MSA Short Course

Neutron Scattering in Earth Sciences

Acknowledgements:

Mineralogical Society of America

DOE-BES

Lujan Center, LANSCE

Spallation Neutron Source

COMPRES-NSF

Thursday

7:30 a.m. Registration and continental breakfast

10:25 Coffee break

12:00 – 1:00 Buffet lunch

3:00 Coffee break

6:30 Reception with cash bar

7:30 Banquet

Friday

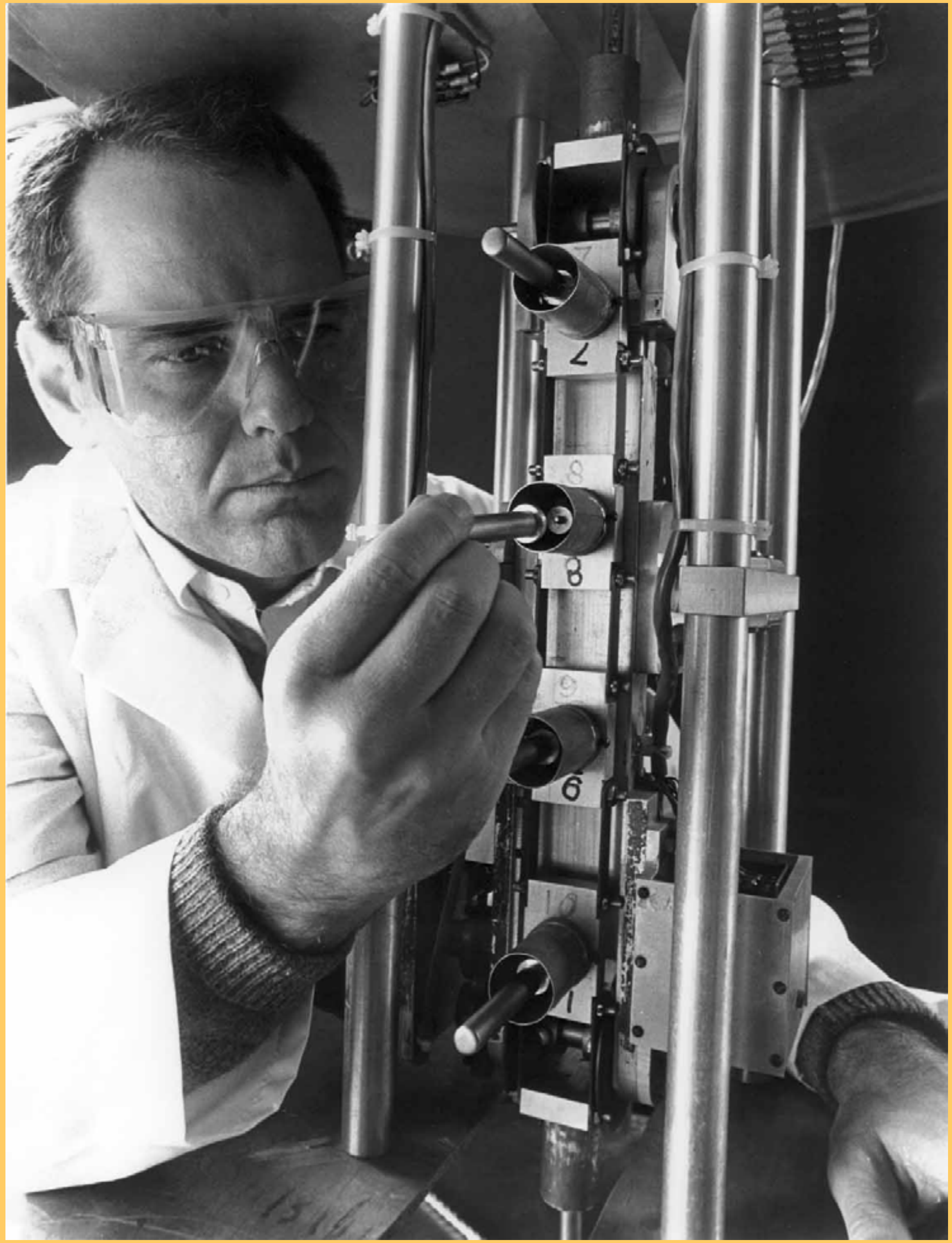
7:30 a.m. Continental breakfast

9:50 Coffee break

12:00 – 1:00 Buffet lunch

3:00-3:15 Coffee break

5:00 Adjourn



Dedicated to James D. Jorgensen 1948-2006

Texture Analysis with Neutron Diffraction

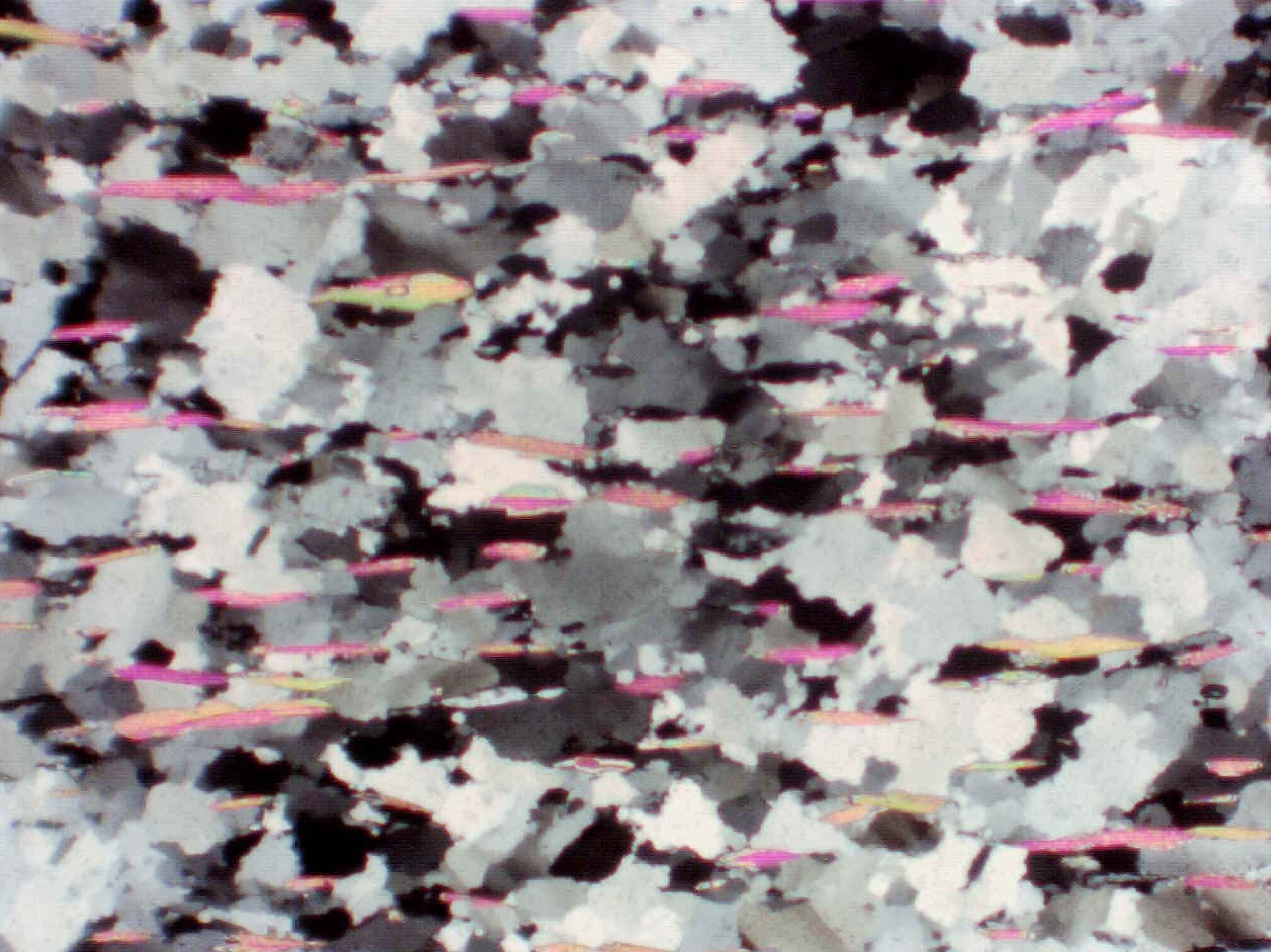
Rudy Wenk
Dept. Earth and Planetary Science, UC Berkeley

- What are textures?
- Representation of textures.
- How do textures form ?
- Texture measurements with neutron diffraction
  - Monochromatic
  - TOF
  - HIPPO
- Texture calculations
  - Pole figures
  - Rietveld

Applications

- Phase transformations / Variant selection
  - Iron (bcc – fcc)
  - Ice
  - Quartz (trigonal – hexagonal)

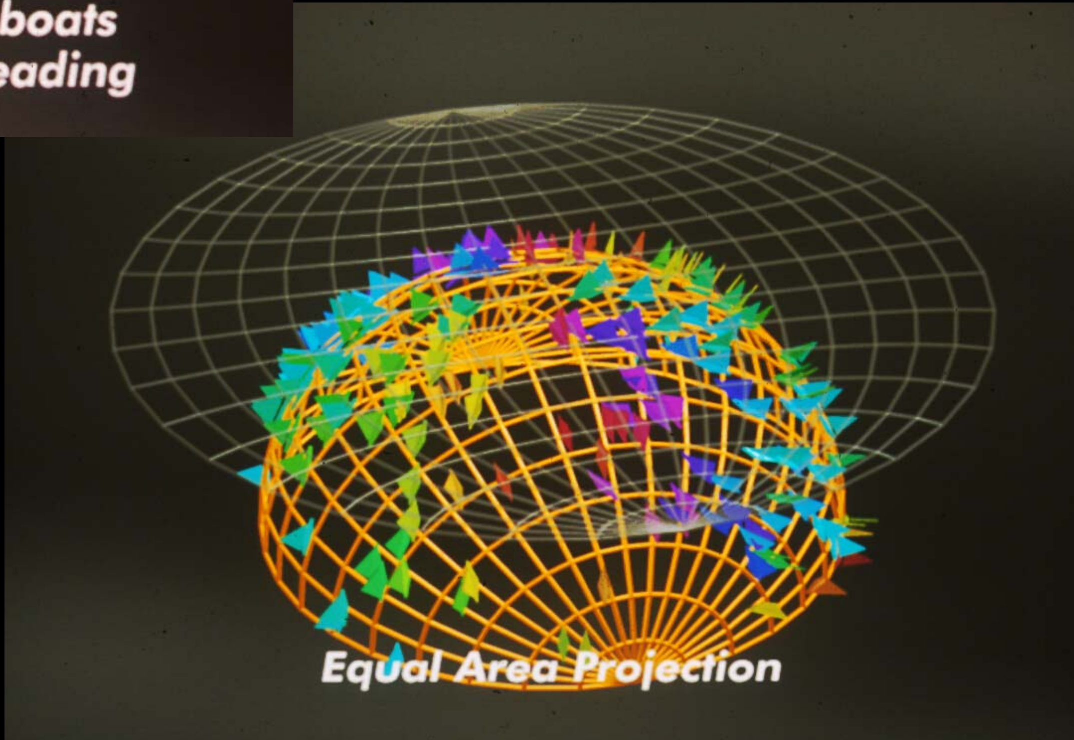
- Geological applications
  - Mechanical twinning in quartz: a paleopiezometer

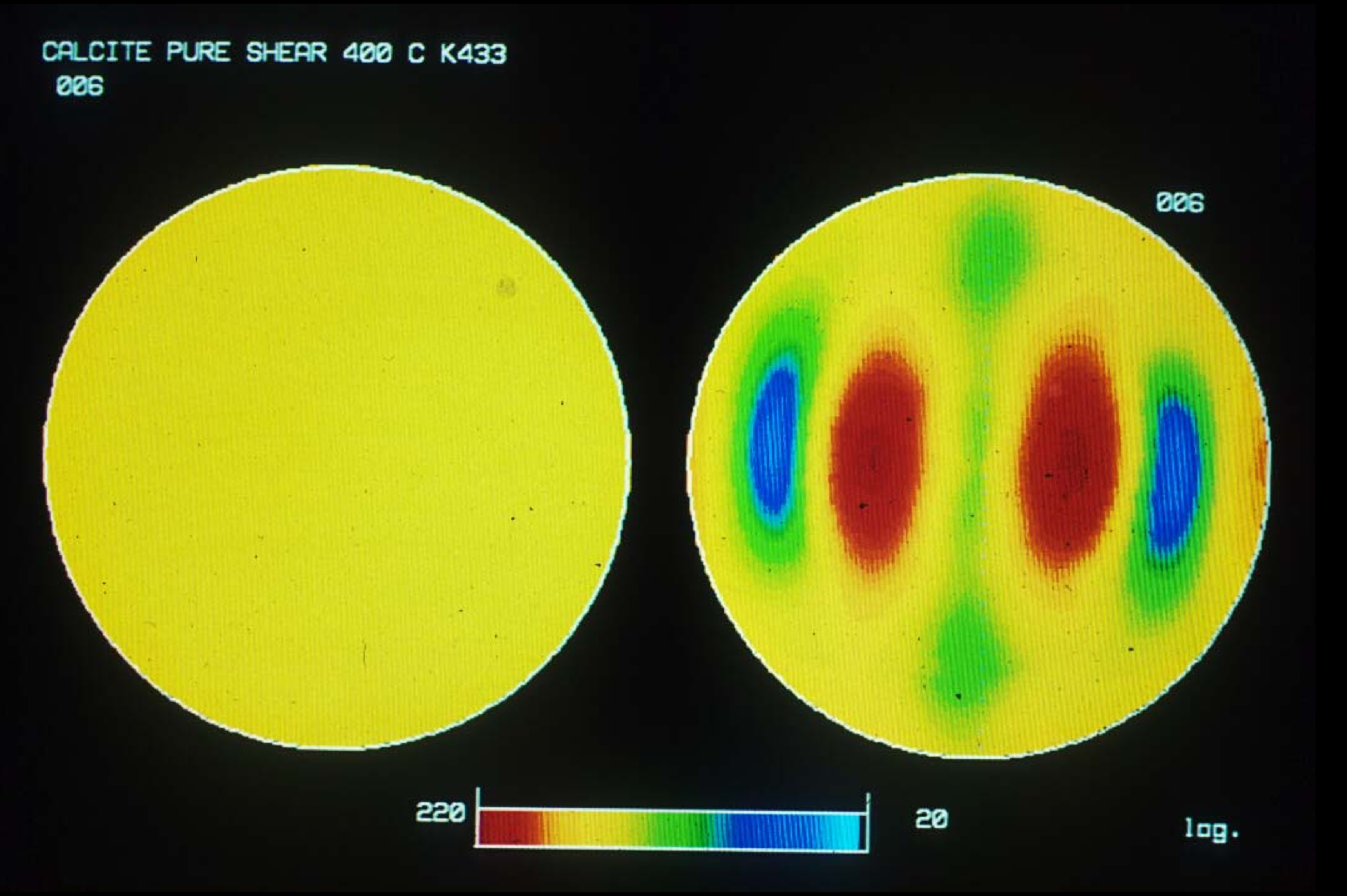


Representation of Preferred Orientation

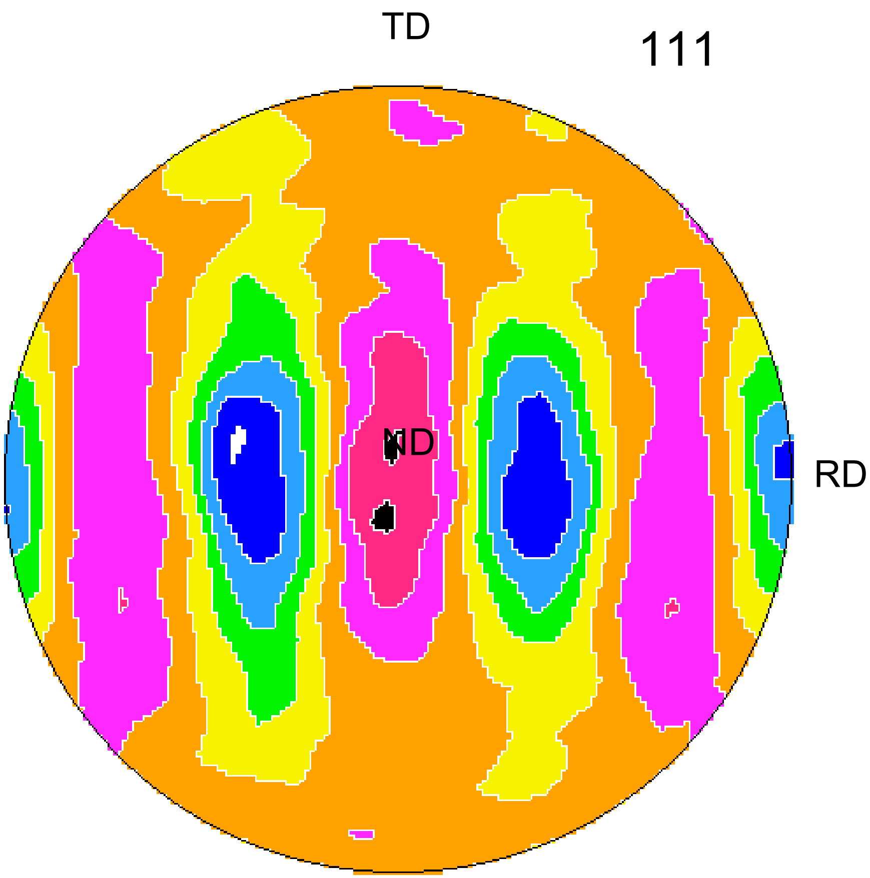
- Orientation Distribution Function (ODF)
- Pole Figures
- Inverse Pole Figures


0°
60°
-60°
120°
-120°
180°
(100) indicated by location of boats
(010) indicated by color and heading

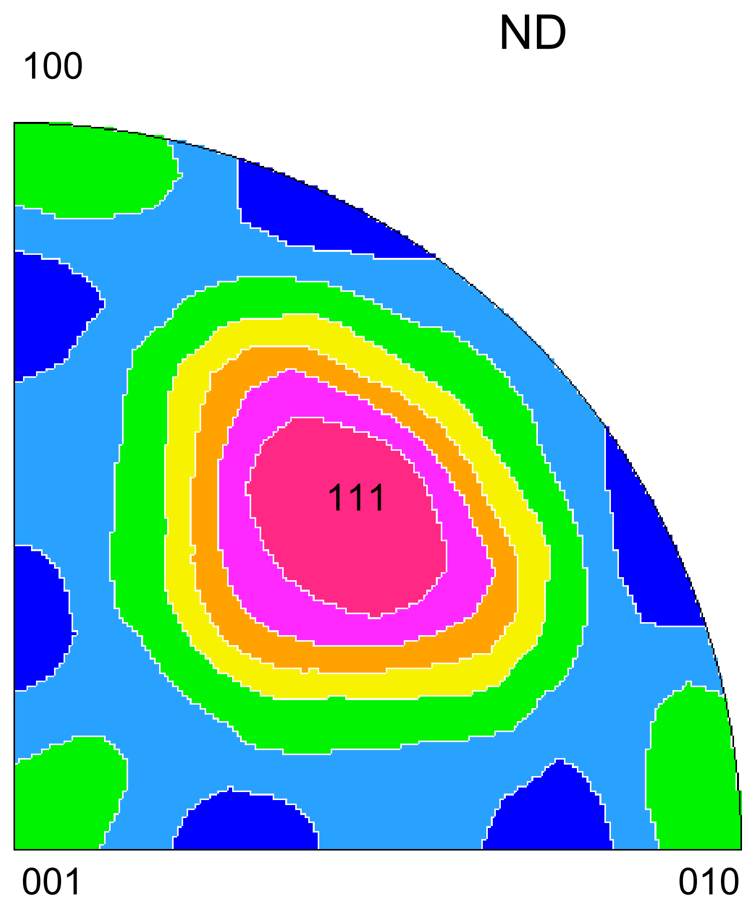

Equal Area Projection

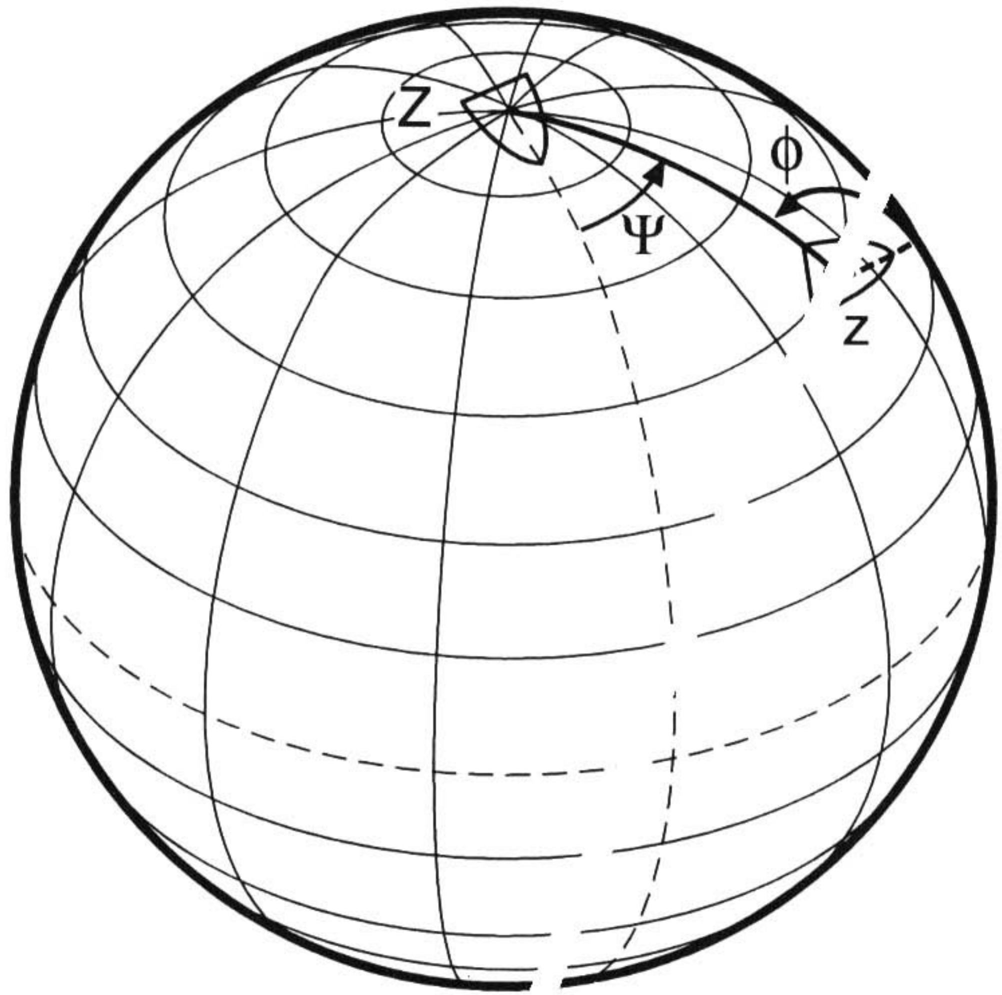

CALCITE PURE SHEAR 400 C K433
006
006
220
20
log.

Pole figure
Sample coordinates



Inverse pole figure
Crystal coordinates

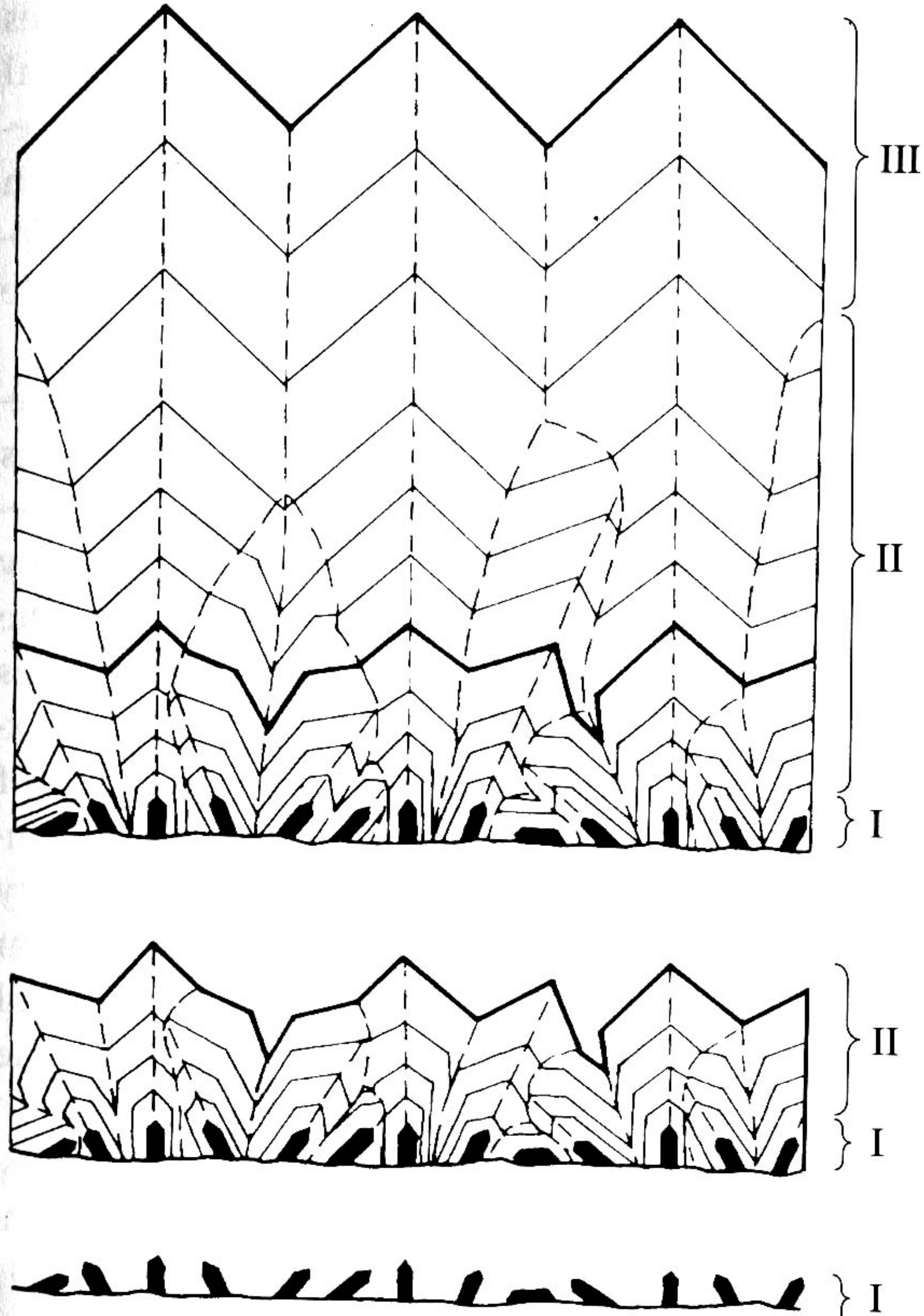




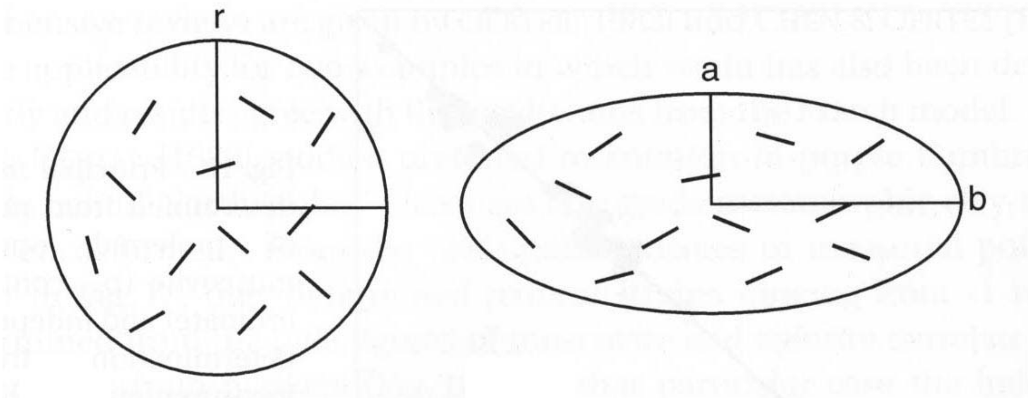
Orientation sphere to define three Euler angles

How do textures form?

- Growth (Topotaxy, epitaxy, temperature gradient, stress field, magnetic field etc.)
- Deformation (Slip, twinning, grain shape)
- Recrystallization
- Phase transformations

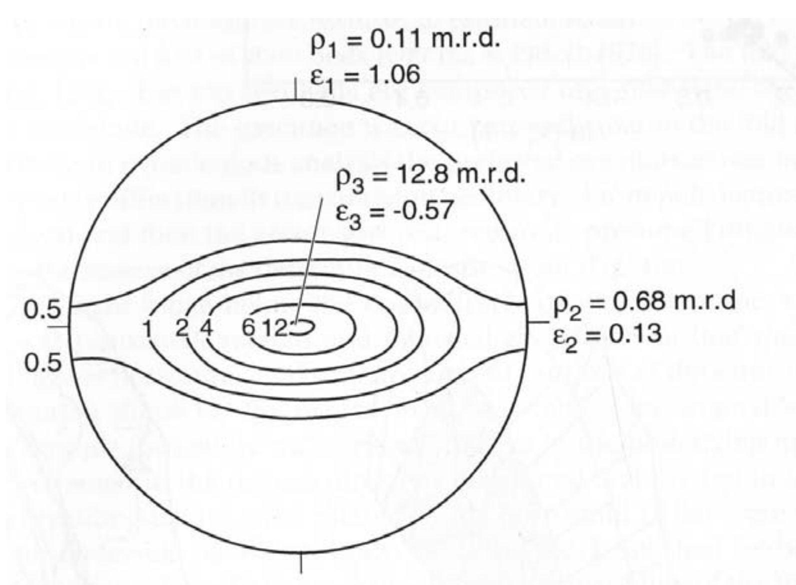

III
II
I
II
I
I

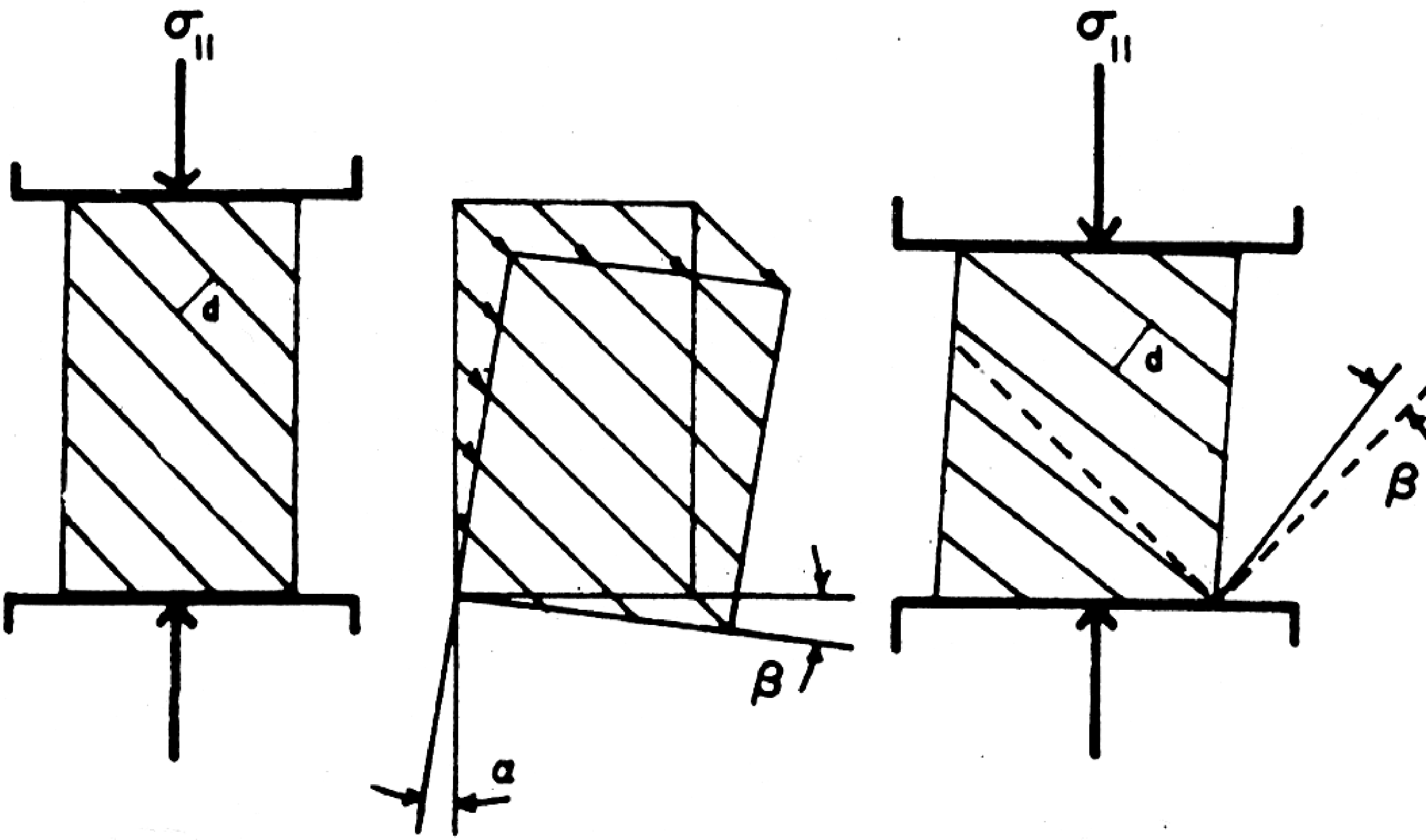
Rigid particles in viscous matrix: Jeffery 1923, March 1932



Compression $\varepsilon_i=\rho_i^{-1/3}-1$

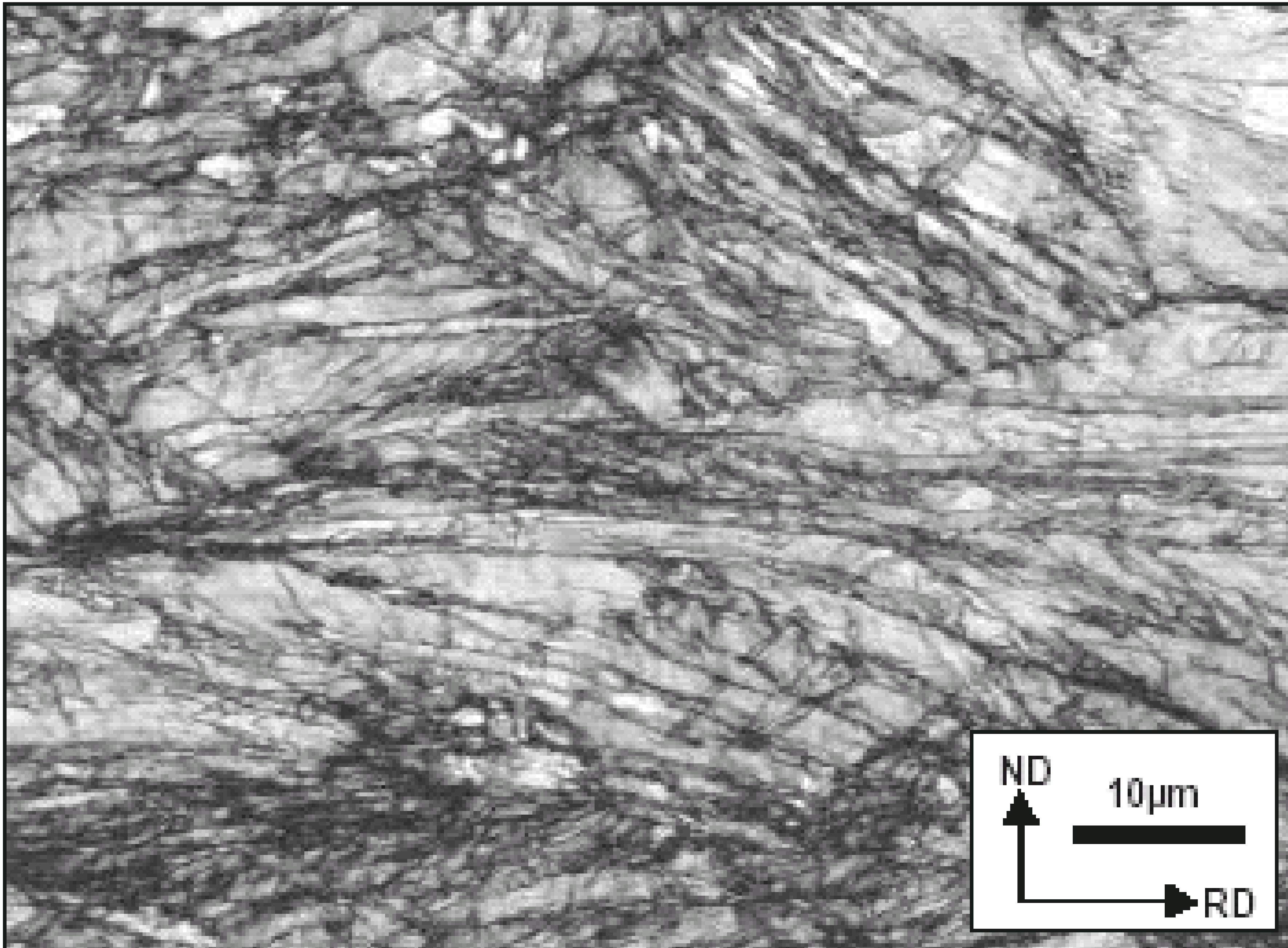
Compaction $\varepsilon_c=\rho_{max}^{-1/2}-1$

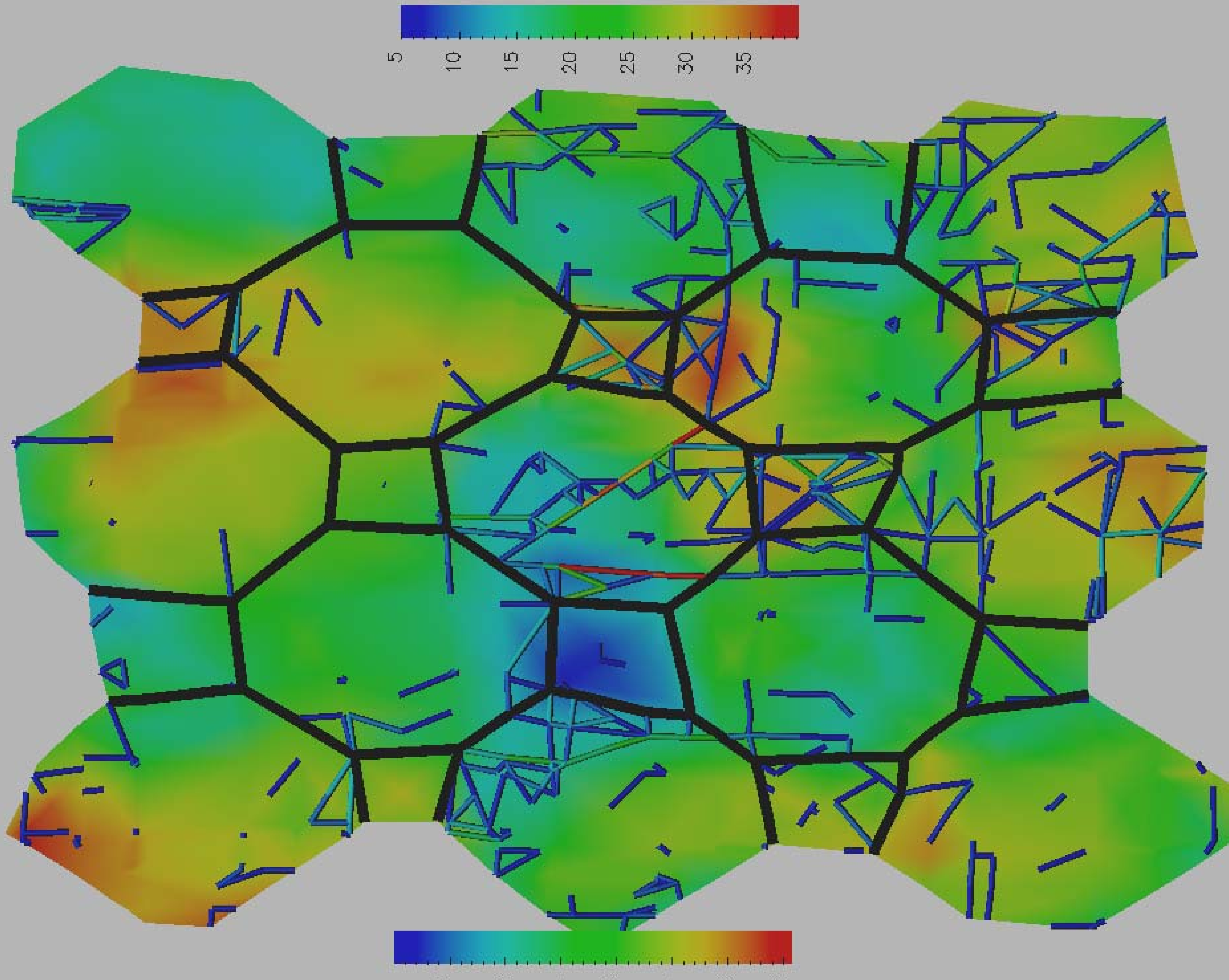




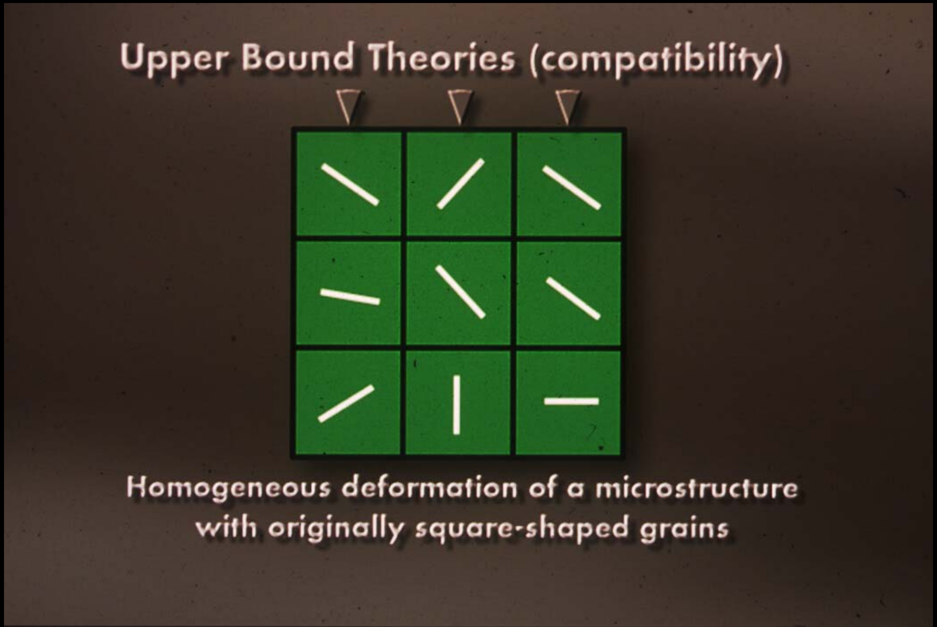
Crystal rotations during deformation by slip

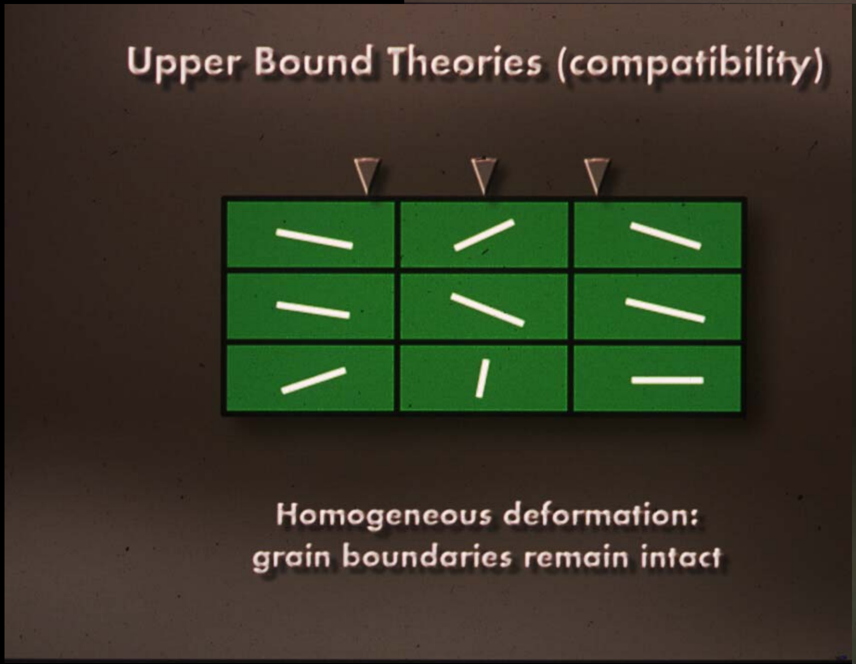
Cold-rolled titanium

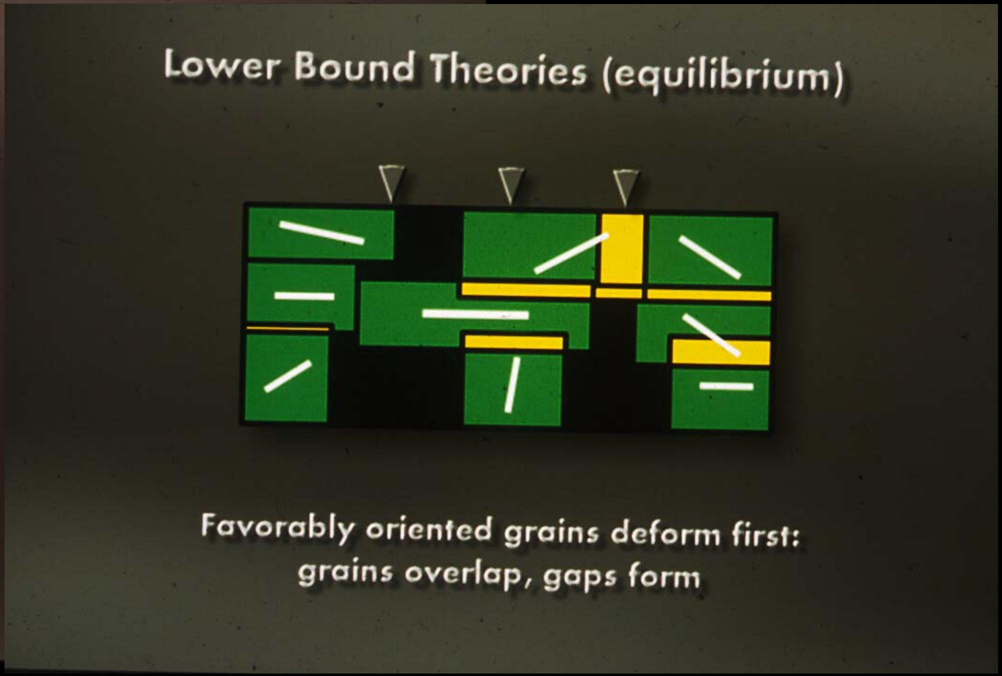




Mika and Dawson, Acta Mater. 47, 1999.


Upper Bound Theories (compatibility)
Homogeneous deformation of a microstructure
with originally square-shaped grains


Upper Bound Theories (compatibility)
Homogeneous deformation:
grain boundaries remain intact


Lower Bound Theories (equilibrium)
Favorably oriented grains deform first:
grains overlap, gaps form

Recrystallization: Modification of Texture

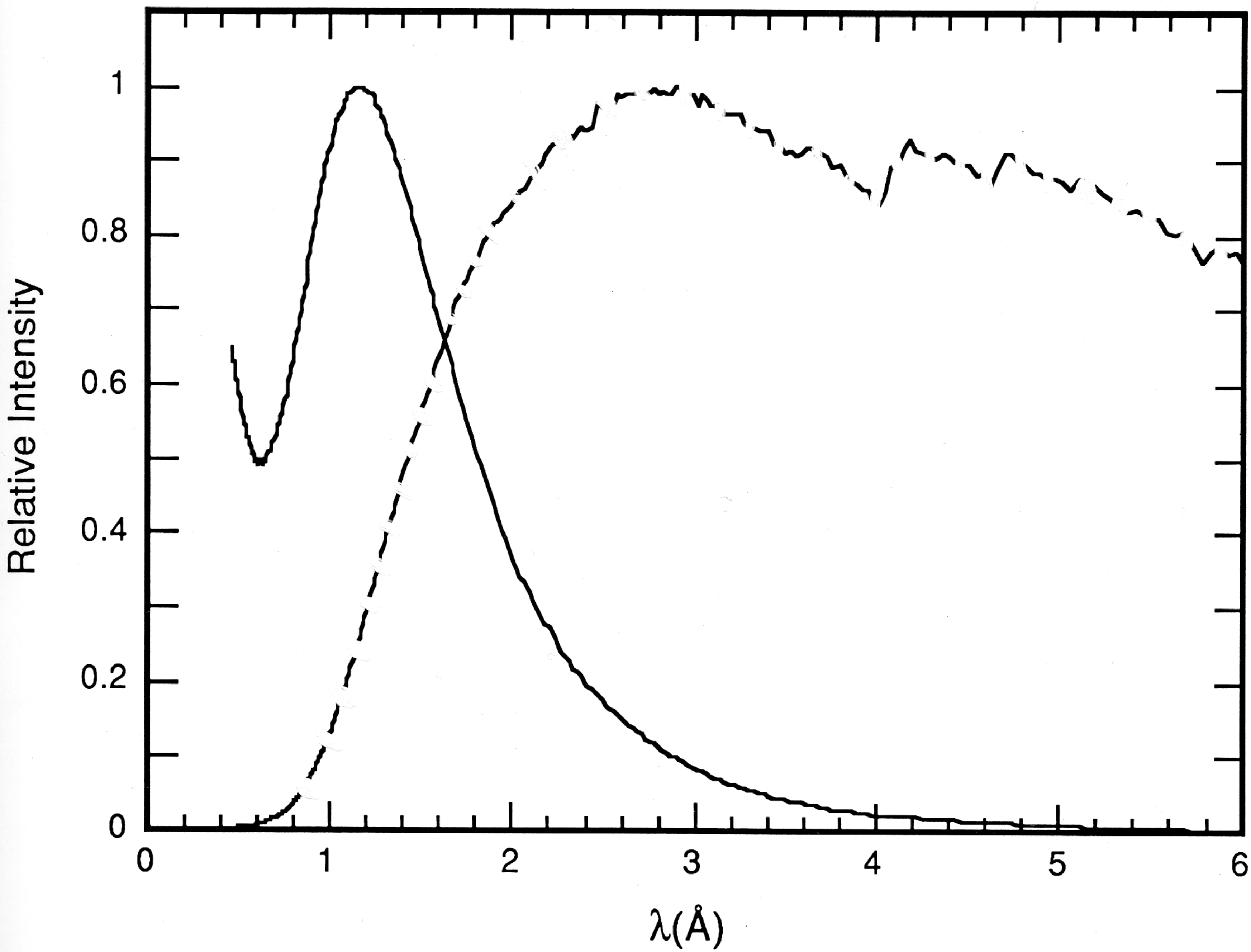
Strain energy is reduced by:

• **Growth** of relatively undeformed grains by grain boundary migration.

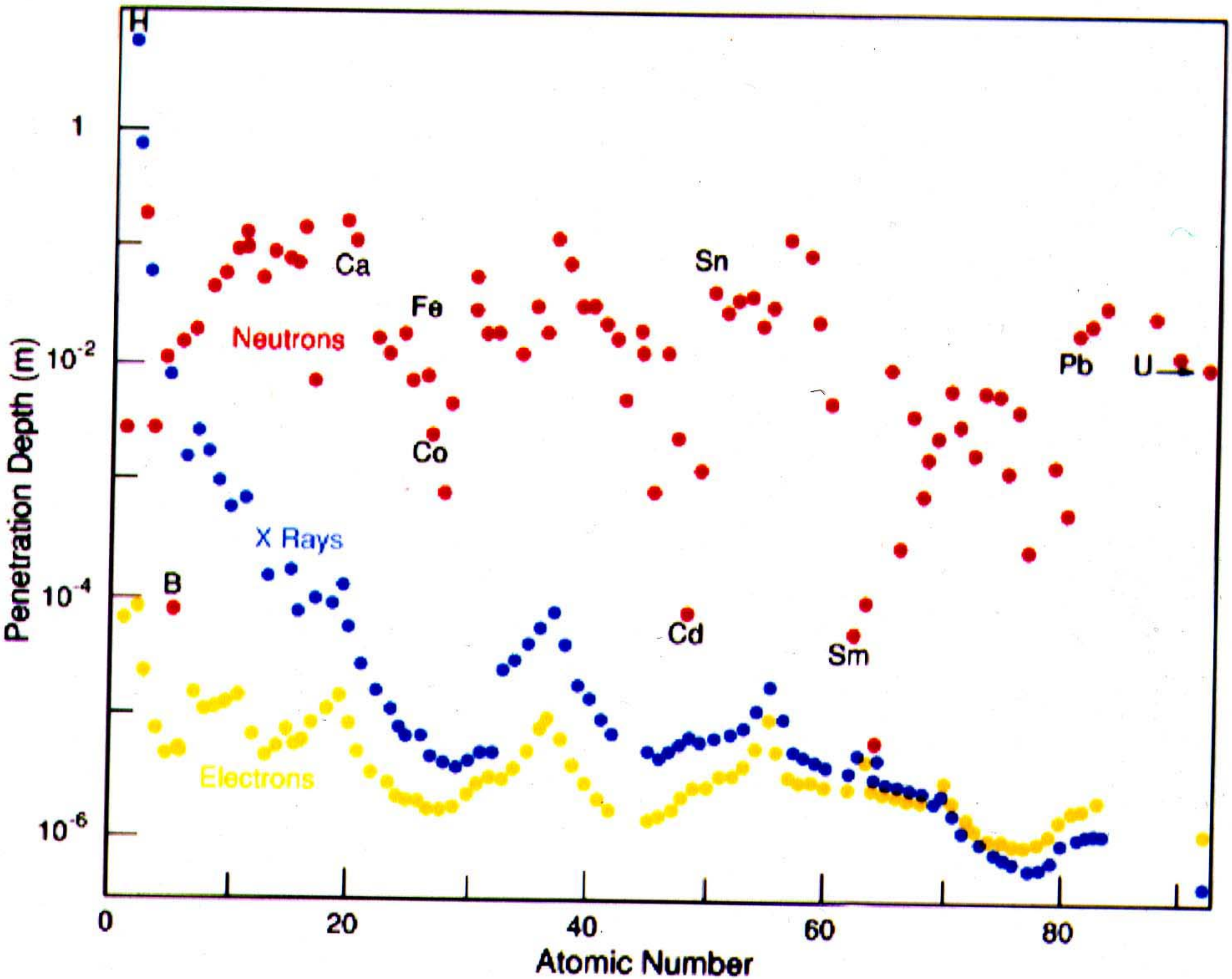
• **Nucleation** of new domains in highly deformed regions.

Texture measurements

Neutron scattering



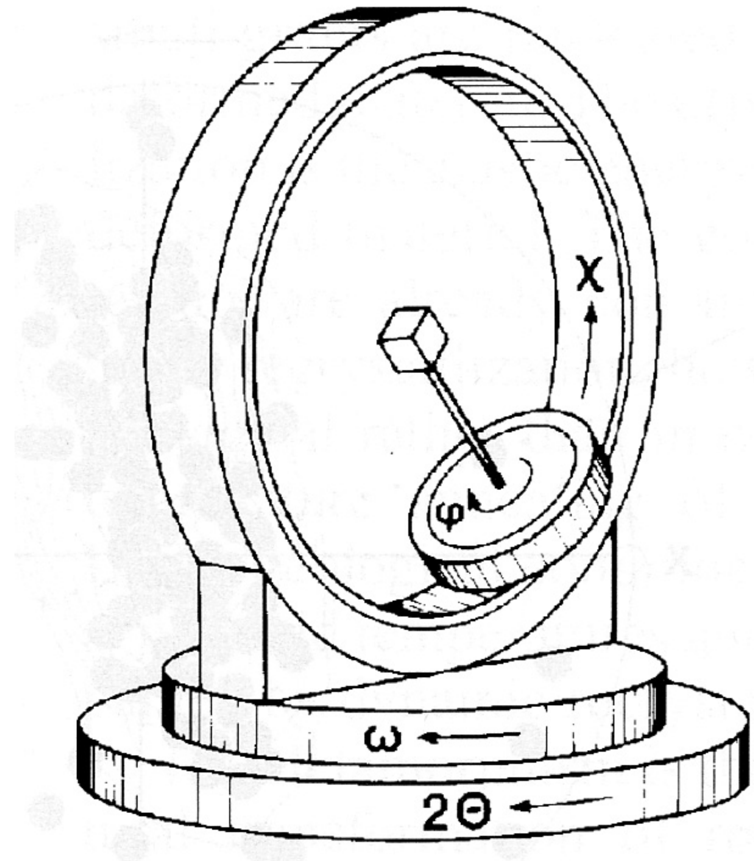
Relative Intensity
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
6
λ(Å)



H
1
Ca
Sn
Fe
Neutrons
10^{-2}
Pb
U
Co
X Rays
B
10^{-4}
Cd
Sm
Electrons
10^{-6}
0
20
40
60
80
Atomic Number
Penetration Depth (m)

Neutron

Monochromatic

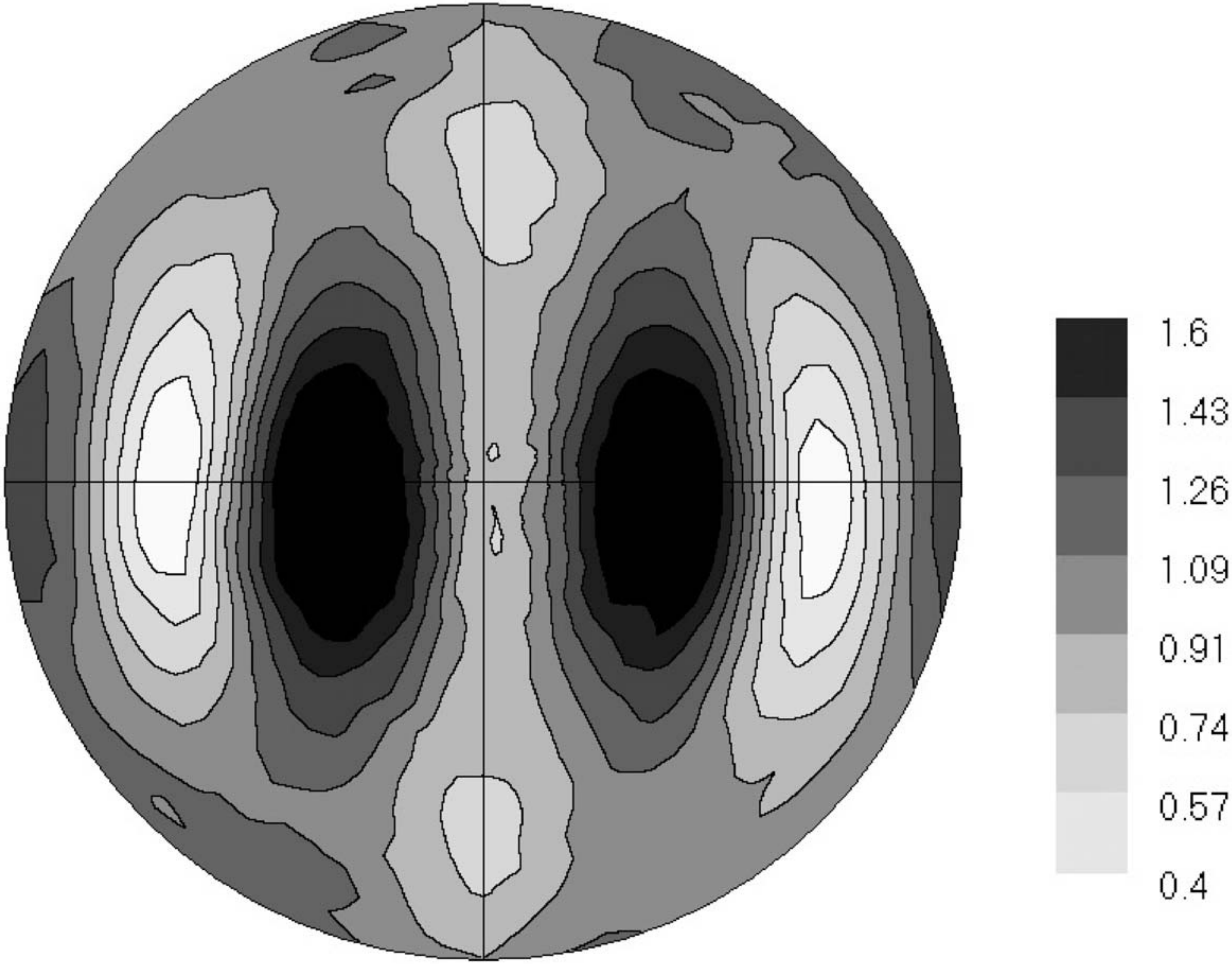


Bragg's Law:

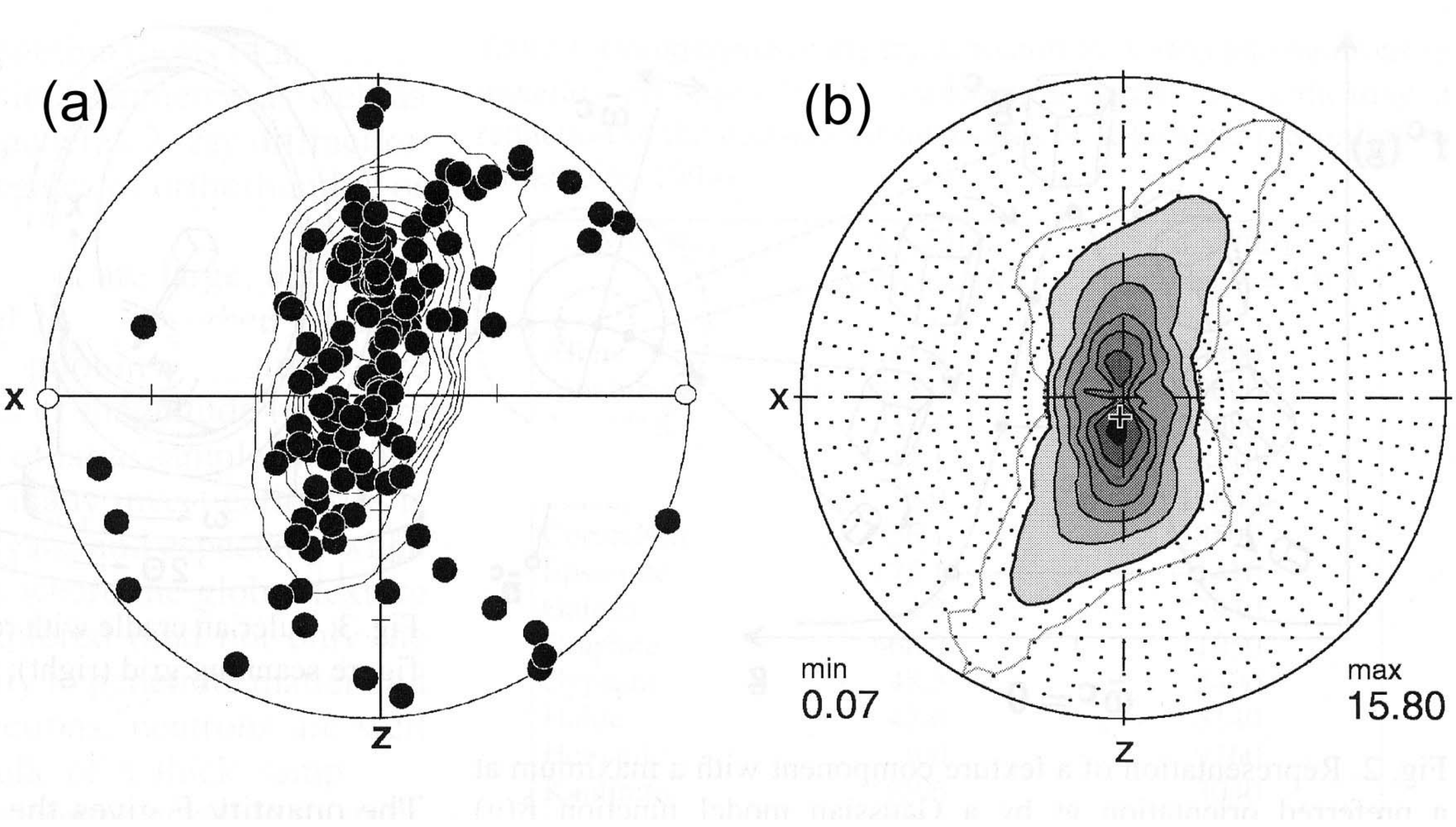
1) $2\, d \sin \theta = n\, \lambda$,

2) reflection on lattice planes

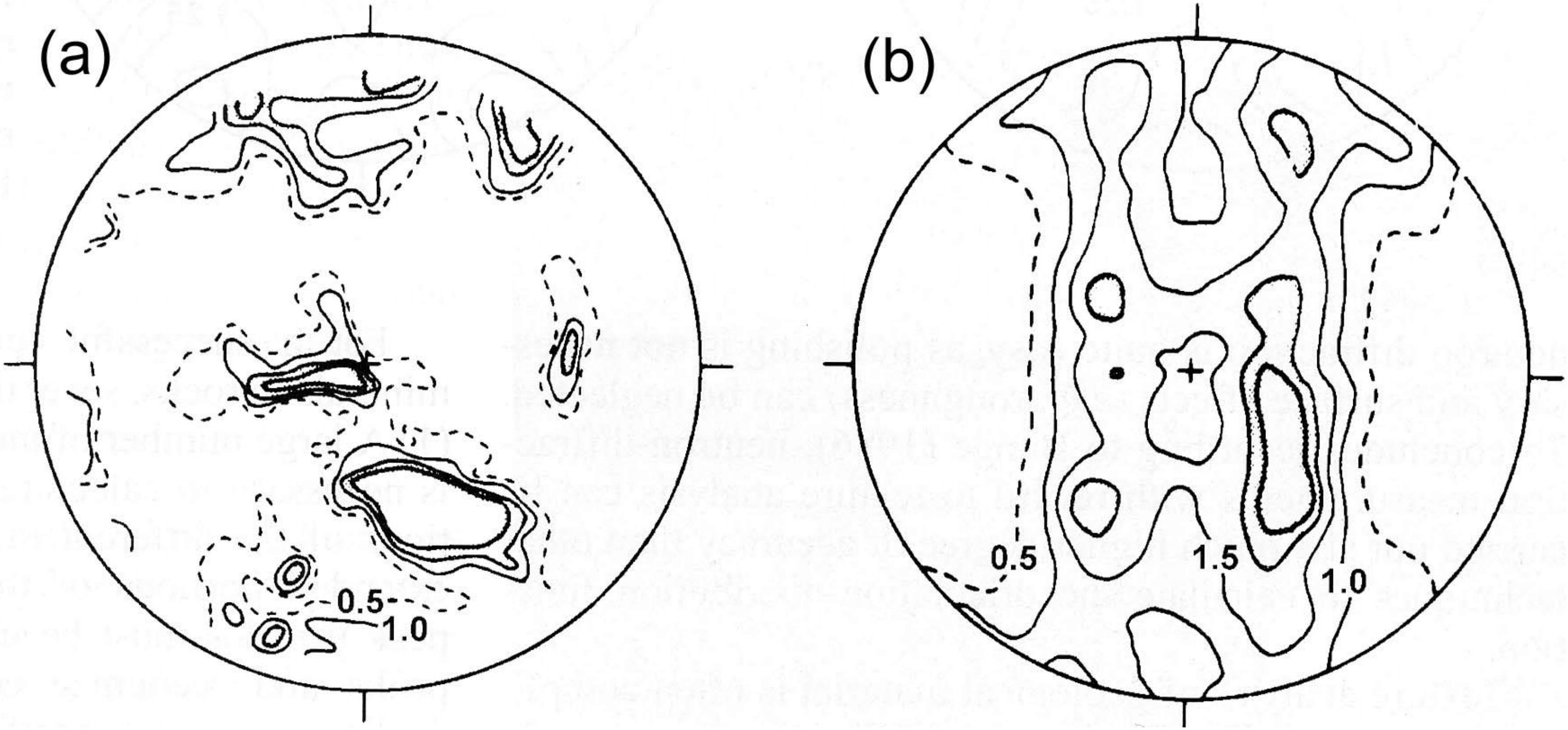
GPPD-IPNS: Kappa Goniometer



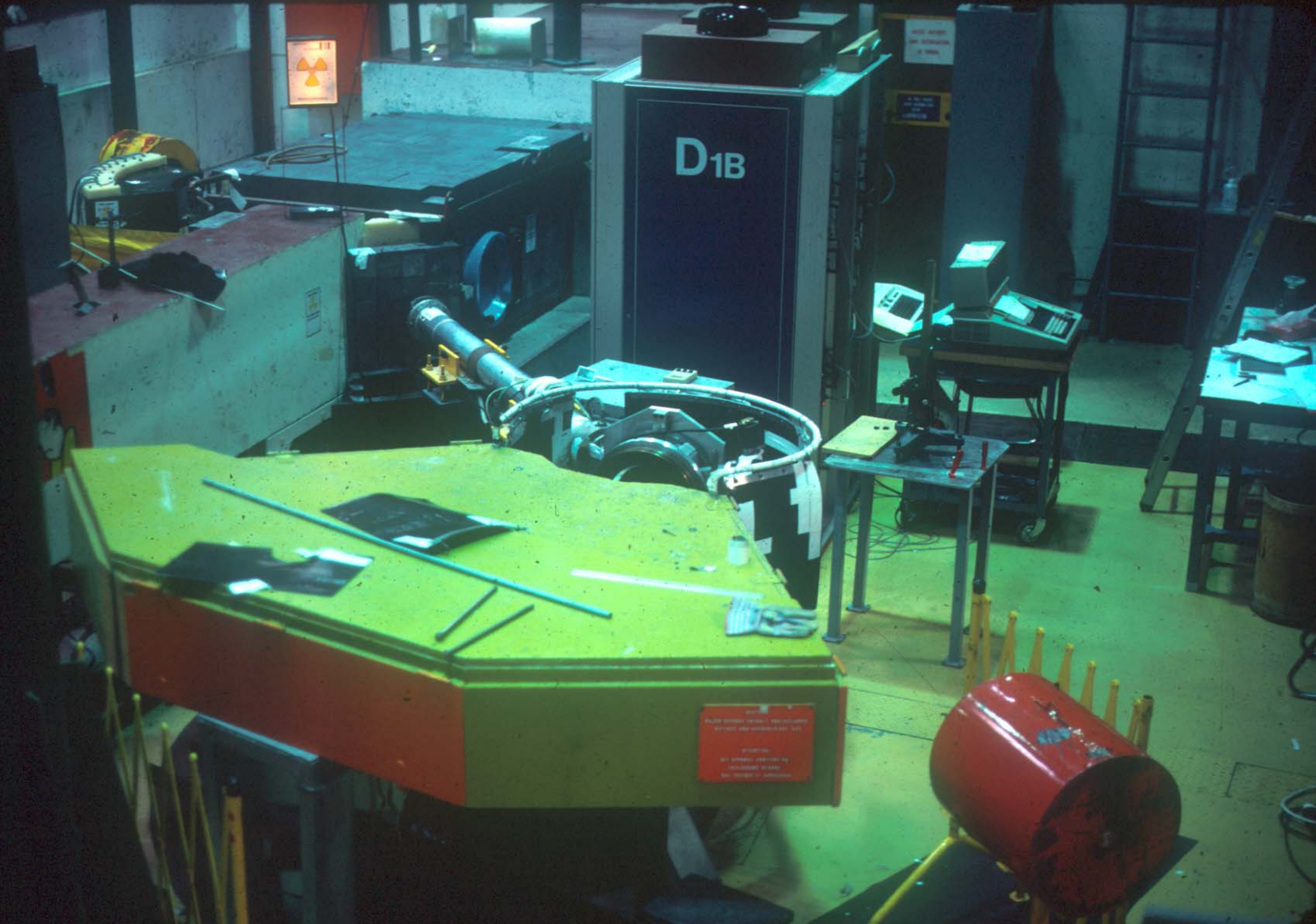
0001 Pole figure of calcite measured at GKSS



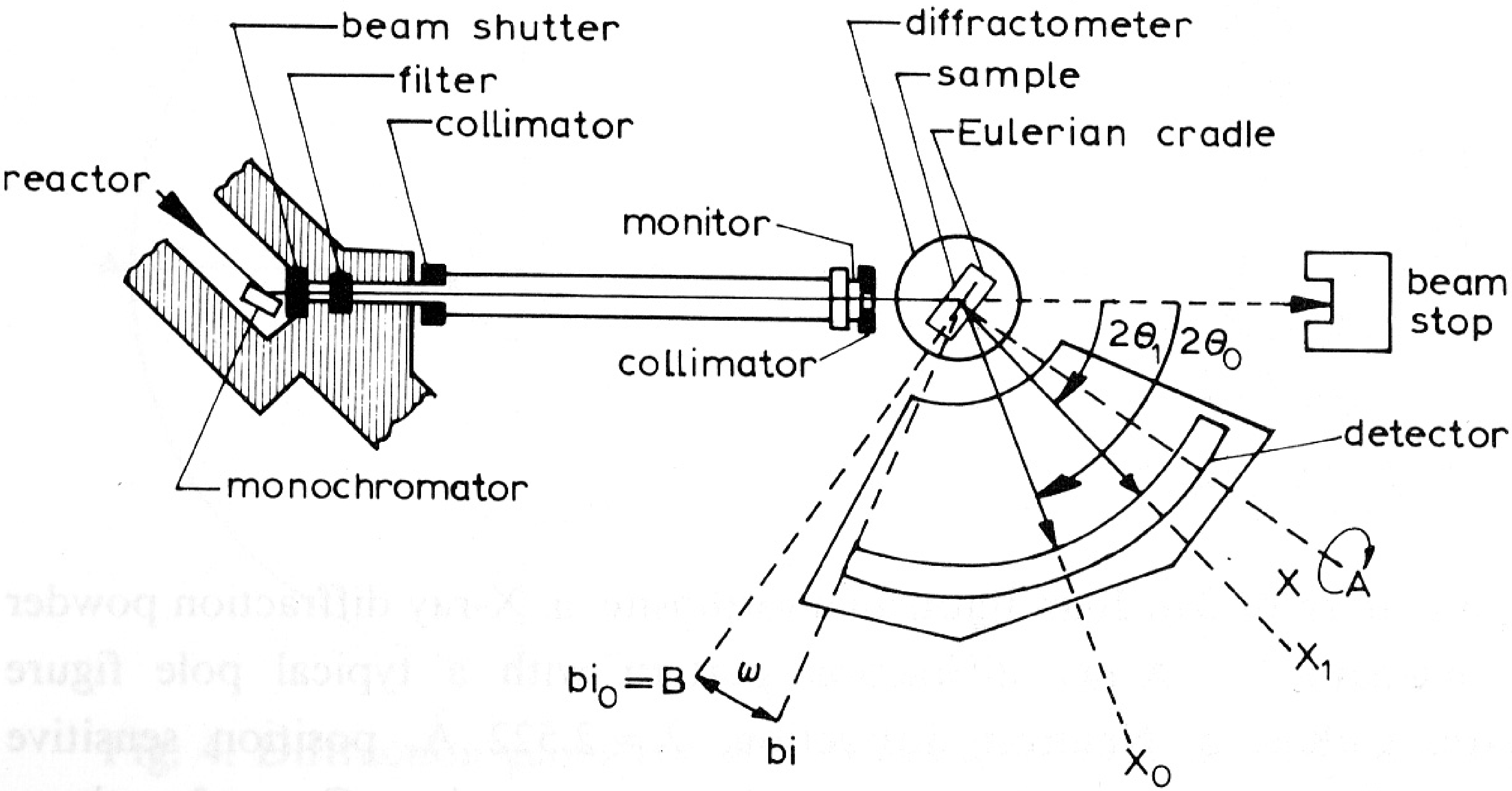
Quartzite 0001: U-stage – Neutron diffraction

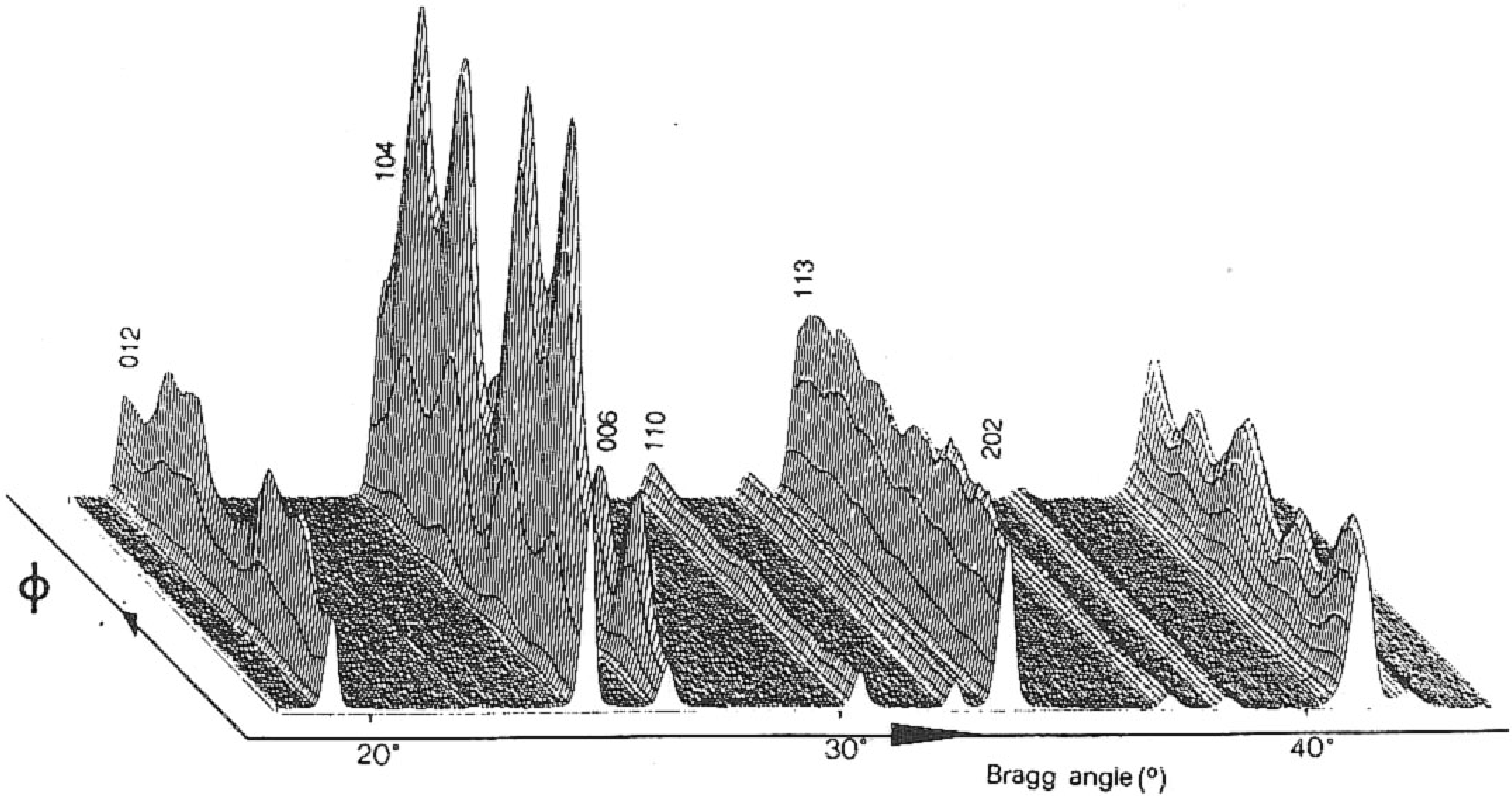


Calcite marble: X-ray – Neutron diffraction



ILL D1B

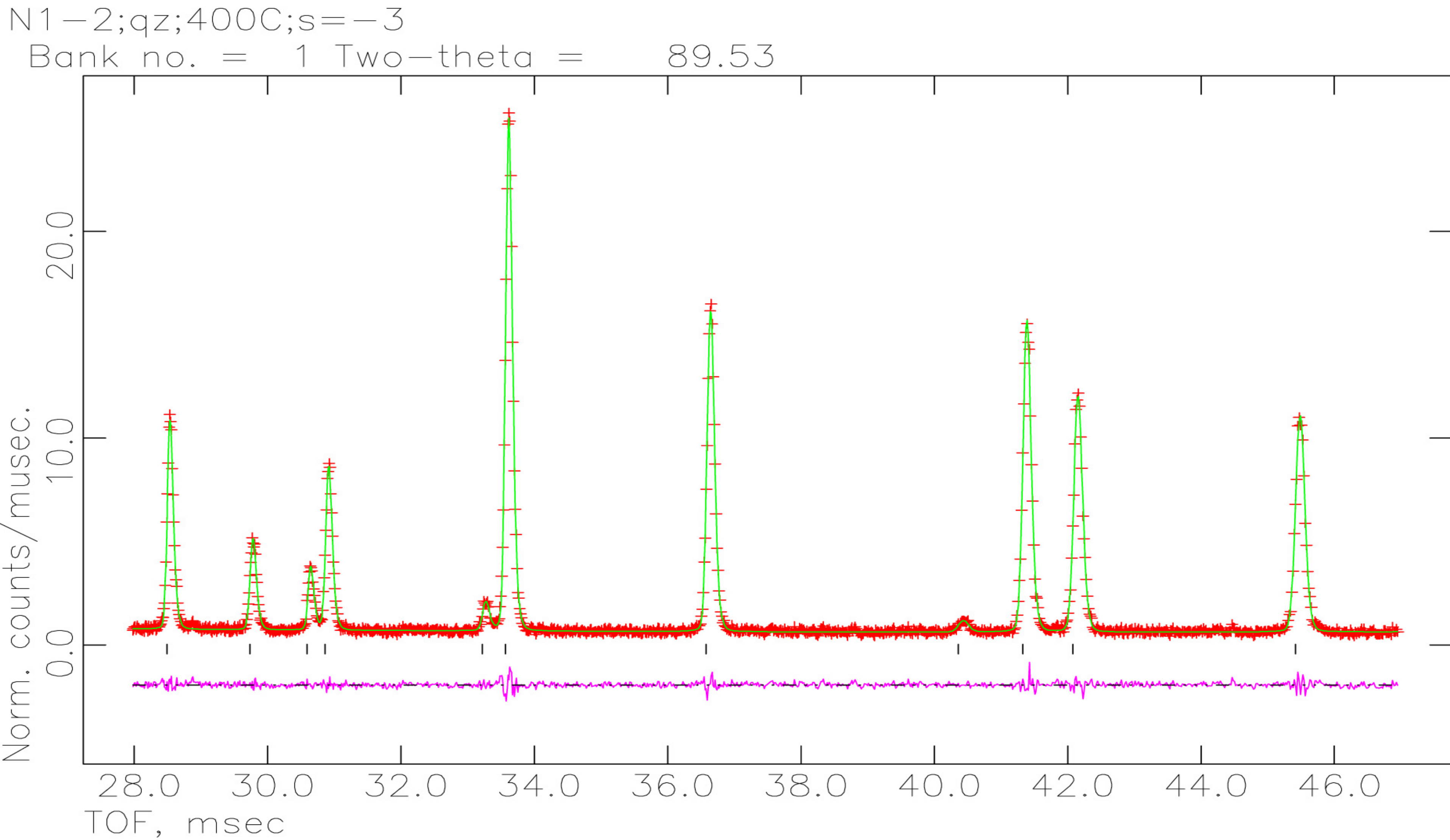

beam shutter
filter
collimator
reactor
monochromator
monitor
collimator
diffractometer
sample
Eulerian cradle
beam stop
2θ1
2θ0
detector
X
A
X1
X0
bi0=B
ω
bi



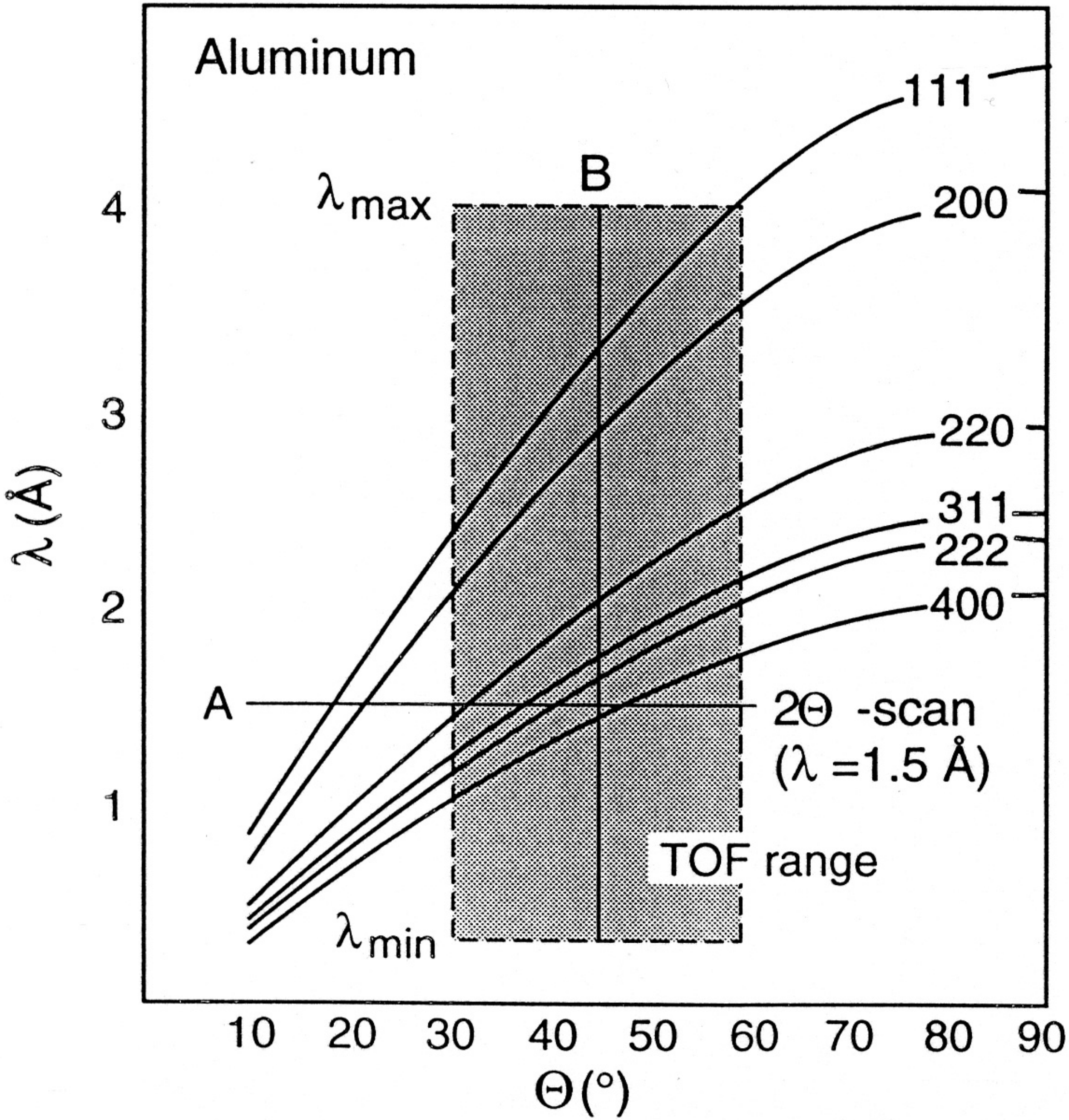
ILL D1B, stack of spectra, limestone

Neutron

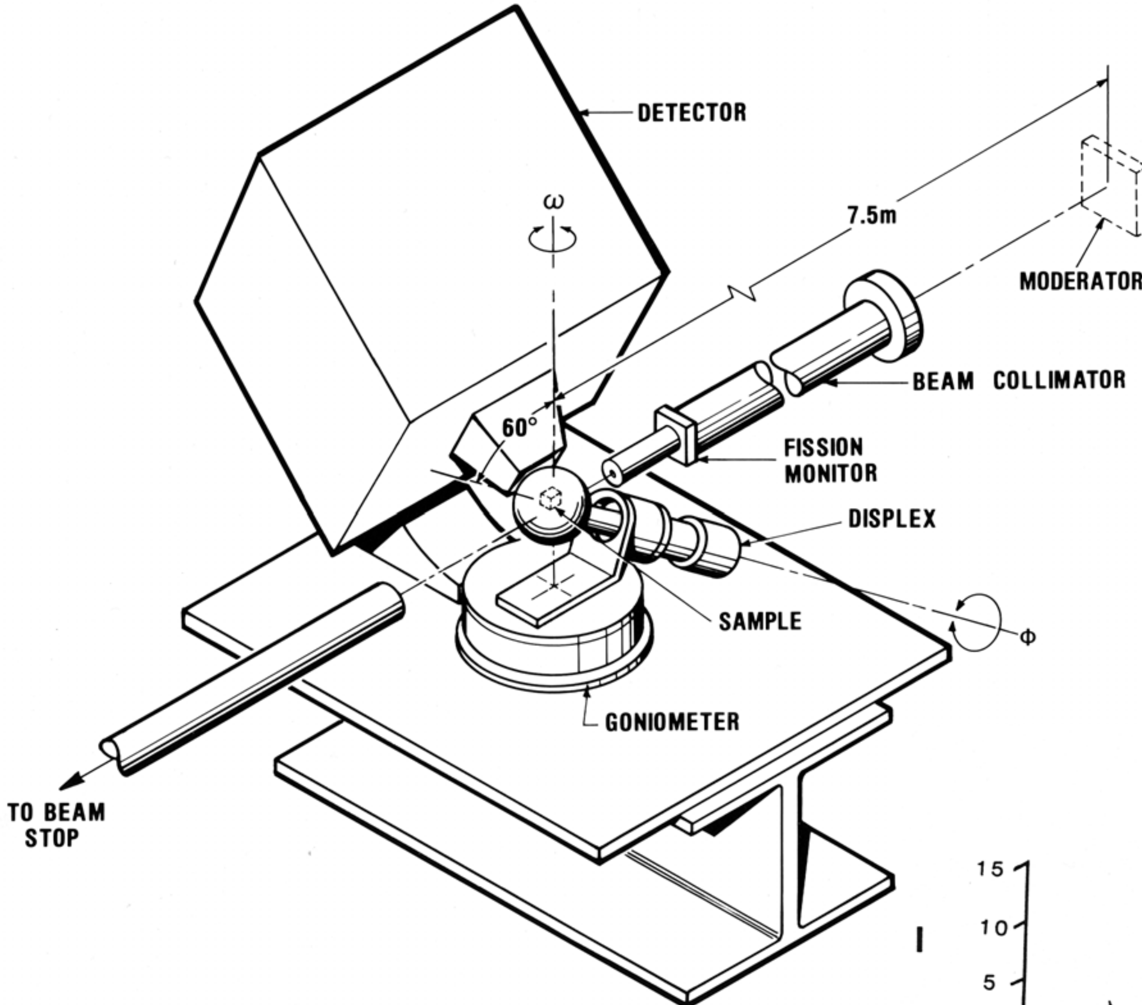
TOF

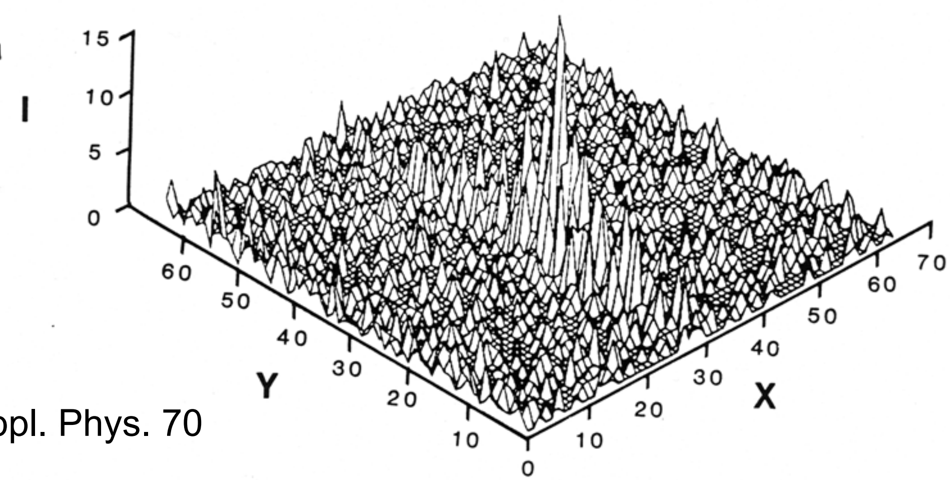


Mouse (keyboard): Left(H) - Height, Right(W) - Location Both(X) - exit

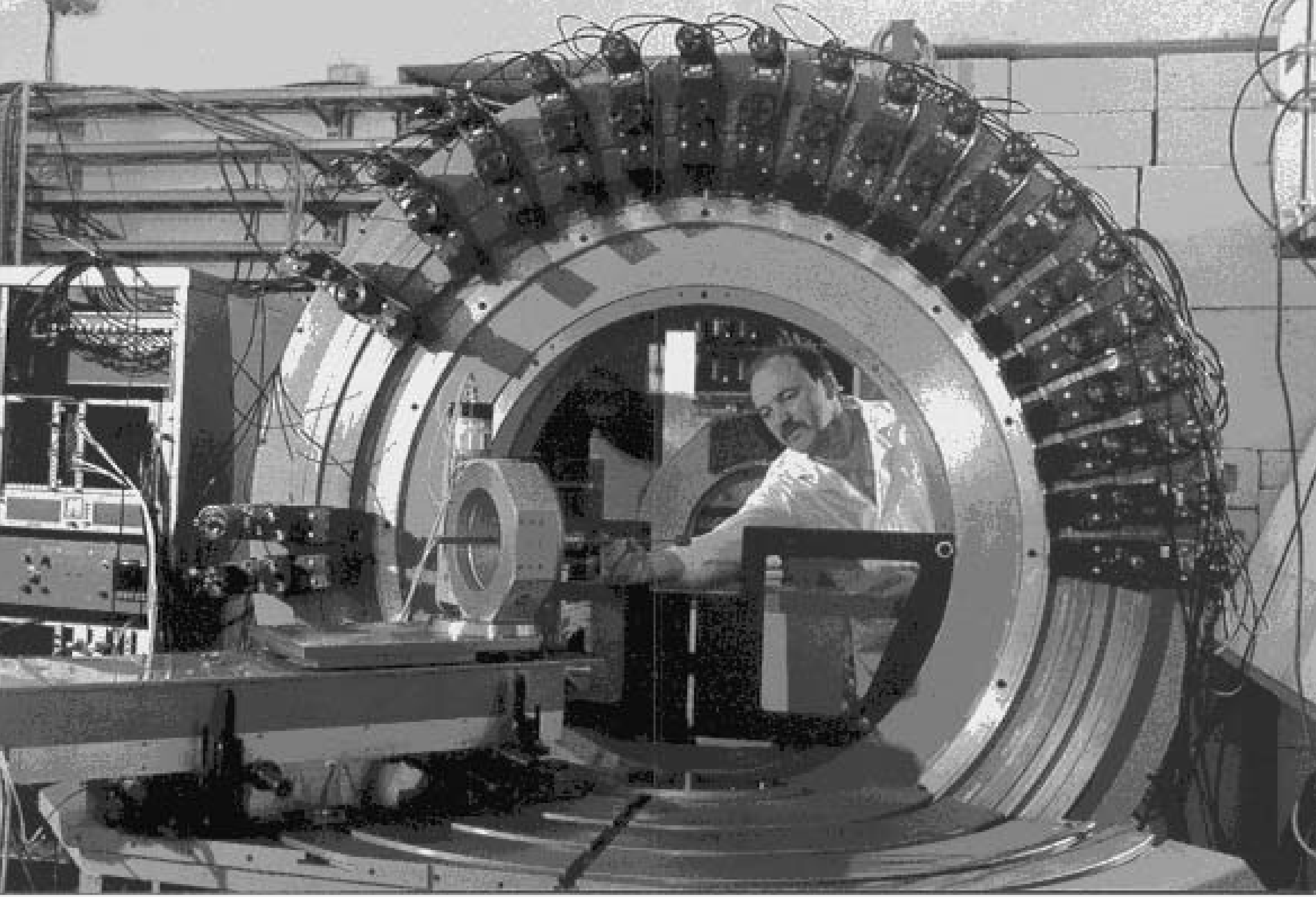


Aluminum
111
200
220
311
222
400
B
λ_{max}
λ_{min}
A
2Θ -scan
(λ =1.5 Å)
TOF range
λ (Å)
4
3
2
1
10 20 30 40 50 60 70 80 90
Θ (°)

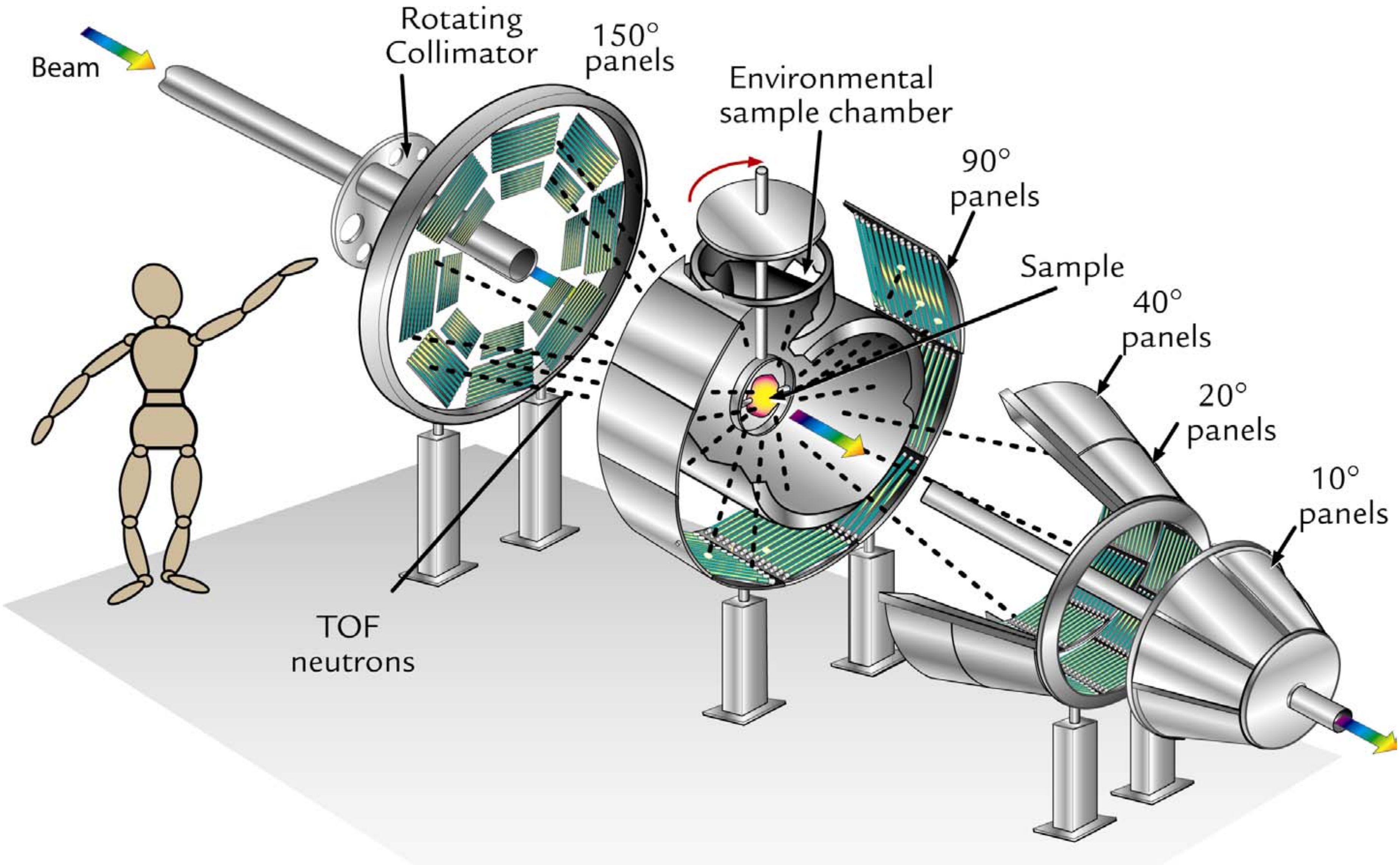




Wenk, Larson, Vergamini and Schultz, 1991, J. Appl. Phys. 70

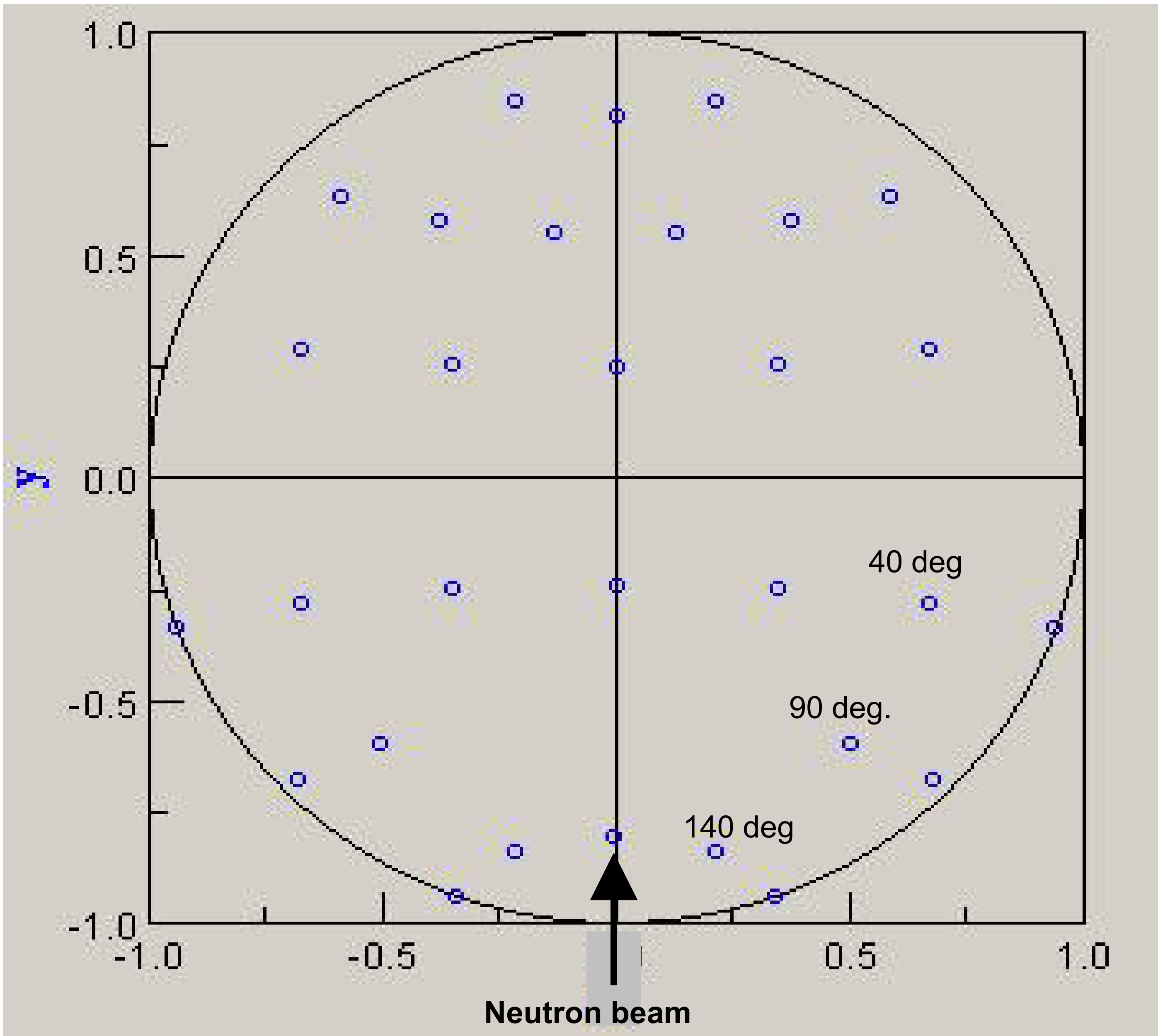


Dubna



UCMRD (University of California Materials Research Diffractometer) or HIPPO (High Pressure Preferred Orientation) at the Lujan Center at LANSCE

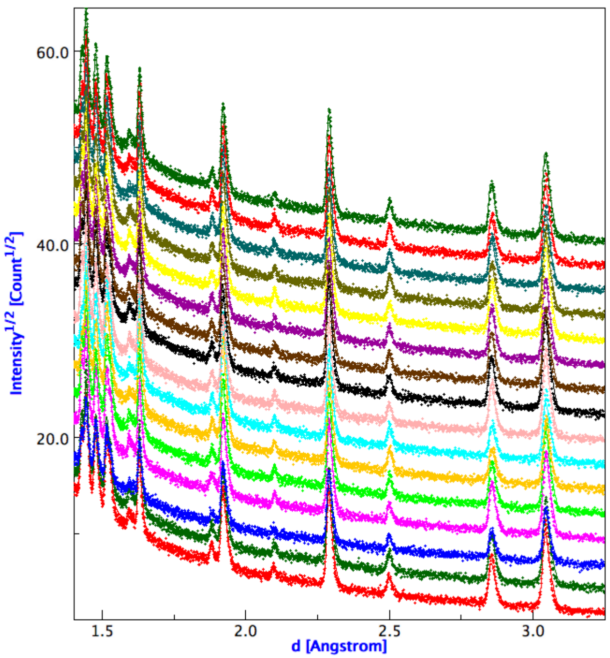
HIPPO Pole Figure Coverage



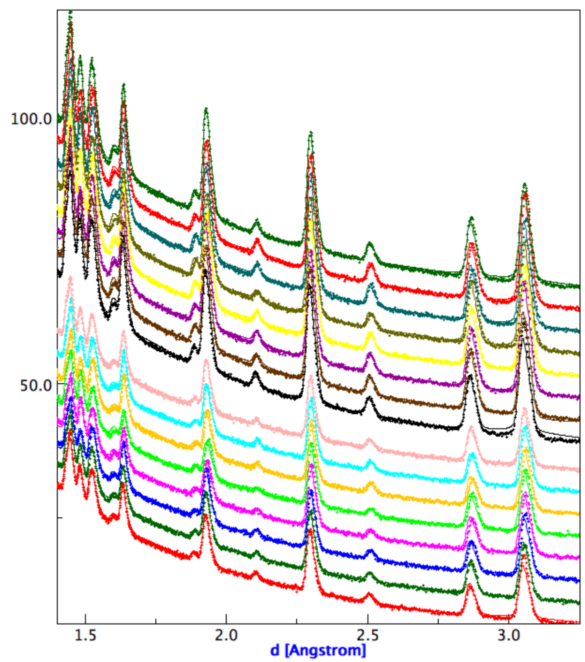
HIPPO: Stacks of diffraction spectra for deformed limestone

Relative intensity differences indicative of texture

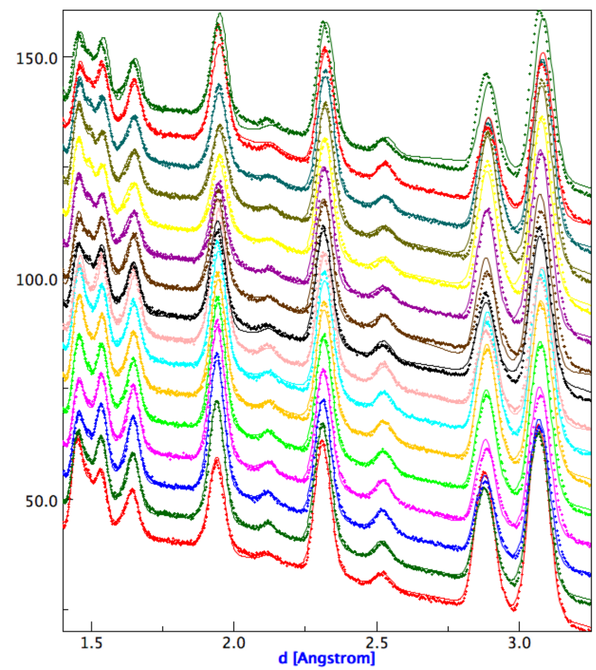
Simultaneous analysis of 384 spectra (48 detectors x 8 rotations) with the Rietveld method



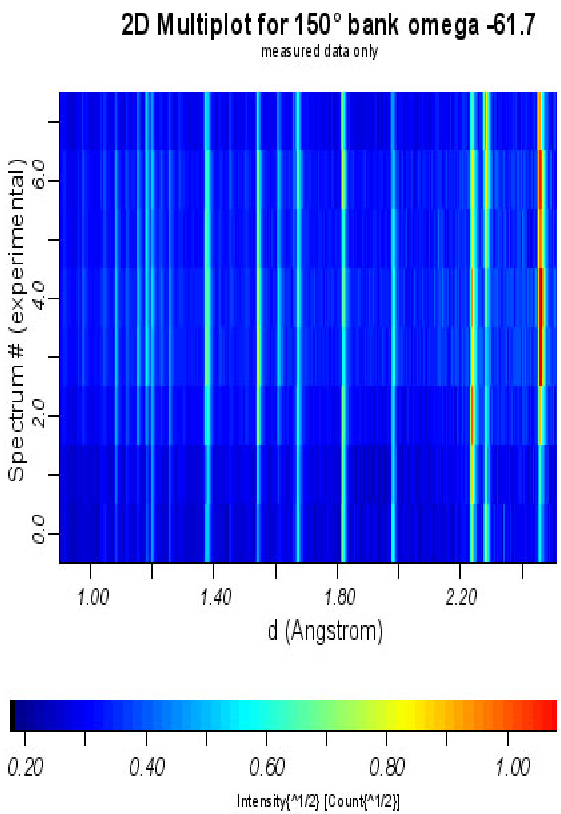
140 deg bank



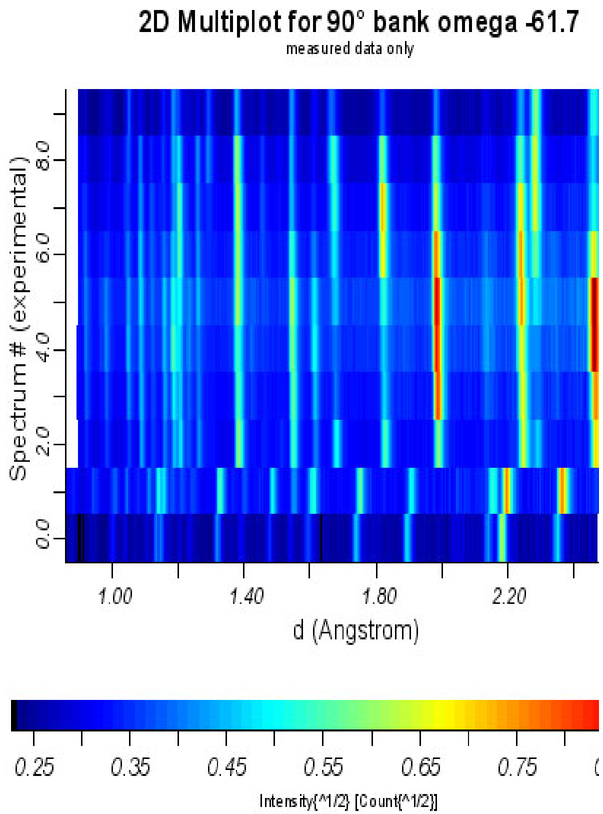
90 deg bank



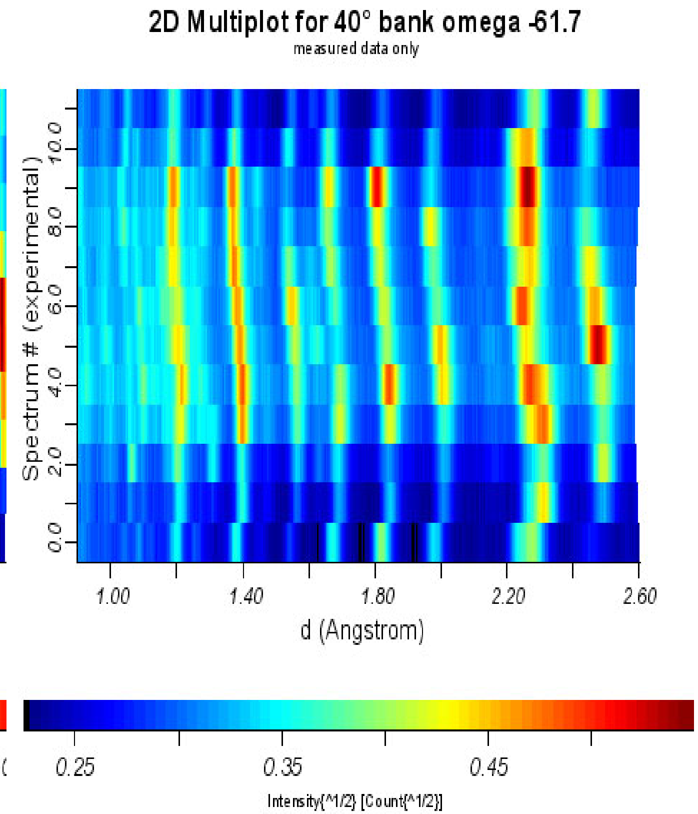
40 deg bank



150 deg bank



90 deg bank



40 deg bank


01 08 2002 09:53
NOTICE
CONTROLLED AREA
DANGER
HIGH RADIATION AREA
WHEN BEAM IS ON

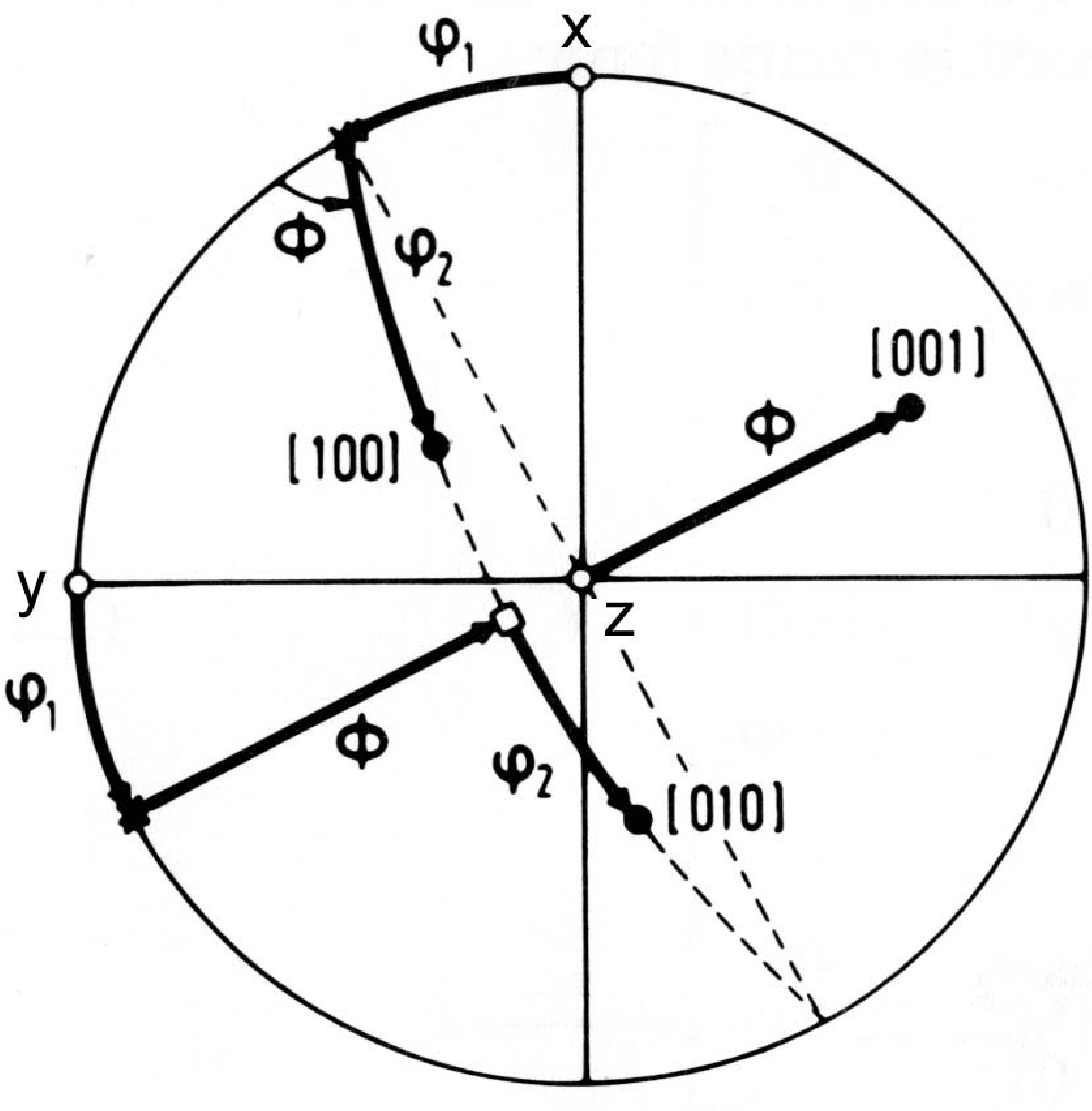
HIPPO Automatic Sample Changer

Rietveld Analysis with MAUD

(Materials Analysis Using Diffraction by Luca Lutterotti)

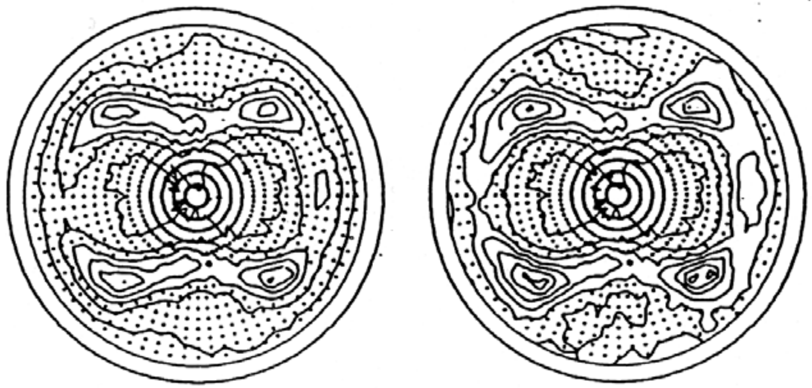
How to get ODF?

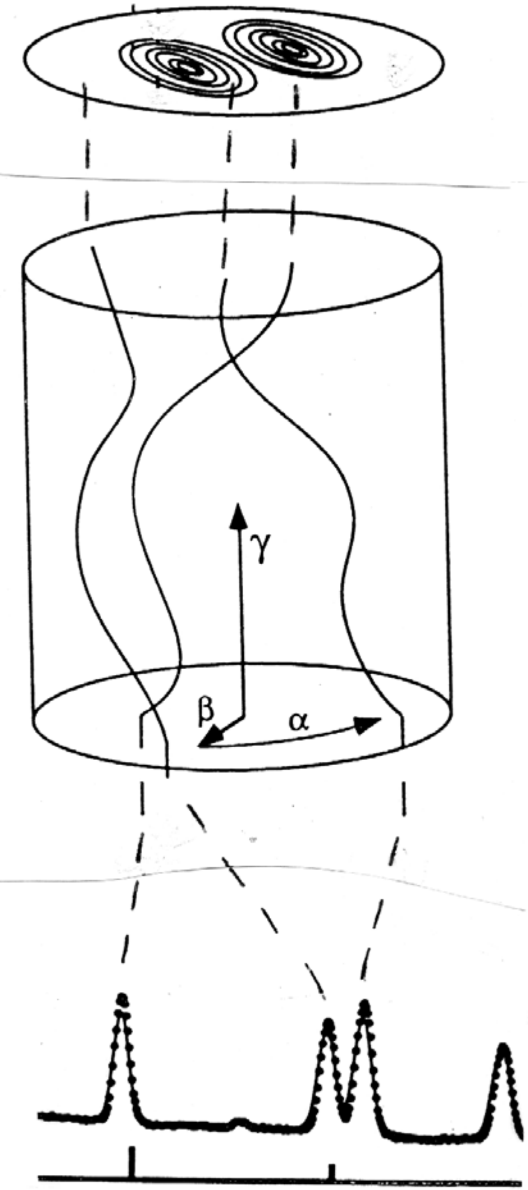
- from individual orientations
- from pole figures
- from diffraction spectra



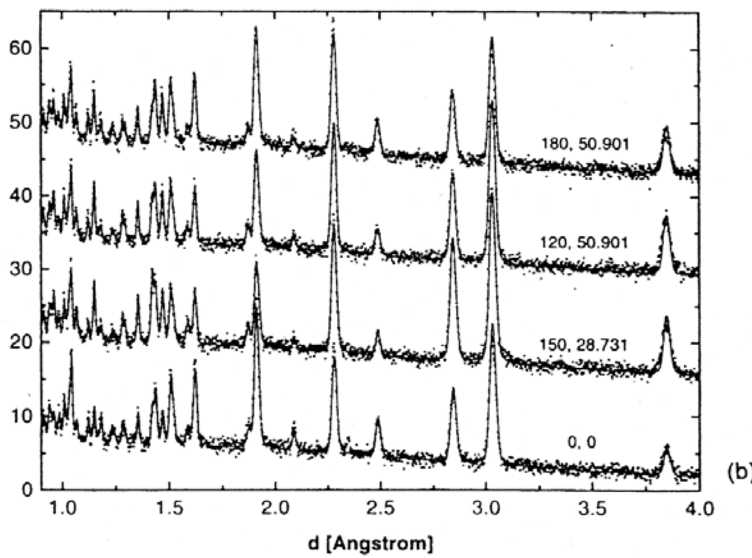
x
φ_1
Φ
φ_2
[001]
Φ
[100]
y
z
φ_1
Φ
φ_2
[010]

Conventional method: from pole figures to ODF

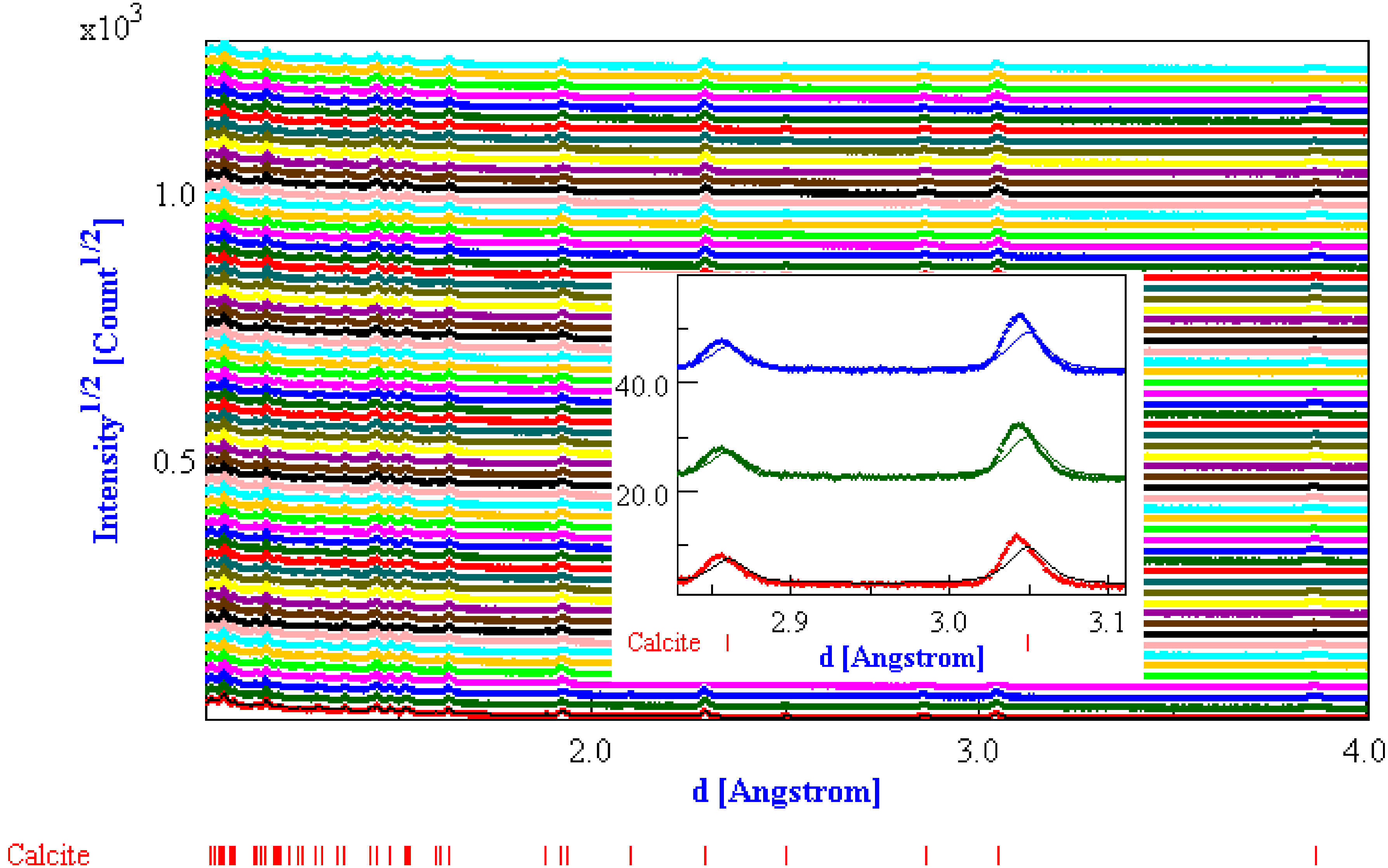




New approach: from diffraction spectra to ODF



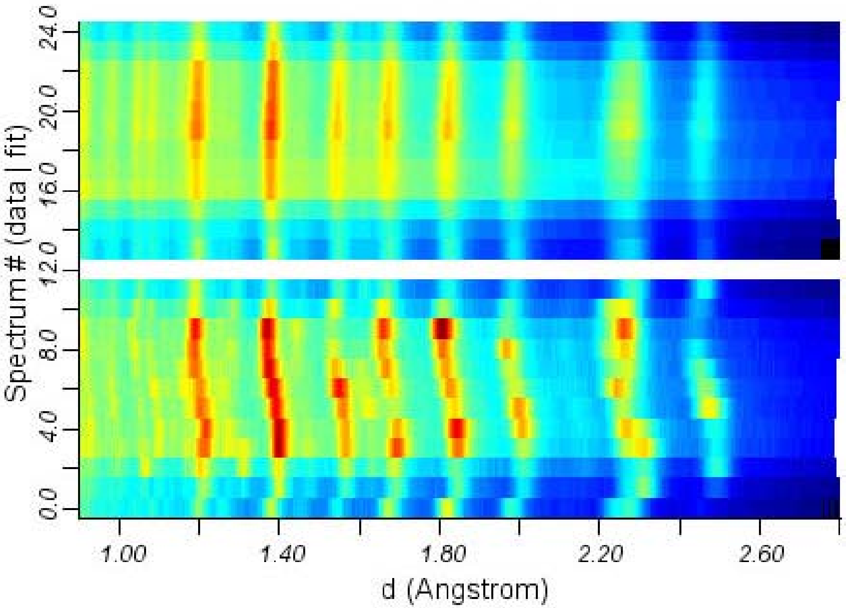
Limestone Standard: Refining 256 Spectra Simultaneously for Texture and Structure with the Rietveld Method (MAUD)



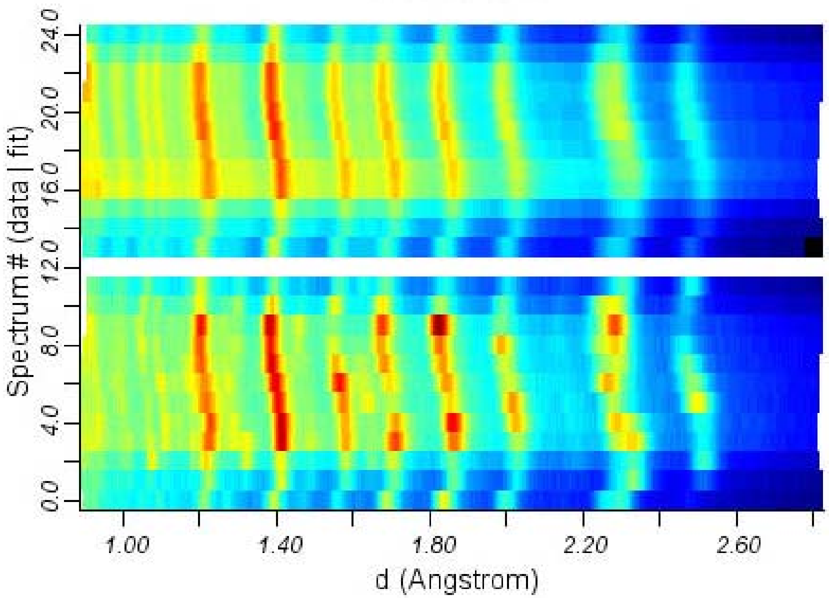
Lutterotti et al. 2002

What influences the spectrum?

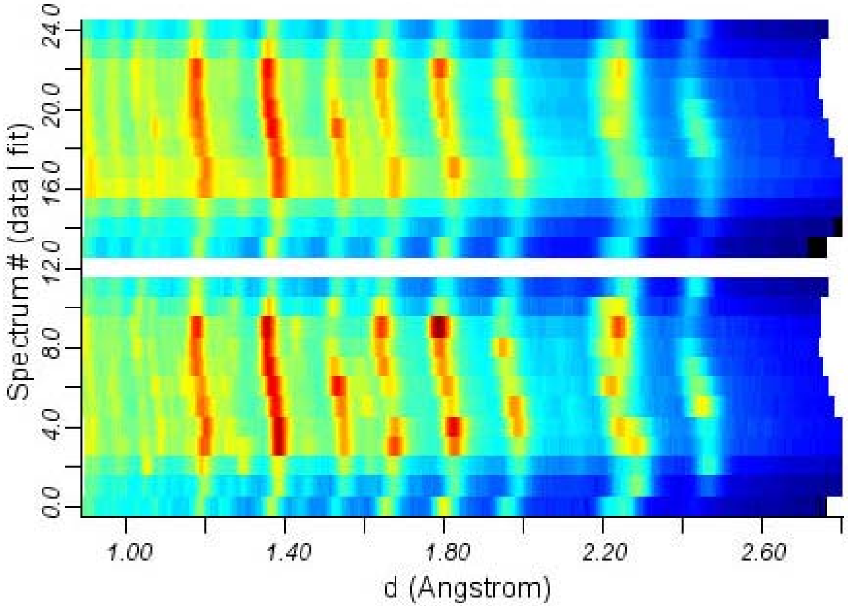
- Instrumental features (wavelength etc.)
- Crystal structure (lattice, atomic positions)
- Microstructure (size, strain)
- Texture (ODF)



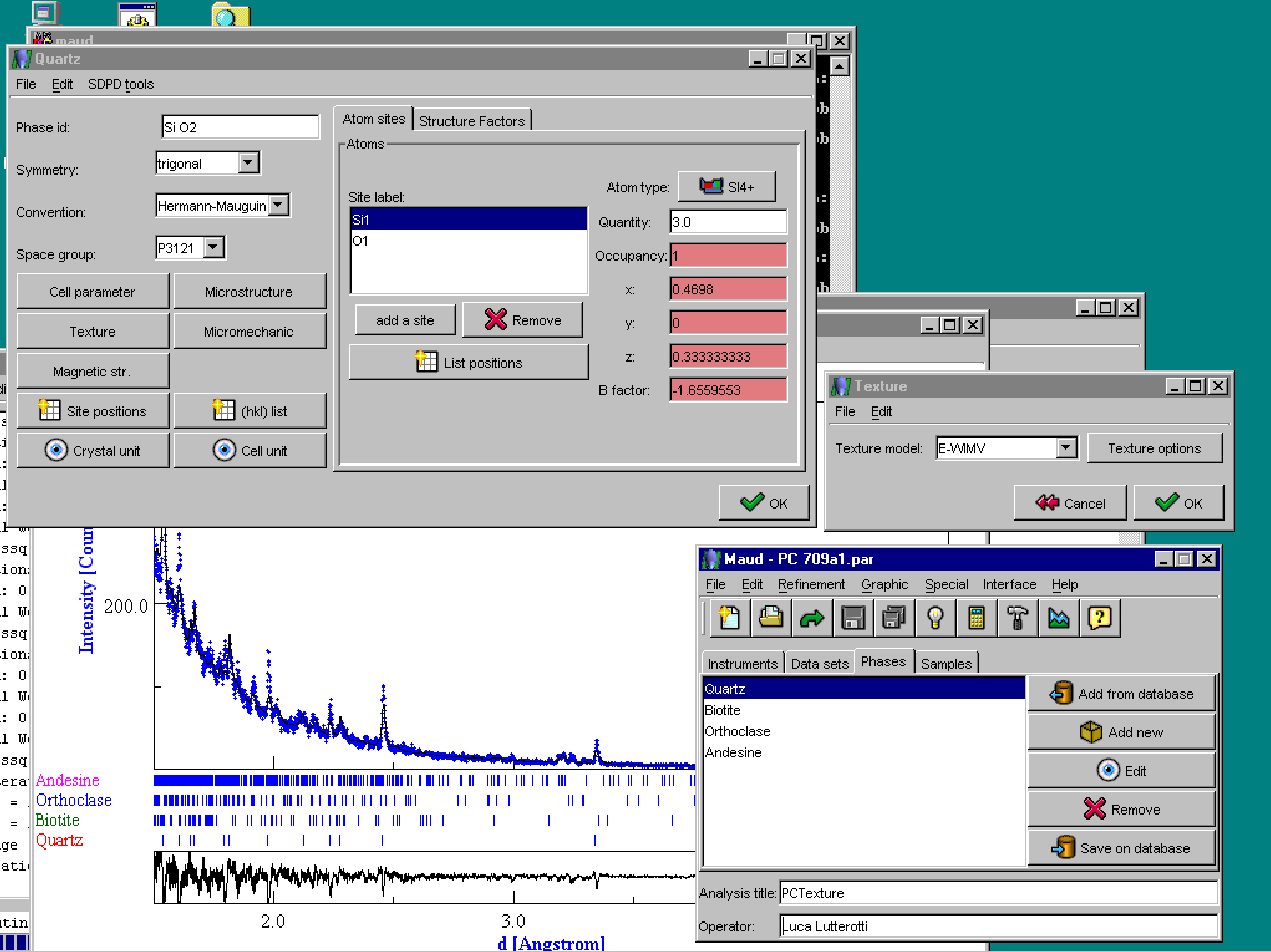
Cycle 1: scale factors and background



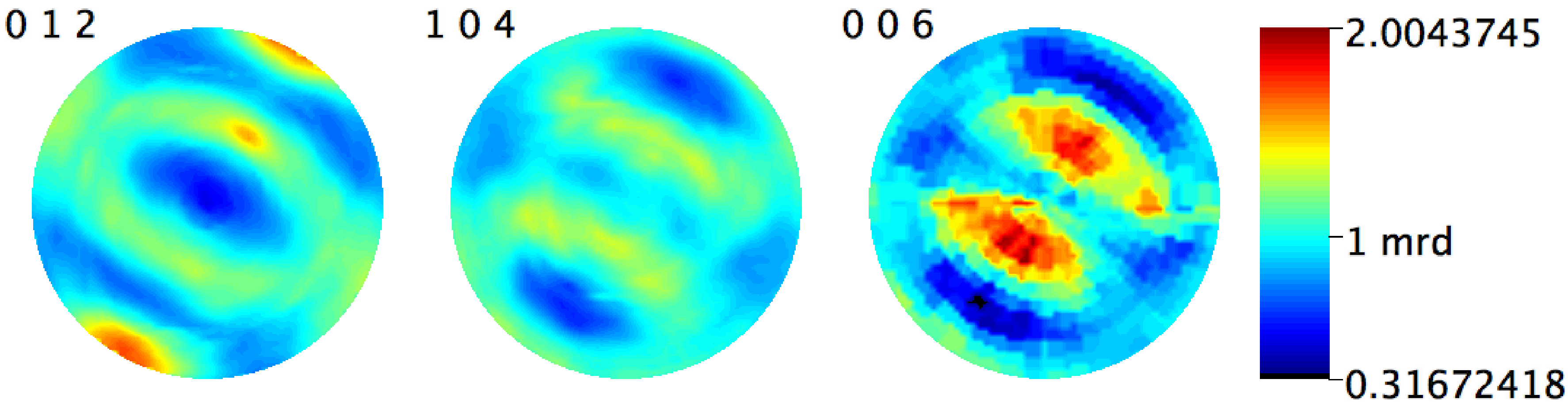
Cycle 2: previous + detector distance



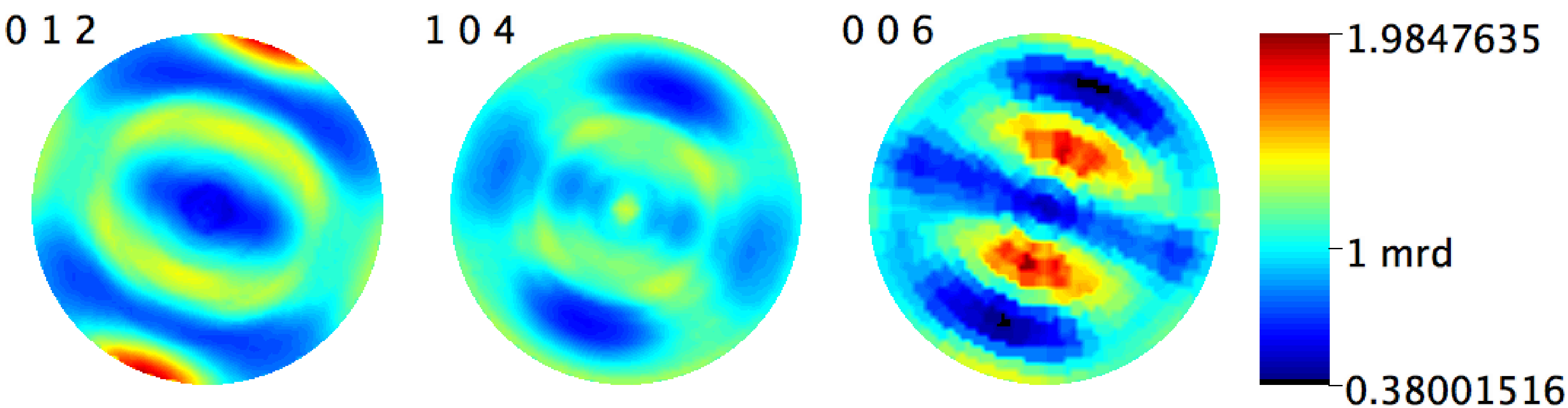
Cycle 3: previous + texture


Quartz
File Edit SDPD tools
Phase id: Si O2
Symmetry: trigonal
Convention: Hermann-Mauguin
Space group: P3121
Cell parameter
Microstructure
Texture
Micromechanic
Magnetic str.
Site positions
(hkl) list
Crystal unit
Cell unit
Atom sites
Structure Factors
Atoms
Site label:
Si1
O1
add a site
Remove
List positions
Atom type: Si4+
Quantity: 3.0
Occupancy: 1
x: 0.4698
y: 0
z: 0.333333333
B factor: -1.6559553
OK
Texture
File Edit
Texture model: E-WIMV
Texture options
Cancel
OK
Maud - PC 709a1.par
File Edit Refinement Graphic Special Interface Help
Instruments
Data sets
Phases
Samples
Quartz
Biotite
Orthoclase
Andesine
Add from database
Add new
Edit
Remove
Save on database
Analysis title: PCTexture
Operator: Luca Lutterotti
Intensity [Cou
200.0
Andesine
Orthoclase
Biotite
Quartz
2.0
3.0
d [Angstrom]

Pole figures for round robin limestone standard

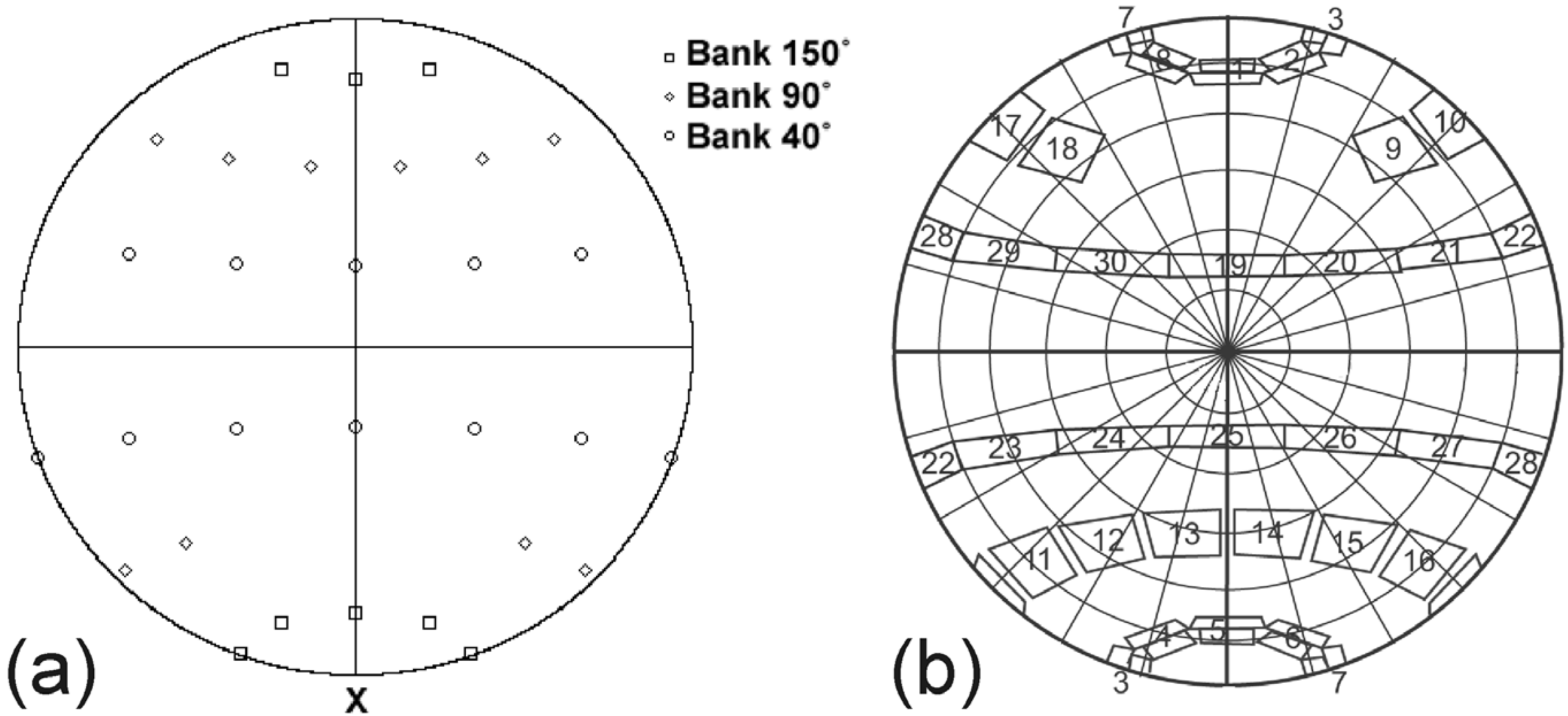


HIPPO Limestone standard, e-WIMV 10 deg



ILL D20 Limestone standard, e-WIMV 10 deg

HIPPO measured in 20 minutes, ILL in 4 hours


Bank 150°
Bank 90°
Bank 40°
(a)
x
(b)
7
3
8
1
2
17
18
9
10
28
29
30
19
20
21
22
22
23
24
25
26
27
28
11
12
13
14
15
16
4
5
6
3
7

Two approaches

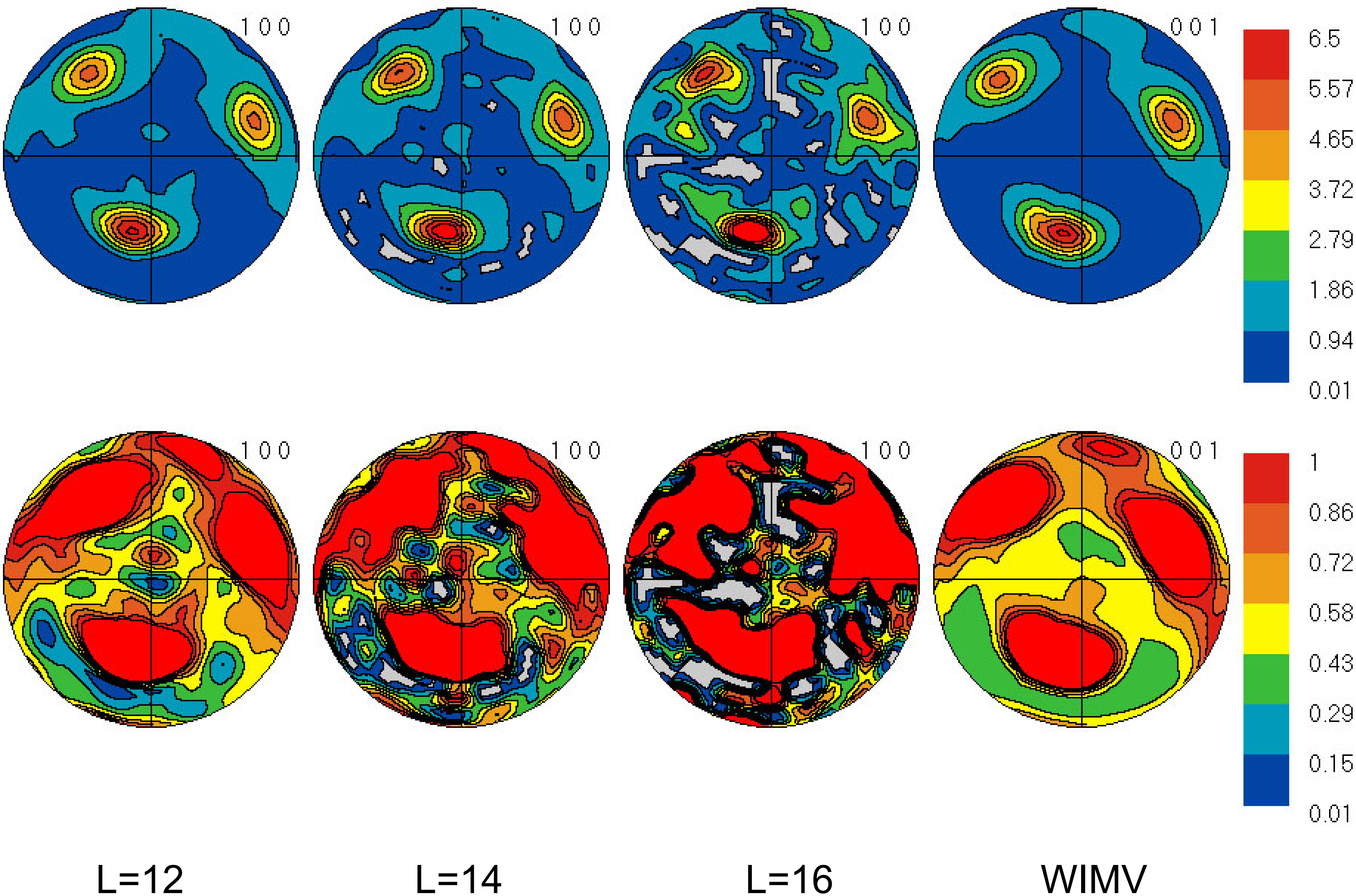
1) Harmonic Method (Fourier approach)

Termination errors, odd coefficients

1) Direct Methods (Tomography)

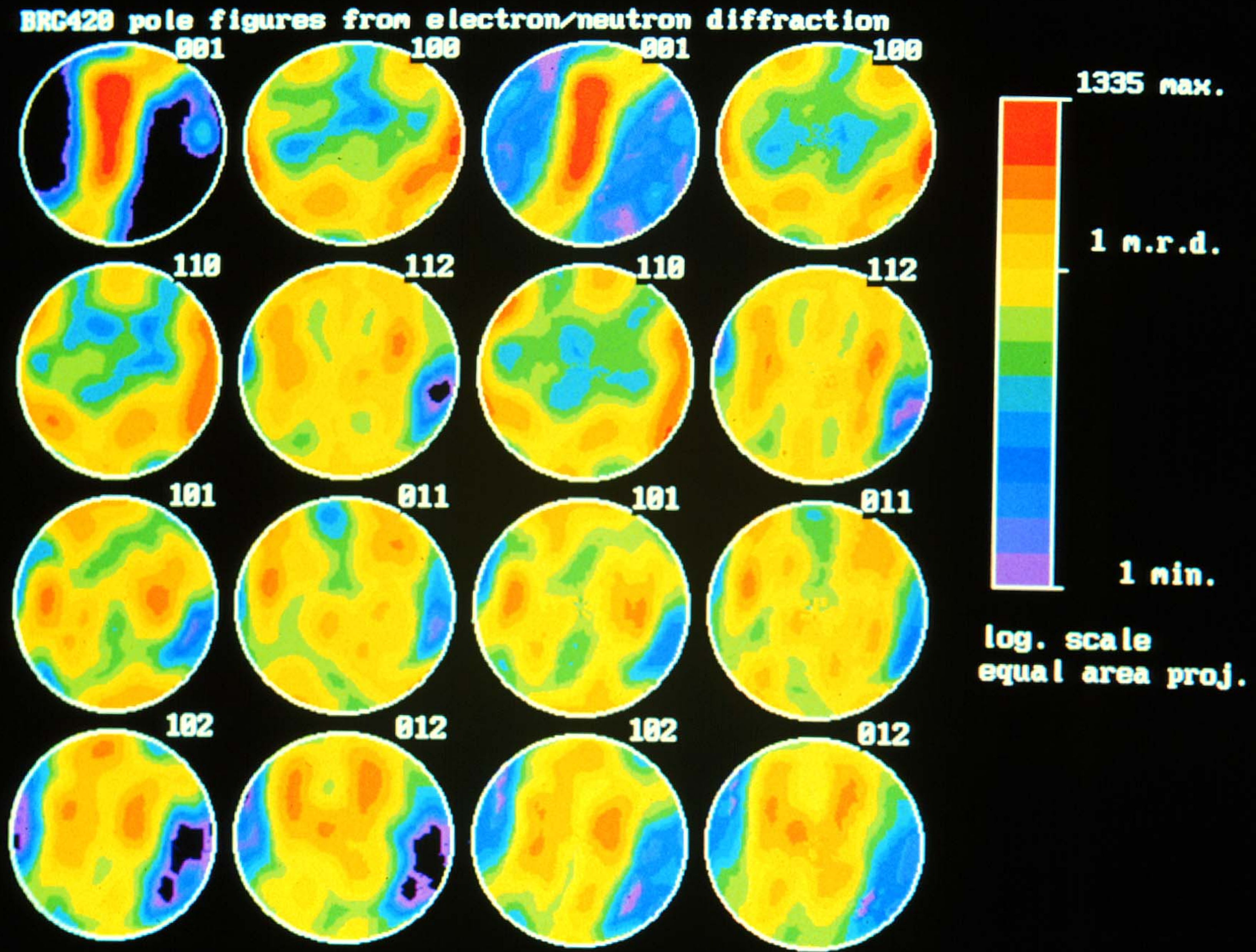
WIMV, Entropy etc.

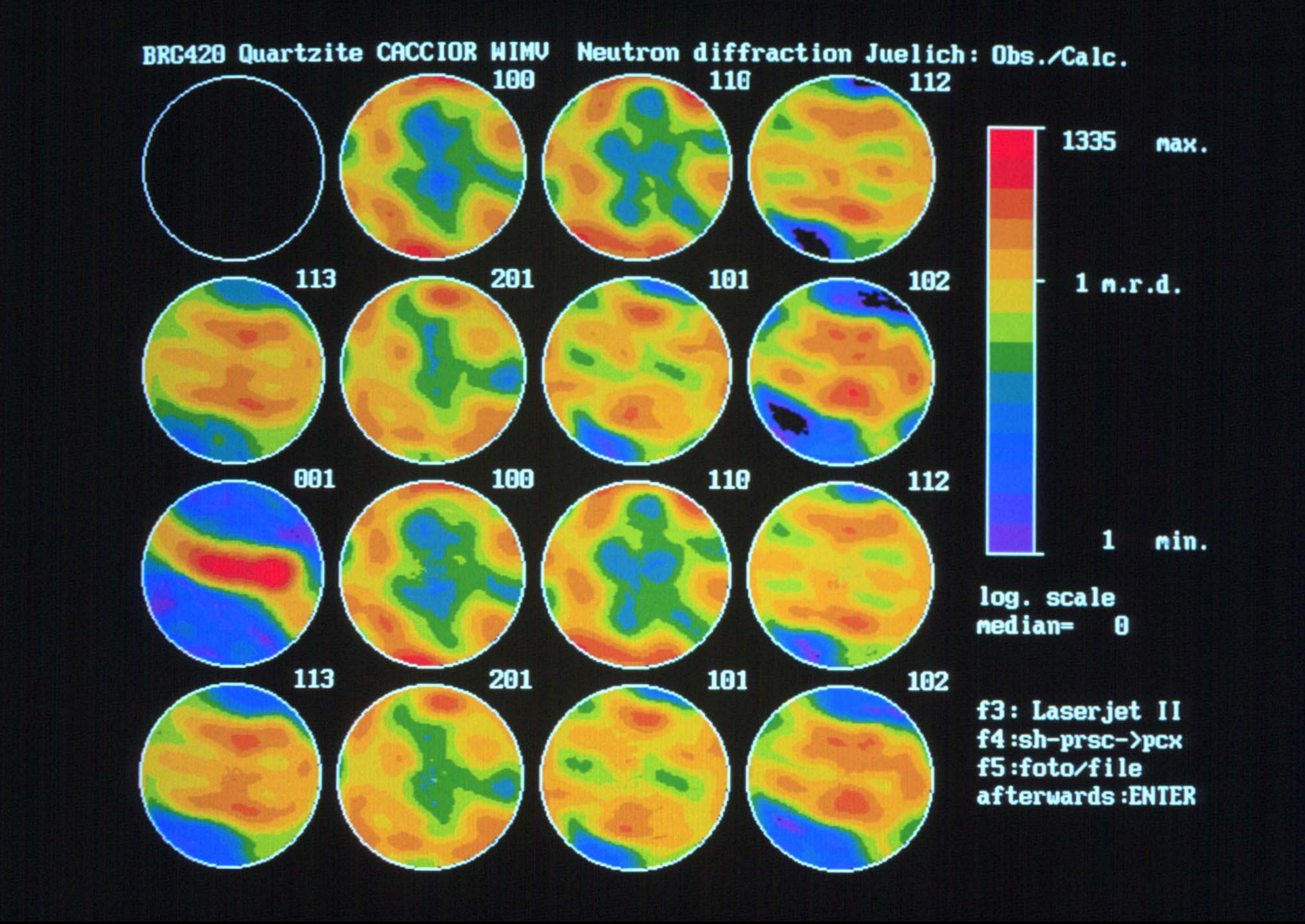
ECAP aluminum

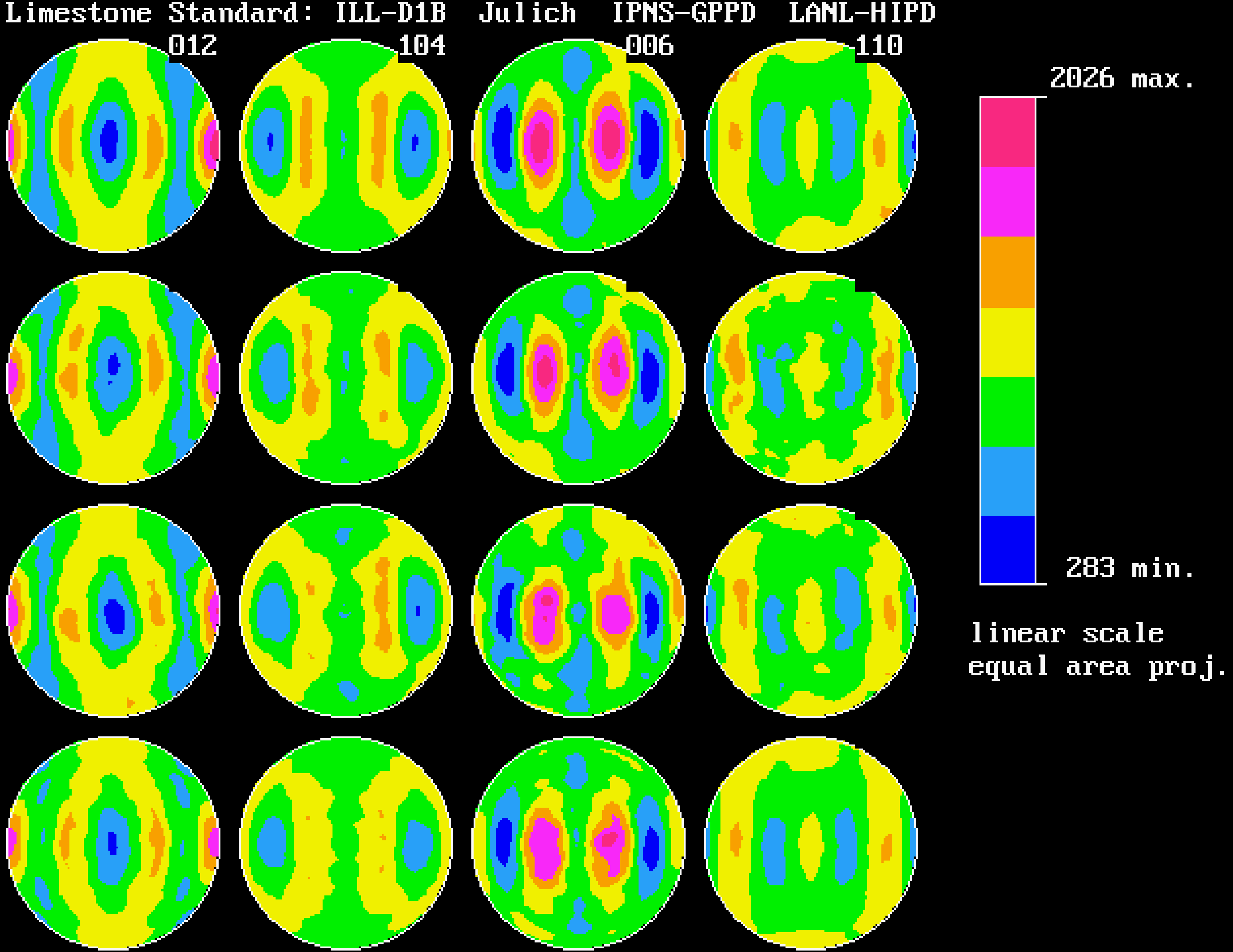


Data Quality

- Comparison with other techniques (neutron-electron)
- Internal consistency (observed-recalculated)
- Round Robin


BRC420 pole figures from electron/neutron diffraction
001
100
001
100
110
112
110
112
101
011
101
011
102
012
102
012
1335 max.
1 m.r.d.
1 min.
log. scale
equal area proj.

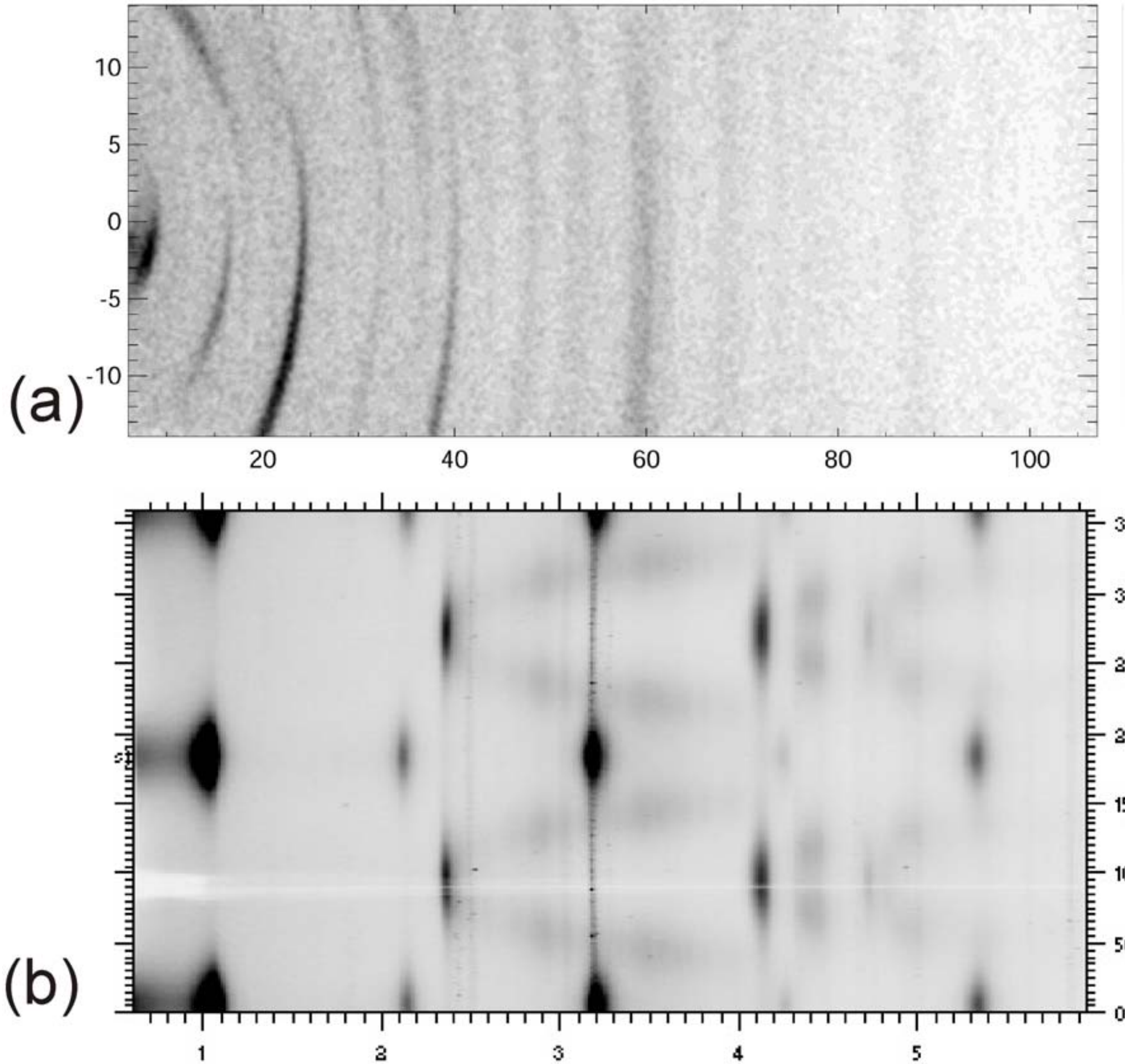

BRG420 Quartzite CACCIOR WIMV Neutron diffraction Juelich: Obs./Calc.
100
110
112
113
201
101
102
001
100
110
112
113
201
101
102
1335 max.
1 m.r.d.
1 min.
log. scale
median= 0
f3: Laserjet II
f4:sh-prsc->pcx
f5:foto/file
afterwards:ENTER



Round Robin limestone

Advantages of neutrons

- Low absorption / high penetration:
  - bulk samples (not surfaces)
  - large samples (coarse grained)
  - environmental stages
- High spectral resolution:
  - low symmetry materials (e.g. minerals, HTS, Pu)
  - Composites (rocks, metal matrix etc.)
- Scattering power:
  - Be, D, D_2O, Al-Si



D20-ILL

11ID-C APS

Illite-rich shale

Neutron Diffraction for Texture and Strain Analysis

Texture

- Geesthacht (monochromatic)
- ILB Saclay (monochromatic)
- ILL D1B, D19 and D20 (monochromatic, banana)
- IPNS GPPD (TOF)
- LANSCE HIPPO (TOF)
- Dubna SKAT (TOF)
- ISIS SXD (TOF)

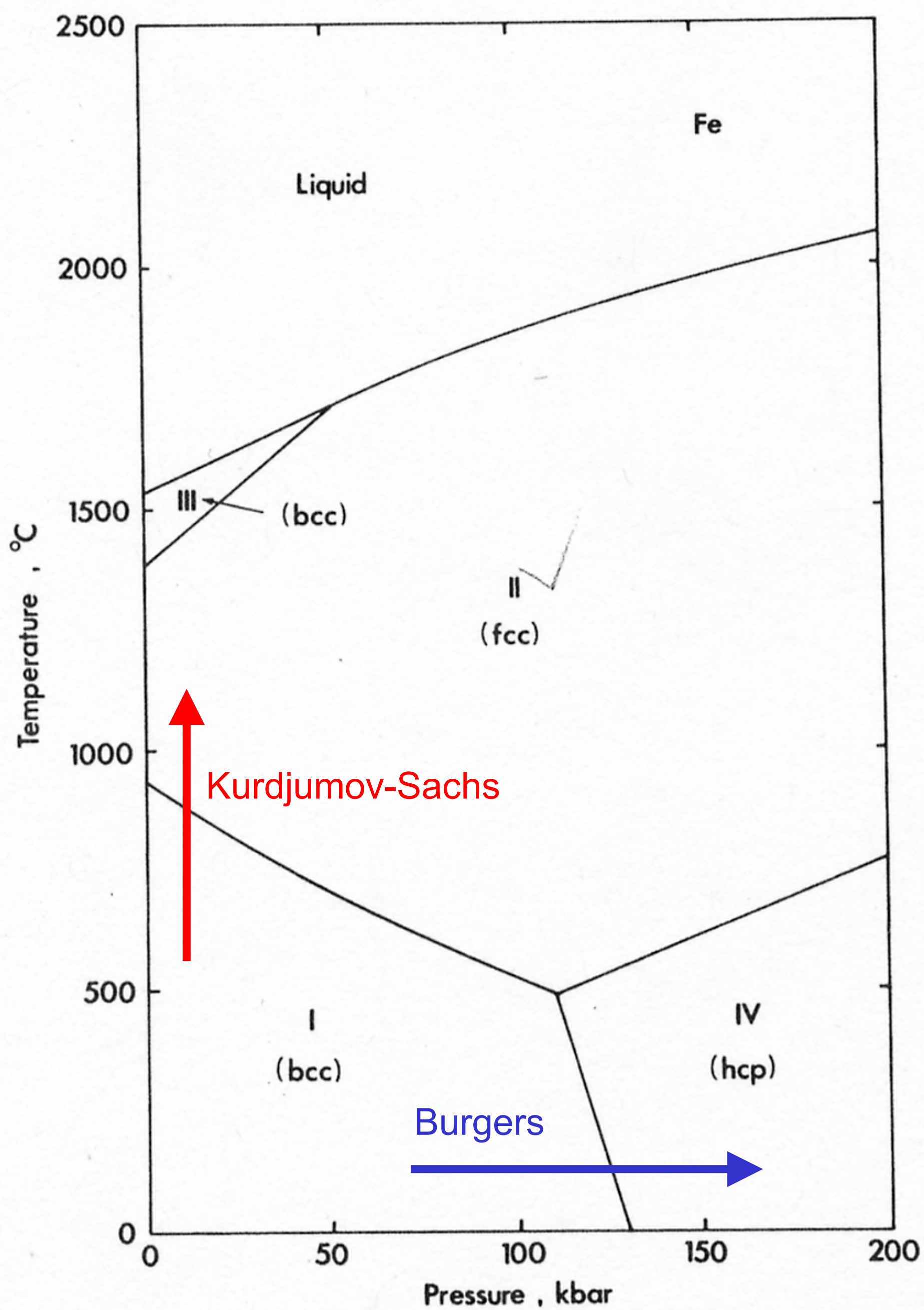
Strain

- Chalk River (monochromatic)
- Dubna EPSILON (TOF)
- IPNS GPPD (TOF)
- LANSCE SMARTS (TOF)
- ISIS ENGIN-X (TOF)
- Geesthacht (monochromatic)

Iron

bcc – fcc – bcc

Fe



2500
2000
1500
1000
500
0
Temperature , °C
Fe
Liquid
III
(bcc)
II
(fcc)
Kurdjumov-Sachs
I
(bcc)
IV
(hcp)
Burgers
0
50
100
150
200
Pressure , kbar

Phase transformations in iron

Kurdjumov-Sachs 1934:

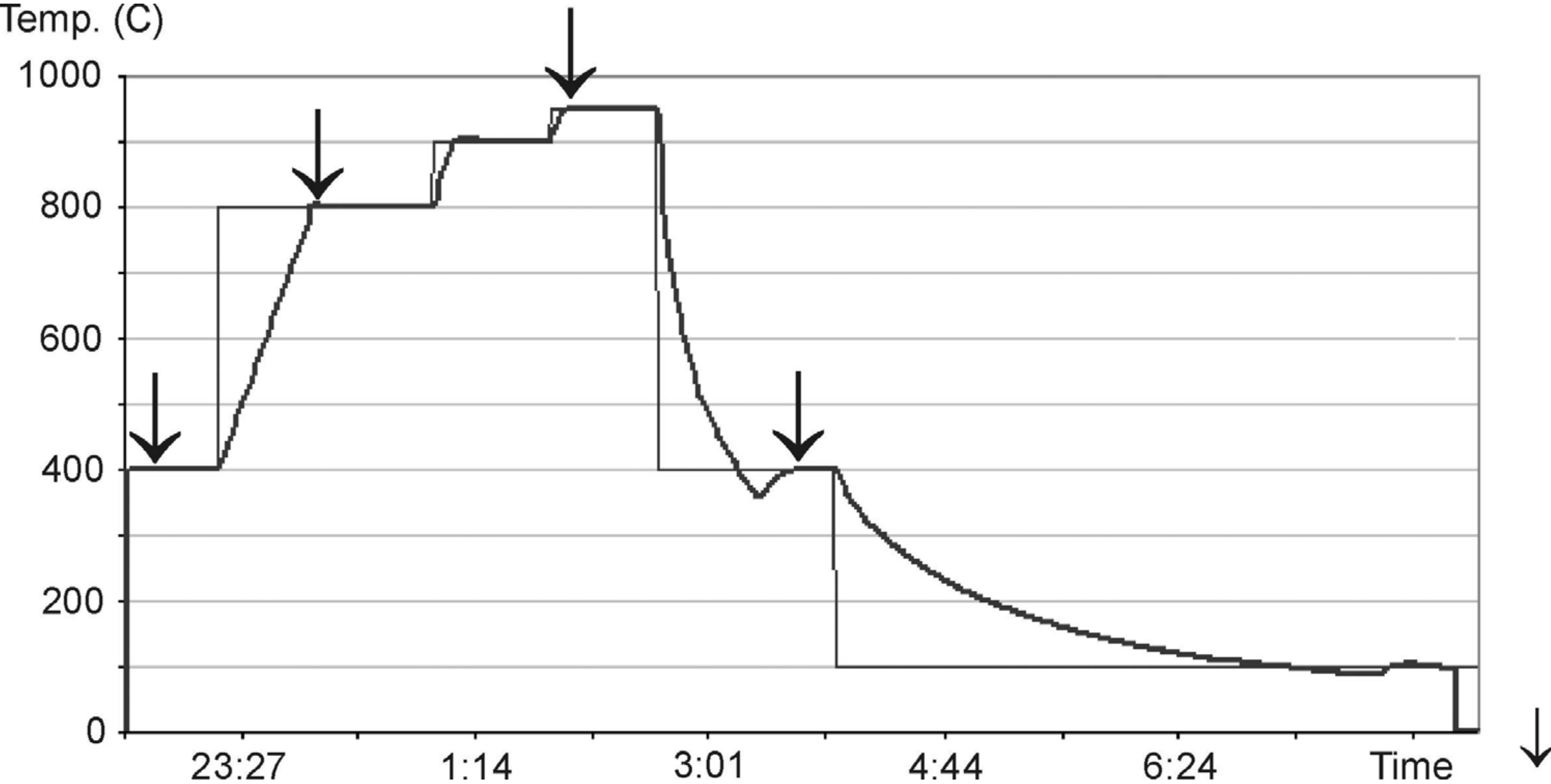
{110}<111> bcc   {111}<110> fcc

{110} is the densest packed plane in bcc, {111} is close-packed plane in fcc, <111> (bcc) and {110} fcc are closest-packed directions

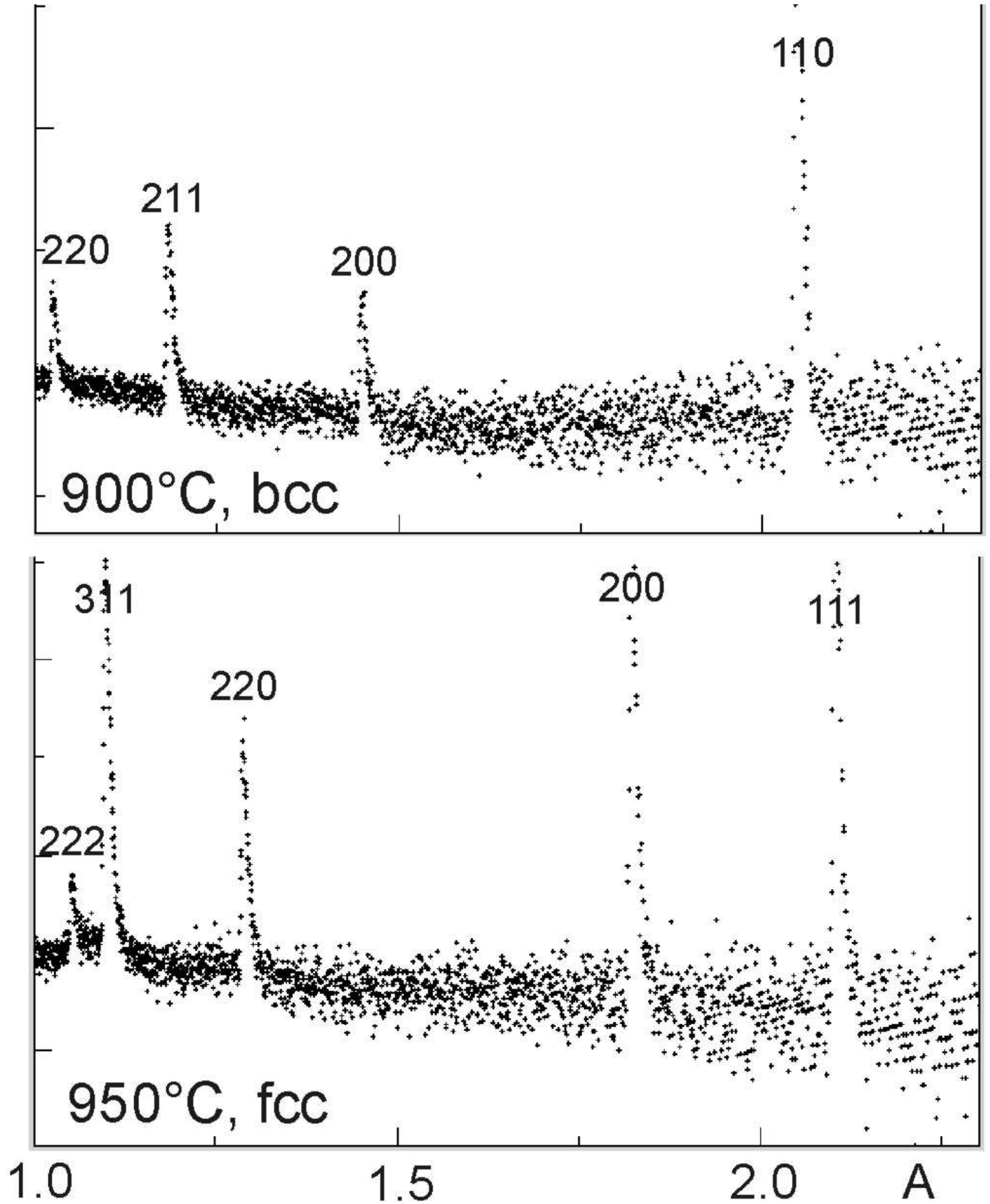
Burgers 1934:

{110}<111> bcc   {0001}<11-20> hcp

{110} is the densest packed plane in bcc, {0001} is close-packed plane in hcp, <111> (bcc) and {11-20} hcp are closest-packed directions

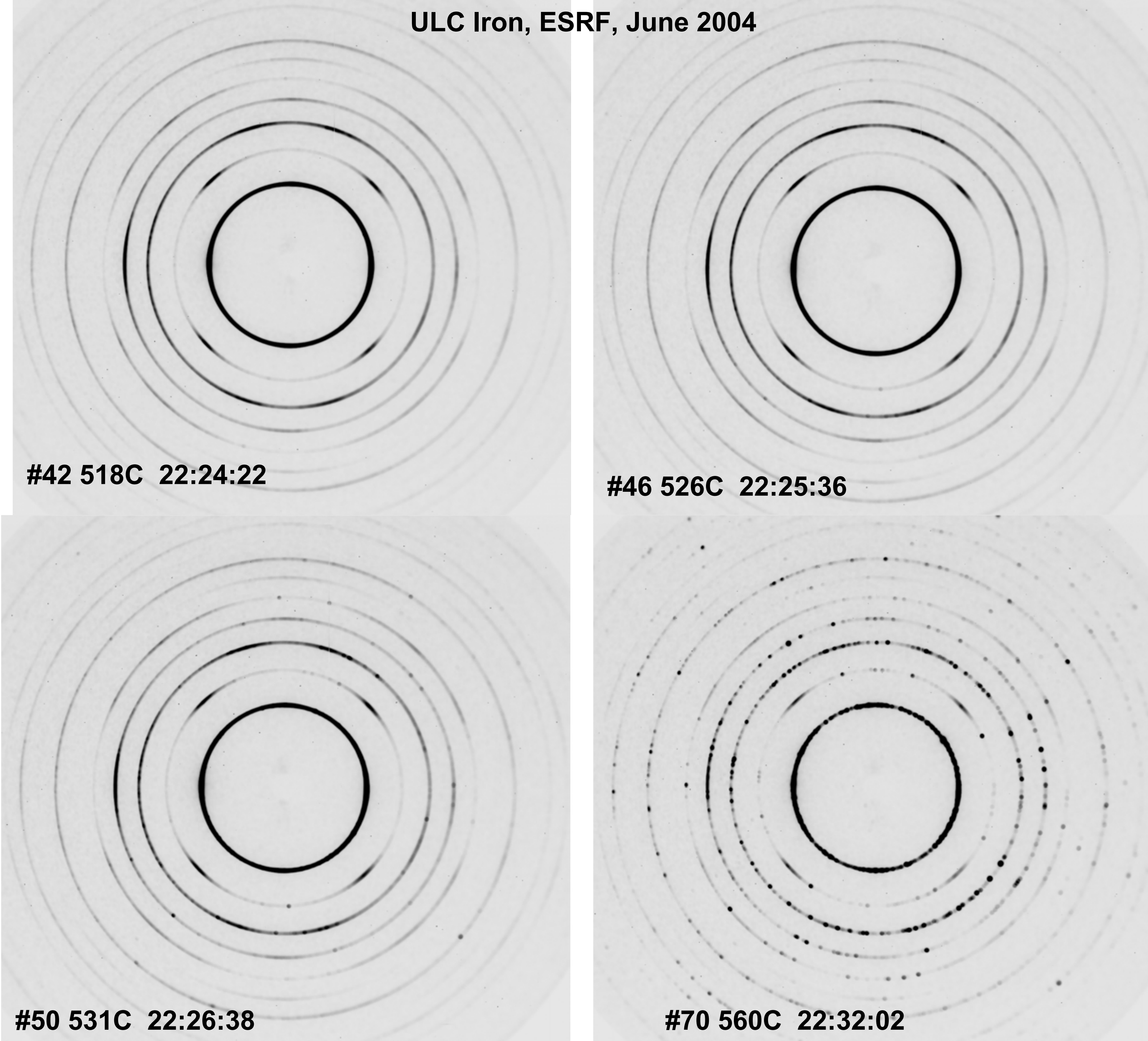


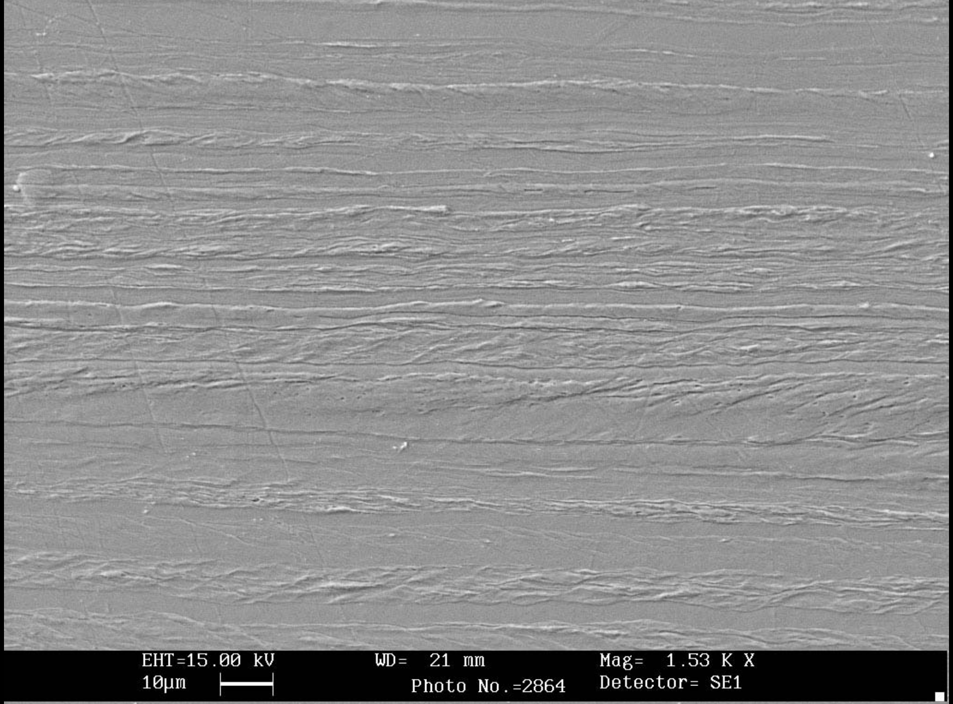
Wenk, H.-R., Huensche, I. and Kestens, L. (2006). ***Mater. Trans*****. (in press)**



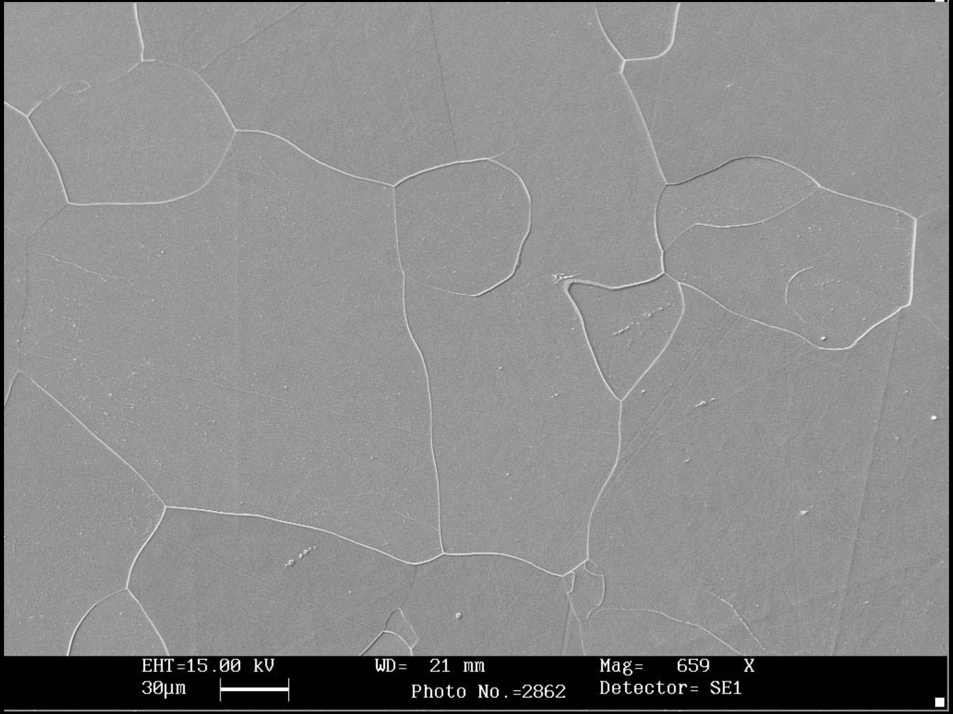
110
211
220
200
900°C, bcc
311
200
111
220
222
950°C, fcc
1.0
1.5
2.0
A

ULC Iron, ESRF, June 2004

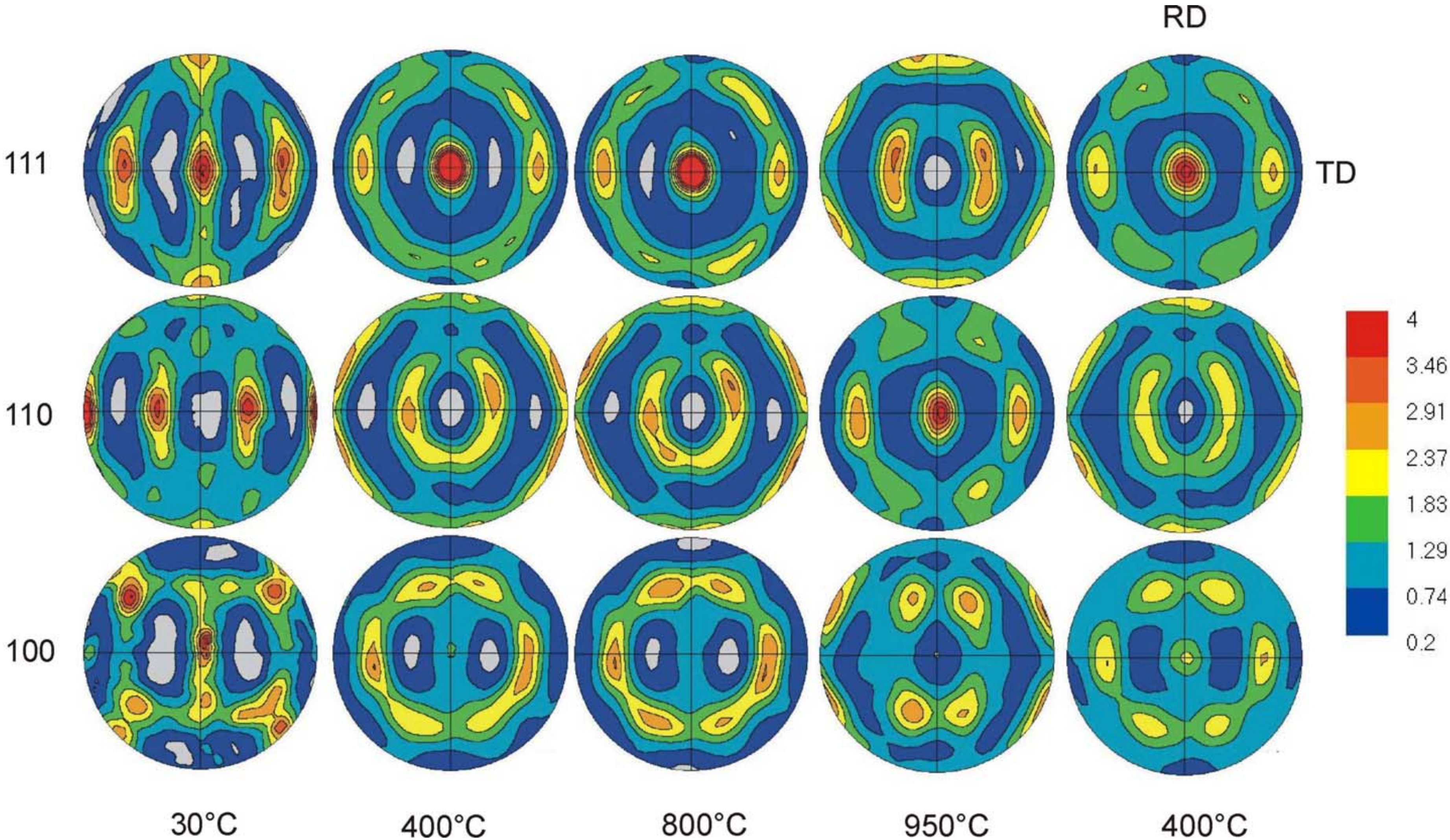




EHT=15.00 kV
10µm
WD= 21 mm
Photo No.=2864
Mag= 1.53 K X
Detector= SE1

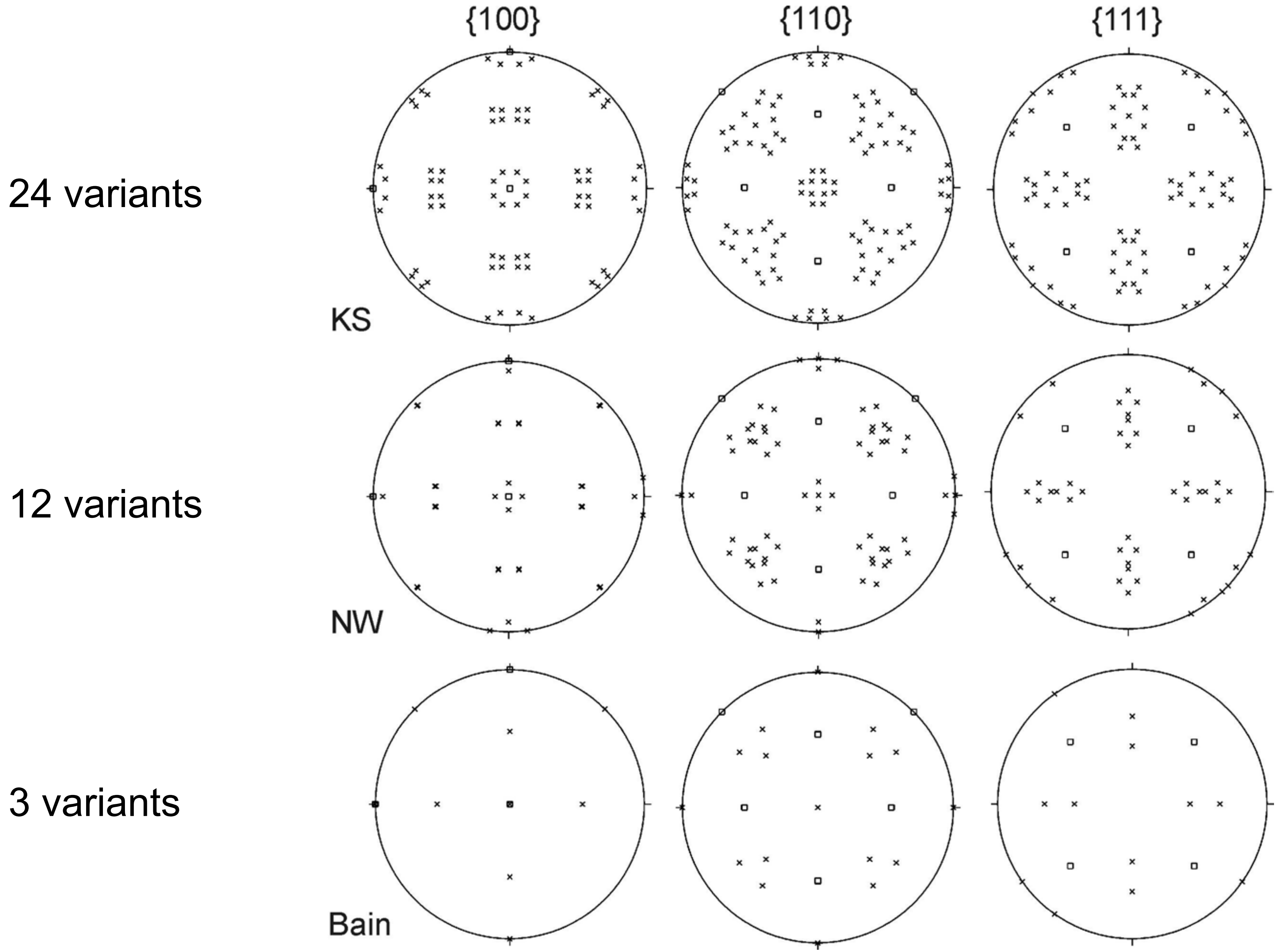


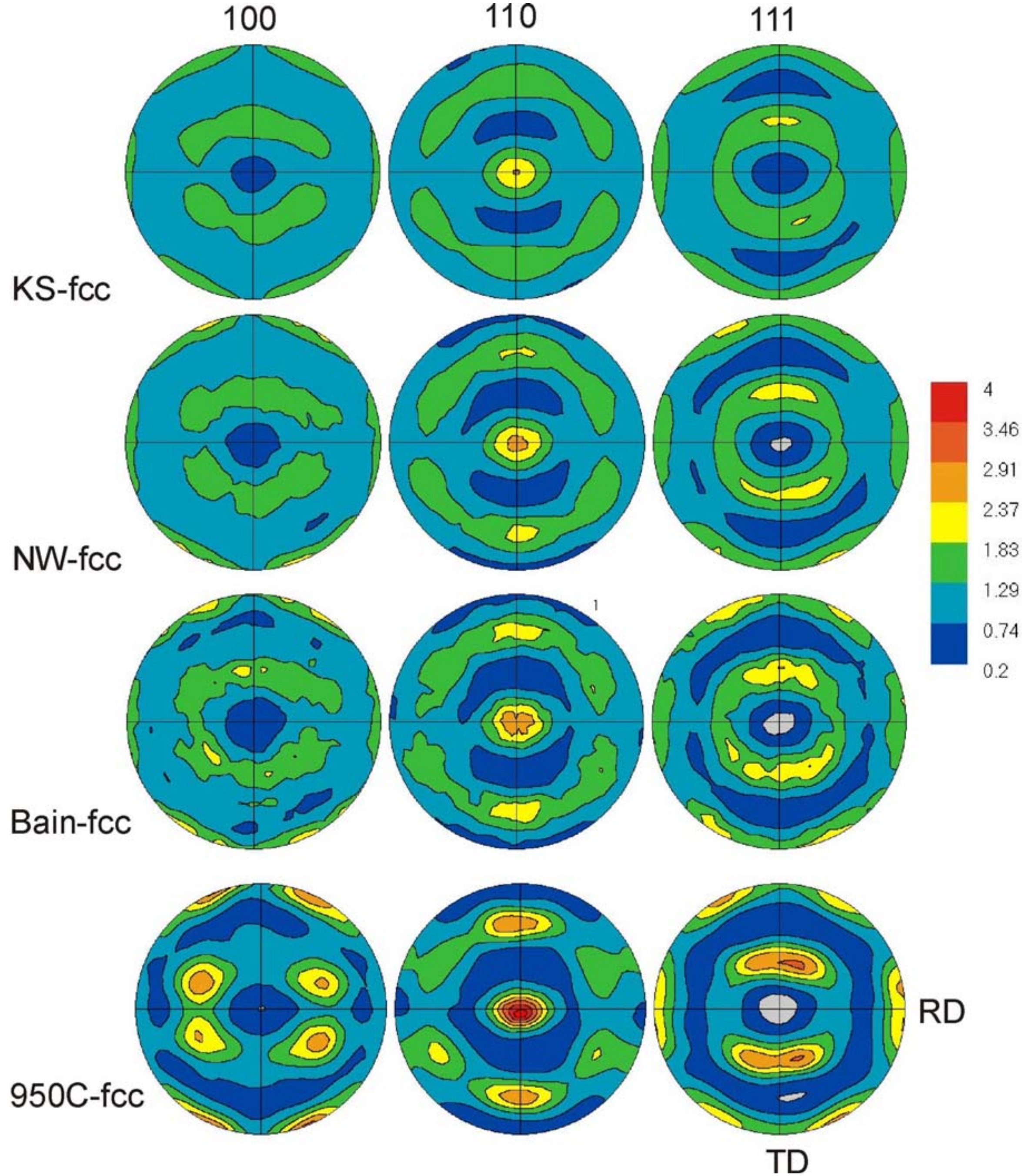
EHT=15.00 kV
30µm
WD= 21 mm
Photo No.=2862
Mag= 659 X
Detector= SE1



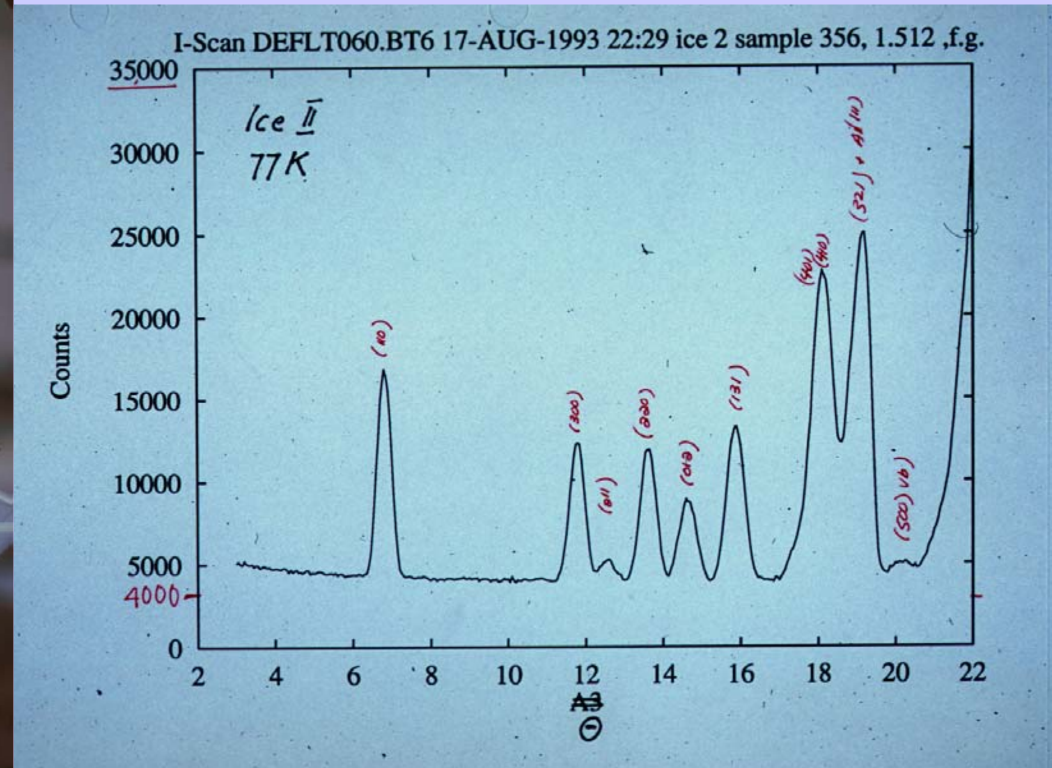
ULC steel, in situ neutron diffraction with HIPPO (LANSCE)

Wenk , Huensche, Kestens Trans. Mat. 2006


{100}
{110}
{111}
24 variants
12 variants
3 variants
KS
NW
Bain

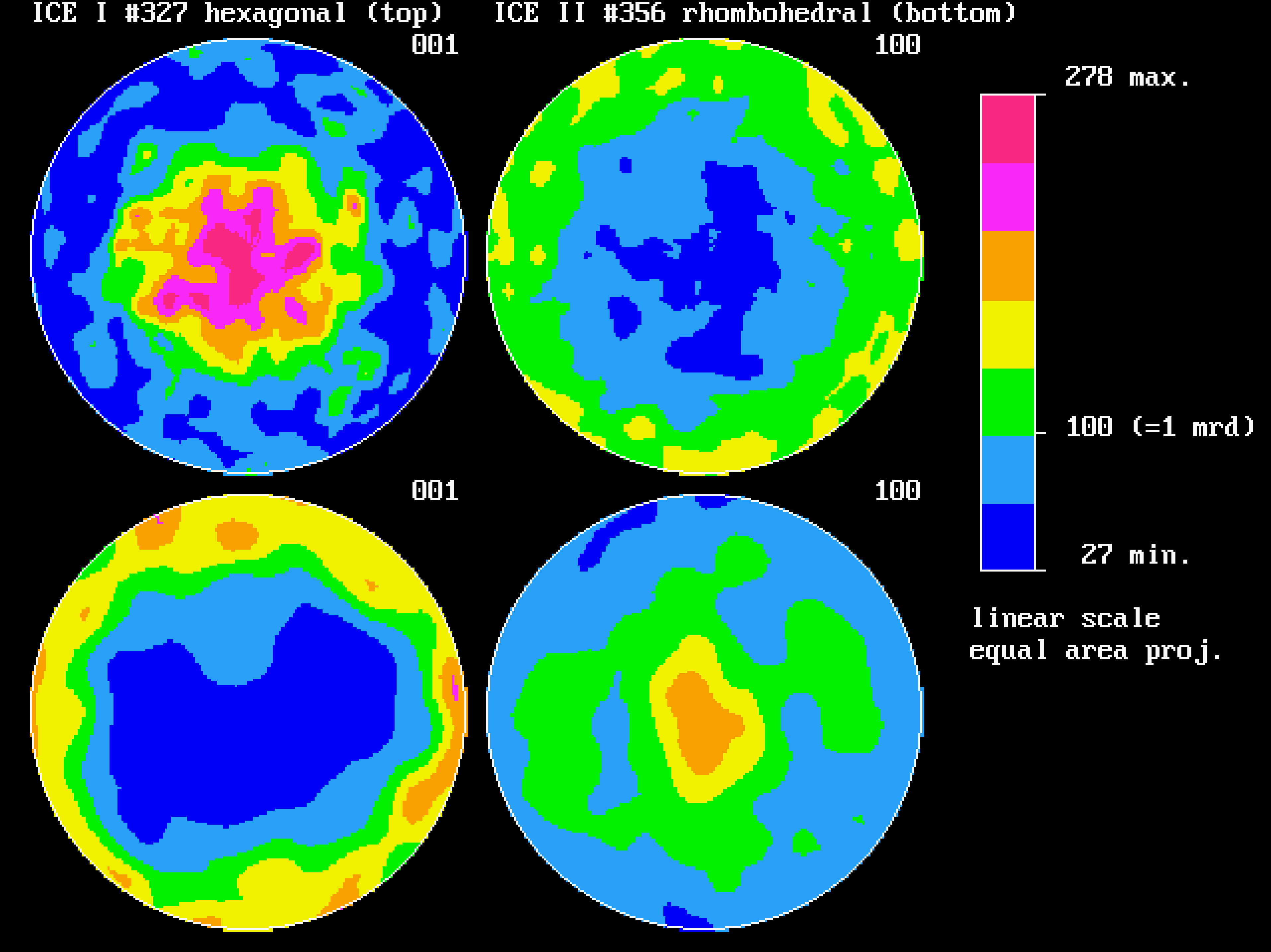

100
110
111
KS-fcc
NW-fcc
Bain-fcc
950C-fcc
4
3.46
2.91
2.37
1.83
1.29
0.74
0.2
RD
TD

ICE



NCD at Lujan

Bennett, Wenk, Durham and Stern (1997) Phil Mag. A76

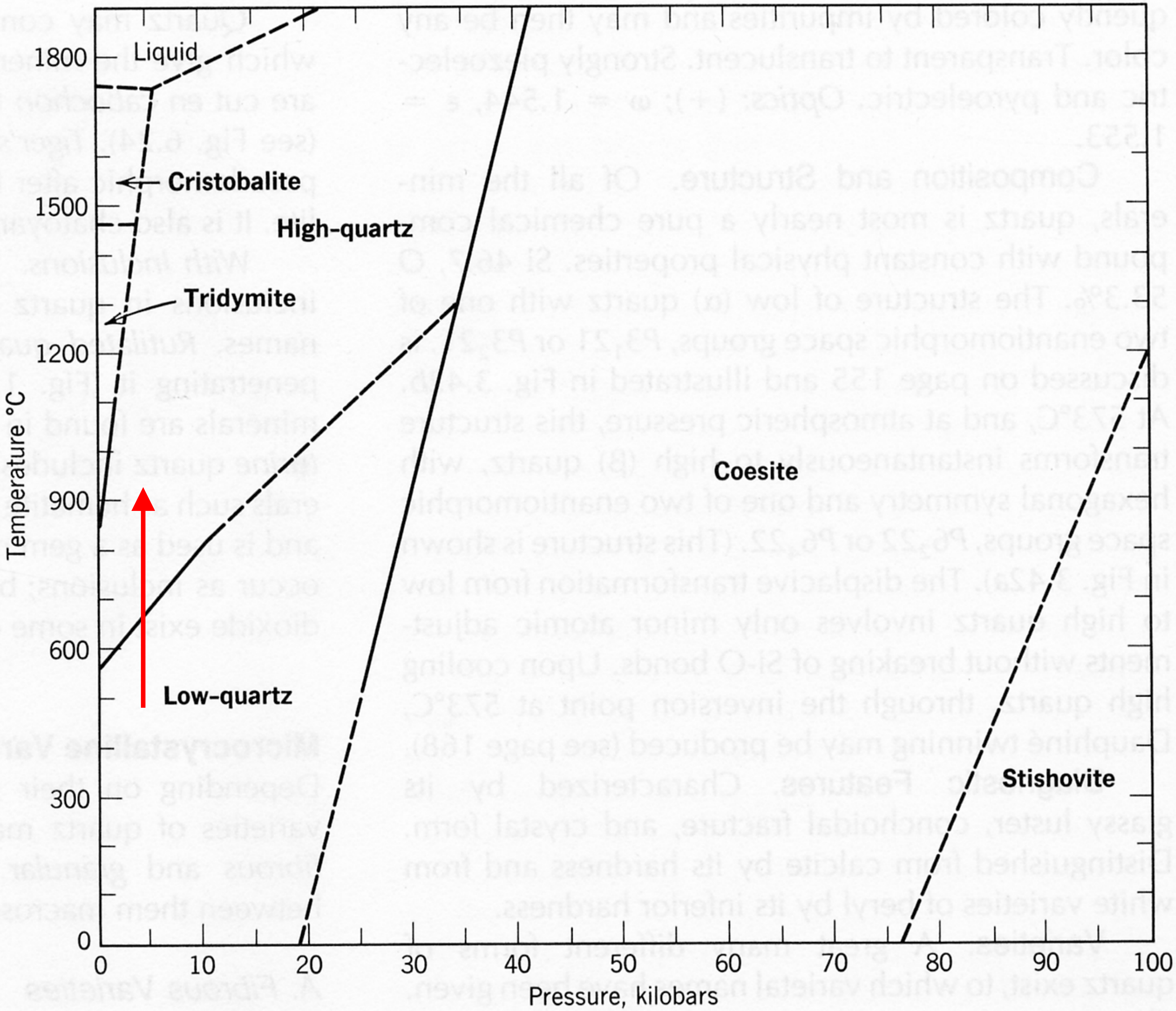


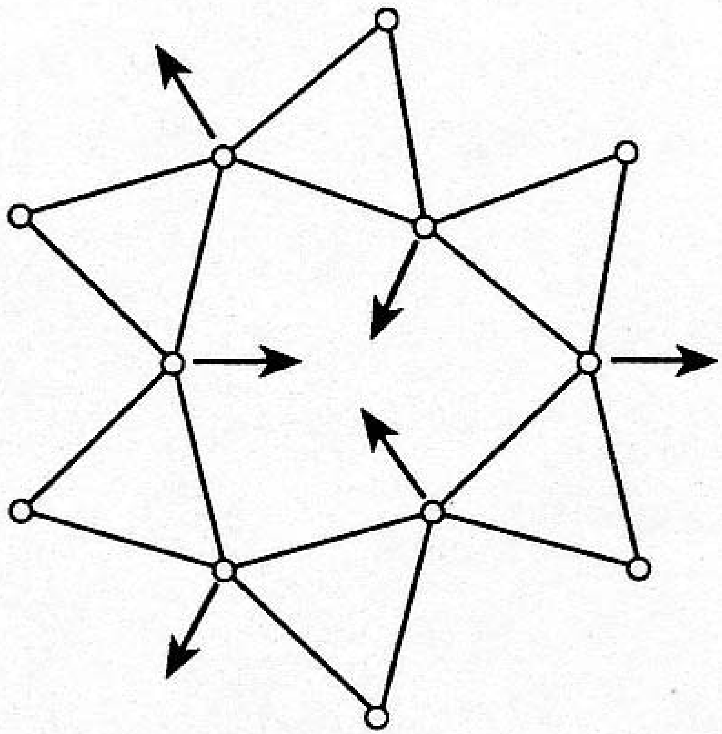
ICE I #327 hexagonal (top)
ICE II #356 rhombohedral (bottom)
001
100
001
100
278 max.
100 (=1 mrd)
27 min.
linear scale
equal area proj.

Quartz

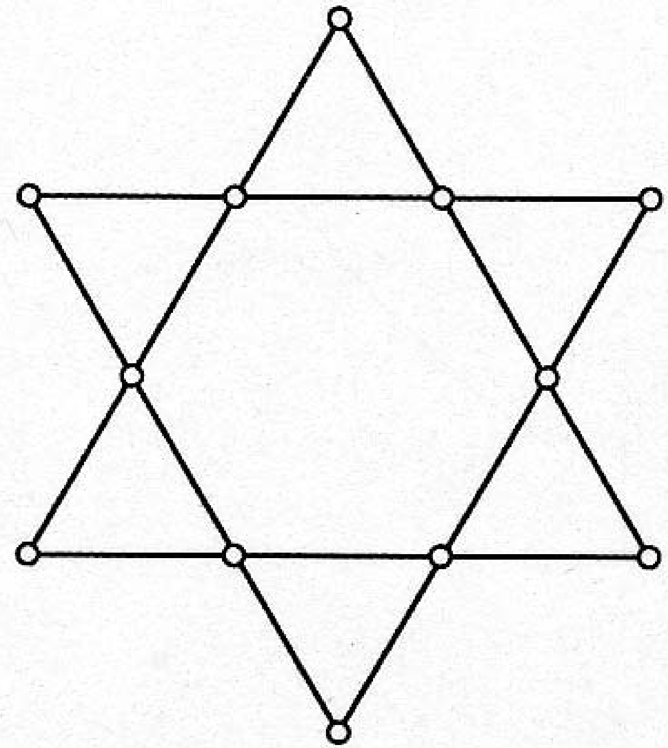
trigonal – hexagonal – trigonal

Texture Memory

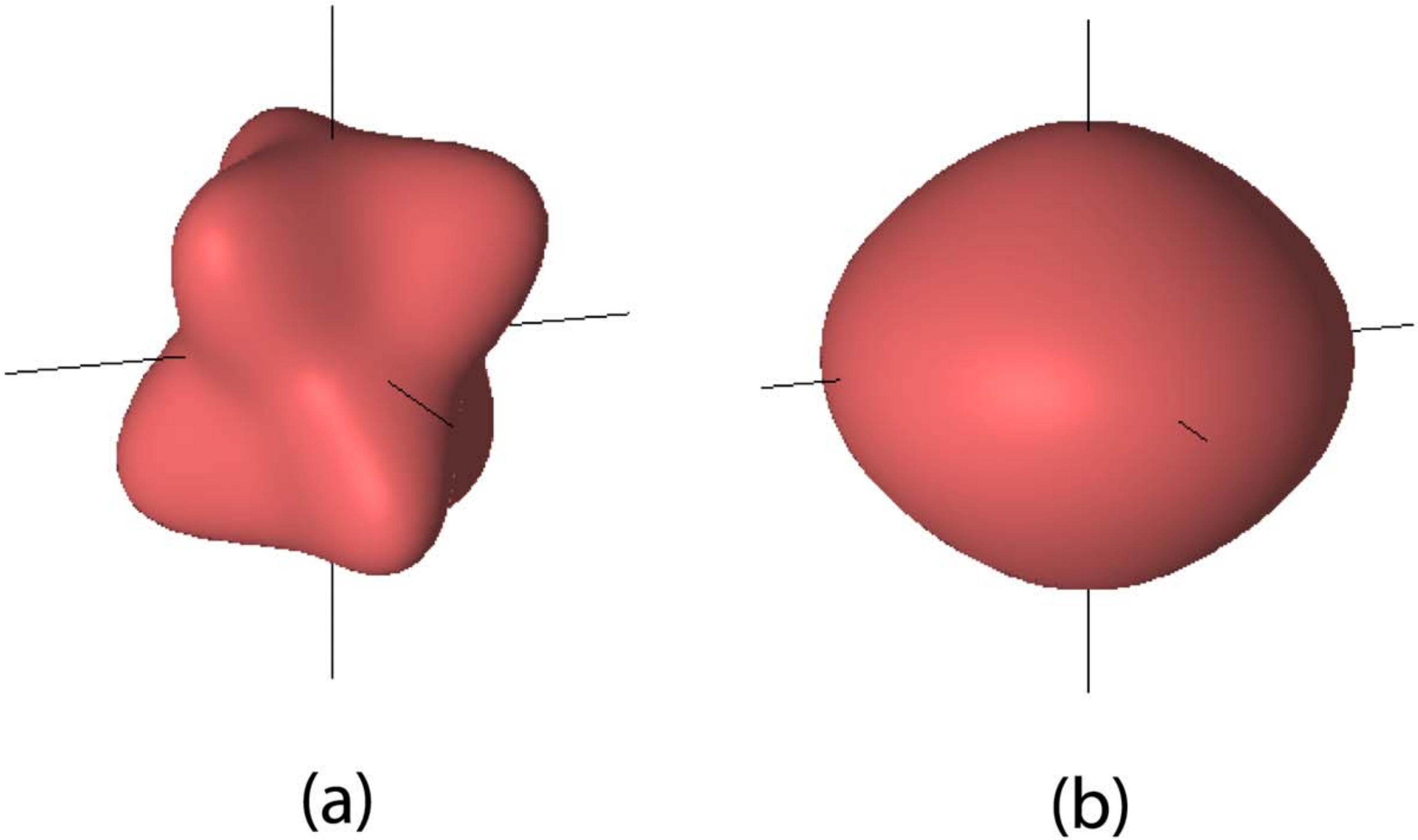

Liquid
Cristobalite
High-quartz
Tridymite
Coesite
Low-quartz
Stishovite
1800
1500
1200
900
600
300
0
0
10
20
30
40
50
60
70
80
90
100
Temperature °C
Pressure, kilobars



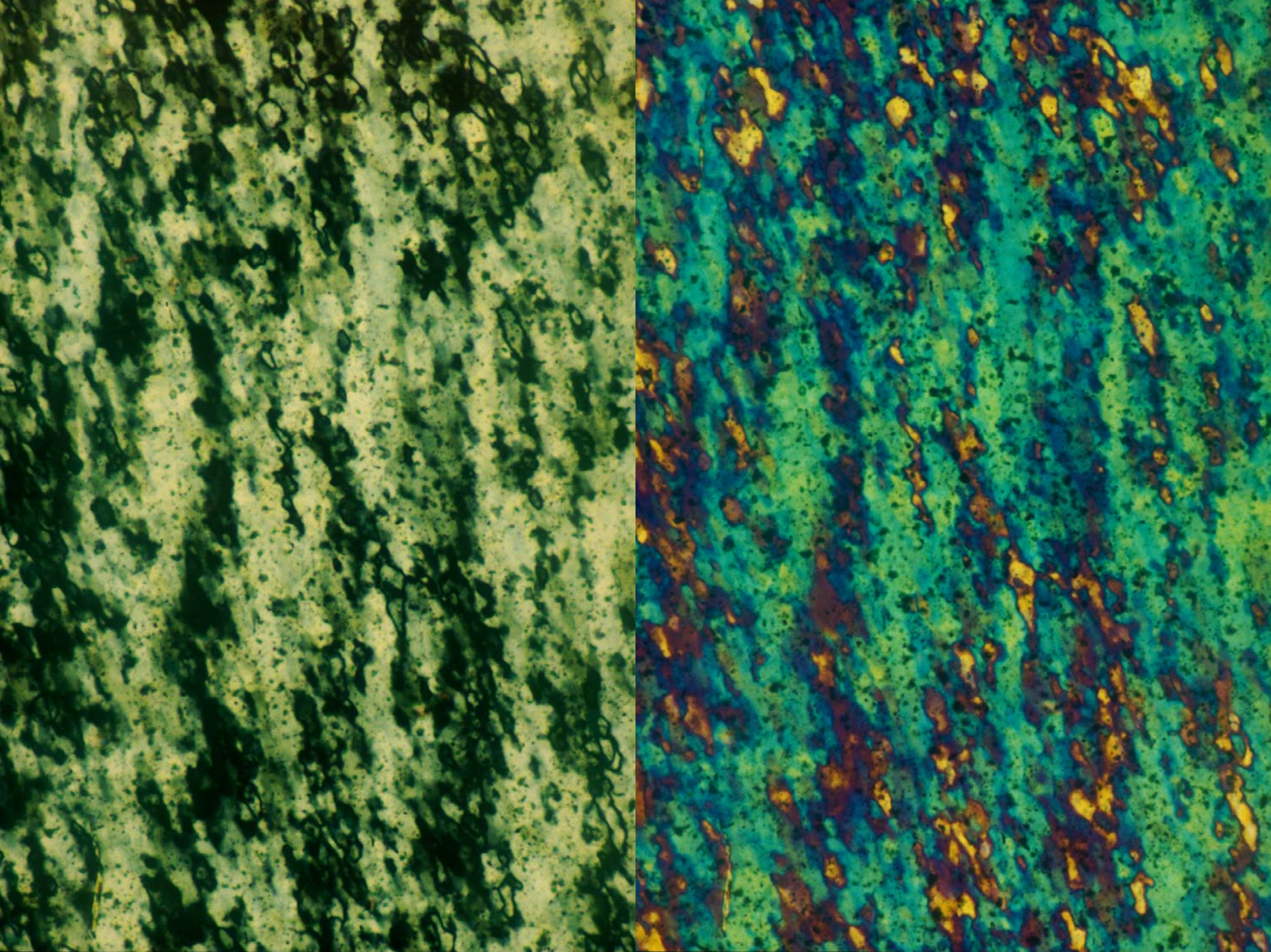
Low quartz (α), trigonal

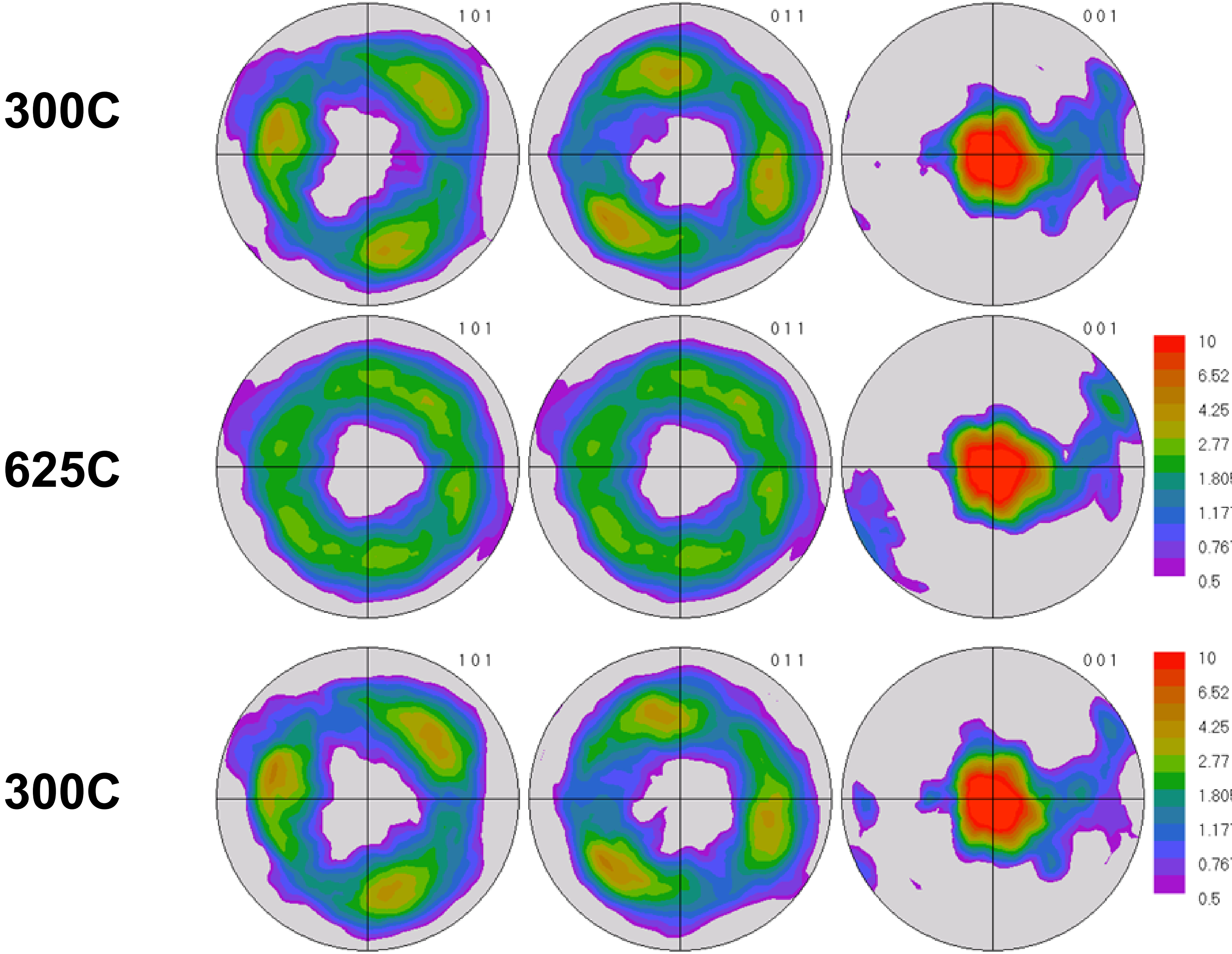


High quartz (β), hexagonal

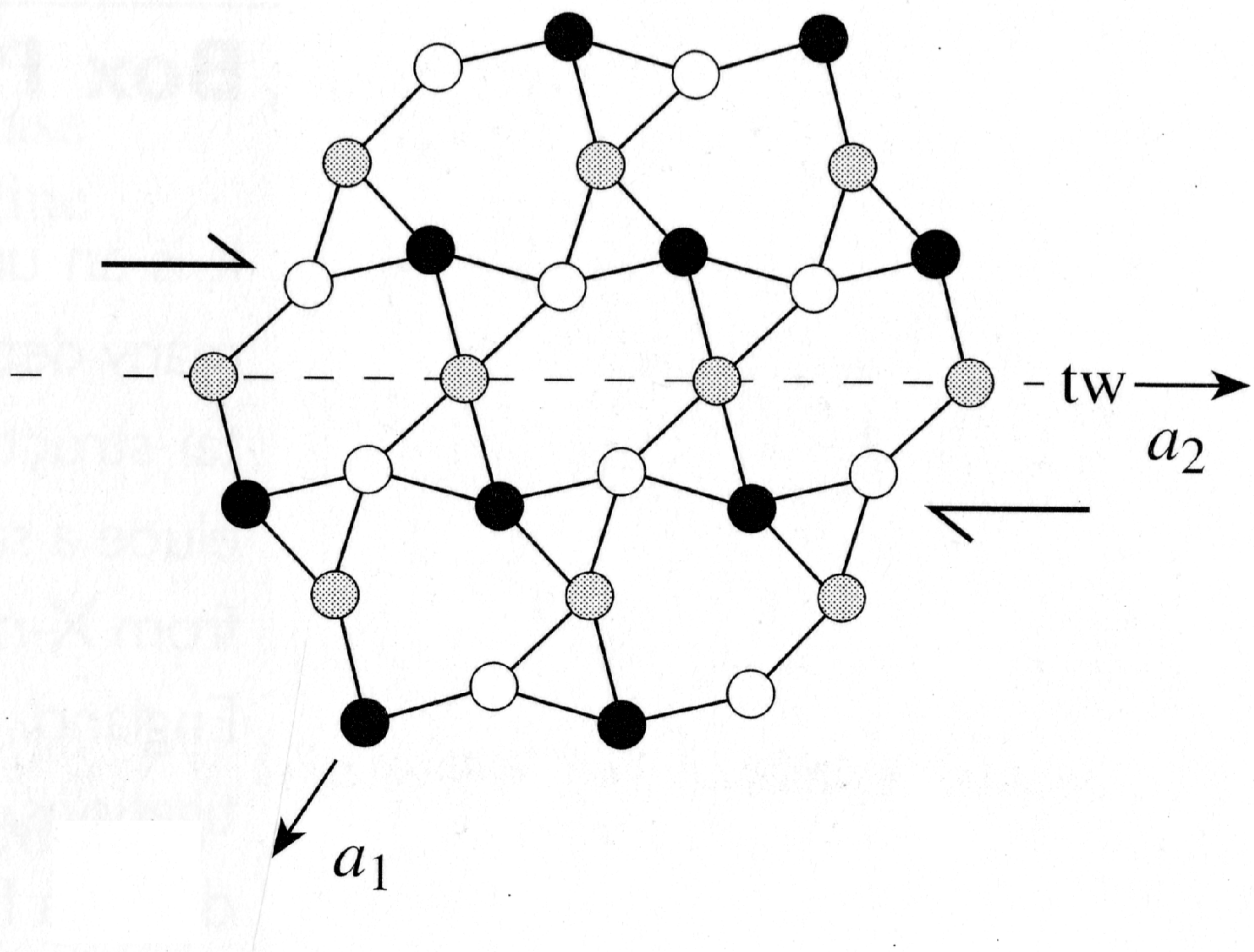


Young's modulus for quartz

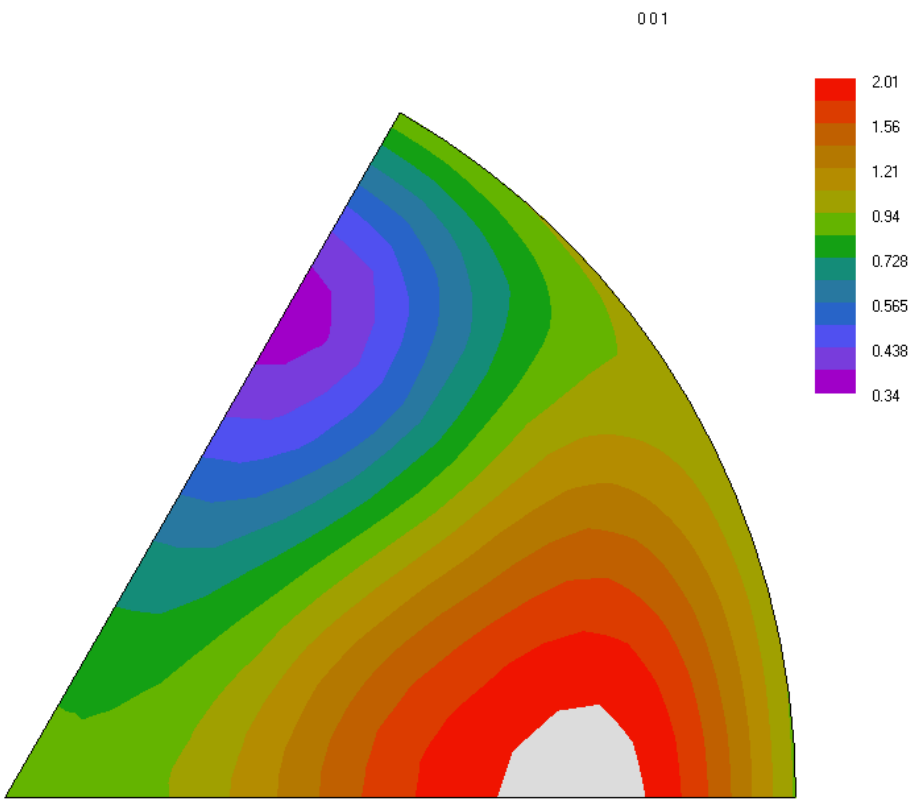


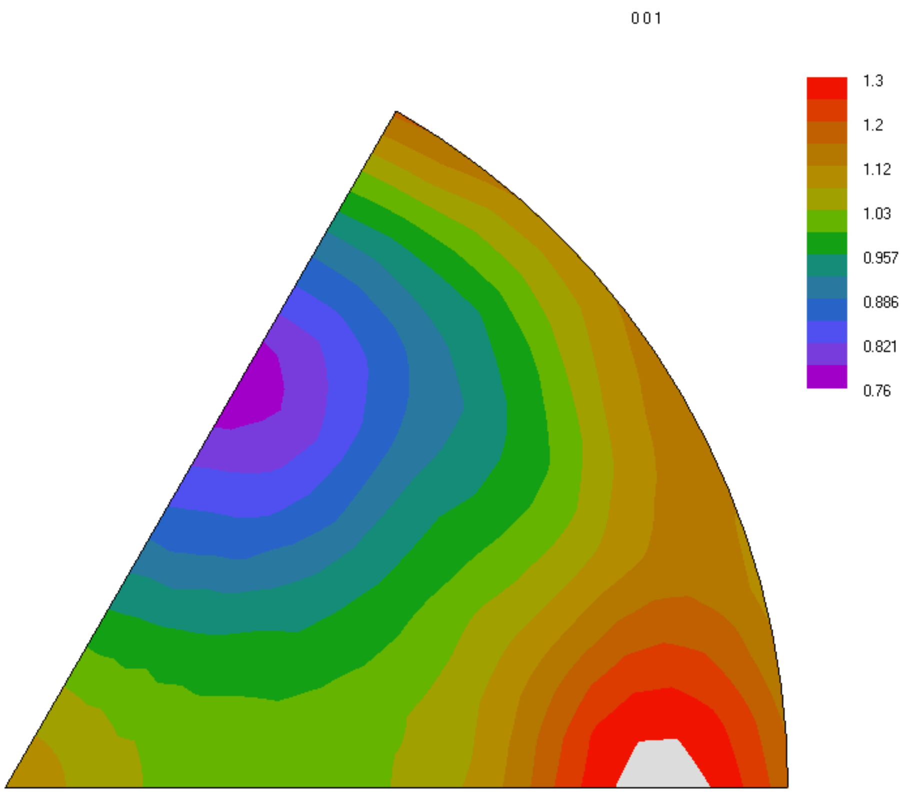


Sci 293 Quartzite mylonite: Texture memory



Mechanical Dauphiné twinning in quartz

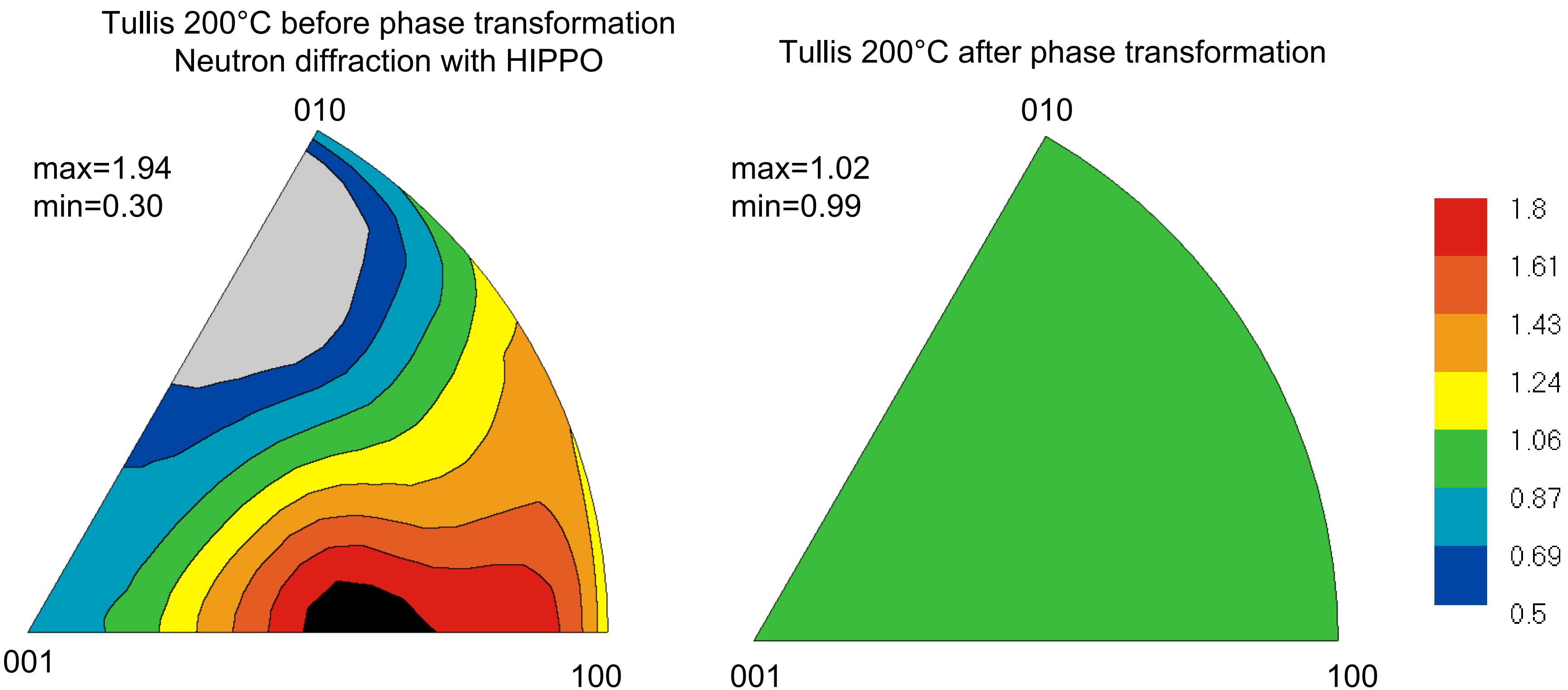




Quartz in compression (Tullis, 1970)

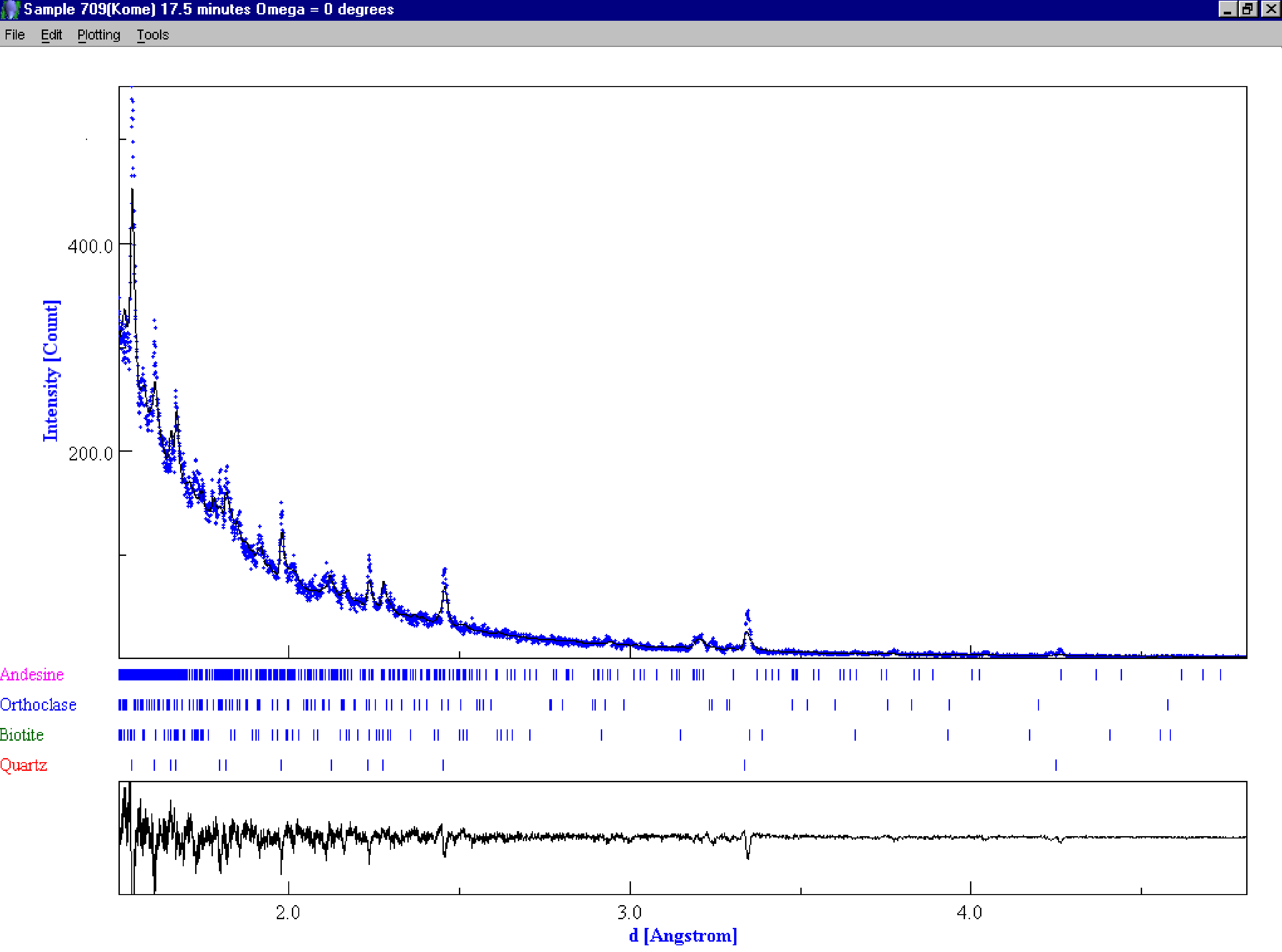
Inverse Young's modulus for quartz

Quartz (Novaculite): IPF before and after heating to 650C, **no texture memory**

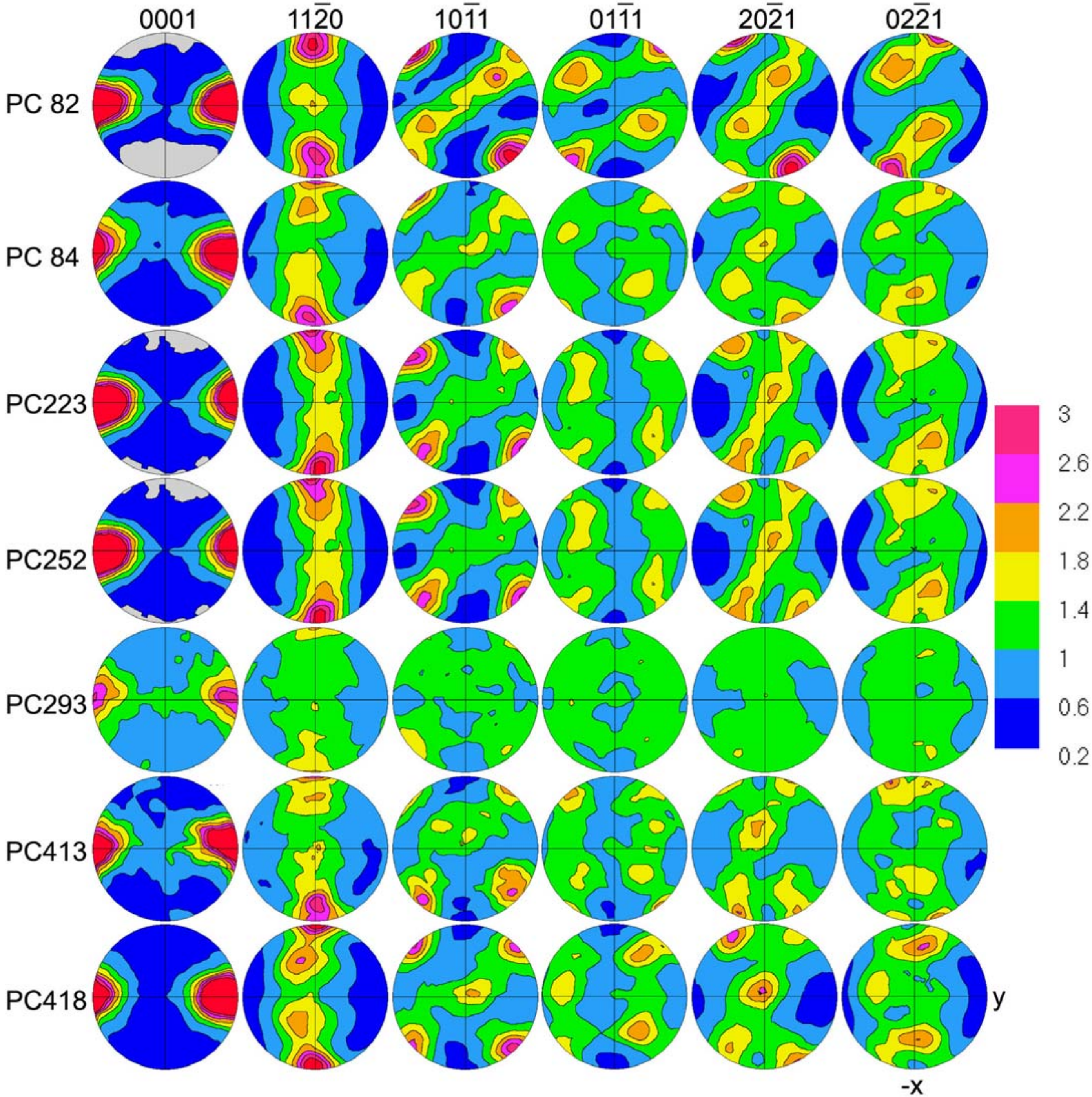


Geological applications

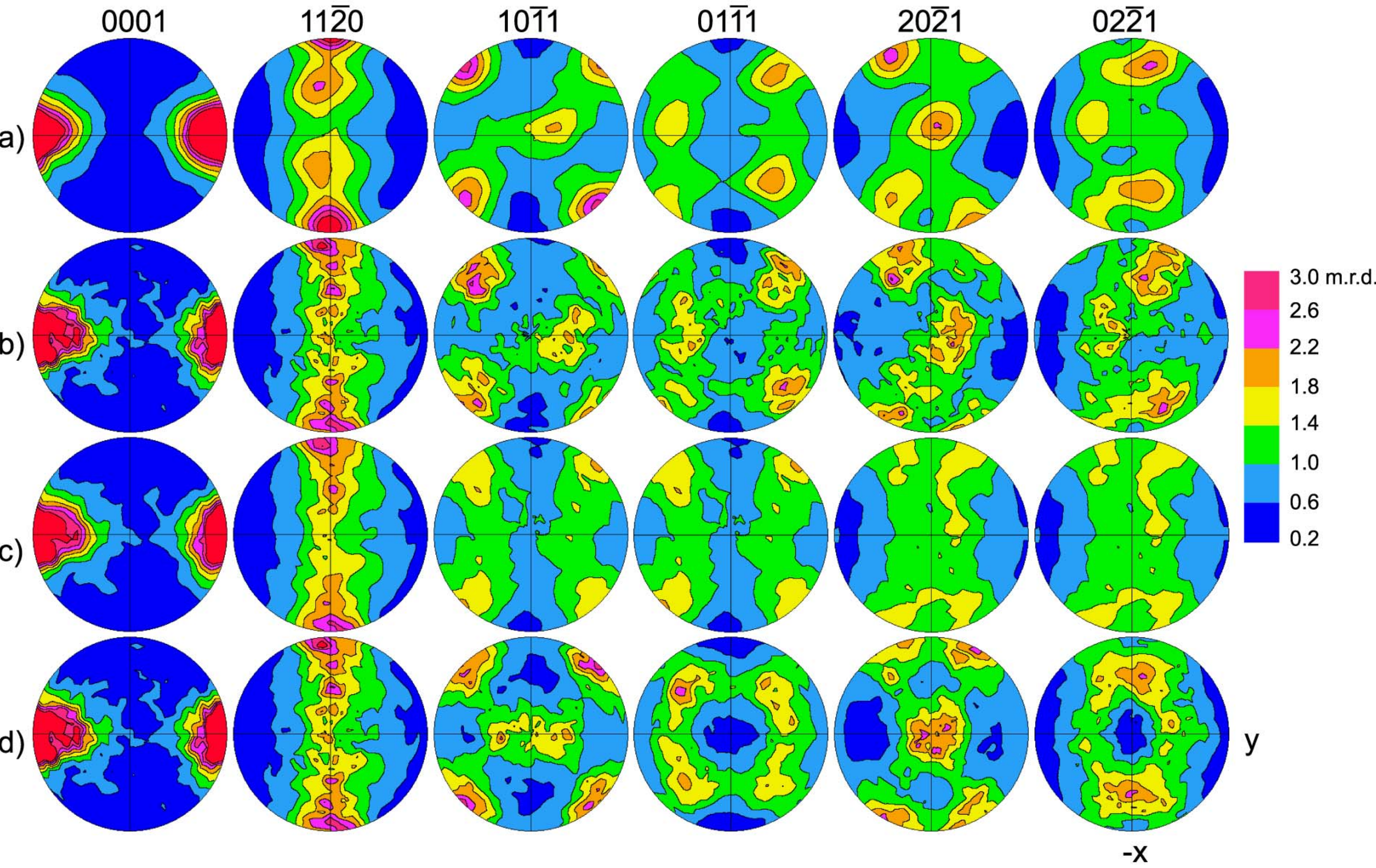
Mechanical twinning in Quartz



Sample 709(Kome) 17.5 minutes Omega = 0 degrees
File
Edit
Plotting
Tools
400.0
200.0
Intensity [Count]
Andesine
Orthoclase
Biotite
Quartz
2.0
3.0
4.0
d [Angstrom]



0001
11$\bar{2}$0
10$\bar{1}$1
01$\bar{1}$1
20$\bar{2}$1
02$\bar{2}$1
PC 82
PC 84
PC223
PC252
PC293
PC413
PC418
3
2.6
2.2
1.8
1.4
1
0.6
0.2
y
-x

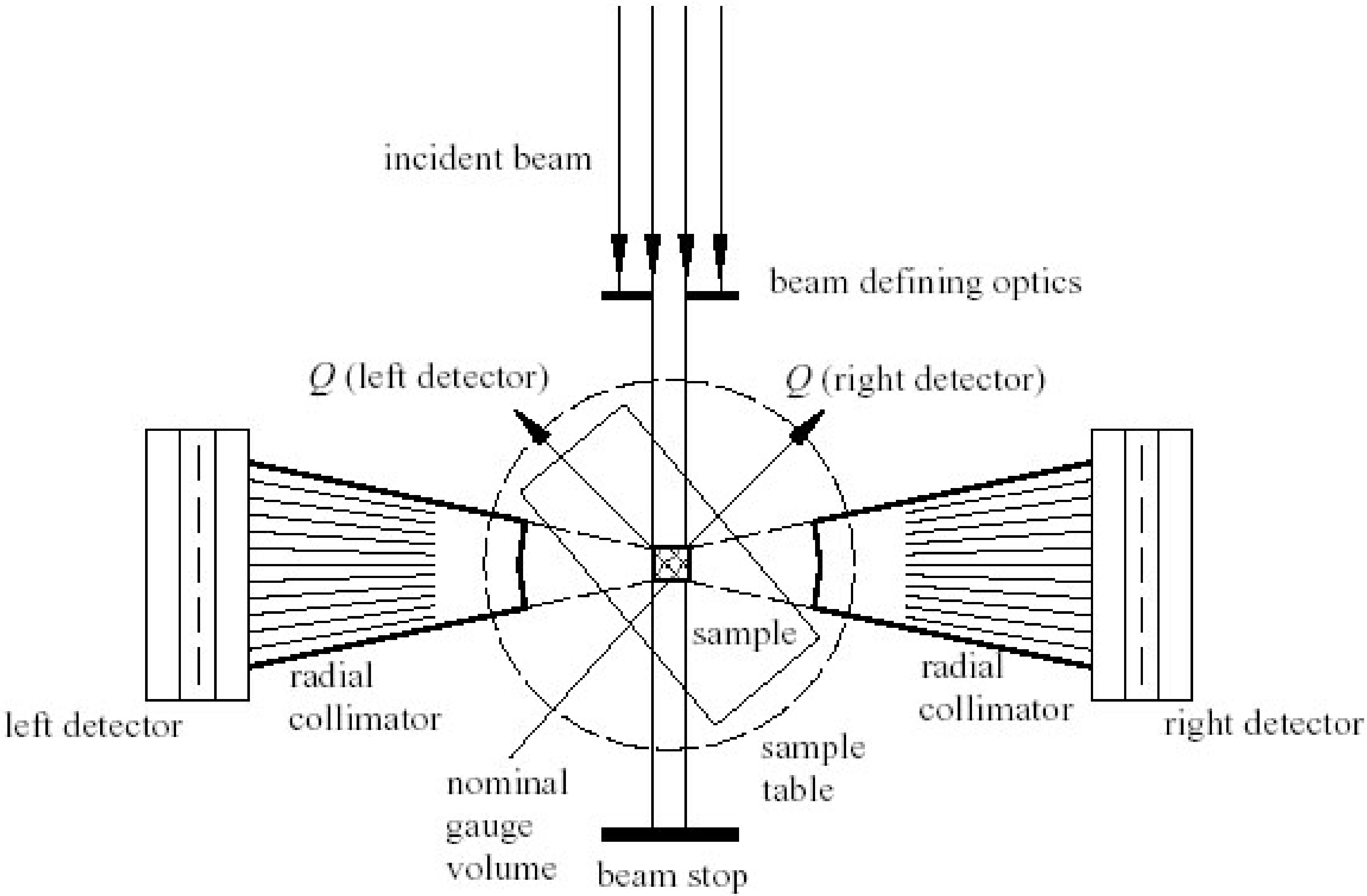


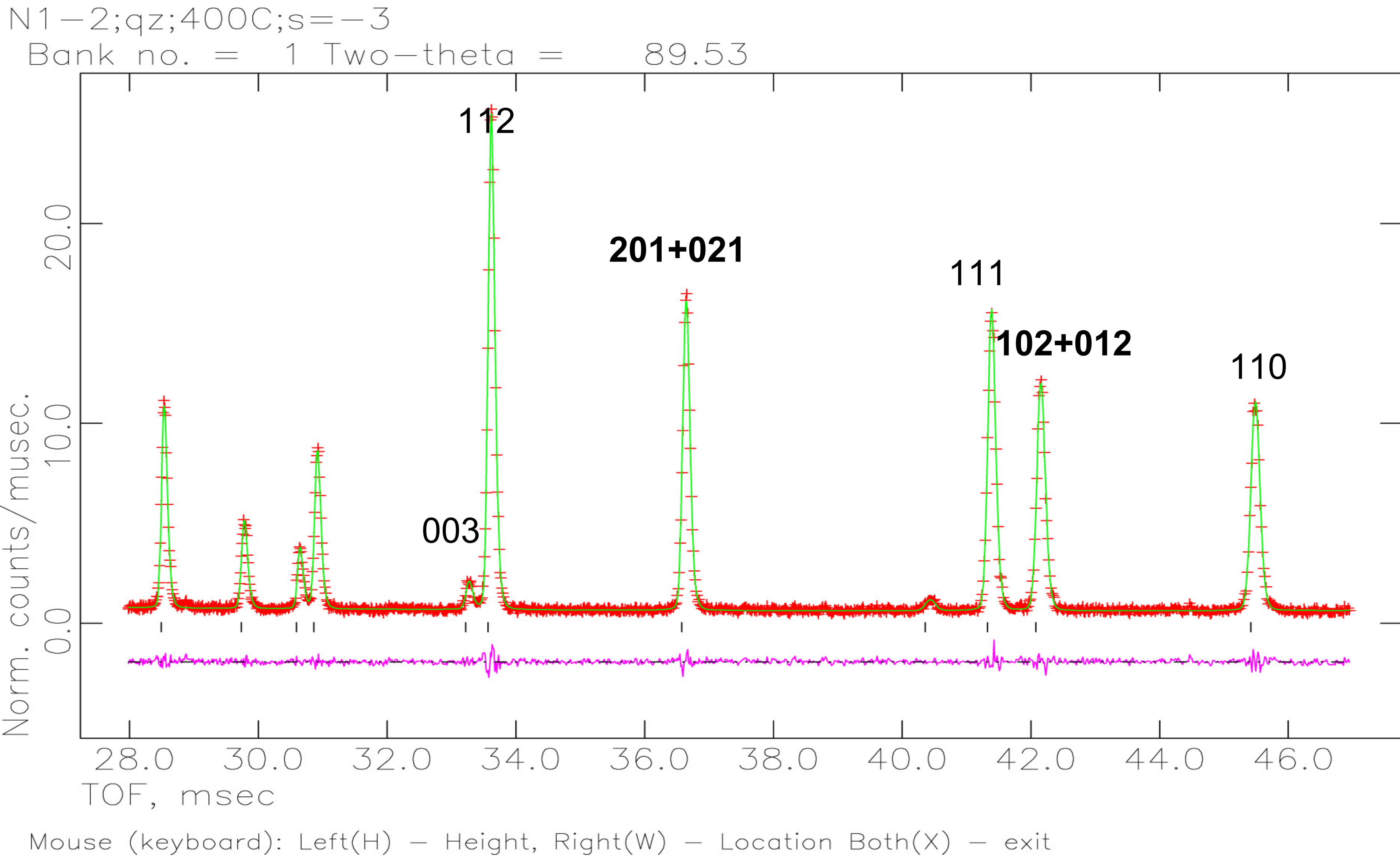
Modeling Dauphiné twinning: A paleo piezometer (Pehl & Wenk, 2005).

In SITU Stressing

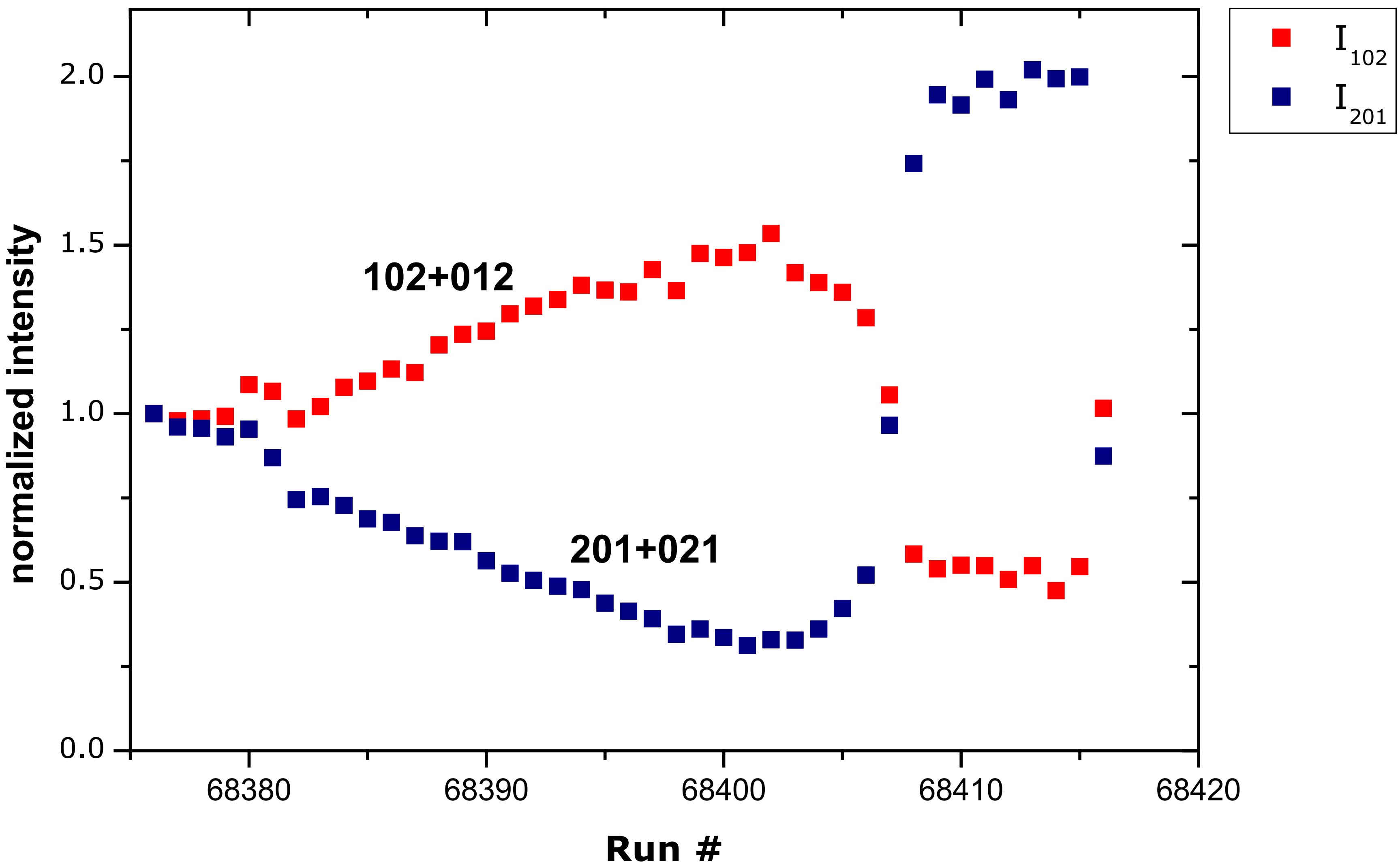
SMARTS, ENGIN-X

ENGIN-X, ISIS

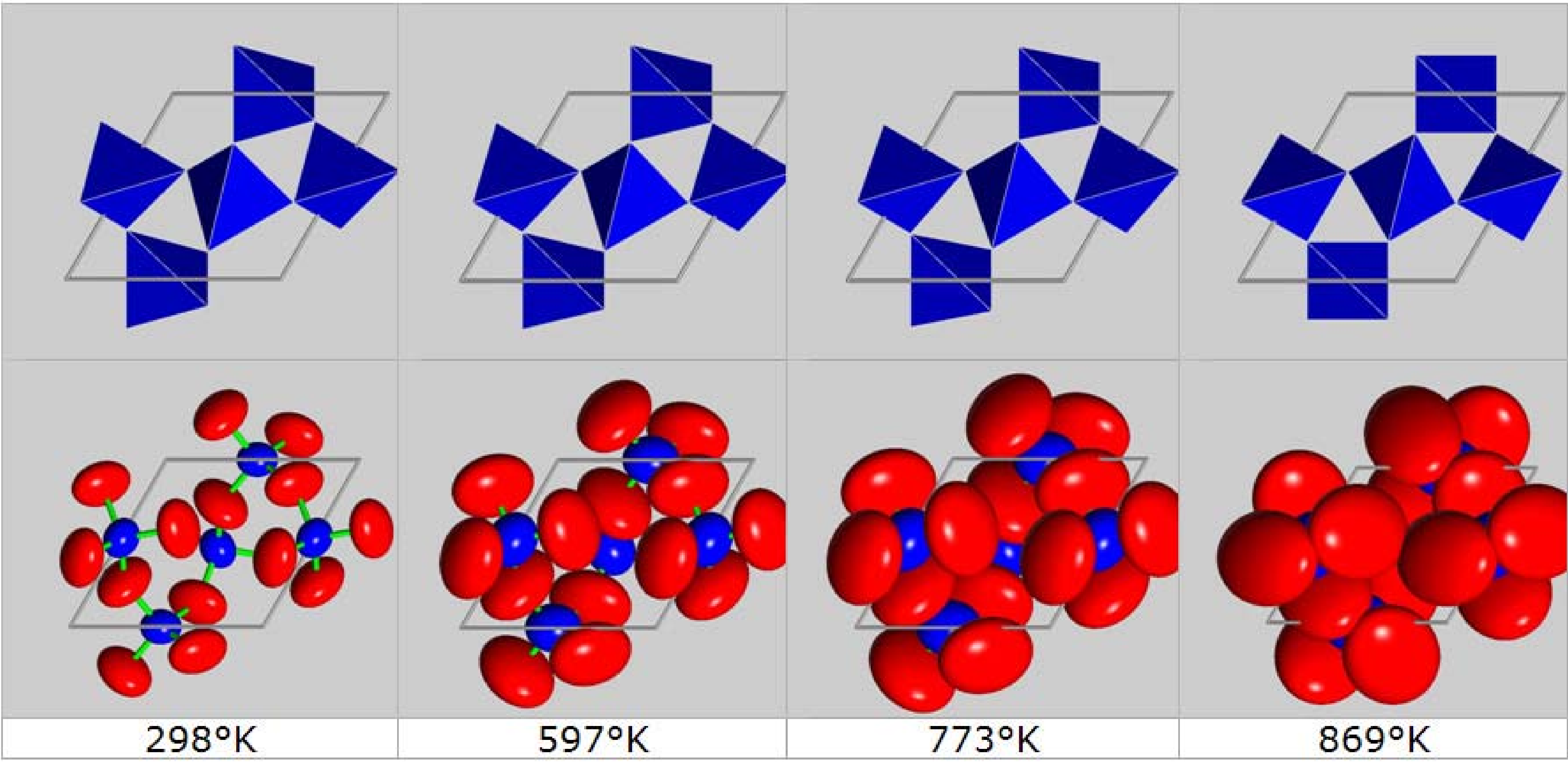

incident beam
beam defining optics
Q (left detector)
Q (right detector)
sample
radial
collimator
left detector
radial
collimator
right detector
nominal
gauge
volume
sample
table
beam stop



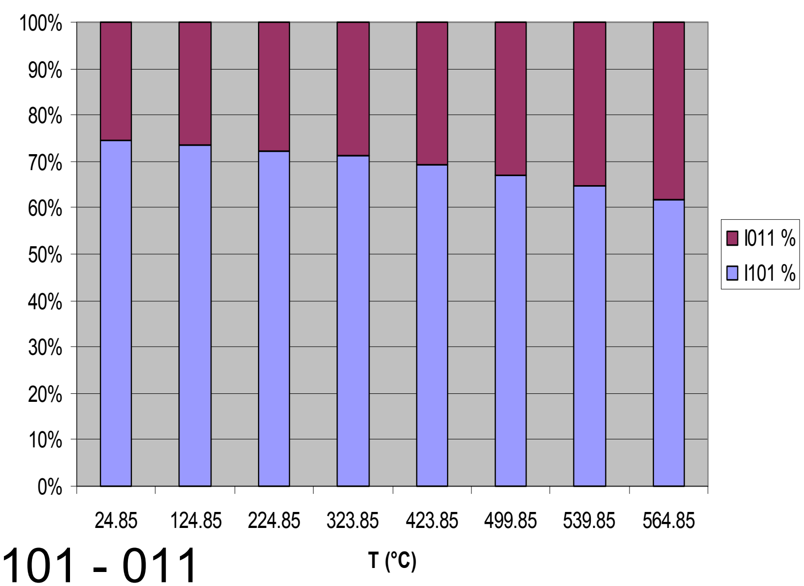
N1-2;qz;400C;s=-3
Bank no. = 1 Two-theta = 89.53
112
201+021
111
102+012
110
003
20.0
10.0
0.0
Norm. counts/musec.
28.0
30.0
32.0
34.0
36.0
38.0
40.0
42.0
44.0
46.0
TOF, msec
Mouse (keyboard): Left(H) - Height, Right(W) - Location Both(X) - exit



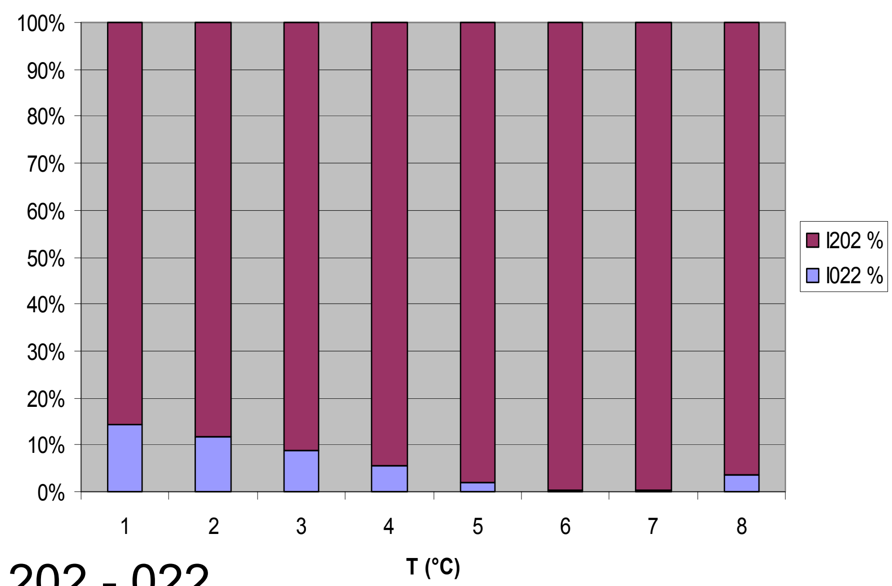
$$I=N\{(1+m)F_{h0l}^2+(1-m)F_{0hl}^2\}$$


298°K
597°K
773°K
869°K

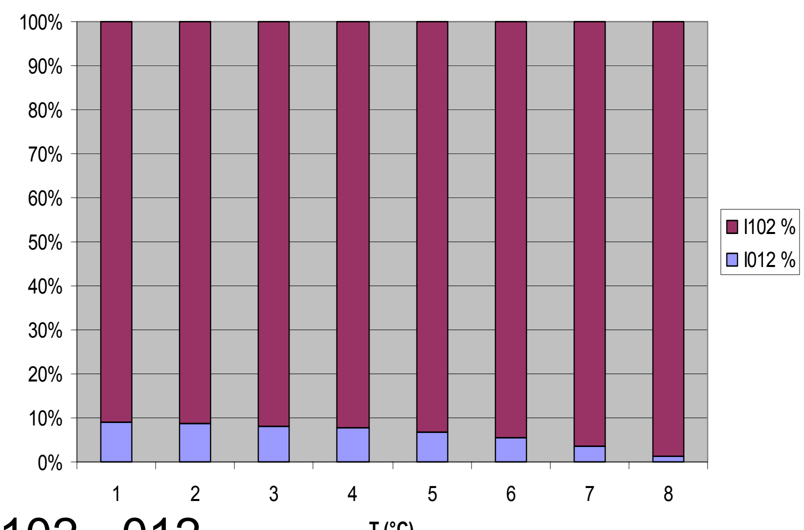
$$100\% = N\,(F_{h0l}^2 + F_{0hl}^2)$$



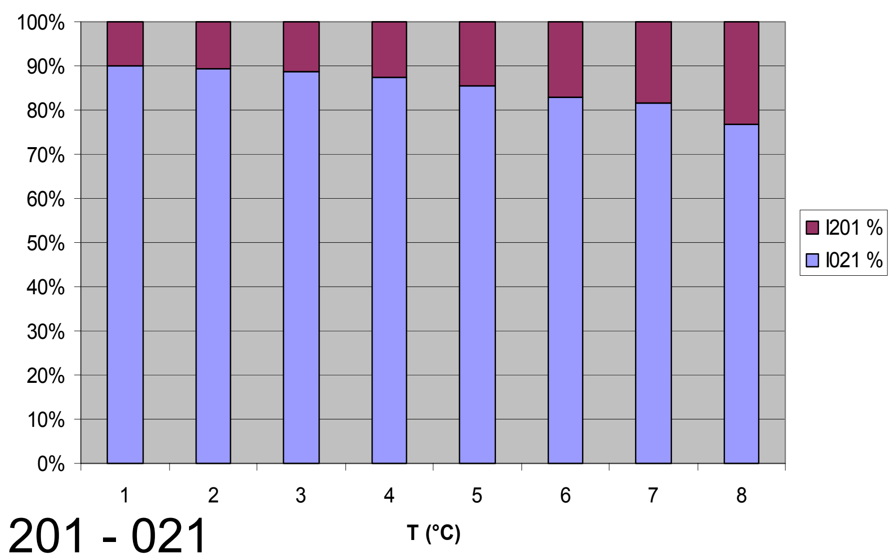
101 - 011



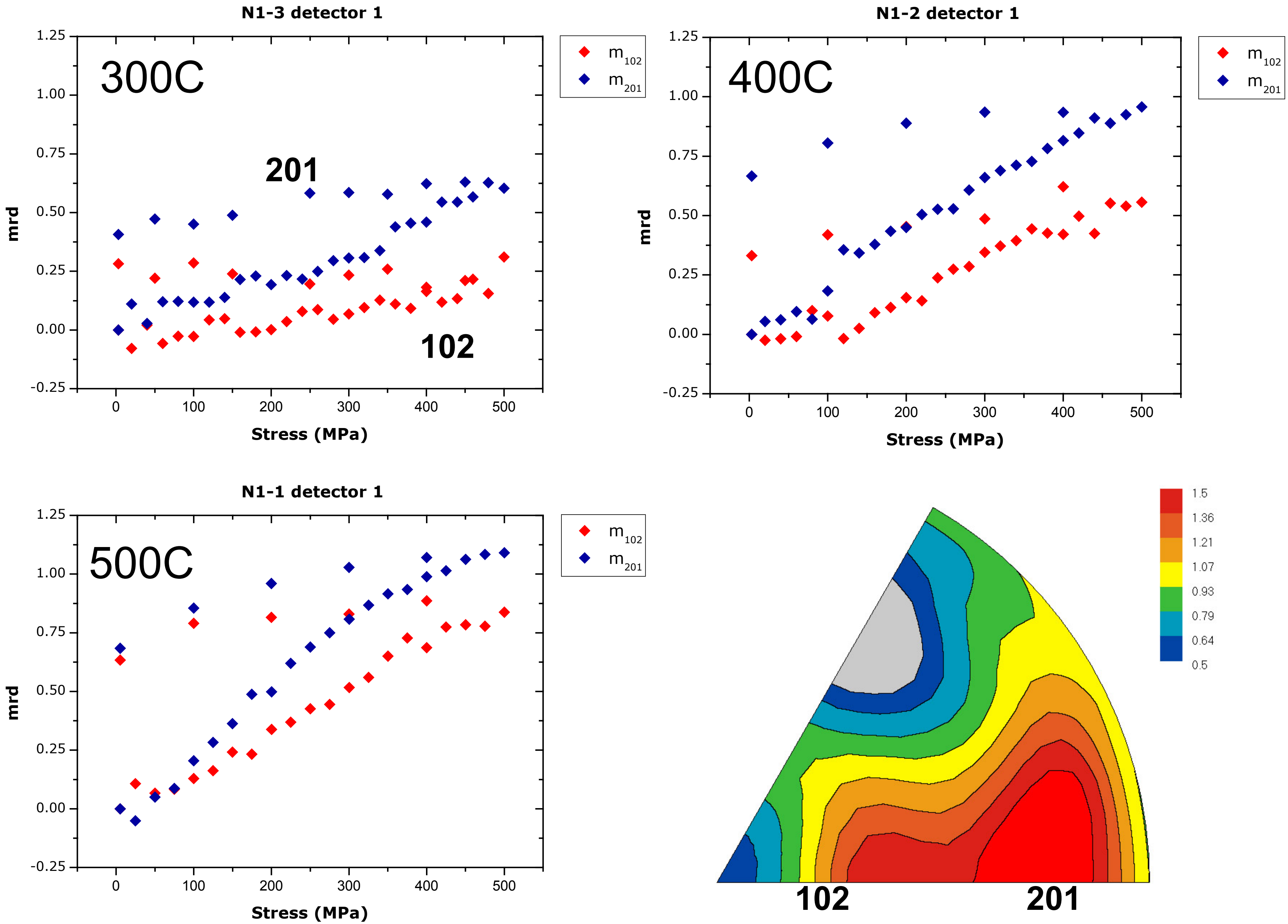
202 - 022



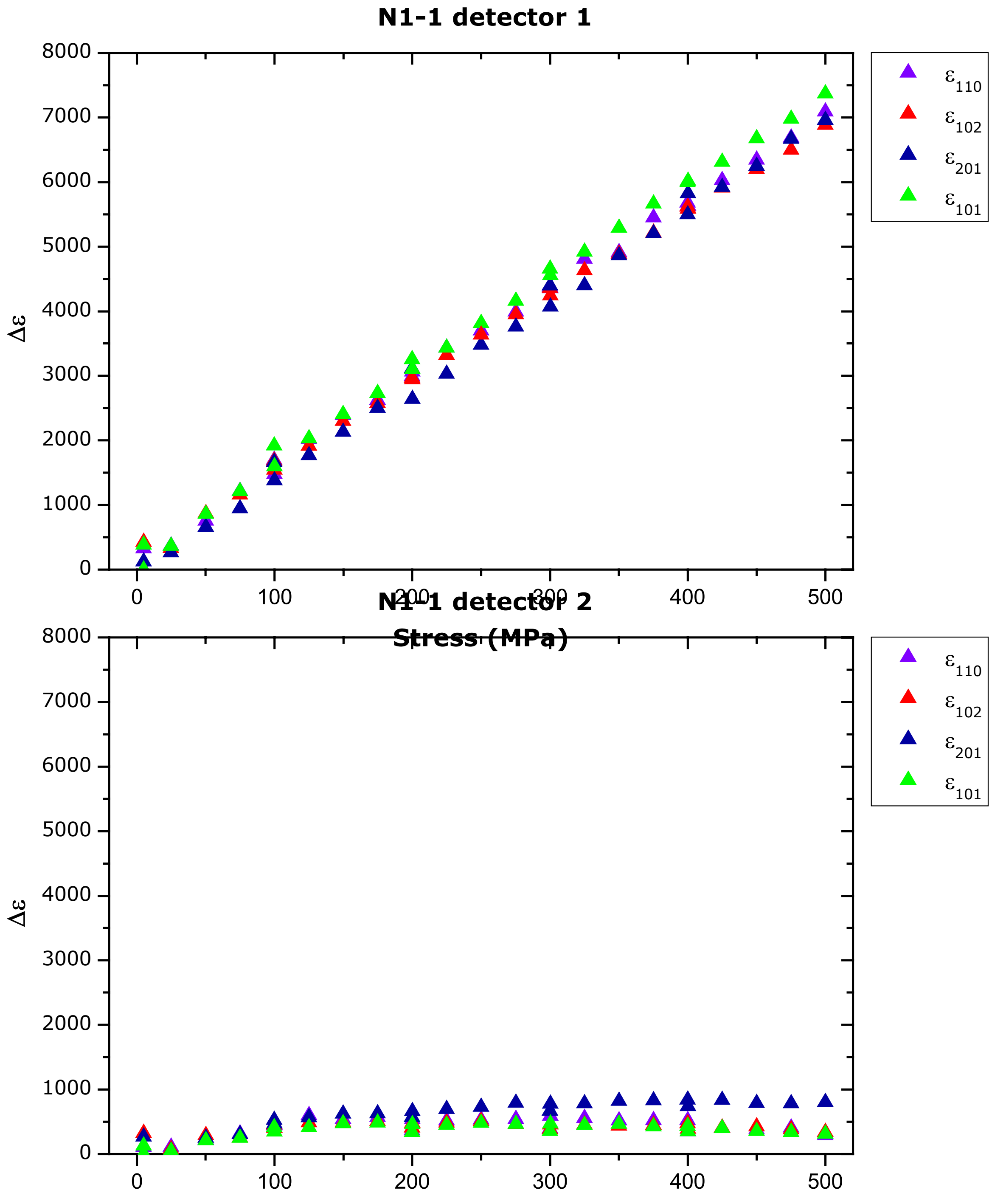
102 - 012



201 - 021



N1-3 detector 1
300C
201
102
mrd
Stress (MPa)
m_{102}
m_{201}
N1-2 detector 1
400C
mrd
Stress (MPa)
m_{102}
m_{201}
N1-1 detector 1
500C
mrd
Stress (MPa)
m_{102}
m_{201}
1.25
1.00
0.75
0.50
0.25
0.00
-0.25
0
100
200
300
400
500
1.5
1.36
1.21
1.07
0.93
0.79
0.64
0.5
102
201



N1-1 detector 1
Δε
Stress (MPa)
ε110
ε102
ε201
ε101
N1-1 detector 2
Δε
ε110
ε102
ε201
ε101

Neutron Diffraction

Main advantages:

- Low absorption (bulk samples, good statistics vs. EBSD, environmental cells: P, T, σ)
- High spectral resolution for composites and low symmetry compounds, no defocusing (Rietveld method)

Main disadvantages:

- Weak scattering
- Complex data processing
- Limited access

Conclusions

- **Neutron diffraction an increasingly used method for quantitative texture analysis.**
- **Neutron diffraction for in situ experiments p, T, σ.**
- **Time-resolved experiments to investigate kinetics.**
- **Neutron diffraction to determine residual strain.**
- **An exciting prospect for students in earth sciences.**