RIETVELD REFINEMENT OF REAL STRUCTURE PARAMETERS OF DISORDERED CLAY MINERALS IN PHASE MIXTURES

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clays and hydrocarbons

project:

Nicht-konventionelle Kohlenwasserstoffe (non-conventional hydrocarbons in Germany)

Germany’s potential for shale oil and shale gas

shale: sedimentary rock which contains quartz, carbonates and clay minerals
clay minerals in shales


carbonates

quartz

brittleness diagram

clay
layer silicates – structural units

SiO$_4$  M(O,OH)$_6$  M: Al$^{3+}$, Mg$^{2+}$, Fe$^{2+/3+}$

dioctahedral  trioctahedral

peak overlapping, rotational/translational disorder, mixed layer stacking

kaolinite
serpentinite
pyrophyllite
talc
smectite
mica
illite
chlorite
turbostratically disordered smectite


turbostratically disordered smectite
supercell approach

Ufer, K. et al. (2004), Z. Kristallogr., 219, 519-527
Rietveld code BGMN

- fundamental parameter approach
- automatic refinement strategy
- spherical harmonics for correction of preferred orientation
- expression interpreter
- solving linear equation systems (complex)
- manipulation of complex structure amplitudes
- ASCII textfile controlled input and output

turbostratically disordered smectite

BGMN structure input file:

PHASE=smectite  SpacegroupNo=5  HermannMauguin=C121
PARAM=A=0.52_0.517^0.521  PARAM=B=0.898_0.894^0.91
PARAM=c0=1.54_1.45^1.6
BETA=100.2

layer==10  // layer: factor for elongation in c direction
C=c0*layer // C: lattice parameter c for supercell…

…
PARAM=GEWICHT=0_0
GEWICHT[1]=GEWICHT*ifthenelse(and(eq(h,0),eq(k,0)),
ifthenelse(mod(l,layer),0,layer),1)

…

* * *

*: quartz, pyrophyllite
artificial mixture “synthetic bentonite”

<table>
<thead>
<tr>
<th></th>
<th>Initial weight-%</th>
<th>calculated wt.-%±3σ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Measurement 0.03° 3 sec 0.02° 20 sec</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R_{exp}$ 5.2 2.6 $R_{wp}$ 7.1 5.4</td>
</tr>
<tr>
<td>smectite</td>
<td>71-73</td>
<td>72.8±2.7 71.3±1.9</td>
</tr>
<tr>
<td>amorphous</td>
<td>4-6</td>
<td>4.5±3.3 6.0±2.1</td>
</tr>
<tr>
<td>plagioclase</td>
<td>5</td>
<td>4.4±0.4 4.5±0.3</td>
</tr>
<tr>
<td>Alkali feldspar</td>
<td>5</td>
<td>5.3±0.6 5.4±0.5</td>
</tr>
<tr>
<td>calcite</td>
<td>3</td>
<td>2.7±0.5 2.5±0.3</td>
</tr>
<tr>
<td>quartz</td>
<td>10</td>
<td>10.2±0.4 10.3±0.3</td>
</tr>
</tbody>
</table>

10% zincite as internal standard

Ufer, K. et al. (2008), Clays and Clay Minerals, 56, 272-282
stacking disorder

- different kinds of layers
- different interlayer spacings
- translations/rotations from one layer to the next

polytypism:
- muscovite 1M, 2M₁, 3T
- new structures:
  - corrensite
  - rectorite,…

statistical description:
- muscovite 1M_d
- illite / smectite ML

ordered

1M

2M₁

3T

disordered
Recursive calculation of structure factors: DIFFaX

\[ \Psi(u) = F(u) + \exp(-2\pi i u \cdot R) \Psi(u) \]

\[ \Psi_i(u) = F_i(u) + \sum_{j=1,2} a_{ij} \exp(-2\pi i u \cdot R_{ij}) \Psi_j(u) \]

Translation, Probabilities

N=3 FMult=3  // N: number of layer types, FMULT: number of subphases
// rotated layers must be introduced as additional subphase
// 0 deg, 120 deg, 240 deg for tv layer types: total of 3 different subphases

// translation in c for illite (absolute scale)
t1=0.39  // stacking vector to compensate monoclinic shift

// probabilities for different stackings
p0=0.75  // p0: probability of 1M "ordered" stacking
p120=0.15  // 120 deg and 240 deg rotations are equiprobable
p240=0.15

// translation matrix t[n,m]: stacking vector from layer n to layer m
// p[n,m]: probability for the occurrence of translation t[n,m]

\[ \begin{align*}
    tx[1,1] &= -tatv \\
    ty[1,1] &= 0.0 \\
    tz[1,1] &= tI/C \\
    p[1,1] &= p0 \\
    tx[1,2] &= -tatv \\
    ty[1,2] &= 0.0 \\
    tz[1,2] &= tI/C \\
    p[1,2] &= p120 \\
    tx[1,3] &= -tatv \\
    ty[1,3] &= 0.0 \\
    tz[1,3] &= tI/C \\
    p[1,3] &= p240 \\
    tx[2,1] &= 0.5*tatv \\
    ty[2,1] &= -tatv*A*cos(30*pi/180)/B \\
    tz[2,1] &= tI/C \\
    p[2,1] &= p240 \\
    tx[2,2] &= 0.5*tatv \\
    ty[2,2] &= -tatv*A*cos(30*pi/180)/B \\
    tz[2,2] &= tI/C \\
    p[2,2] &= p0 \\
    tx[2,3] &= 0.5*tatv \\
    ty[2,3] &= -tatv*A*cos(30*pi/180)/B \\
    tz[2,3] &= tI/C \\
    p[2,3] &= p120 \\
    tx[3,1] &= 0.5*tatv \\
    ty[3,1] &= tatv*A*cos(30*pi/180)/B \\
    tz[3,1] &= tI/C \\
    p[3,1] &= p120 \\
    tx[3,2] &= 0.5*tatv \\
    ty[3,2] &= tatv*A*cos(30*pi/180)/B \\
    tz[3,2] &= tI/C \\
    p[3,2] &= p240 \\
    tx[3,3] &= 0.5*tatv \\
    ty[3,3] &= tatv*A*cos(30*pi/180)/B \\
    tz[3,3] &= tI/C \\
    p[3,3] &= p0
\end{align*} \]


// recursive structure factor calculation
\[ F = \text{cat}(i=1, \text{while}(i<N), j=1, \text{while}(j<N), \text{while}(j<i), \text{while}(j<i)) \]
\[ FT = \text{detune}(p[i,j], p[i,j] = 2*pi^i * h(tx[i,j], ty[i,j], tz[i,j]), \text{Treal}(i,j) = \text{FT} * \text{cos}(phi[i,j]), \text{Timag}(i,j) = \text{FT} * \text{sin}(phi[i,j]), \text{Freal}(i,j), \text{Fimag}(i,j) = \text{sqrt}(F(i,j)) \]

disorder models

applicable for:
• stacking of different kinds of layers (even with different thicknesses)
• translations of layers parallel to each other
• rotation of layers parallel to each other

existing models:
• illite and glauconite (rotational disorder)*
• illite/smectite mixed layering*
• kaolinite (enantiomorph layers, b/3 translations)
• pyrophyllite (different translation vectors)
• talc (rotational disorder)
• chlorite (b/3 translations)
• opal-ct
• layered double hydroxides*

* published
illite/smectite mixed layered minerals

- 00l reflections
- Smectitic interlayers:
  - Turbostratic disorder
  - Different layer thicknesses
  - Long range ordering ("Reichweite")
  - Reichweite => range of influence

- Hk reflections
- Illitic interlayers:
  - Translational / Rotational disorder

- 2 different effects / classes!

Jagodzinski, H. (1949), Acta Crystallographica, 2, 201-207
**illite/smectite mixed layered minerals**

**model for 00l reflections:**
- different junctions of illite, smectite(1w), smectite(2w)
- short- or long-range ordering; Reichweite R0-R3
- proportions (wI, wS) and stacking probabilities (pII, pIS,..)

**model for hk reflections:**
- n120° rotational disorder (0°, 120°, 240°)
- different translation vectors

**global (shared) parameters**
- lattice parameter
- atomic positions
- occupancies
- scaling factor, P.O. factor

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Bundesanstalt für Geowissenschaften und Rohstoffe

GEOZENTRUM HANNOVER
illite/smectite pure sample

separate but connected models:
n120° rotational disorder
R3 illite/smectite(1w)/smectite(2w)

control file *.sav:
%
% connected parameters
PARAM[3]=GEWICHTconnected=0.01_0
PARAM[4]=prefercconnected=0_-2^2
PARAM[5]=Aconnected=0.52_0.5^0.528
PARAM[6]=tIconnected=1=0.98^1.02
...

structure file 00l.str:
...
// Scaling of intensity and correction of preferred orientation
GEWICHT=GEWICHTconnected
preferc=prefercconnected
GEWICHT[1]=layer*anisosqr(1-preferc/2,1-preferc/2,1+preferc)*GEWICHT
...

structure file hk.str:
...
// Scaling of intensity and correction of preferred orientation
GEWICHT=GEWICHTconnected
preferc=prefercconnected
GEWICHT[1]=layer*anisosqr(1-preferc/2,1-preferc/2,1+preferc)*GEWICHT
...
smectite / IS mixtures

- **Pure IS**
  - $w_I = 0.8718$
  - $p_0 = 0.6597$

- **66.7 wt.-% IS, 33.3 wt.-% smectite**
  - $w_I = 0.8459$
  - $p_0 = 0.6408$
  - 65.1 wt.-% IS
  - 31.9 wt.-% smectite
  - 3.0 wt.-% quartz

- **33.3 wt.-% IS, 66.7 wt.-% smectite**
  - $w_I = 0.8329$
  - $p_0 = 0.5805$
  - 34.1 wt.-% IS
  - 63.8 wt.-% smectite
  - 2.1 wt.-% quartz

- **10.0 wt.-% IS, 90.0 wt.-% smectite**
  - $w_I = 0.7966$
  - $p_0 = 0.5430$
  - 22.0 wt.-% IS
  - 76.6 wt.-% smectite
  - 1.4 wt.-% quartz

- **33.3 wt.-% IS, 66.7 wt.-% smectite**
  - $w_I = 0.8329$
  - $p_0 = 0.5805$
  - 34.1 wt.-% IS
  - 63.8 wt.-% smectite
  - 2.1 wt.-% quartz
artificial mixture “synthetic shale” - QPA

1/3 IS, 2/3 smectite: 30 wt.-%
1/2 quartz, 1/2 calcite: 70 wt.-%

10 wt.-% illite/smectite
20 wt.-% smectite
35 wt.-% quartz
35 wt.-% calcite

refinement result:
11.2 wt.-% illite/smectite
18.4 wt.-% smectite
35.0 wt.-% quartz
35.4 wt.-% calcite
### "synthetic shale" – structural parameters

#### Refinement result:

<table>
<thead>
<tr>
<th></th>
<th>Pure IS</th>
<th>30:70 Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>$w_l$</td>
<td>0.8718</td>
<td>0.8368</td>
</tr>
<tr>
<td>$p_0$</td>
<td>0.6597</td>
<td>0.333</td>
</tr>
</tbody>
</table>

The diagram shows the X-ray diffraction peaks for different minerals in synchrotron X-ray diffraction (SXRD) data, indicating the structural parameters of the synthetic shale. The peaks are color-coded for different minerals: illite-smectite (yellow), smectite (blue), quartz (green), and calcite (red).
smectite / IS mixtures: simulations

input (simulation)

50 wt.-% smectite (40% 1w)
50 wt.-% IS (R0, 40% 1w)

wl=0.6
p0=0.333

parameter reduction,
additional information:

wl=0.6 (fixed) + chemical composition of IS

output (refinement)

42.5 wt.-% smectite
57.5 wt.-% IS

wl=0.4765
p0=0.411

input (simulation)

50 wt.-% smectite (0% 1w)
50 wt.-% IS (R0, 0% 1w)

wl=0.6
p0=0.334

output (refinement)

50.5 wt.-% smectite
49.5 wt.-% IS

p0=0.334
combined refinement

Preparation of random powder sample and oriented mounts under different conditions ("multi-specimen")

Suspension of clay minerals on glass slides or ceramic tiles

15 global parameters

I/S(1w,2w) 6 individual parameters

EG intercalated I/S 7 individual parameters

I/S1w2w 1Md, cv/tv, 120° rot. 18 individual parameters

Air-dried

EG intercalated

Rand. powdered

wl=0.86+-0.0012

Sakharov, B.A. et al. (1999), Clays and Clay Minerals, 47, 555-566
statistical tools for sample selection

Posidonia shale
72 core samples, 1 sample per meter

correlation matrix from XRF chemical data

cluster analysis from XRD data
QPA with 4 different models

Reichweite 0
\[ R_{wp} = 7.45\% \]

Reichweite 1
\[ R_{wp} = 7.40\% \]

Reichweite 2
\[ R_{wp} = 7.41\% \]

Reichweite 3
\[ R_{wp} = 7.56\% \]
### QPA with different models

<table>
<thead>
<tr>
<th>Mineral Type</th>
<th>IS, R0 (%)</th>
<th>IS, R1 (%)</th>
<th>IS, R2 (%)</th>
<th>IS, R3 (%)</th>
<th>Turbostratic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illite/Smectite</td>
<td>32.9</td>
<td>32.3</td>
<td>32.4</td>
<td>33.4</td>
<td>15.6</td>
</tr>
<tr>
<td>Smectite</td>
<td>15.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>21.5</td>
<td>21.3</td>
<td>21.3</td>
<td>21.4</td>
<td>15.7</td>
</tr>
<tr>
<td>Chlorite</td>
<td>4.3</td>
<td>4.7</td>
<td>5.0</td>
<td>4.6</td>
<td>16.7</td>
</tr>
<tr>
<td>Muskovite 2M1</td>
<td>8.5</td>
<td>8.7</td>
<td>8.6</td>
<td>8.5</td>
<td>19.3</td>
</tr>
<tr>
<td>Quartz</td>
<td>18.0</td>
<td>18.0</td>
<td>17.9</td>
<td>17.8</td>
<td>16.2</td>
</tr>
<tr>
<td>Calcite</td>
<td>5.2</td>
<td>5.2</td>
<td>5.2</td>
<td>5.1</td>
<td>5.0</td>
</tr>
<tr>
<td>Siderite</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.6</td>
</tr>
<tr>
<td>Ankerite</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>2.4</td>
<td>2.3</td>
</tr>
<tr>
<td>Plagioclase (16An)</td>
<td>1.2</td>
<td>1.2</td>
<td>1.3</td>
<td>1.1</td>
<td>2.9</td>
</tr>
<tr>
<td>Rutile</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Anatase</td>
<td>1.5</td>
<td>1.5</td>
<td>1.4</td>
<td>1.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Pyrite</td>
<td>2.6</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.8</td>
</tr>
</tbody>
</table>

### Notes
- QPA independent of the choice of model for Reichweite even with wrong smectite model the same sum of clay
conclusion

• disordered clay minerals can reliably be quantified in mixtures with the Rietveld method

• even mixtures of very similar structures like smectite and IS can be quantified, if the degree of disorder is not too high and sensible constraints/fixations were made

• for a reliably structural characterisation detailed examinations are necessary

• the sum of all clay minerals can be achieved even with unfavorable models