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

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TECHNISCHE UNIVERSITÄT BERGAKADEMIE FREIBERG
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Bundesanstalt für Geowissenschaften und Rohstoffe
GEOZENTRUM HANNOVER

clays and hydrocarbons

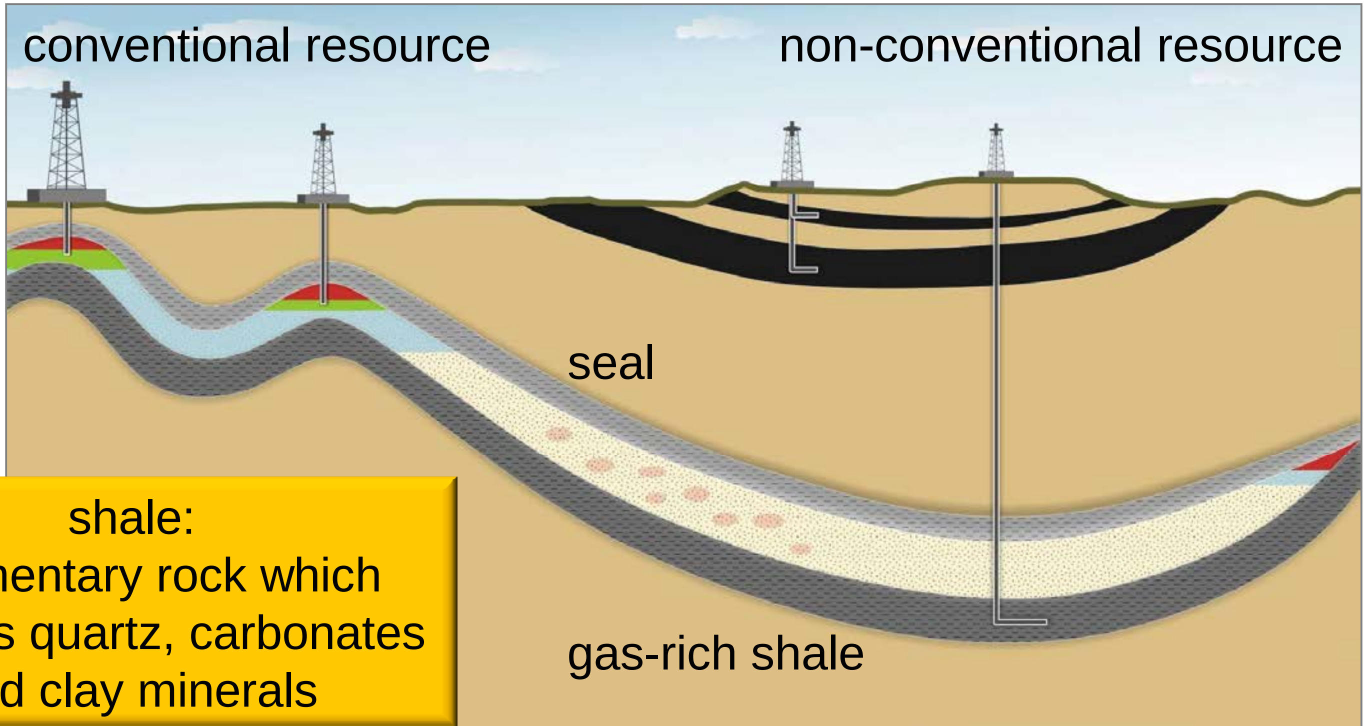
project:

NIKO

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

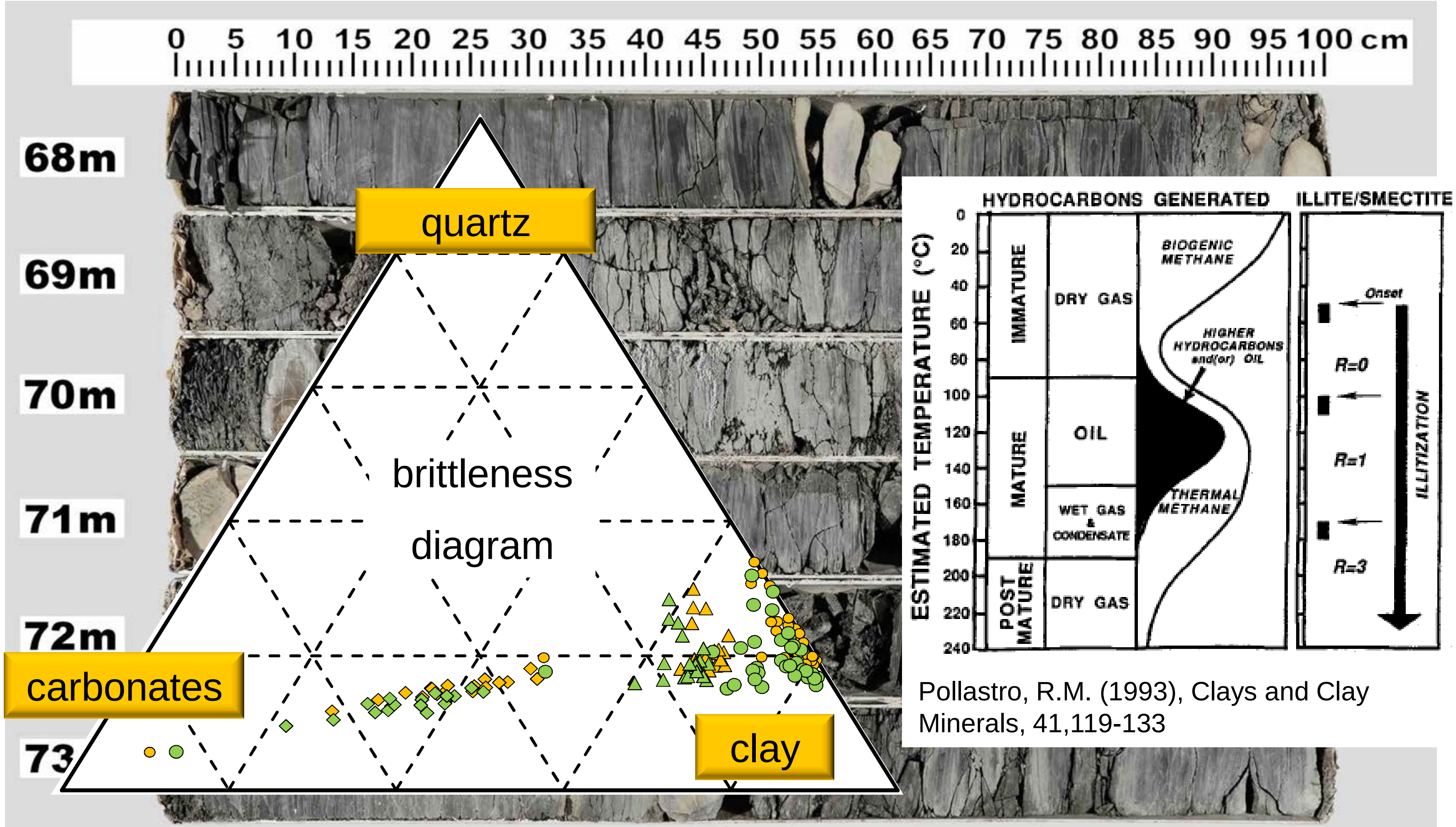
Bundesministerium
für Wirtschaft
und Technologie

Germany's potential for shale oil and shale gas



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

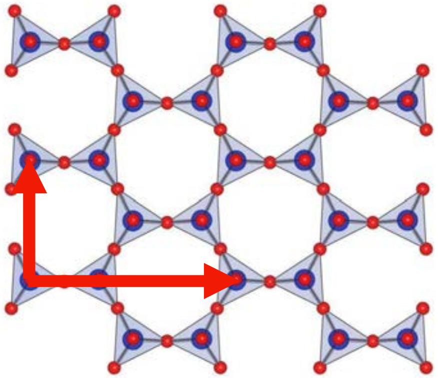
clay minerals in shales



Pollastro, R.M. (1993), Clays and Clay Minerals, 41,119-133

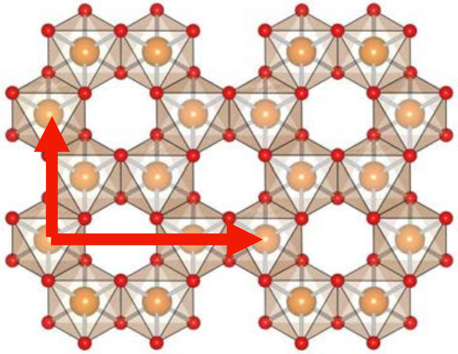
layer silicates – structural units

SiO_4

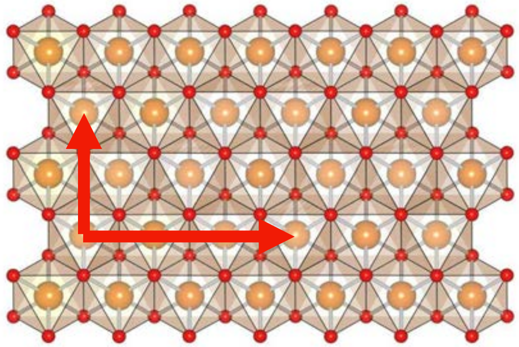


a = ~5.2 Å, b= ~9.0 Å

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



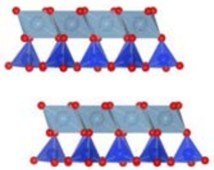
dioctahedral



trioctahedral

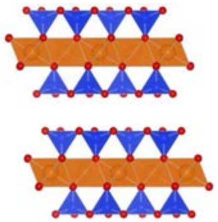
peak overlapping, rotational/translational disorder, mixed layer stacking

T
O

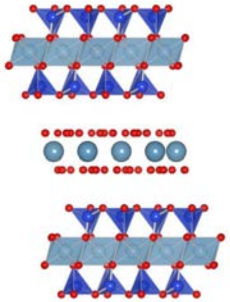


kaolinite
serpentinite

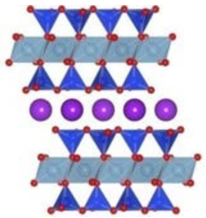
T
O
T



pyrophyllite
talc

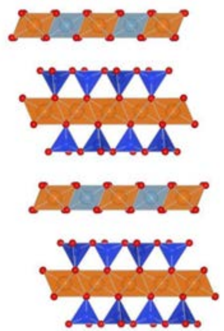


smectite



mica
illite

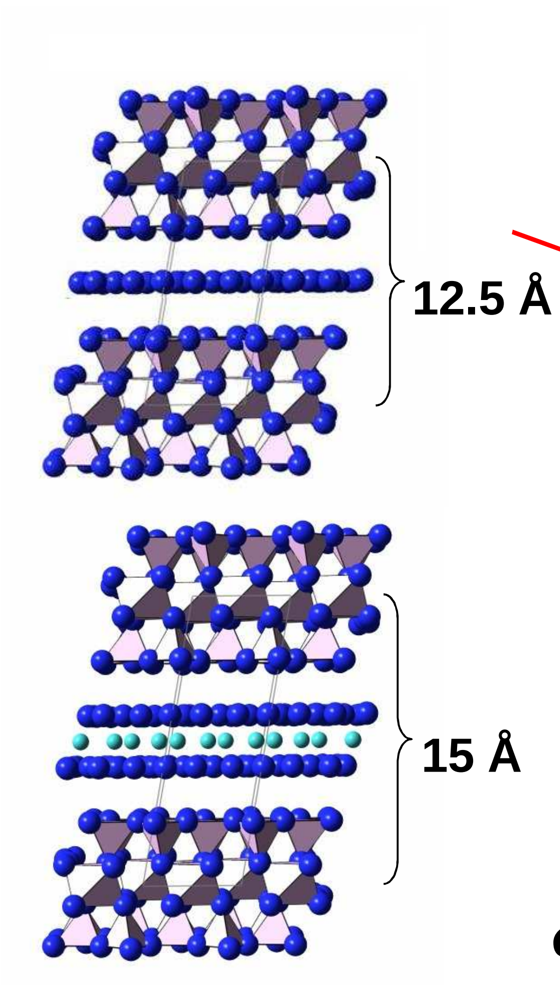
T
O
T
O

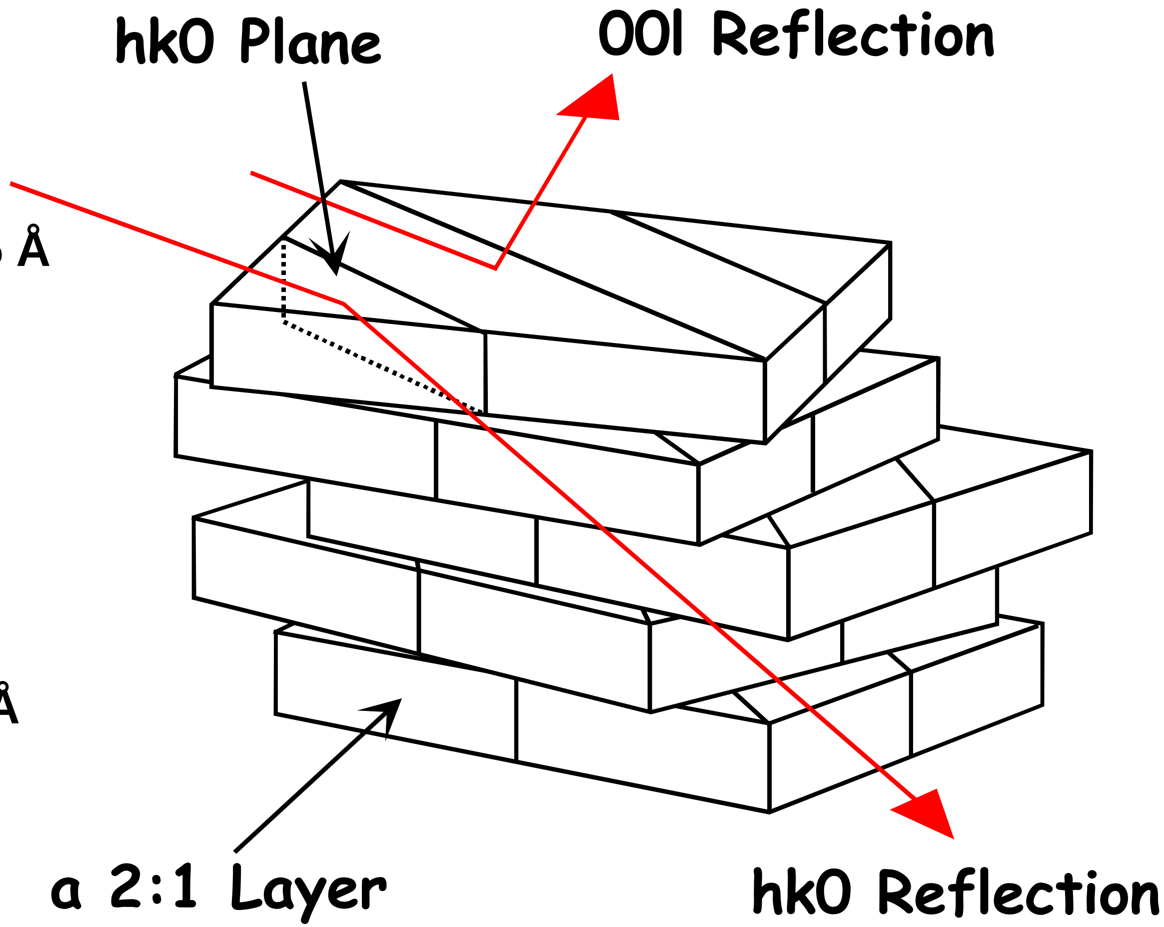


chlorite

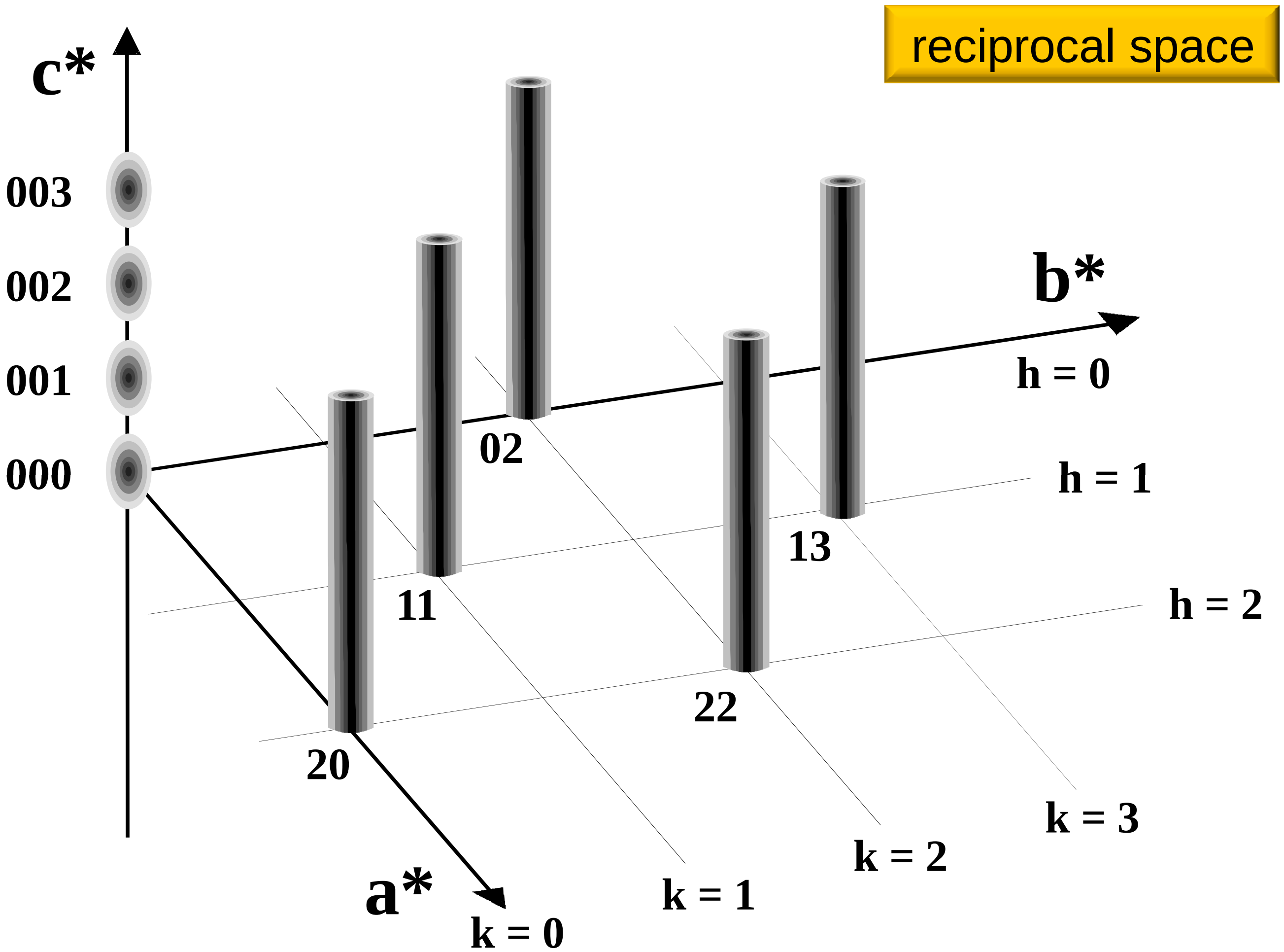
turbostratically disordered smectite

Warren, B.E. (1941), Physical Review, 59**,** 693-698

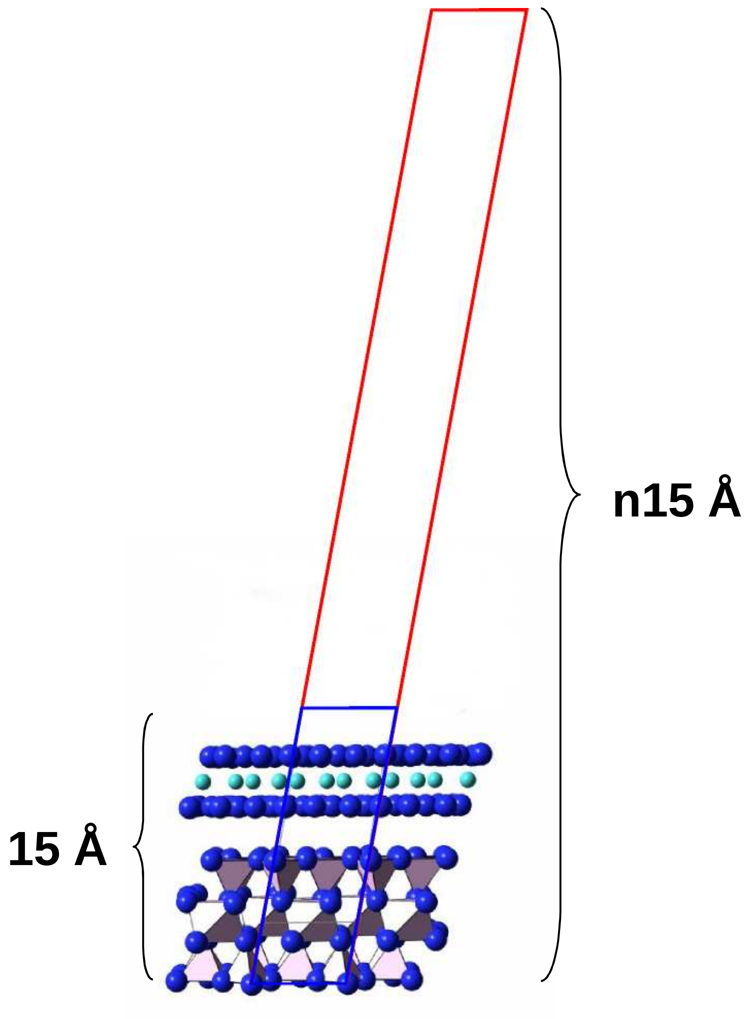


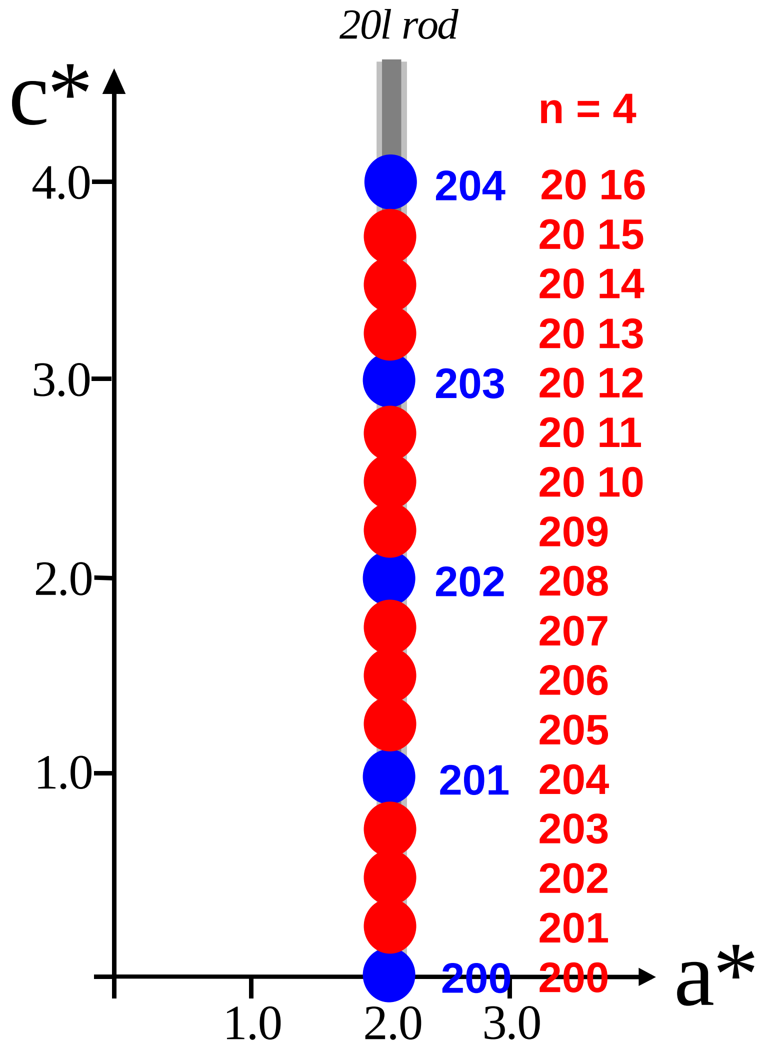


turbostratically disordered smectite



supercell approach





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

Rietveld code BGMN

BGMNwin

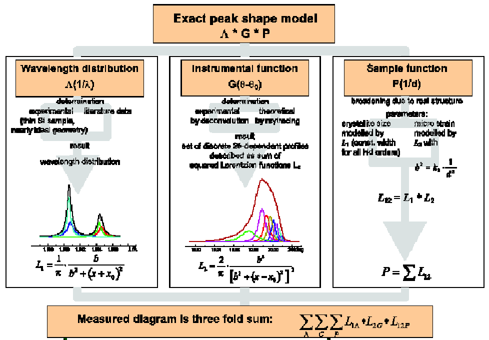
File Run Tools Configuration Windows Help

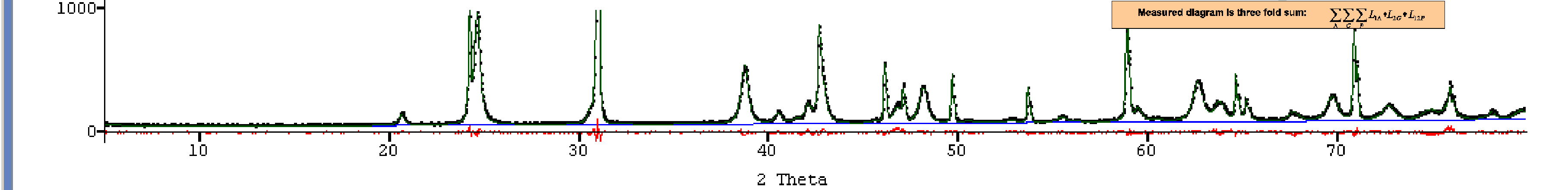
Jörg Bergmann, Dresden

2 GoethiteQuartz.dia

Calculated Profiles: ---------- Database Lines: ----------

- 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





Bergmann, J. & Kleeberg, R. (1998), Materials Science Forum, 278-281, 300-305

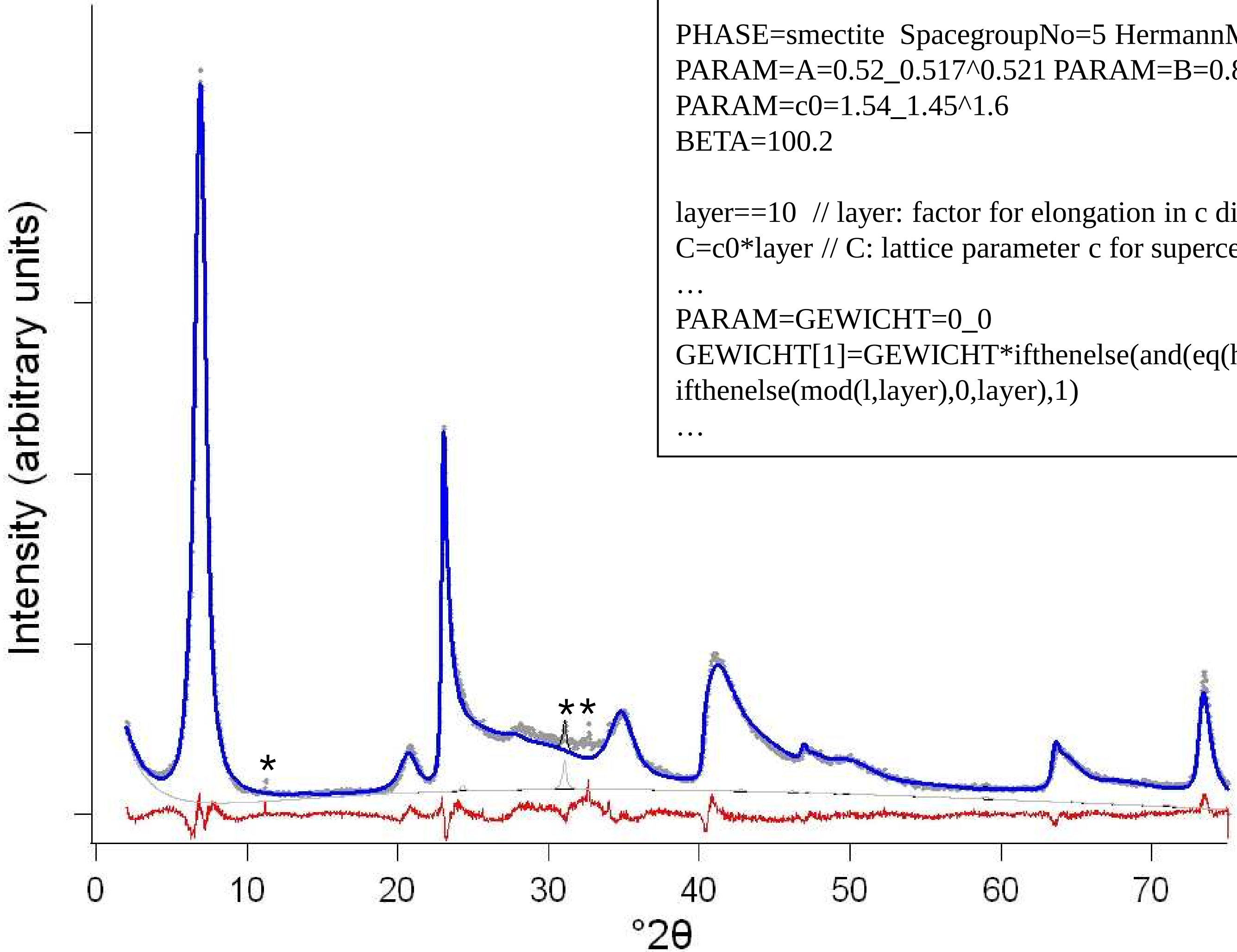
BGR Bundesanstalt für Geowissenschaften und Rohstoffe
GEOZENTRUM HANNOVER

turbostratically disordered smectite

BGMN structure input file:

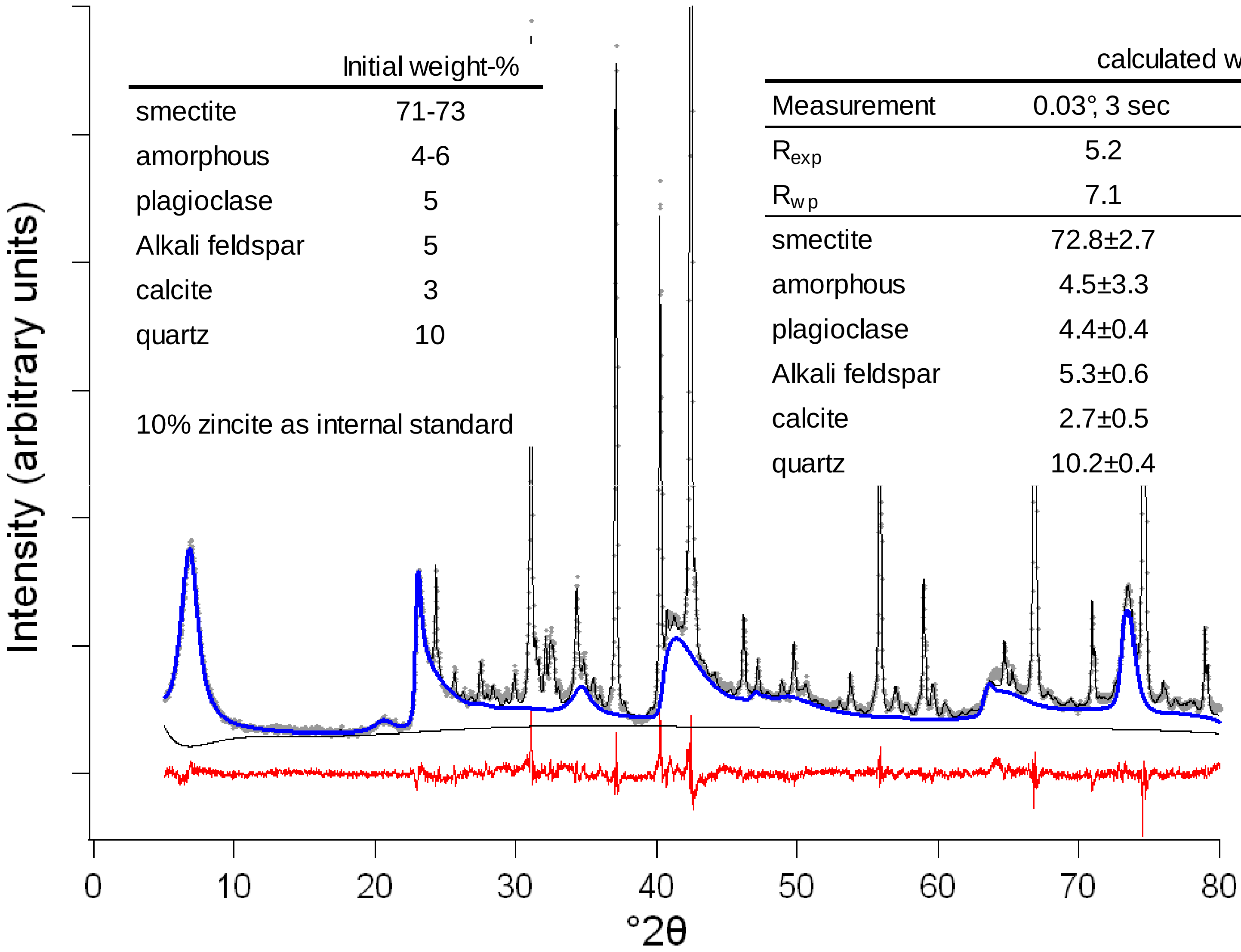
PHASE=smectite SpacegroupNo=5 HermannMauguin=C121
PARAM=A=0.52_0.517^0.521 PARAM=B=0.898_0.894^0.91
PARAM=c0=1.54_1.45^1.6
BETA=100.2

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"



	Initial weight-%
smectite	71-73
amorphous	4-6
plagioclase	5
Alkali feldspar	5
calcite	3
quartz	10

10% zincite as internal standard

	calculated wt.-%±3σ	
Measurement	0.03°, 3 sec	0.02°, 20 sec
R_{exp}	5.2	2.6
R_{wp}	7.1	5.4
smectite	72.8±2.7	71.3±1.9
amorphous	4.5±3.3	6.0±2.1
plagioclase	4.4±0.4	4.5±0.3
Alkali feldspar	5.3±0.6	5.4±0.5
calcite	2.7±0.5	2.5±0.3
quartz	10.2±0.4	10.3±0.3

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

ordered

disordered

<u>polytypism:</u>

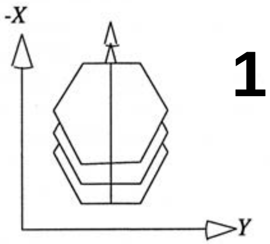
- muscovite 1M, $2M_1$, 3T

<u>new structures:</u>

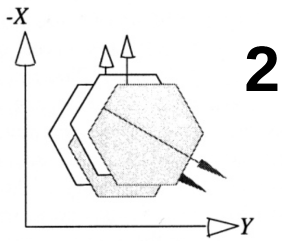
- corrensite
- rectorite,…

<u>statistical description:</u>

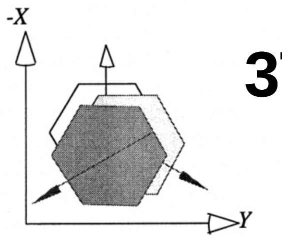
- muscovite $1M_d$
- illite / smectite ML



1M

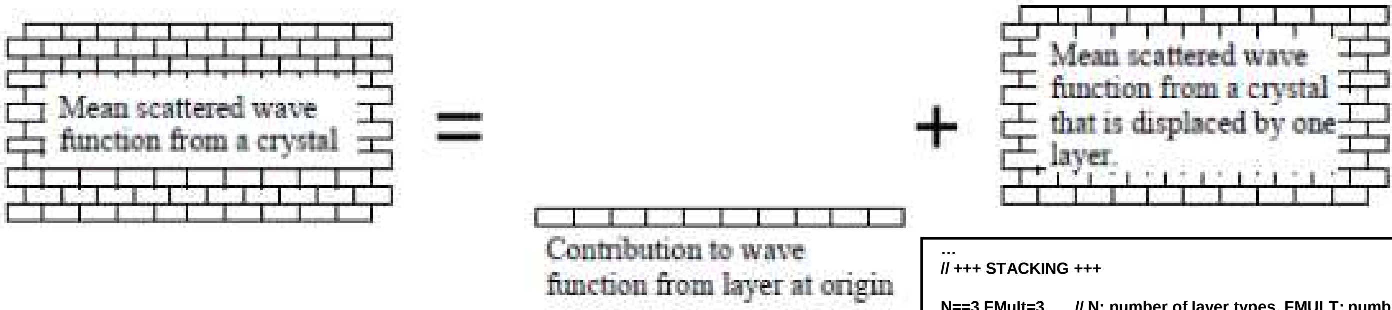


$2M_1$



3T

recursive calculation of structure factors: DIFFaX



$$\Psi(\mathbf{u}) = F(\mathbf{u}) + \exp(-2\pi i \mathbf{u} \cdot \mathbf{R})\,\Psi(\mathbf{u})$$

$$\Psi_i(\mathbf{u}) = F_i(\mathbf{u}) + \sum_{j=1,2} \alpha_{ij} \exp(-2\pi i \mathbf{u} \cdot \mathbf{R}_{ij})\,\Psi_j(\mathbf{u})$$

translations

probabilities

```
...
// +++ STACKING +++

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

tl=1          // translation in c for illite (absolute scale)
tatv=0.39     // stacking vector to compensate monoclinic shift

// probabilities for different stackings
p0=0.75                          // p0: probability of 1M "ordered" stacking
p120=(1-p0)/2 p240=(1-p0)/2  // 120 deg and 240 deg rotations are equiprobable

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

tx[1,1]==-tatv ty[1,1]==0.0 tz[1,1]==tl/C p[1,1]==p0     //    0 deg tv-tv
tx[1,2]==-tatv ty[1,2]==0.0 tz[1,2]==tl/C p[1,2]==p120  // 120 deg tv-tv
tx[1,3]==-tatv ty[1,3]==0.0 tz[1,3]==tl/C p[1,3]==p240  // 240 deg tv-tv

tx[2,1]==0.5*tatv ty[2,1]==-tatv*A*cos(30*pi/180)/B tz[2,1]==tl/C p[2,1]==p240  // 240 deg tv-tv
tx[2,2]==0.5*tatv ty[2,2]==-tatv*A*cos(30*pi/180)/B tz[2,2]==tl/C p[2,2]==p0     //    0 deg tv-tv
tx[2,3]==0.5*tatv ty[2,3]==-tatv*A*cos(30*pi/180)/B tz[2,3]==tl/C p[2,3]==p120  // 120 deg tv-tv

tx[3,1]==0.5*tatv ty[3,1]==tatv*A*cos(30*pi/180)/B tz[3,1]==tl/C p[3,1]==p120 // 120 deg tv-tv
tx[3,2]==0.5*tatv ty[3,2]==tatv*A*cos(30*pi/180)/B tz[3,2]==tl/C p[3,2]==p240 // 240 deg tv-tv
tx[3,3]==0.5*tatv ty[3,3]==tatv*A*cos(30*pi/180)/B tz[3,3]==tl/C p[3,3]==p0    //    0 deg tv-tv

p[1]==1/3 p[2]==1/3 p[3]==1/3 // proportion of subphases

// recursive structure factor calculation

F=cat(i==1,while(le(i,N),j==1,while(le(j,N),
FT==detune*p[i,j],phi==2*pi*(h*tx[i,j]+k*ty[i,j]+l*tz[i,j]),
Treal[i,j]==-FT*cos(phi),Timag[i,j]==-FT*sin(phi),j==j+1),
Treal[i,i]==Treal[i,i]+1,
Freal[i]==F[i]*cos(phi[i]*pi/180),Fimag[i]==F[i]*sin(phi[i]*pi/180),i==i+1),
cgauss(Treal,Timag,phireal,phiimag,Freal,Fimag,1E-6,N),
f2==0,i==1,while(le(i,N),
f2==f2+p[i]*(2*(Freal[i]*phireal[i]+Fimag[i]*phiimag[i])
-sqr(Freal[i])-sqr(Fimag[i])),i==i+1),sqrt(f2)
```


Treacy, M.M. et al. (1991), Proc. R. Soc. London Ser. A, 433, 499-520

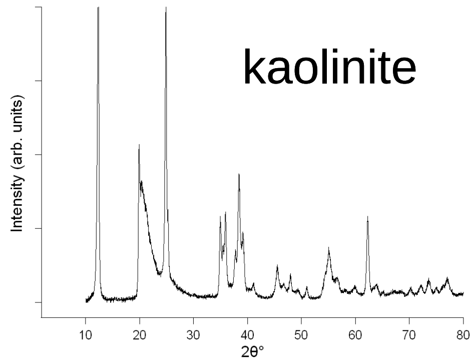
disorder models

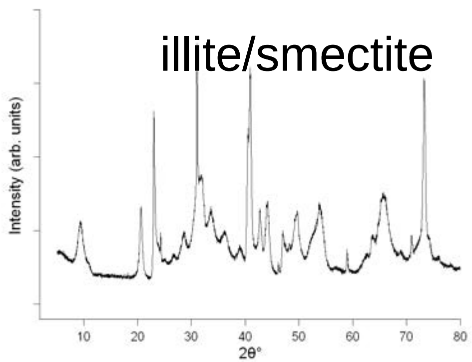
applicable for:

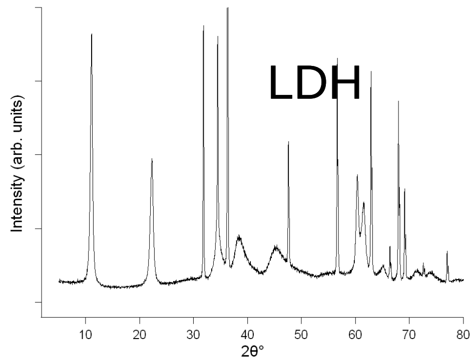
- stacking of different kinds of layers (even with different thicknesses)
- translations of layers parallel to each other
- rotation of layers parallel to each other

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*

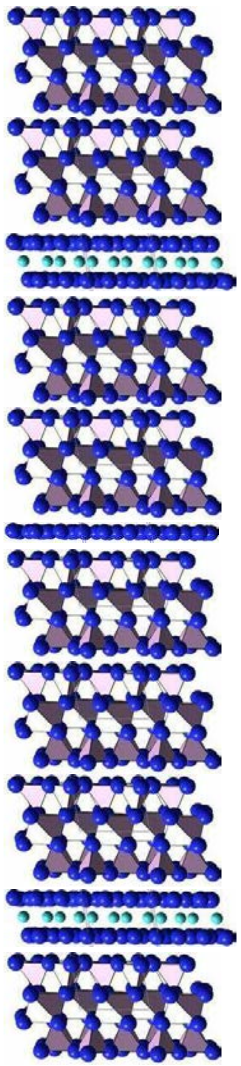






* published

illite/smectite mixed layered minerals



00l reflections

<u>smectitic interlayers:</u>
- turbostratic disorder
- different layer thicknesses
- long range ordering („Reichweite“)
- Reichweite => range of influence

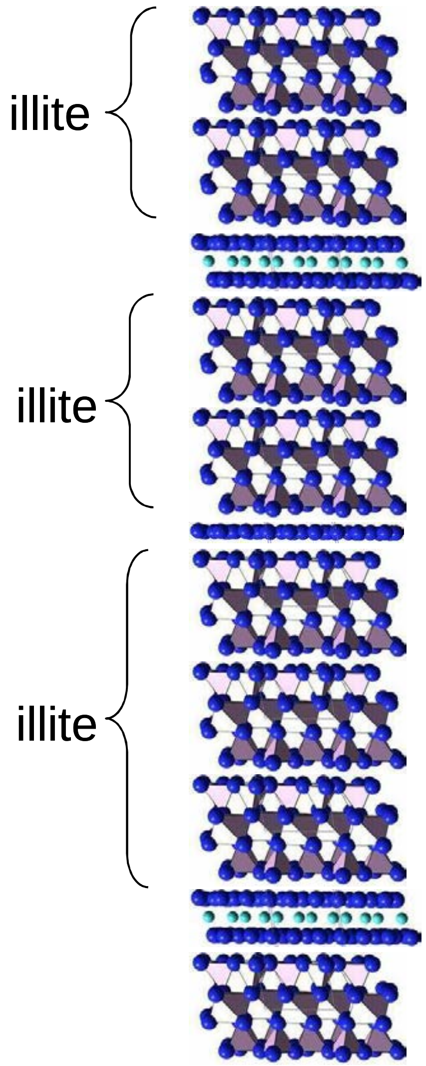
hk reflections

<u>illitic interlayers:</u>
translational / rotational disorder

2 different
effects / classes!

Jagodzinski, H. (1949), Acta Crystallographica, 2, 201-207

illite/smectite mixed layered minerals



<u>model for 00l reflections:</u>

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

<u>model for hk reflections:</u>

- n120° rotational disorder (0°, 120°, 240°)
- different translation vectors

<u>global (shared) parameters</u>

- lattice parameter
- atomic positions
- occupancies
- scaling factor, P.O. factor

illite/smectite pure sample

separate but connected models:

n120° rotational disorder

R3 illite/smectite(1w)/smectite(2w)

control file *.sav:

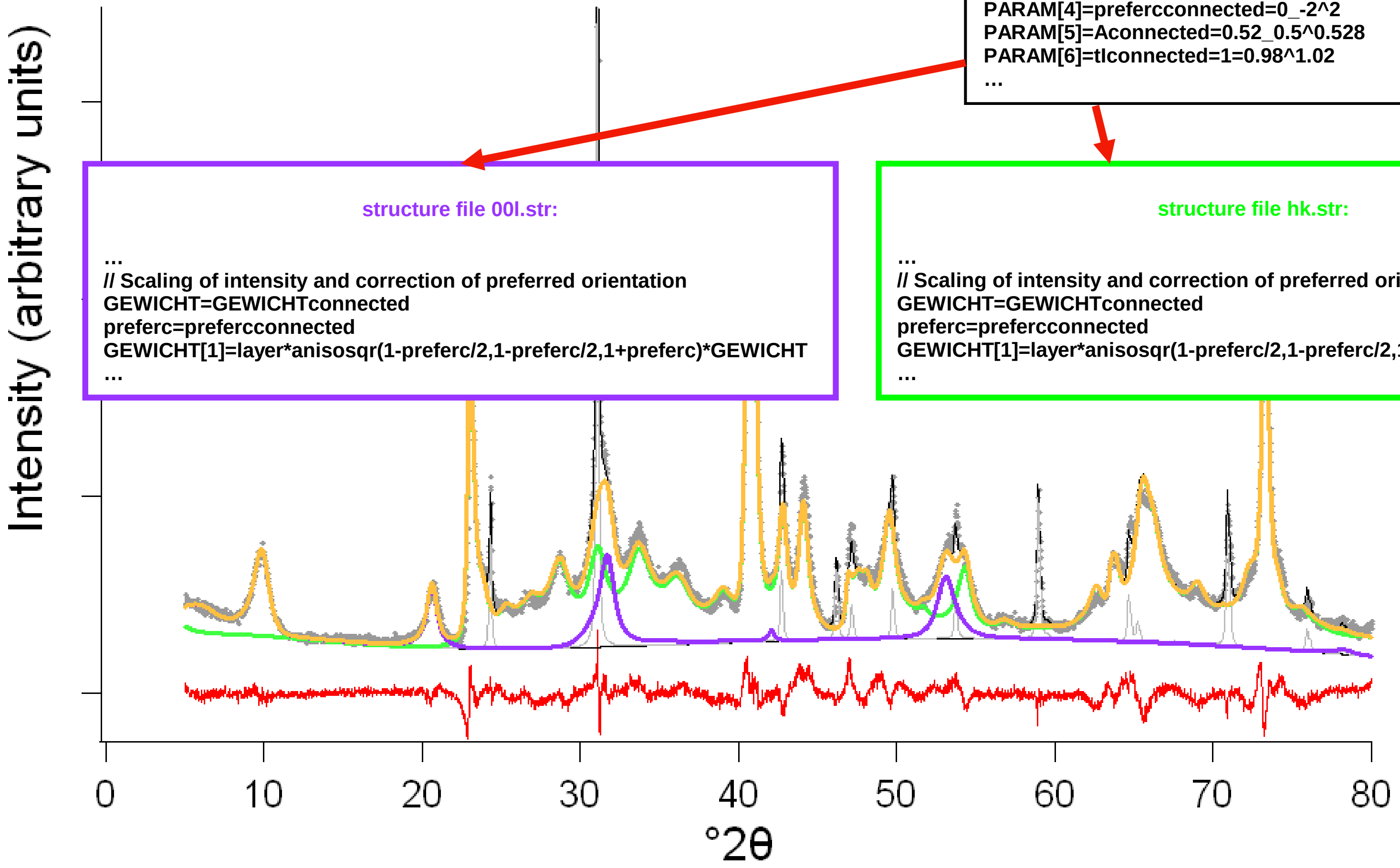
...
% connected parameters
PARAM[3]=GEWICHTconnected=0.01_0
PARAM[4]=prefercconnected=0_-2^2
PARAM[5]=Aconnected=0.52_0.5^0.528
PARAM[6]=tlconnected=1=0.98^1.02
...

structure file 00l.str:

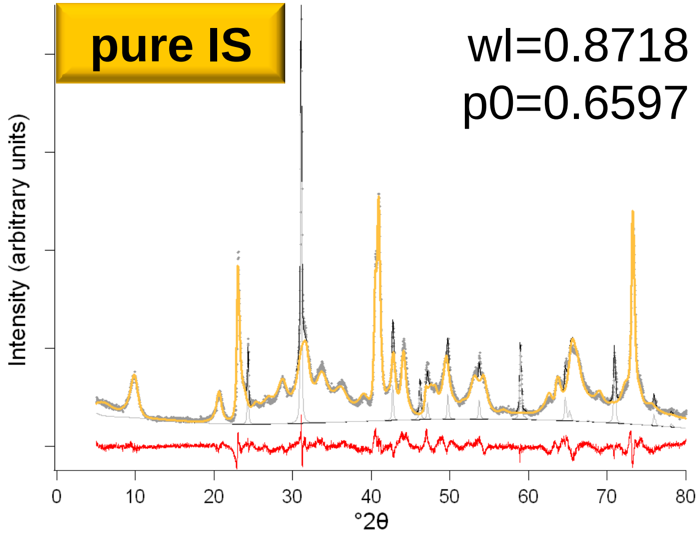
...
// Scaling of intensity and correction of preferred orientation
GEWICHT=GEWICHTconnected
preferc=prefercconnected
GEWICHT[1]=layer*anisosqr(1-preferc/2,1-preferc/2,1+preferc)*GEWICHT
...

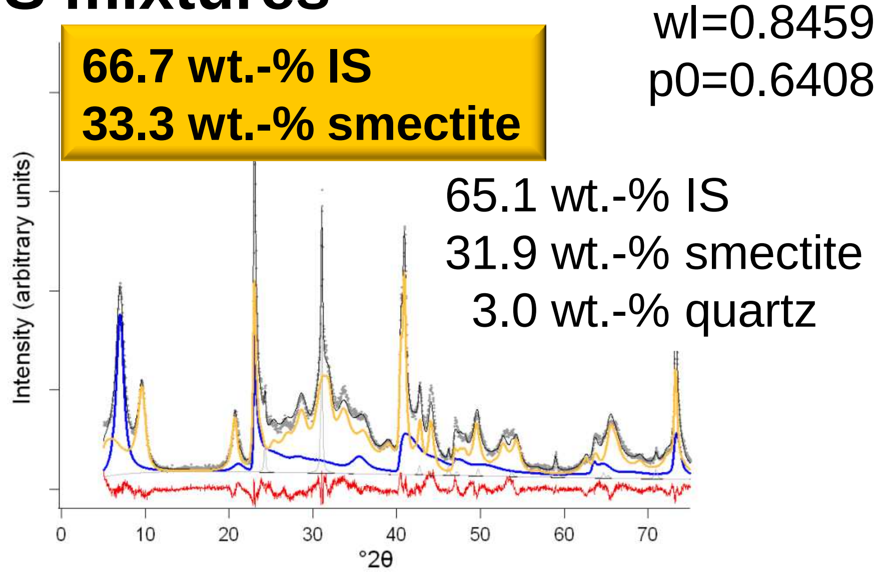
structure file hk.str:

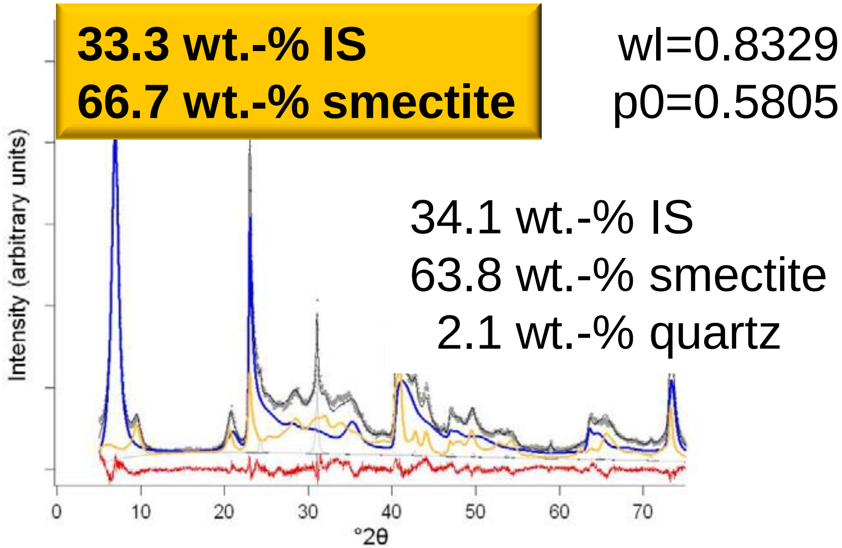
...
// Scaling of intensity and correction of preferred orientation
GEWICHT=GEWICHTconnected
preferc=prefercconnected
GEWICHT[1]=layer*anisosqr(1-preferc/2,1-preferc/2,1+preferc)*GEWICHT
...

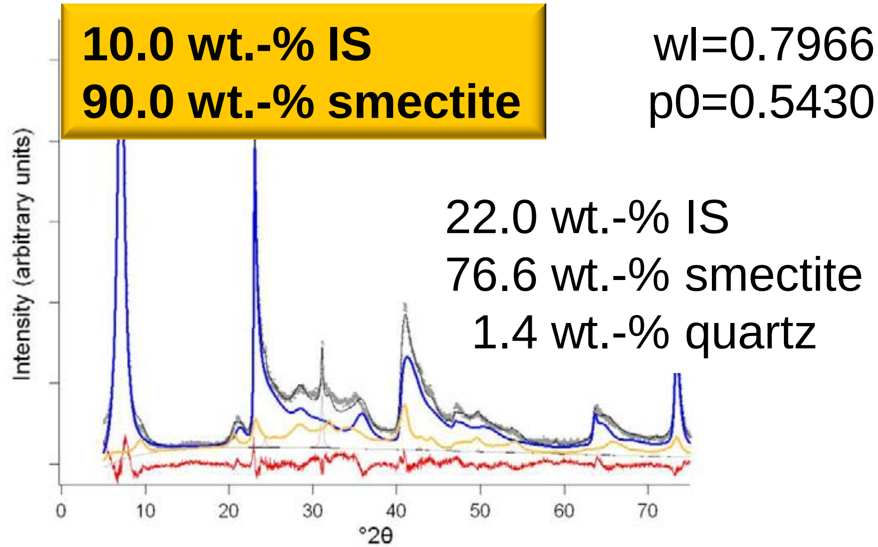


smectite / IS mixtures





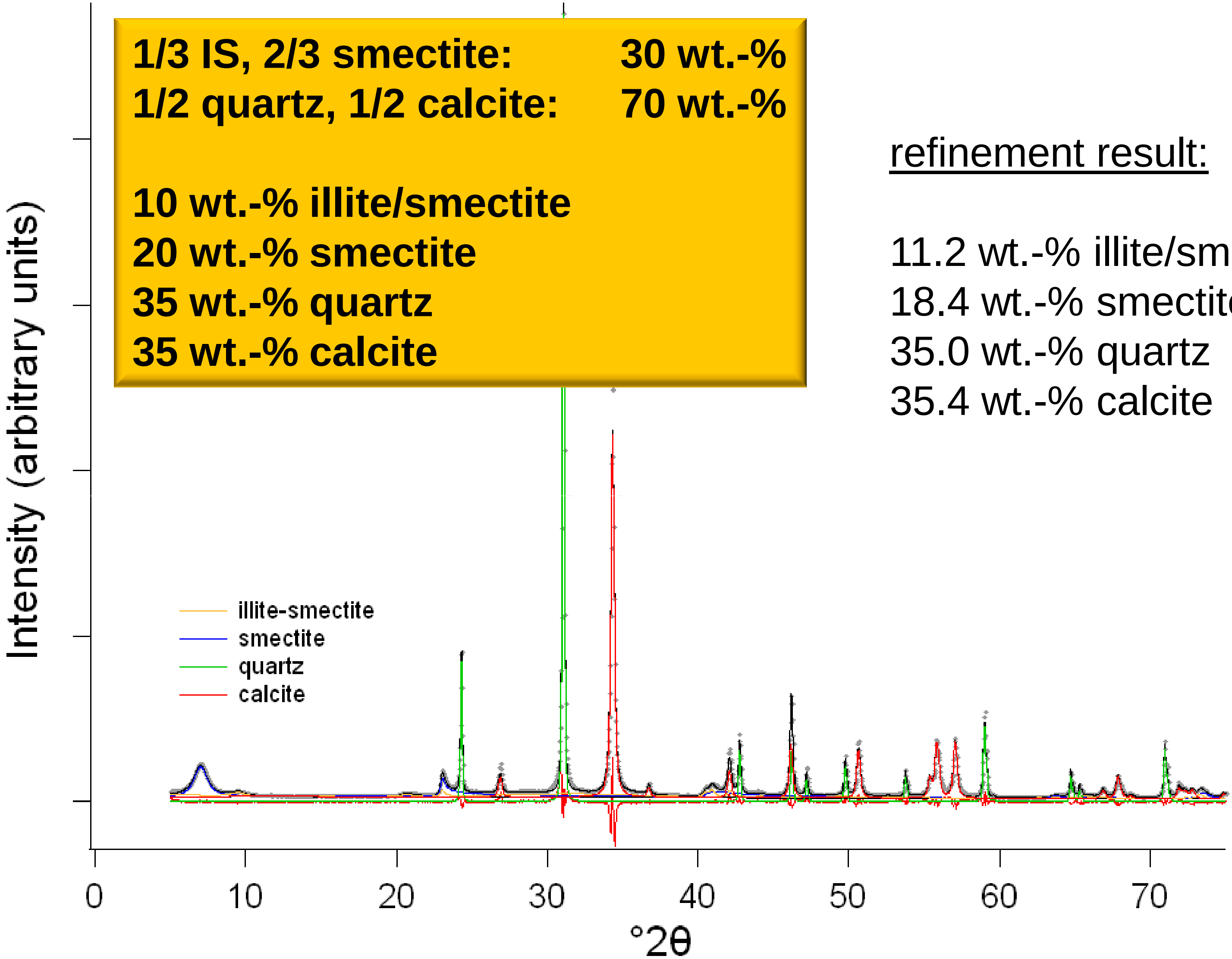




artificial mixture “synthetic shale” - QPA

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



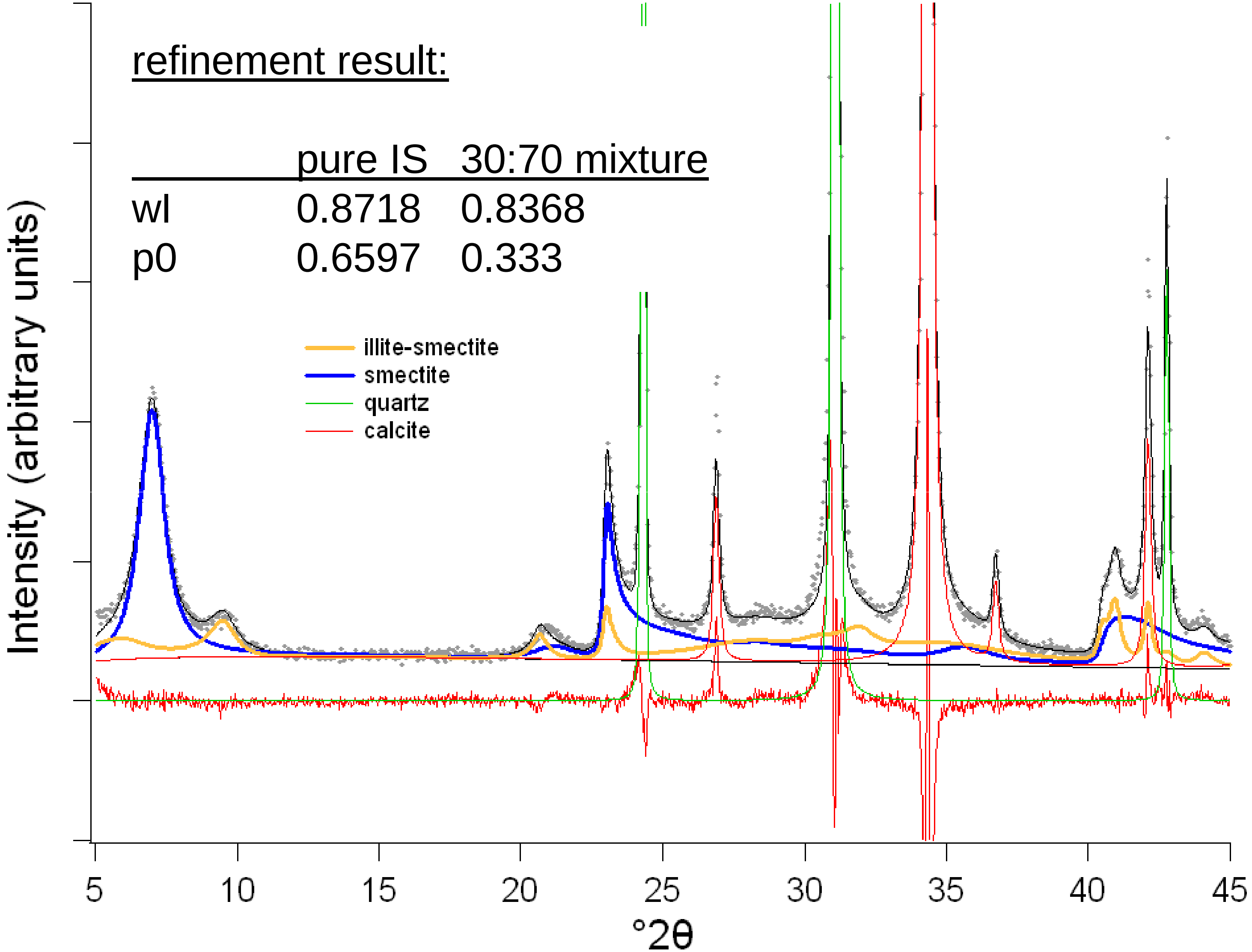
refinement result:

11.2 wt.-% illite/smectite
18.4 wt.-% smectite
35.0 wt.-% quartz
35.4 wt.-% calcite

"synthetic shale" – structural parameters

refinement result:

	pure IS	30:70 mixture
wl	0.8718	0.8368
p0	0.6597	0.333



smectite / IS mixtures: simulations

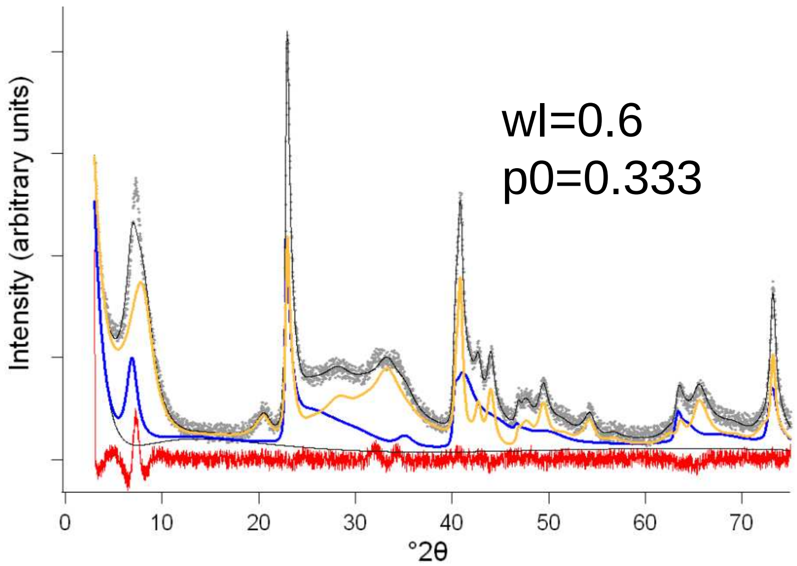
input (simulation)

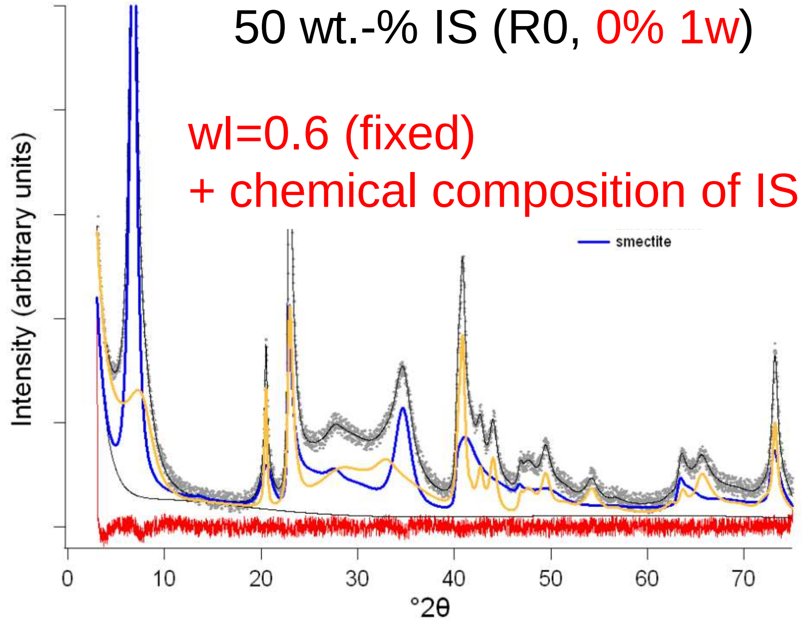
50 wt.-% smectite (40% 1w)
50 wt.-% IS (R0, 40% 1w)

parameter reduction, additional information:

input (simulation)

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





output (refinement)

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

wl=0.4765
p0=0.411

output (refinement)

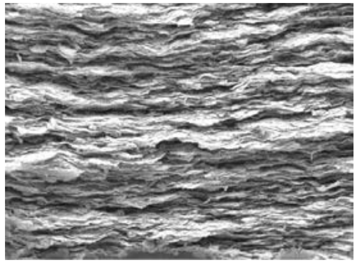
50.5 wt.-% smectite
49.5 wt.-% IS

p0=0.334

combined refinement

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

suspension of clay minerals on glas slides or ceramic tiles

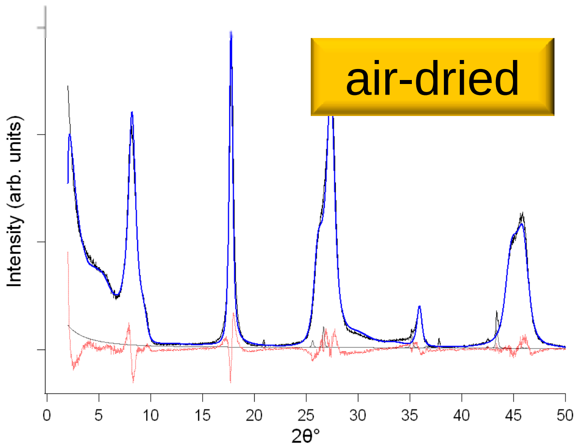


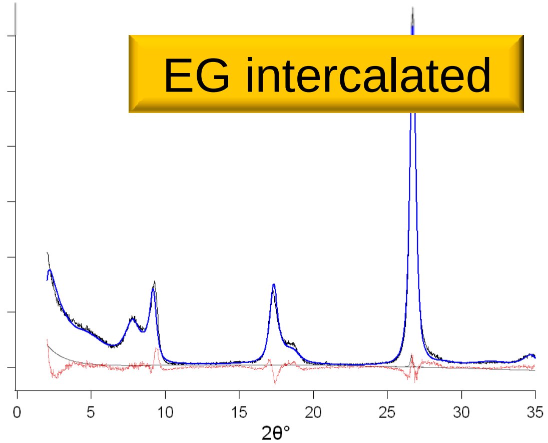
15 global parameters

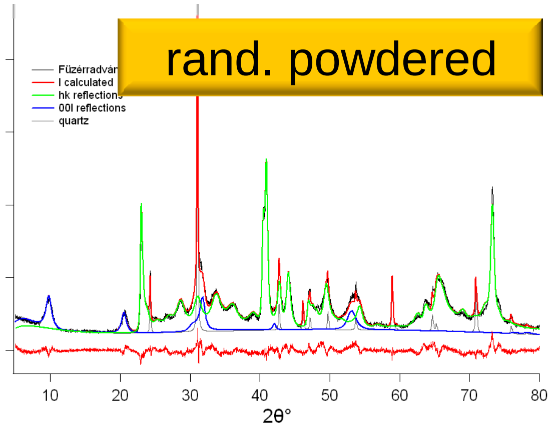
I/S(1w,2w)
6 individual parameters

EG intercalated I/S
7 individual parameters

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



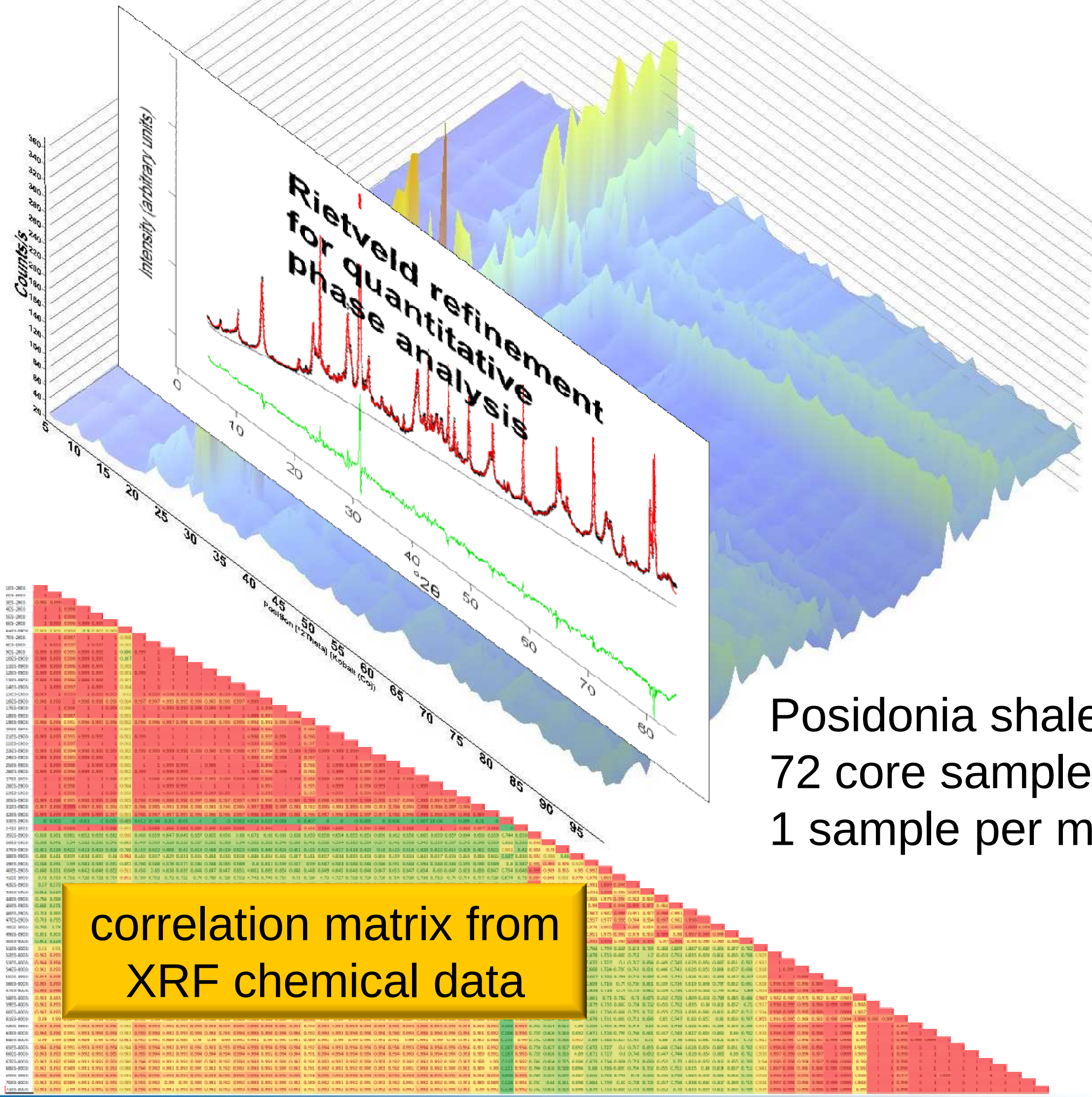




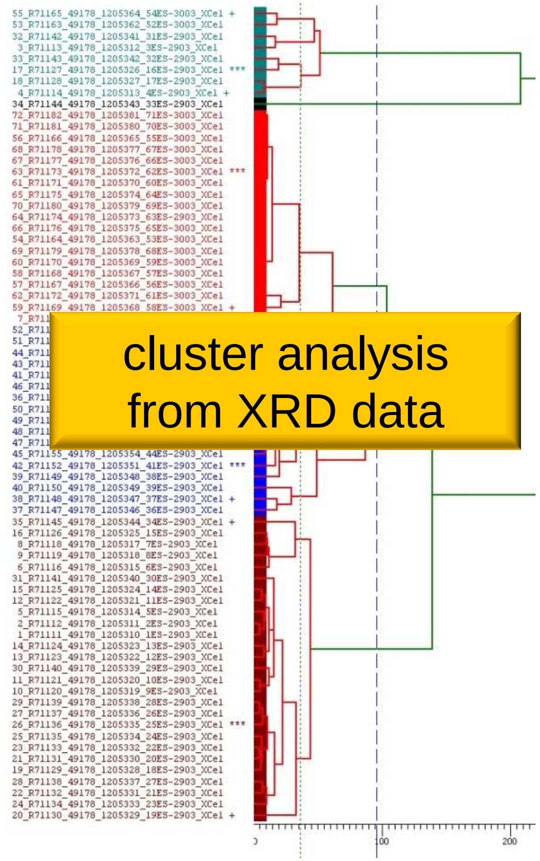
wl=0.86+-0.0012

Sakharov, B.A. et al. (1999), Clays and Clay Minerals, 47, 555-566

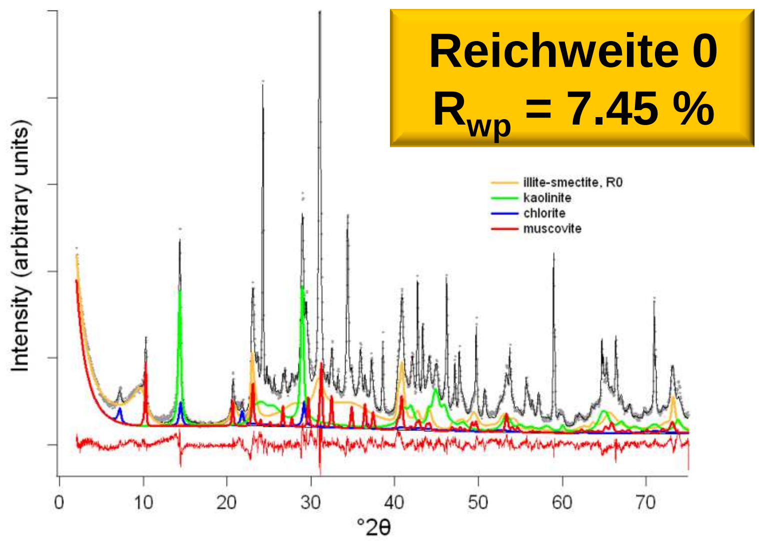
statistical tools for sample selection

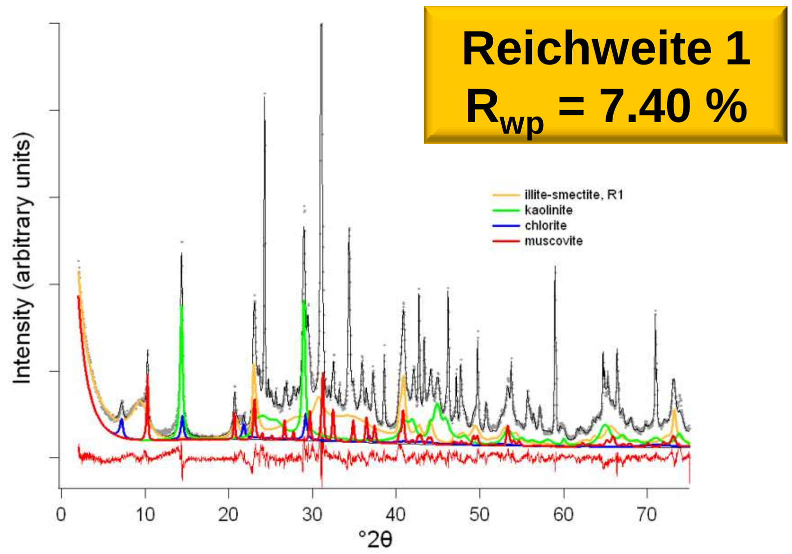


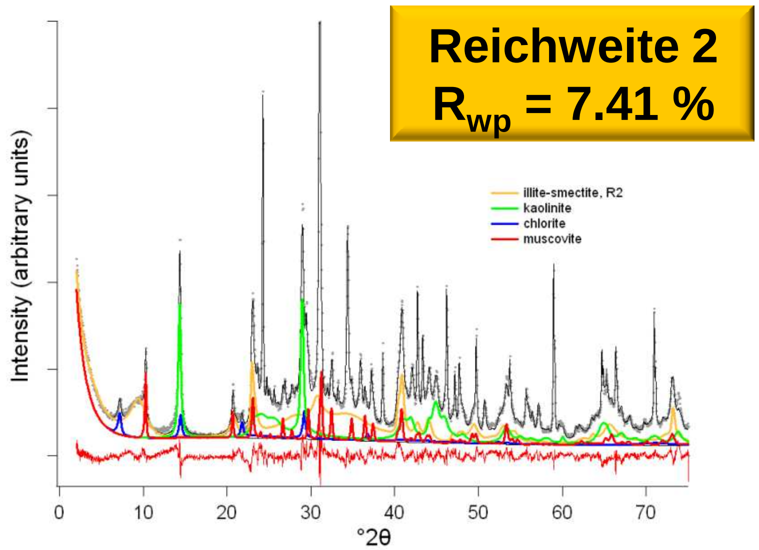
Posidonia shale
72 core samples,
1 sample per meter

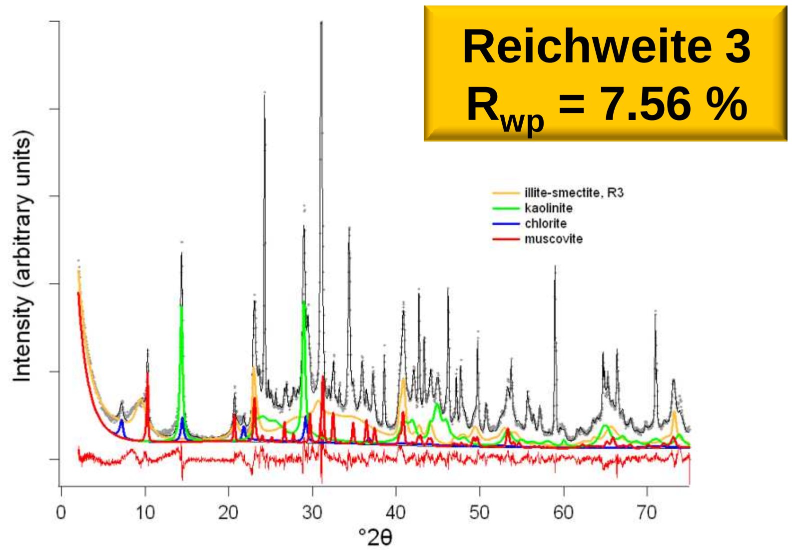


QPA with 4 different models







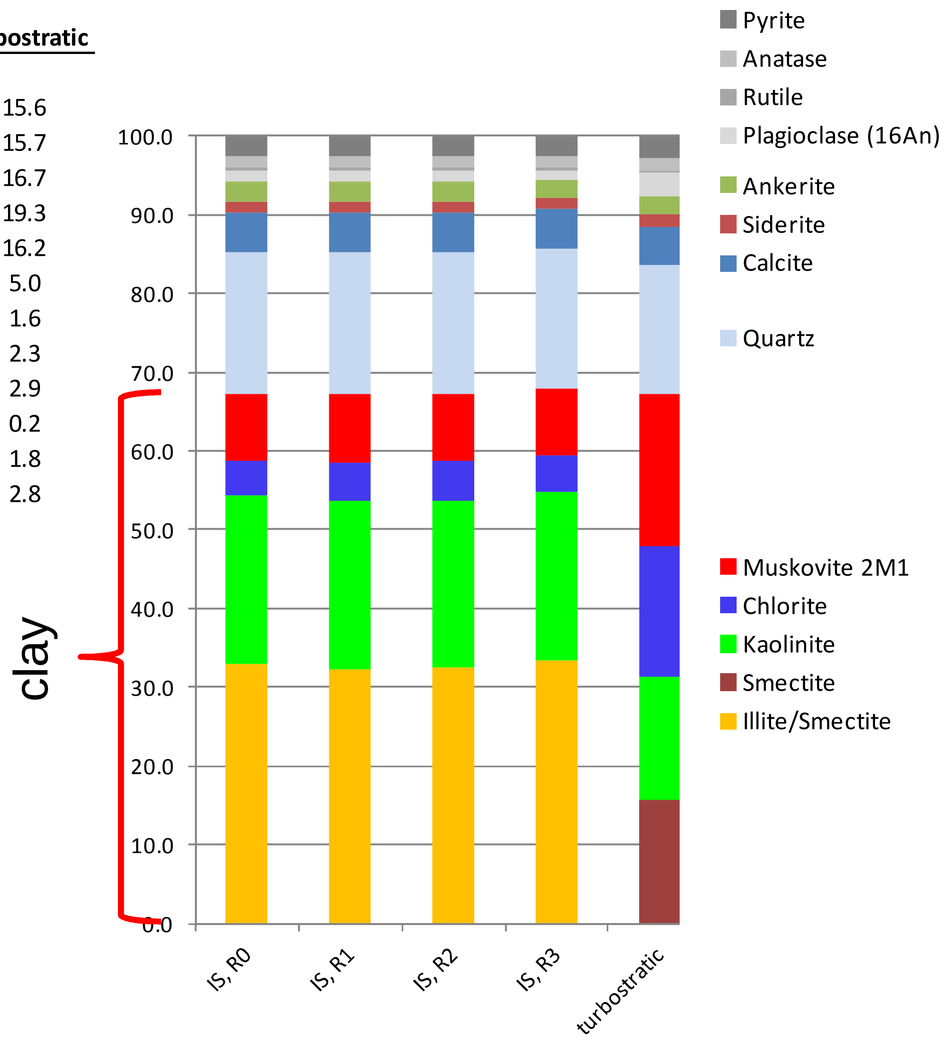


QPA with different models

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

QPA independant of the choice of model for Reichweite

even with wrong smectite model the same sum of clay



Bundesanstalt für Geowissenschaften und Rohstoffe

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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 achived even with unfavorable models