to the foliation plane. Maximum (001) pole densities are similar to those reported for Zechezstein shales (Sintubin, 1994a; 4–6 MRD), Gulf Coast mudstones (Ho et al., 1995; 2–7 MRD), and mudstones from Pennsylvania (Ho et al., 1995; 2–5 MRD) but considerably weaker than muscovite in metamorphic slates (Oertel and Phakey, 1972; 16 MRD; Sintubin, 1994b; 5–18 MRD). All these previous studies used single peak intensity measurements, which can be unreliable for interlayer clays with diffuse peaks and background uncertainties. Our method relied on full spectra deconvolution.

If the ODs and the elastic constants of single crystals for each phase are known, averaging procedures can be applied to evaluate the elastic properties of the polycrystal. Unfortunately, elastic properties of clay minerals are poorly known (Katahara, 1996), and for this study we have used experimental elastic stiffness moduli of muscovite measured with Brillouin scattering (Vaughan and Guggenheim, 1986) and kaolinite elastic constants derived from first-principles studies (Sato et al., 2005). Muscovite is treated as monoclinic, and kaolinite is treated as triclinic.

Results for aggregate elastic constants weighted by the OD are shown in Table 3. The Voigt and Reuss values provide upper and lower bounds, assuming uniform strain and uniform stress, respectively, throughout the textured aggregate. A geometric mean averaging is intermediate (Matthies and Humbert, 1993). From aggregate elastic constants obtained by the geometric mean, we calculated phase velocity surfaces \( (V_{pa}, V_{ps}, V_{ps}) \). Figure 10 gives the 1D profiles of \( V_{pa}, V_{ps}, (V_{pa} - V_{ps}) \) from a position perpendicular to the foliation plane \( (0^\circ) \) to the position parallel to the foliation plane \( (90^\circ) \). Anisotropies (in percent) for the clay mineral components \( A = 200(V_{max} - V_{min})/(V_{max} + V_{min}) \) are in the range of 10%. From elastic coefficients, we can also calculate Thomsen parameters that are used in exploration seismology (Thomsen, 1986). For the two shales analyzed in this study, anisotropy is moderate (Table 3). This is because by using muscovite elastic moduli for I/S, we assume that any interlayer water is pore water. The elastic anisotropy calculated

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Table 2. Quantitative texture information for OD and pole figures in multiples of a random distribution (MRD). F2 is the texture strength.

<table>
<thead>
<tr>
<th>Sample phase</th>
<th>F2 (max/min)</th>
<th>OD (max/min)</th>
<th>(001) (max/min)</th>
<th>(100) (max/min)</th>
</tr>
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<tbody>
<tr>
<td>Hard shale</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I/S</td>
<td>1.43</td>
<td>4.21/0.28</td>
<td>3.01/0.37</td>
<td>1.39/0.62</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1.38</td>
<td>3.68/0.35</td>
<td>2.63/0.50</td>
<td>1.30/0.70</td>
</tr>
<tr>
<td>Soft shale</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I/S</td>
<td>1.64</td>
<td>5.82/0.27</td>
<td>4.91/0.33</td>
<td>1.45/0.38</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1.03</td>
<td>1.38/0.84</td>
<td>1.18/0.89</td>
<td>1.06/0.94</td>
</tr>
</tbody>
</table>
Figure 6. (100) and (001) I/S pole figures recalculated from the OD: (a) hard shale and (b) soft shale. An equal area projection. The pole density scale is in multiples of random distribution (MRD).

Figure 7. Kaolinite pole figures (100) and (001), recalculated from the OD: (a) hard shale and (b) soft shale. An equal area projection. The pole density is scale in MRD.
Figure 8. (a) I/S and (b) kaolinite (001) pole figures recalculated from the OD for three different spots of the hard shale sample. An equal area projection. The pole density is in MRD.

Figure 9. The (001) kaolinite peak for hard (a) and soft shale (b). The image shows intensity variation in 36 spectra (from 0° to 360°) from the 2D synchrotron image at ω = 30° (tilting angle) for each spot analyzed. Notice the different intensity scales for (a) and (b).
with this technique comes from the texture of the nonporous material, and the effect of low-aspect ratio pores (interlayer water) aligned with the bedding is neglected.

For bulk rock seismic properties, not only does crystal orientation need to be considered but also other contributions to anisotropy in shales, such as oriented fractures, degree of porosity, and water content (O’Connell and Budiansky, 1976; Crampin, 1981; Hornby et al., 1994; Schoenberg and Sayers, 1995). The difference between texture-derived wave-velocity contributions and experimental velocity measurements can be interpreted in terms of direct porosity effects, such as low-aspect ratio pores, preferred orientation of low-aspect ratio pores, and pore interactions (Ullemeyer et al., 2006). Unfortunately, in the case of these samples, no velocity measurements are available.

The role of porosity in the development of intrinsic anisotropy described by Wang (2002) (more compacted shales equal a higher degree of anisotropy) is only partially confirmed. The I/S in soft shale (less compacted with 26% of porosity) is more strongly aligned than I/S in hard shale (more compacted with only 6% of porosity). However, the rule applies to kaolinite, whereas soft shale the texture is almost random.

### CONCLUSIONS

Our study demonstrated the feasibility of extracting orientation distributions of individual mineral components in shales. With the advances in X-ray diffraction methods and Rietveld texture analysis, we are now able to obtain quantitative texture information with a high degree of resolution for complicated multiphase materials. Quantification of the texture-derived contribution to anisotropy of clay minerals in shales opens the possibility to determine a lower limit of anisotropy caused by crystallite orientation and thus advance our understanding of the importance of pores by comparing predicted and measured seismic velocities. With such information, comprehensive models for seismic wave anisotropy in clay-rich sedimentary rocks can be developed.

### ACKNOWLEDGMENTS

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### REFERENCES


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Table 3. Elastic stiffness of I/S and kaolinite aggregates using the geometric mean (Geo), Voigt average (upper limit), Reuss average (lower limit), and calculated Thomsen anisotropy parameters. The reference single-crystal values assume monoclinic symmetry for muscovite (Vaughan and Guggenheim, 1986) and triclinic symmetry for kaolinite (Sato et al., 2005). Only the most significant elastic constants are shown.

<table>
<thead>
<tr>
<th>Sample/phase</th>
<th>Averages</th>
<th>Elastic constants (GPa)</th>
<th>Thomsen parameters</th>
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<tr>
<td></td>
<td></td>
<td>C\textsubscript{11}</td>
<td>C\textsubscript{33}</td>
</tr>
<tr>
<td>Hard shale</td>
<td></td>
<td>111.4</td>
<td>102.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>130.7</td>
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<td></td>
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<td>89.5</td>
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<td></td>
<td></td>
<td>79.3</td>
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<td></td>
<td>121.1</td>
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</tr>
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<td></td>
<td></td>
<td>48.1</td>
<td>45.2</td>
</tr>
<tr>
<td>Kaolinite</td>
<td></td>
<td>114.3</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>133.9</td>
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<td></td>
<td></td>
<td>91.8</td>
<td>81.9</td>
</tr>
</tbody>
</table>

Figure 10. Calculated seismic velocities for I/S (hard and soft shale) and kaolinite (hard shale). (a) P-waves, (b) ΔS-waves versus the angle to the bedding plane.


