Structural Studies at High Pressures and High Temperatures using High Energy X-ray Powder Diffraction

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- Why?
- How?
  - Technical Developments
- Results of some challenging materials
  - Anhydrite, Dolomite
- Preliminary results on modeling total scattering
  - Quantitative PDF from analysis of total scattering from DAC
- Collaborators: Sytle Antao, Dave Martin, Stony Brook; Wilson Crichton, Grenoble; Peter Chupas, Peter Lee & Savjit Shastri, APS, Argonne
- Support NSF-EAR

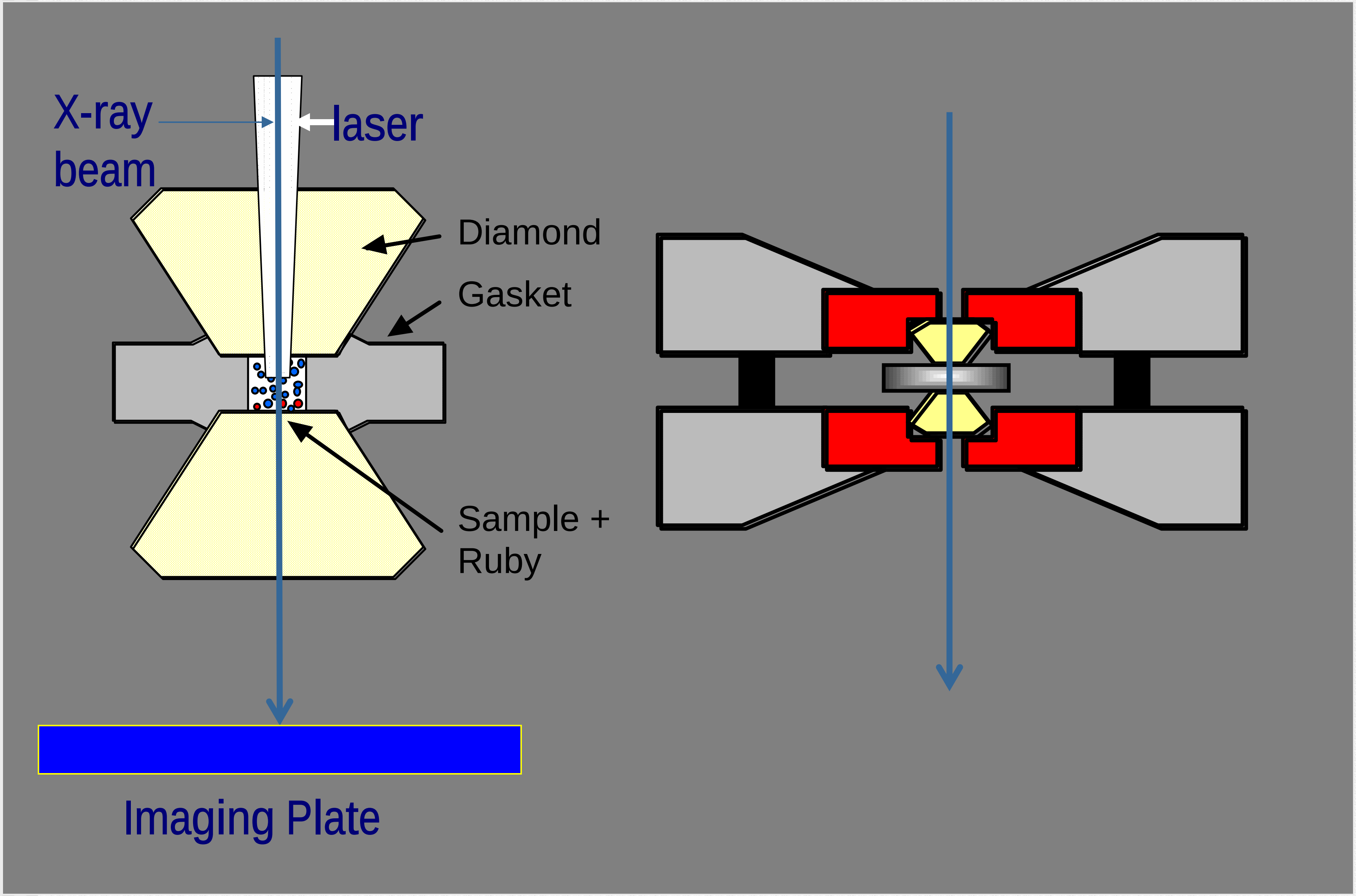
high energy?

- Science: Order-disorder affects thermodynamic and physical properties (think dielectric loss, oxygen ordering in superconductors, Al/Si ordering in silicates)
- Pressure: Competition between entropic gain (disorder) and cases where pressure favors ordering
  - High PT studies relevant to planetary and novel materials
- *In Situ:* State of order in quench sample?
  - protocols for *in situ* diffraction data collection now established
  - Kinetic studies might provide activation energies and

How? Accurate crystallographic studies at high PT

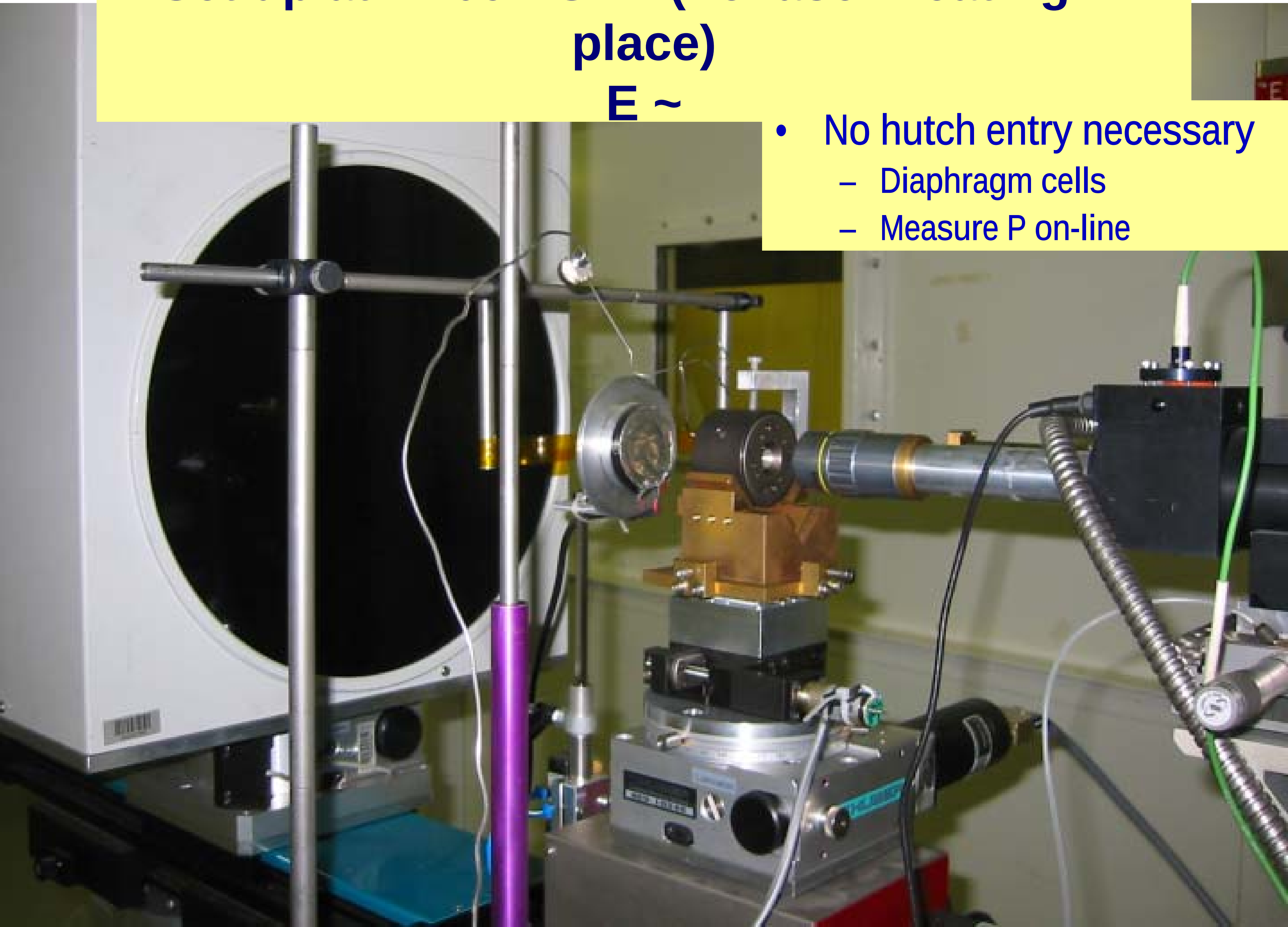
- *Versatile beamlines designed for*
  - (A) Reconnaissance - rapid survey of phase space
  - (B) Accurate structures - *f*(P,T,*t*) (kinetics)
- *Pressure Cells*
  - *Opposed anvil devices*
    - *Diamond cell*
    - *Large volume devices*

(A) Example of Reconnaissance study at Hi-PT - Laser heated DAC (diamond anvil cell) study of $CaSO_4$ (anhydrite)



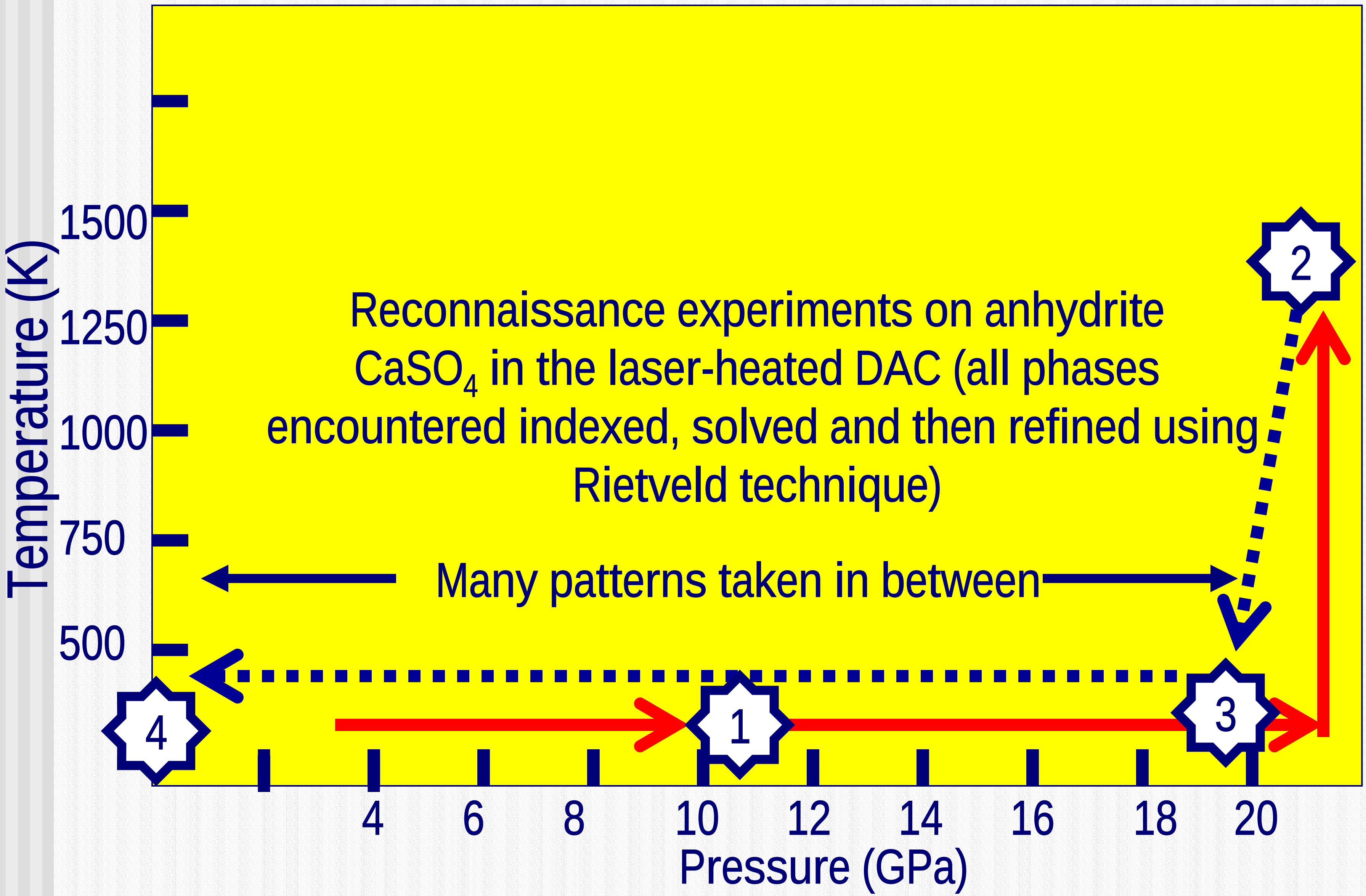
Set up at ID-09 ESRF (no laser heating in place)
E ~

- No hutch entry necessary
  - Diaphragm cells
  - Measure P on-line

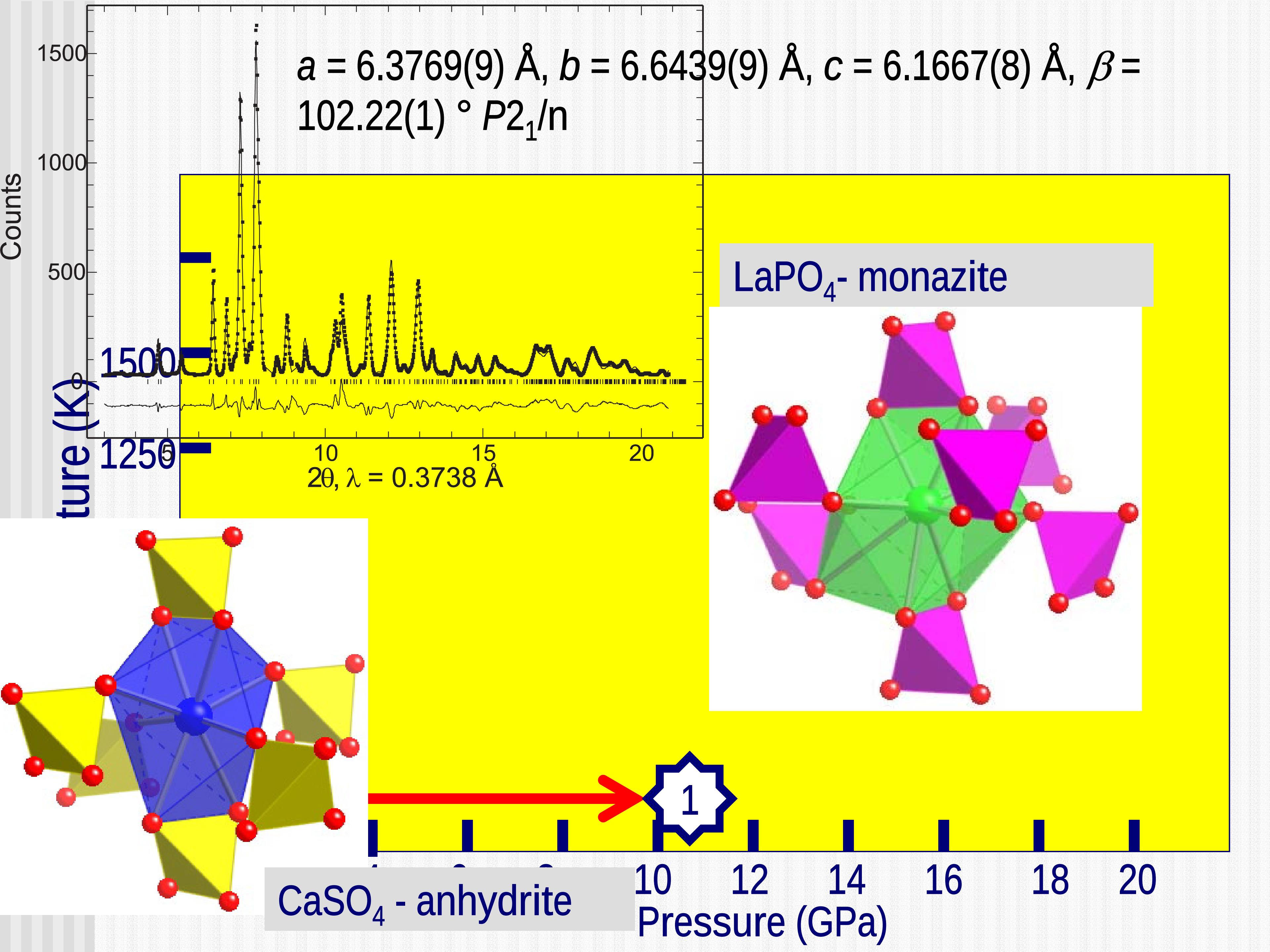


(A) Reconnaissance: possible HP-HT structure-types of $CaSO_4$ ($A^{2+}B^{6+}O_4$)

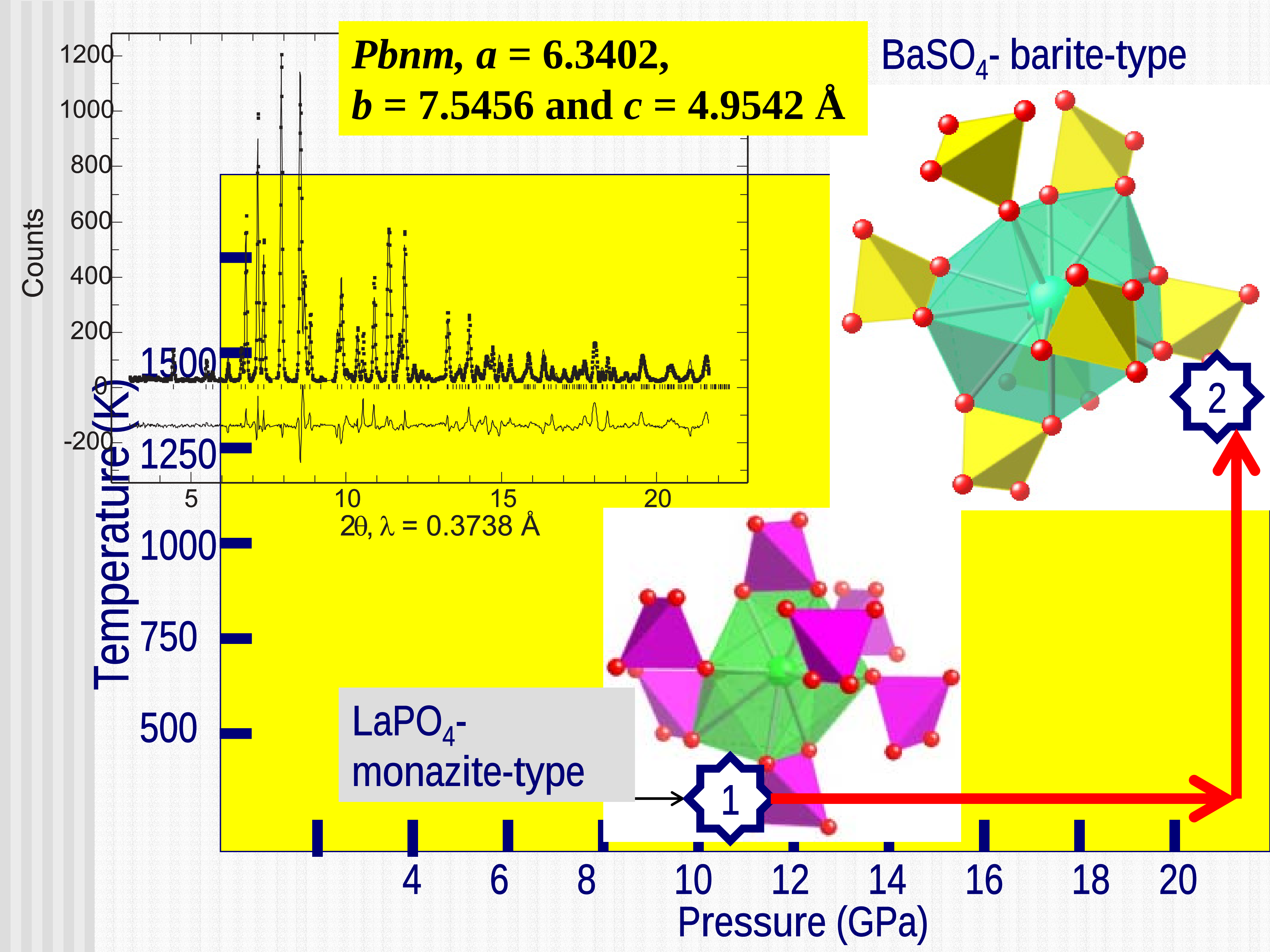
- Anhydrite structure unique in $A^{2+}B^{6+}O_4$ chemistry
- Beginning of anticipated transitions from
  - "low-pressure" small-cation BO_4^{6+} (B=S, Zr, Cr) .
  - "moderate-pressure" (larger cation) monazite-and barite-type structures
  - "high-pressure" tungstates with barite- and scheelite structures.



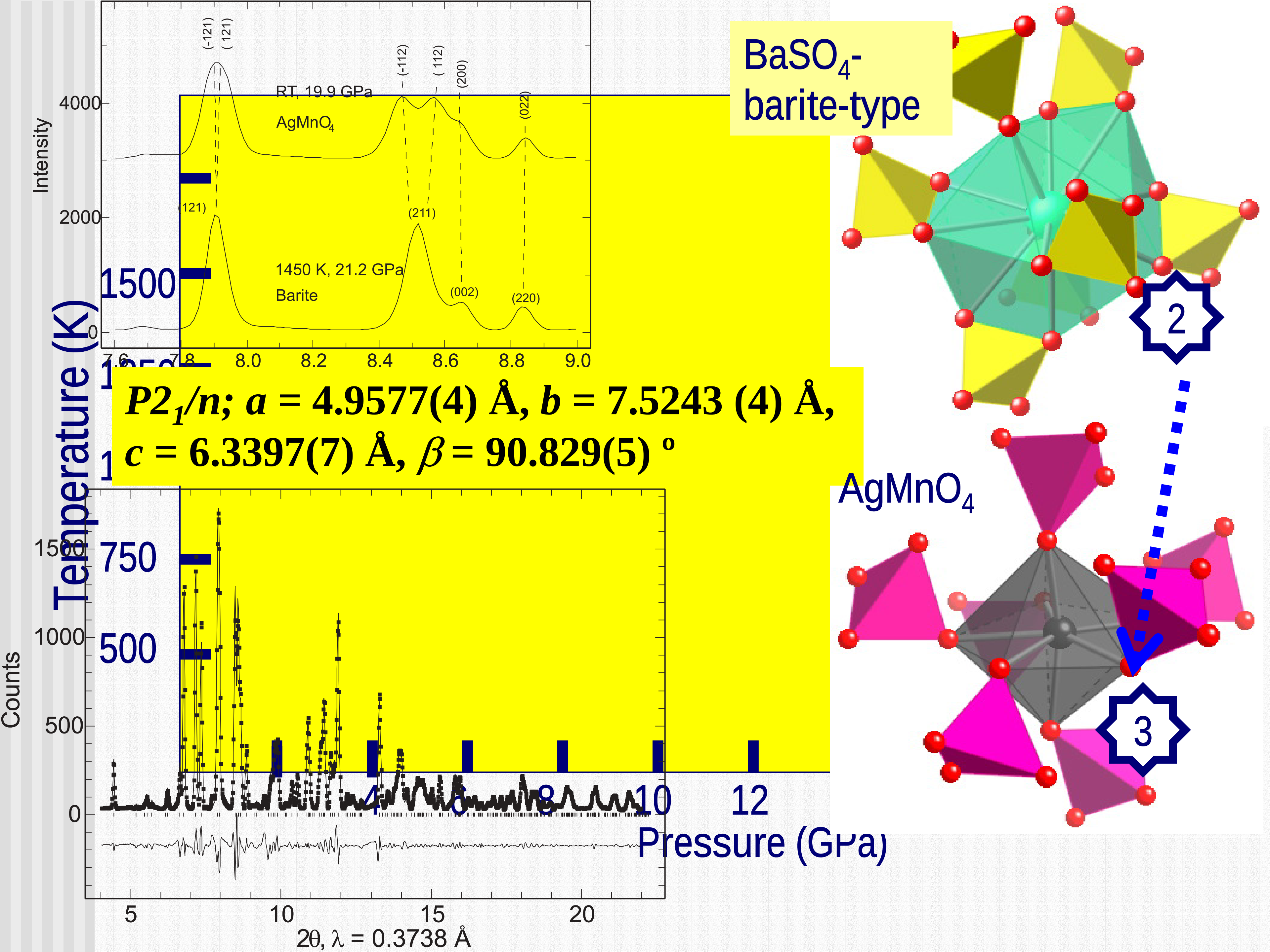
Temperature (K)
1500
1250
1000
750
500
Reconnaissance experiments on anhydrite CaSO4 in the laser-heated DAC (all phases encountered indexed, solved and then refined using Rietveld technique)
Many patterns taken in between
1
2
3
4
4
6
8
10
12
14
16
18
20
Pressure (GPa)

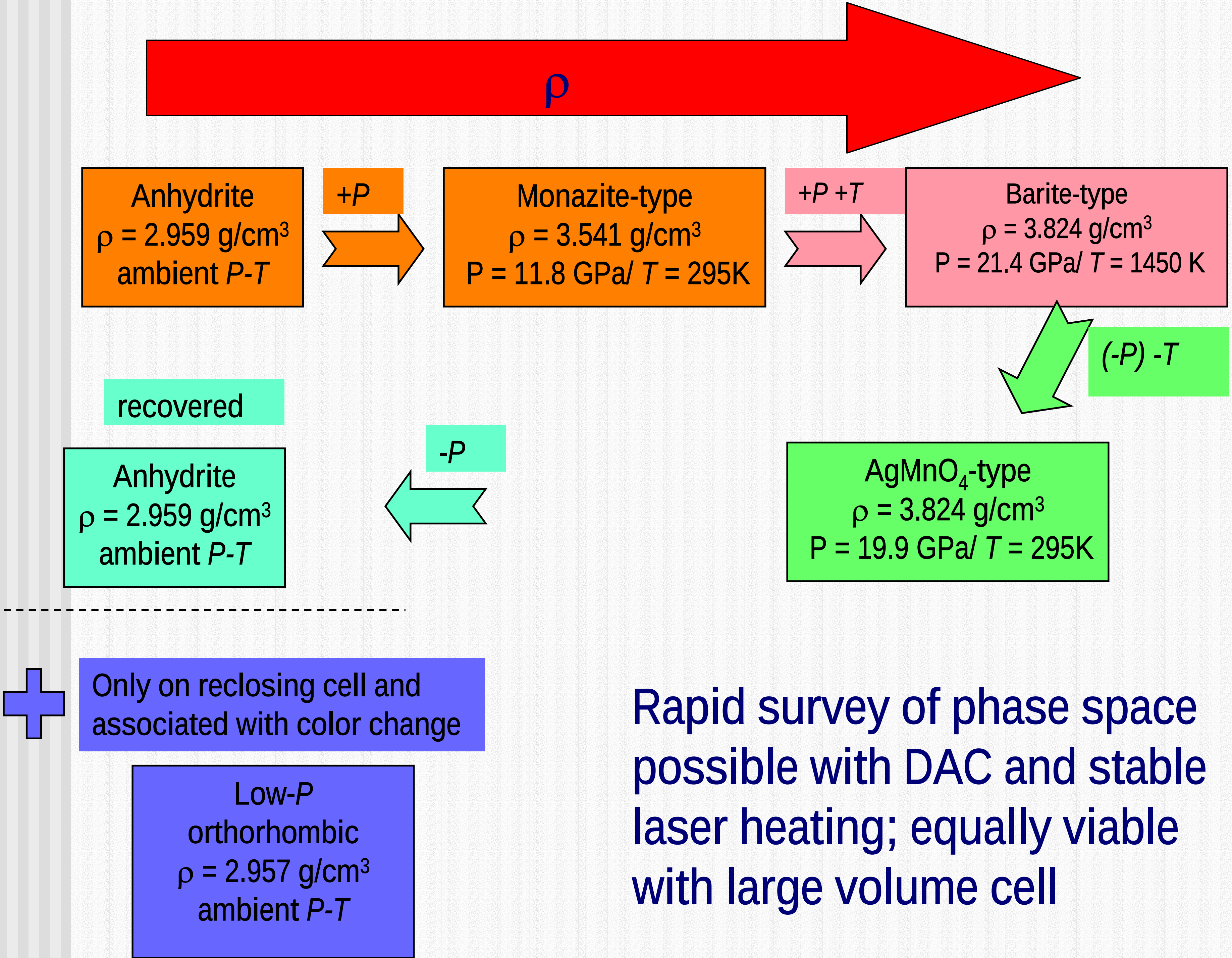


a = 6.3769(9) Å, b = 6.6439(9) Å, c = 6.1667(8) Å, β = 102.22(1) ° P2$_1$/n
Counts
1500
1000
500
0
5
10
15
20
2θ, λ = 0.3738 Å
LaPO$_4$- monazite
CaSO$_4$ - anhydrite
1500
1250
10
12
14
16
18
20
Pressure (GPa)
1



Pbnm, a = 6.3402,
b = 7.5456 and c = 4.9542 Å
BaSO4- barite-type
Counts
1200
1000
800
600
400
200
0
-200
5
10
15
20
2θ, λ = 0.3738 Å
Temperature (K)
1500
1250
1000
750
500
LaPO4-
monazite-type
1
2
4
6
8
10
12
14
16
18
20
Pressure (GPa)


BaSO4-barite-type
AgMnO4
P2₁/n; a = 4.9577(4) Å, b = 7.5243 (4) Å, c = 6.3397(7) Å, β = 90.829(5) º
RT, 19.9 GPa
AgMnO4
1450 K, 21.2 GPa
Barite
(-121)
(121)
(-112)
(112)
(200)
(022)
(211)
(002)
(220)
Intensity
Counts
2θ, λ = 0.3738 Å
Temperature (K)
Pressure (GPa)
2
3



Rapid survey of phase space possible with DAC and stable laser heating; equally viable with large volume cell

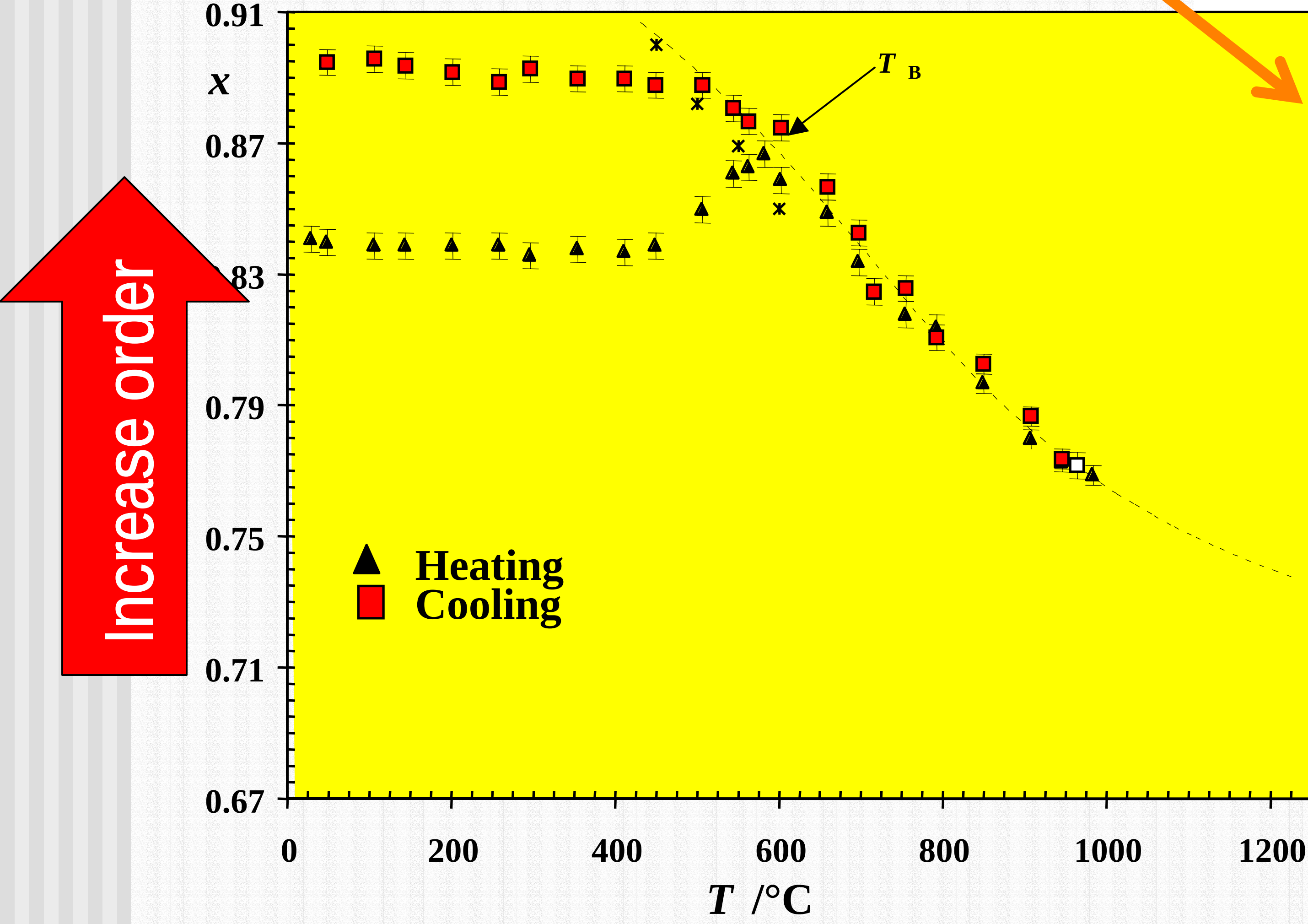
Structural basis for physical properties

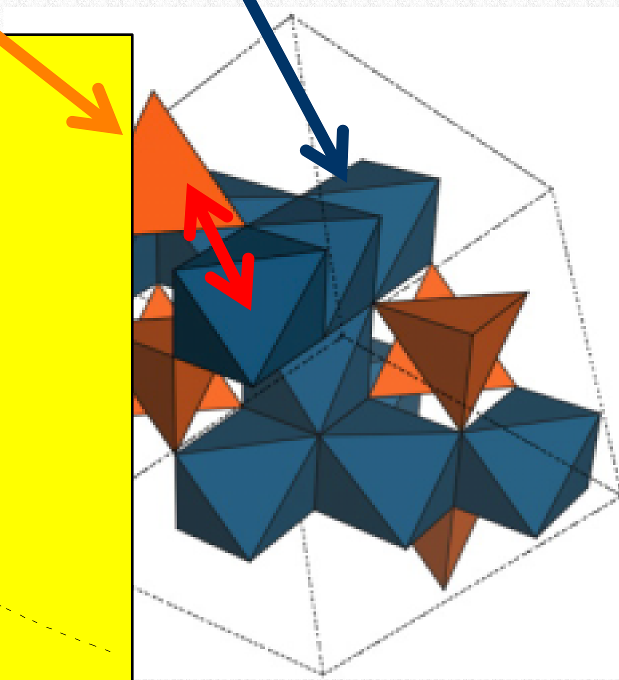
- Emerging perspectives
  - Sound velocities can be affected near phase transitions and as function of cation order
  - Stability dramatically enhanced
  - Structural basis for these phenomena?
- Advantageous to measure both properties and scattering suitable for derivation of accurate structure models
  - This can be *sometimes* be easier in Large Volume High Pressure Devices

Order-disorder in spinels

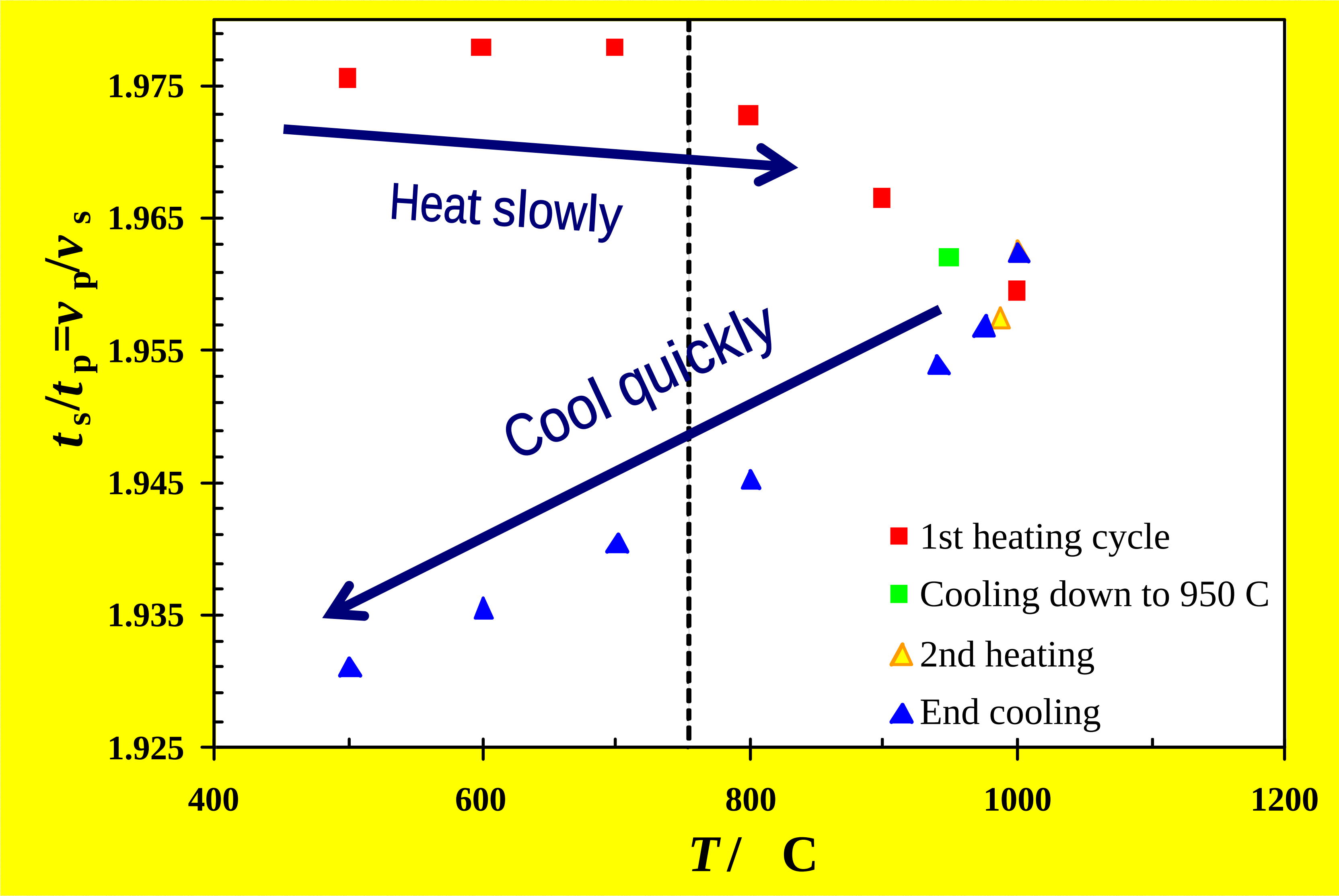
Inversion parameter (x)

${}^{iv}[A_{1-x}B_x]^{vi}[A_{x/2}B_{1-x/2}]_2O_4$





Order-disorder and physical properties: Changes in sound velocity in $MgFe_2O_4$ spinel



Structural basis for physical properties

- Emerging perspectives
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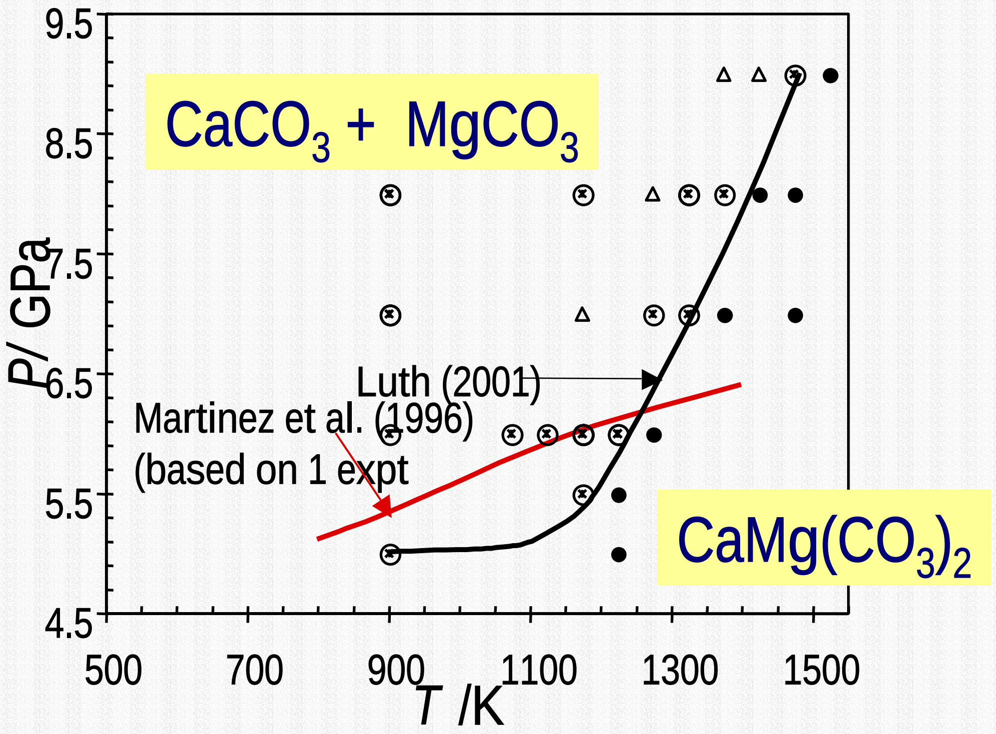
Order-disorder and thermodynamic properties: reason for dolomite's enhanced stability at high PT?



Structural basis for this dramatic increase in stability at HT?

Pressure dependence?

Structural basis for physical properties

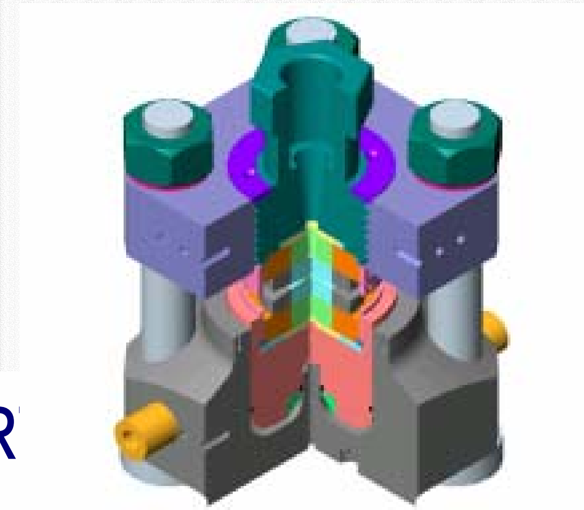
- Emerging perspectives
  - Order-disorder affects:
    - Sound velocities
    - Stability
  - Structural basis for these phenomena?
- Advantageous to measure both properties and scattering suitable for derivation of accurate structure models
  - This can *sometimes* be easier in Large Volume High Pressure Devices (T stability, large volume -> higher signal provided sensitivity maintained)

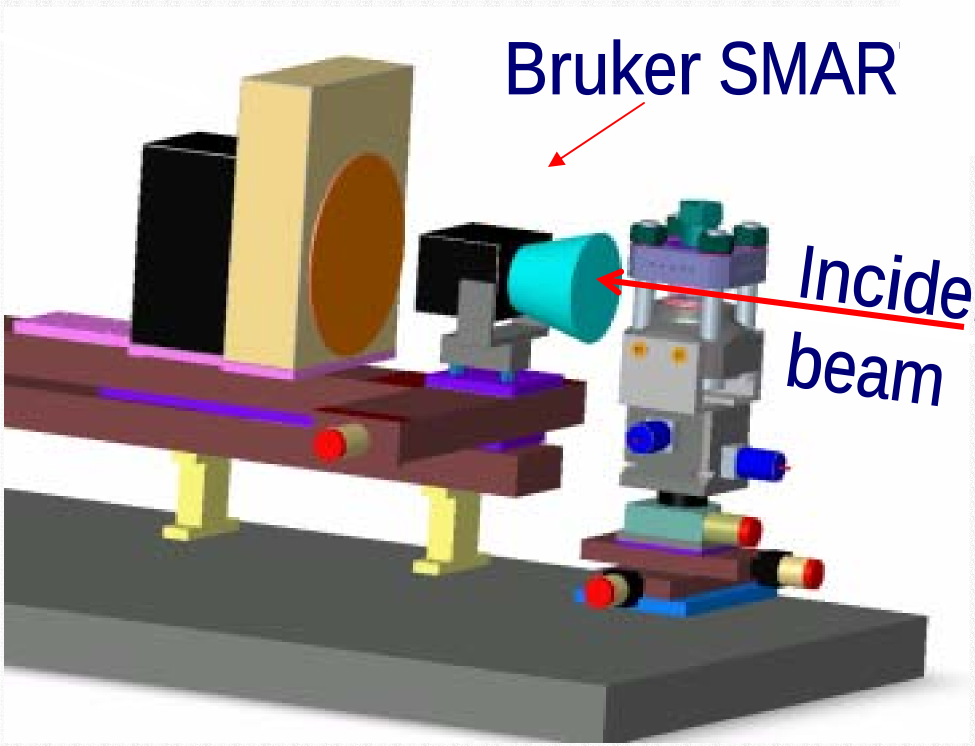
Large volume devices

- Advantages
  - Sample volume ~ 10^4 x DAC
    - Especially useful in case of amorphous materials
  - Heating stability, control and measurement
  - Simultaneous property/diffraction (sound velocity)
  - Easier control of pO_2, pCO_2 etc, reaction buffers
- Disadvantages
  - Single crystal studies difficult
  - Pressure range limited < 40 GPa
  - Parasitic scattering from cell assembly

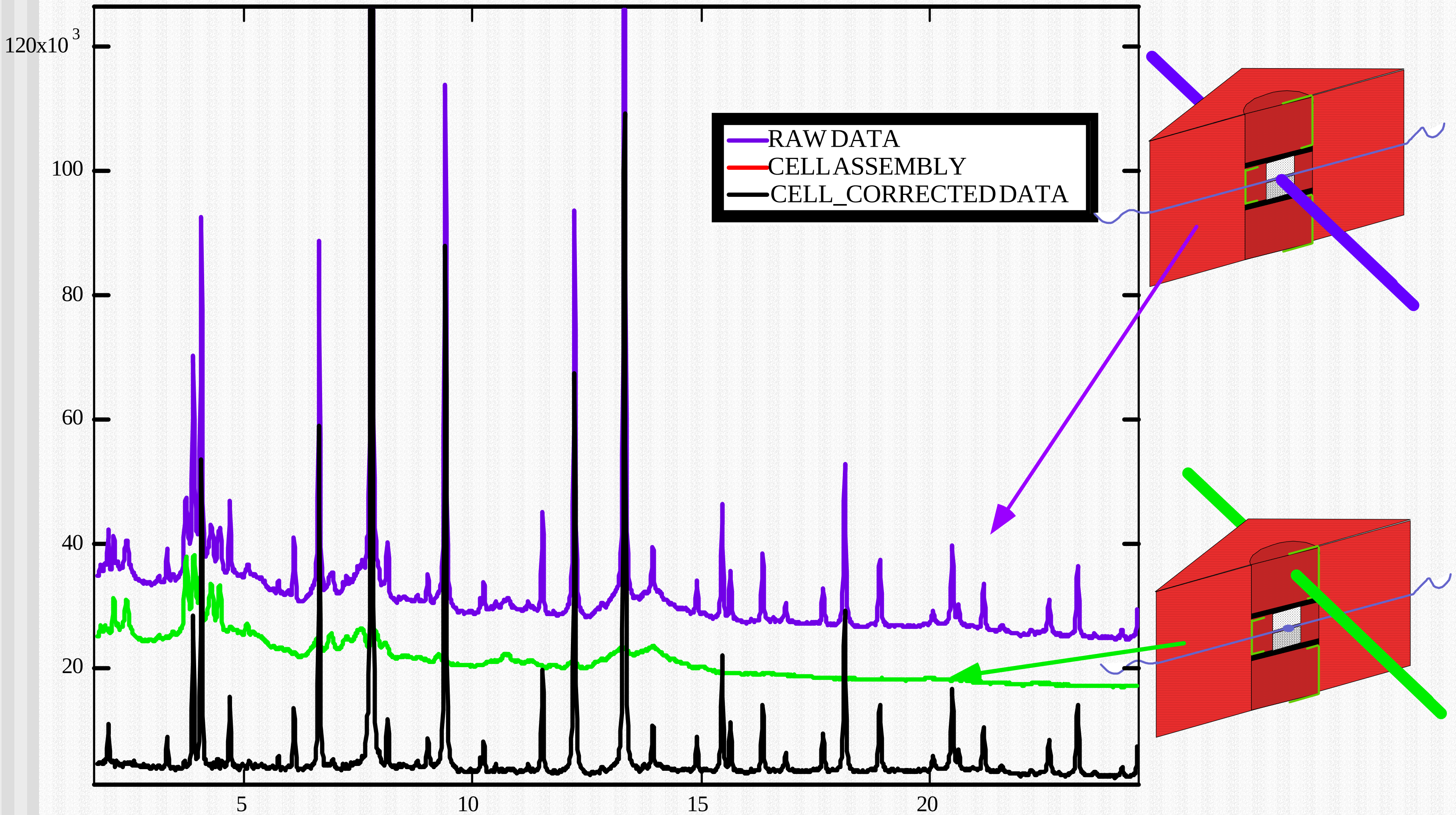
Paris-Edinburgh set-up at ID30, (ESRF W. Crichton), 11-ID (Tulk and Benmore - see Frontiers 2004 in Guest House)

- Unfocused beam, 0.1mm(h) x 0.25mm(v) on sample
- Energies > 40keV)
- slits required (single or radial)





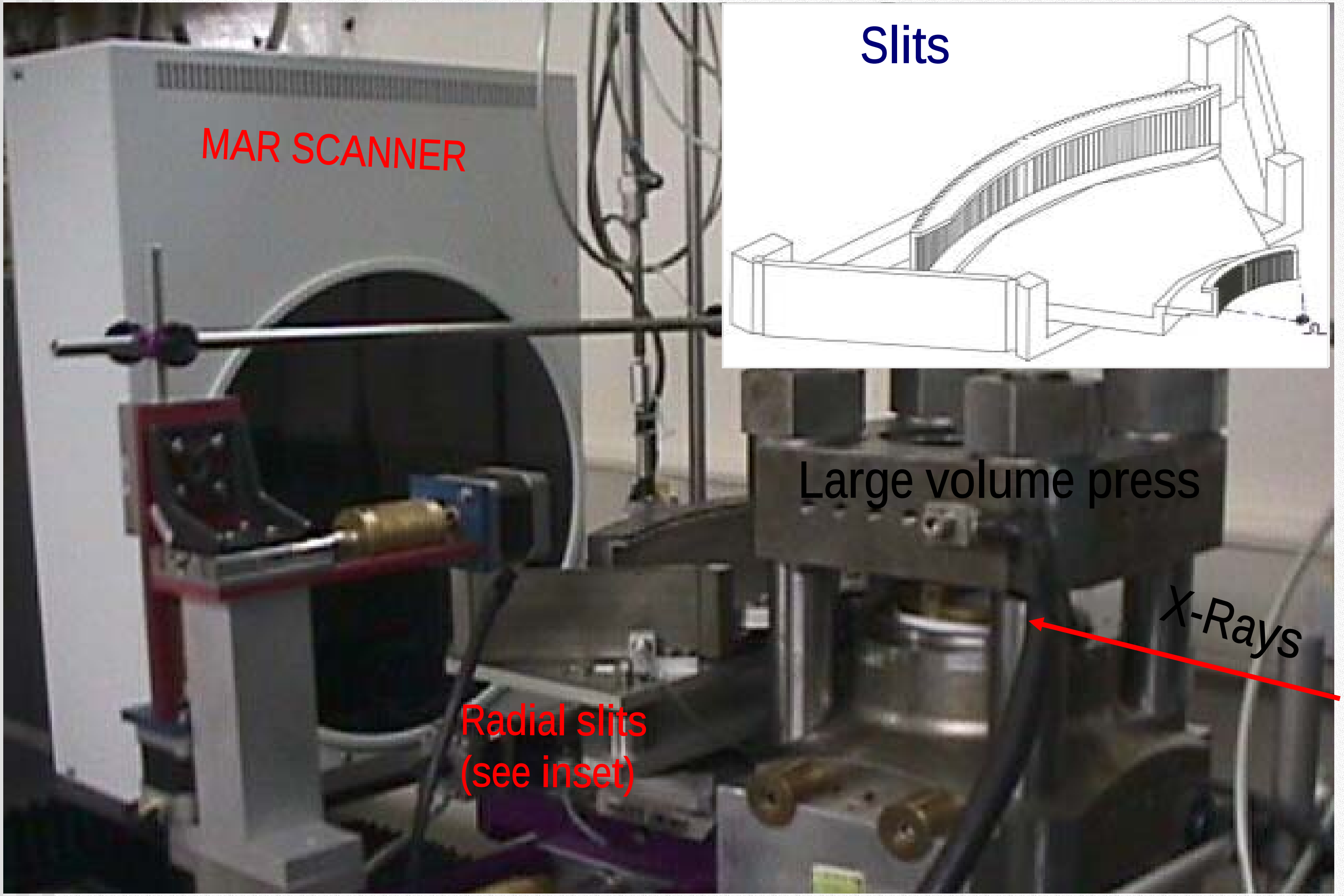
SUBTRACTION OF CELL ASSEMBLY-CONTRIBUTION TO OBSERVED DIFFRACTION PATTERN



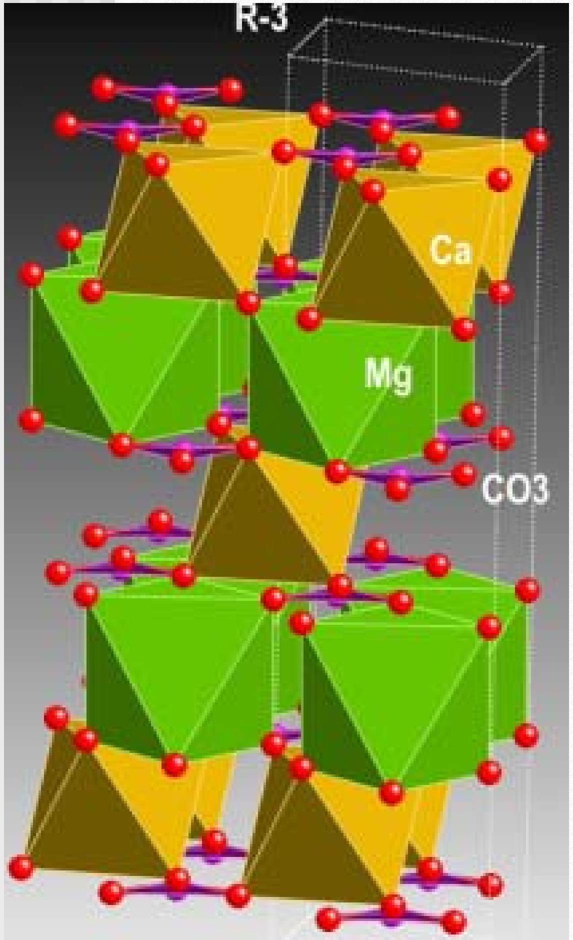
Problematic for complex patterns with weak low angle ordering peaks (like dolomite) - better to eliminate parasitic scattering in such cases.

Paris-Edinburgh set-up at ID30, (ESRF W. Crichton)

- Radial slits mounted on translation between detector and cell

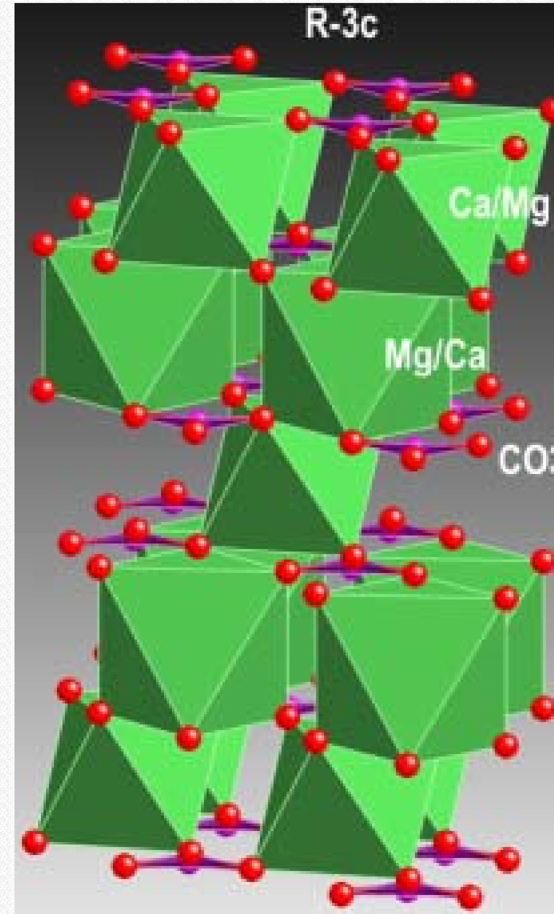


disorder in dolomite: $R\bar{3}c$ -> $R\bar{3}$ transition



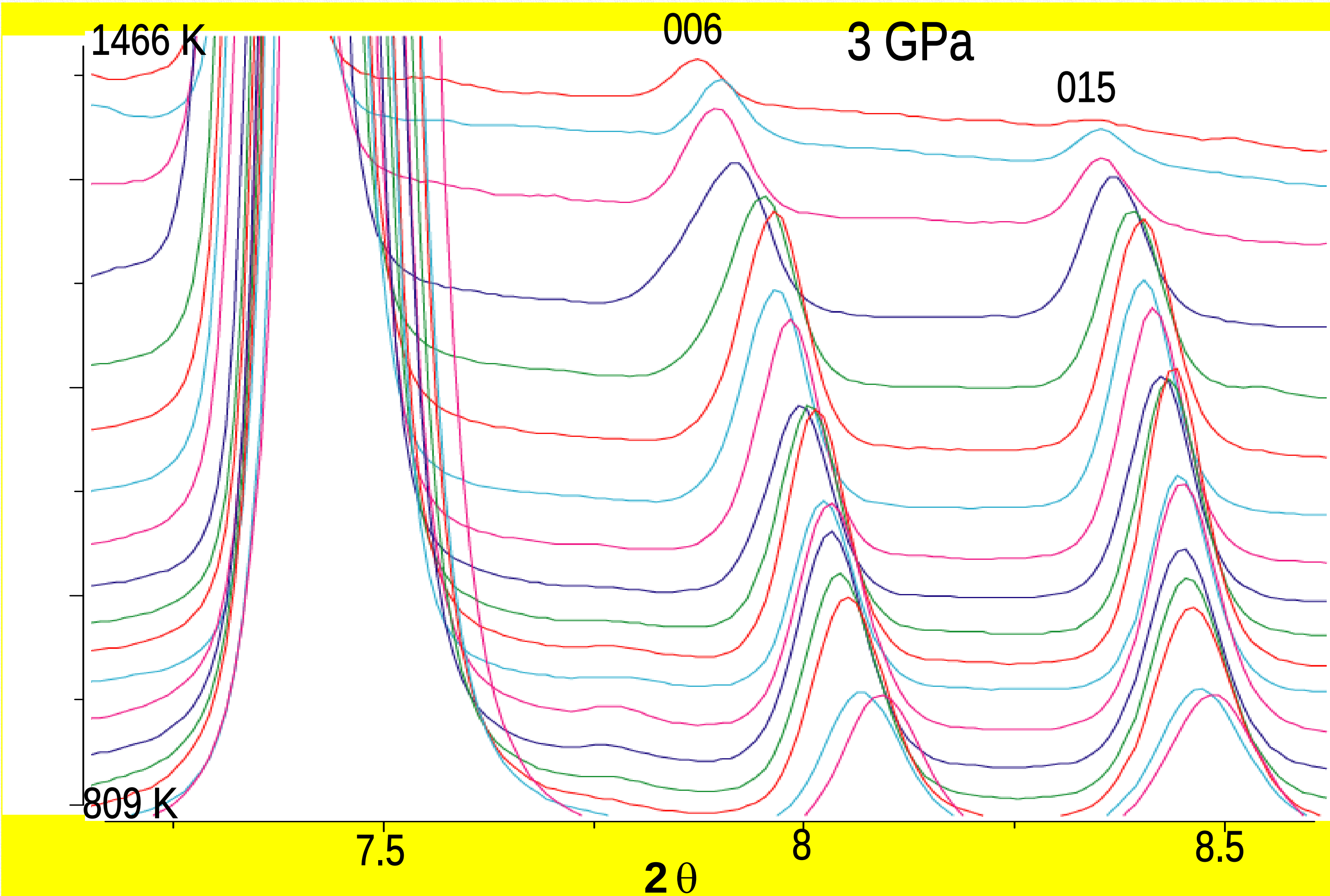
Decrease intensity of "ordering"

Reflections near transition

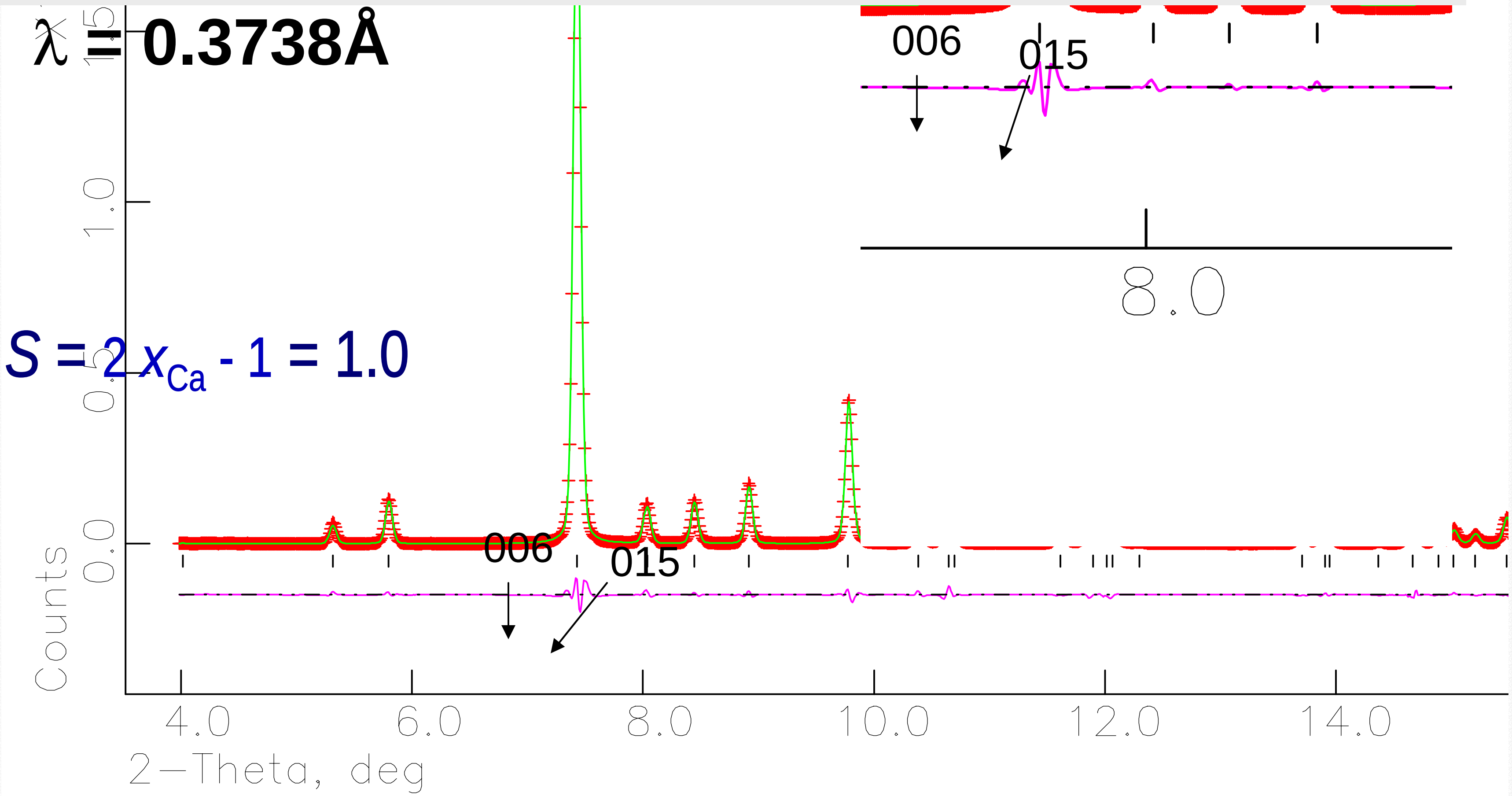


Order parameter $s = 2\,x_{Ca} - 1$, varies from $s = 1$ (where $x_{Ca} = 1$) for a completely ordered dolomite to $s = 0$ (where $x_{Ca} = 0.5$)

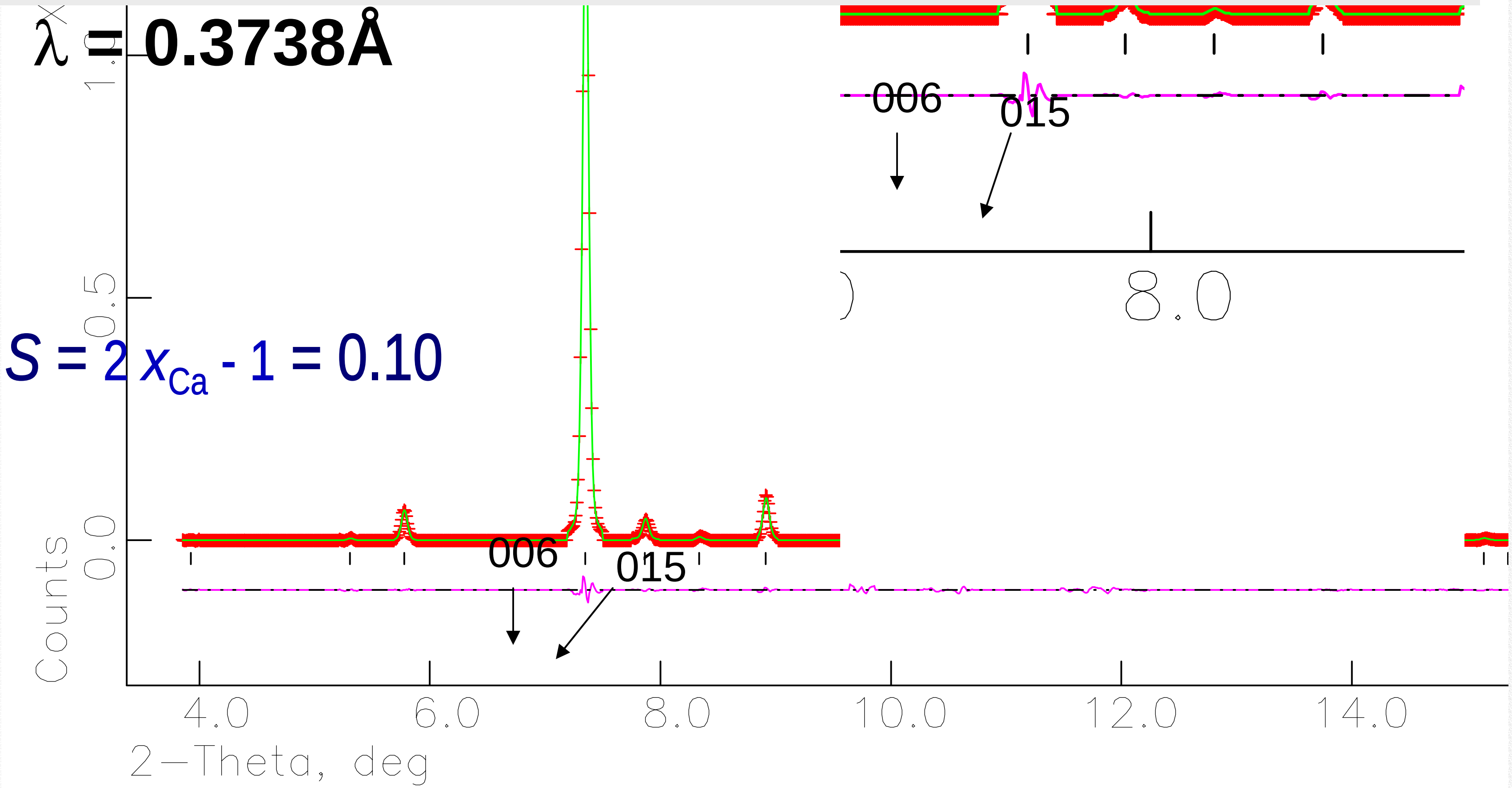
Disorder in dolomite ($R\bar{3}c$ -> $R\bar{3}$) leads to disappearance of c-glide dependent absence (015); how good an indicator of disorder is I_{015}/I_{006}?

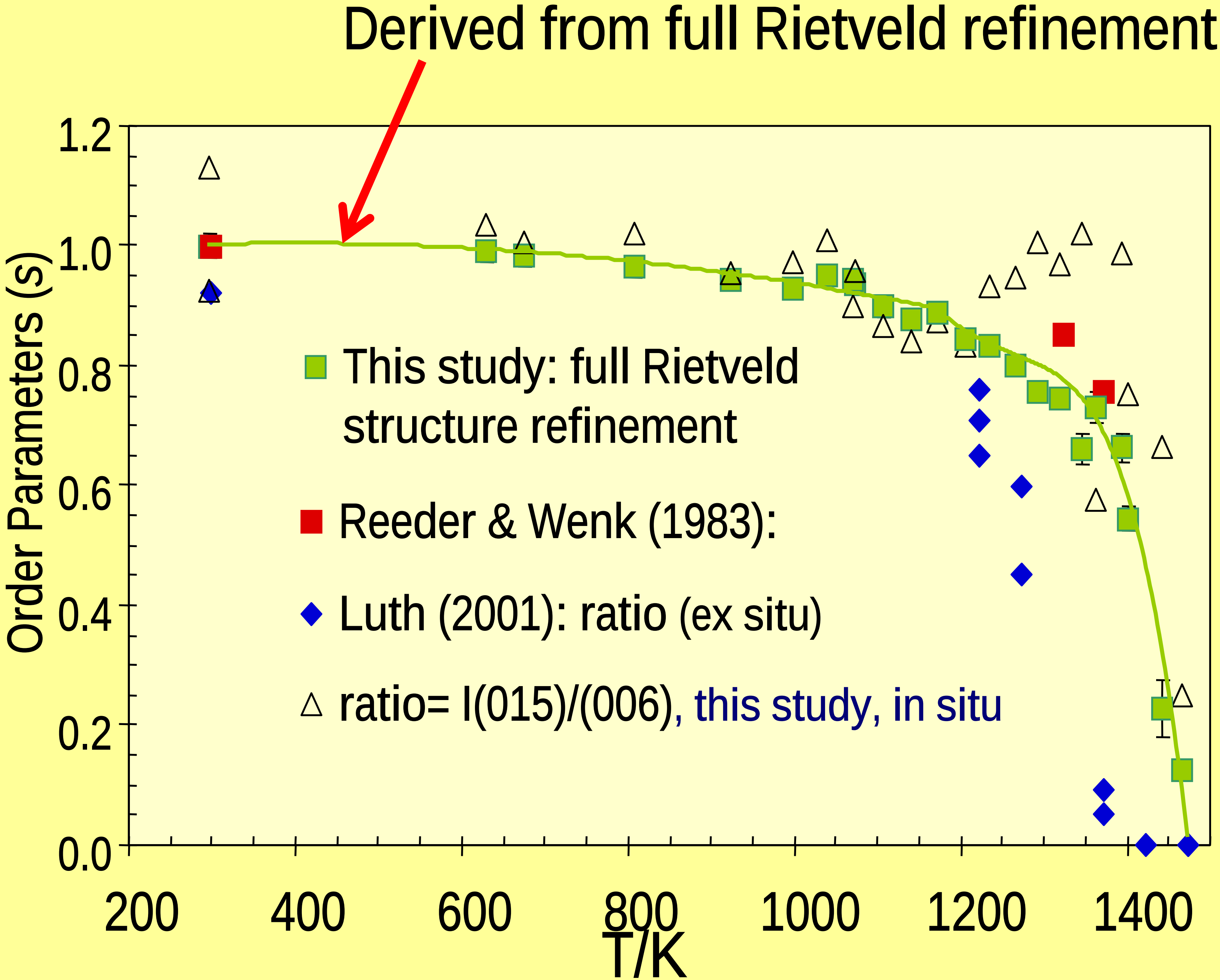


Pattern collected with slits room PT in cell - no parasitic scattering



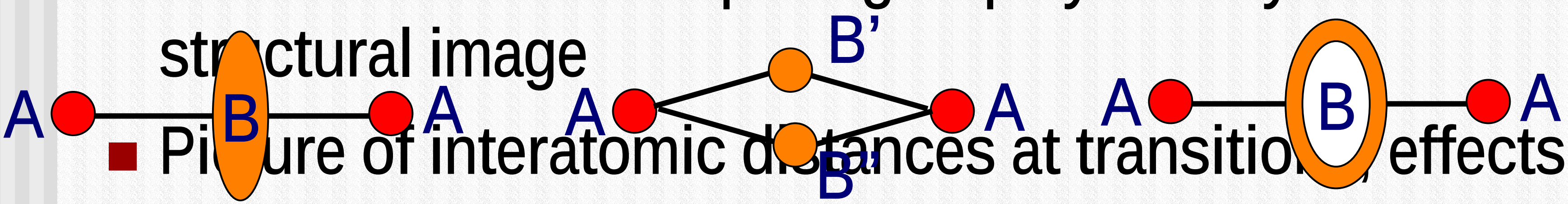
Pattern collected with slits at 3 GPa, 1466 K - no parasitic scattering




Derived from full Rietveld refinement
This study: full Rietveld structure refinement
Reeder & Wenk (1983):
Luth (2001): ratio (ex situ)
ratio= I(015)/(006), this study, in situ
Order Parameters (s)
T/K
0.0
0.2
0.4
0.6
0.8
1.0
1.2
200
400
600
800
1000
1200
1400

Short Range order in crystalline materials

- Bragg scattering gives average picture
  - Short range order interpreted in context of space group picture (split atom sites)
- Direct Fourier transform of the diffraction pattern
  - Includes all (elastic) scattering, including diffuse scattering
    - correspond to "instantaneous" image - information of interatomic distances "unfiltered" by space group constraints
    - (Ambiguity often remains though)
  - Lose the comfort of space group symmetry and structural image



  - Picture of interatomic distances at transition, effects of surface reconstruction

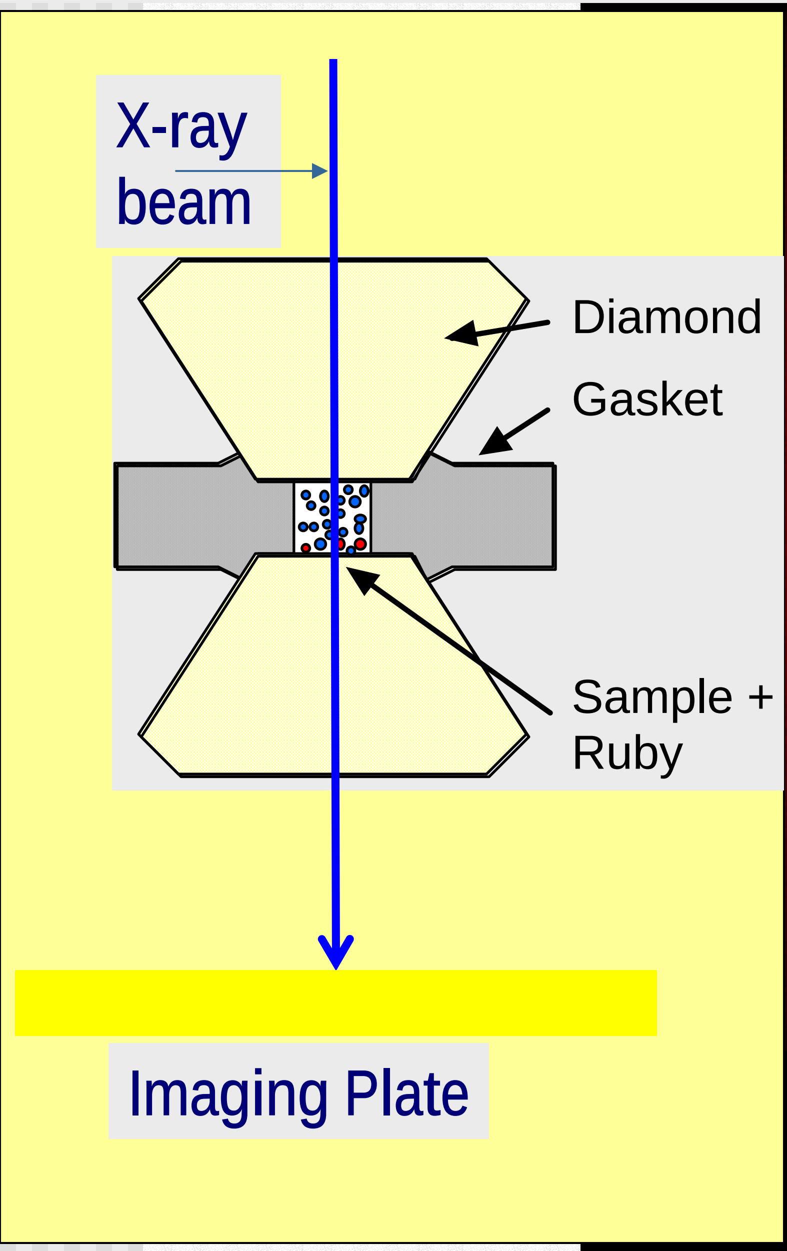
Pair distribution function analysis using High Pressure data (HP-PDF)- why?

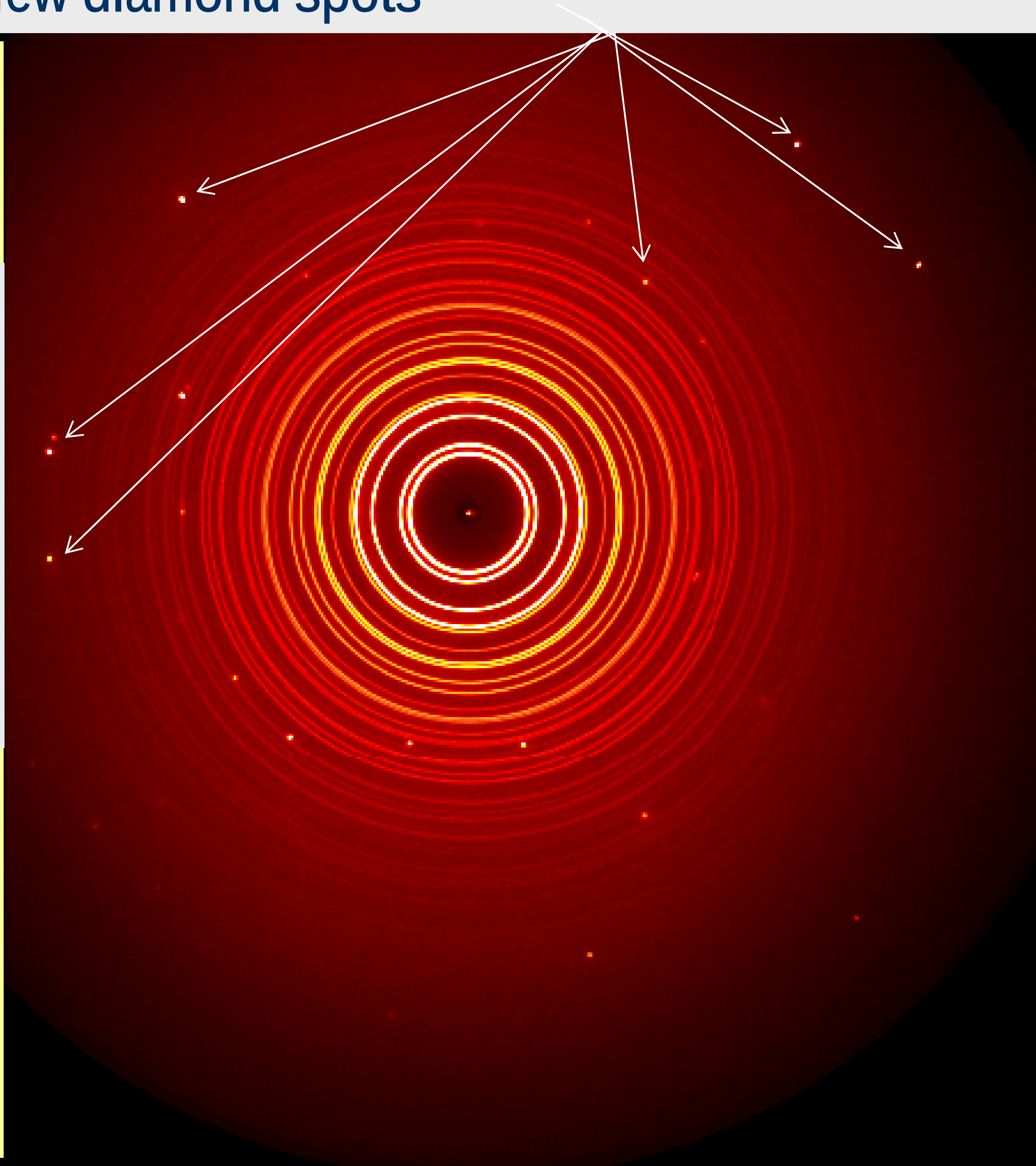
- Order-disorder inherently short -range phenomenon and pressure promotes transitions
  - Long range order established over time - nucleation Vs. martensitic mechanisms (eg PRLs, 83, 328; 86, 4072) of phase transformation at HP for hcp -> ccp
  - Effects of deviatoric stress on transition mechanism
- Pair distribution function + modeling offers a way forward

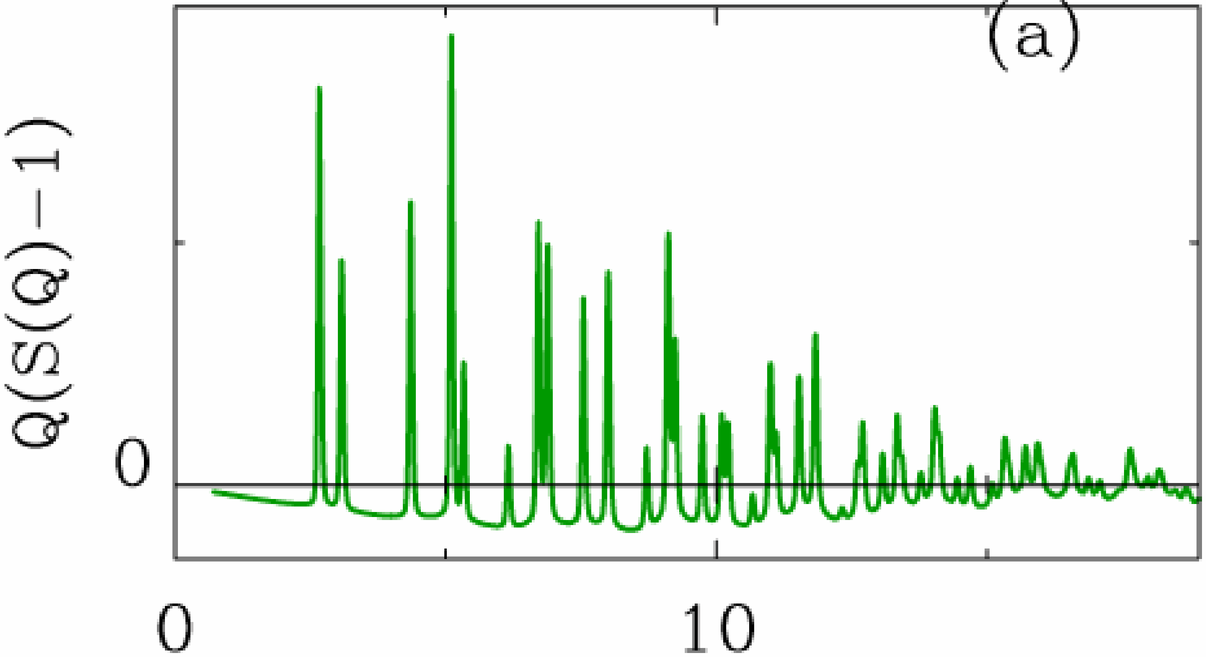
Quantitative (Q)HP-PDF - how?

- Difficulties doing QHP-PDF
  - Interference (scattering, Compton) from cell
    - Slits and LVHPD
    - Diamond anvil cell with thin diamonds and larger sample size
  - Limited data range - trade-offs in PT, cell opening/access
    - use high energy
  - Small sample size in DAC
    - Brightest possible (focused) beams
- Trial experiments
  - nanocrystalline gold (50 nm diameter) in DAC RT, 0- 10 GPa. Excellent data

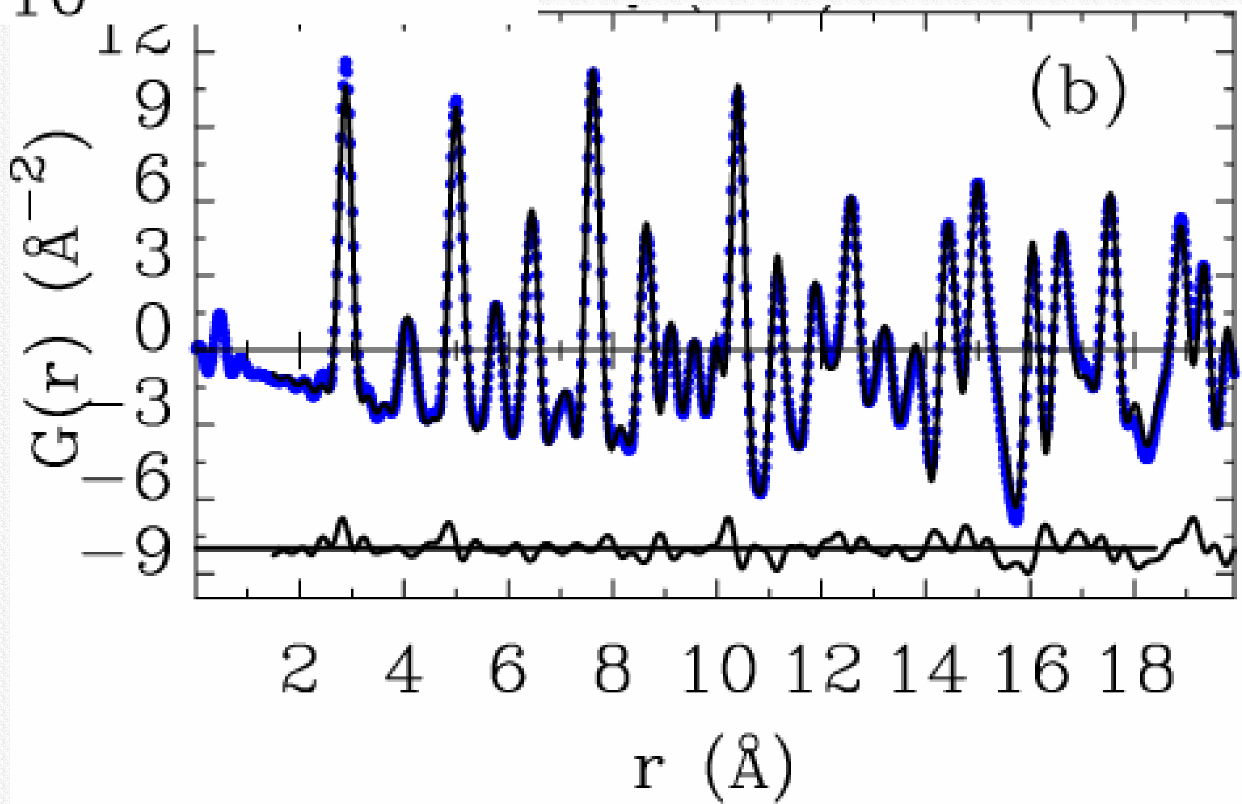
PDF measurements in a DAC on nanocrystalline Au (1-ID-C, E = 80 keV, λ = 0.10557 Å). Image plate data: few diamond spots



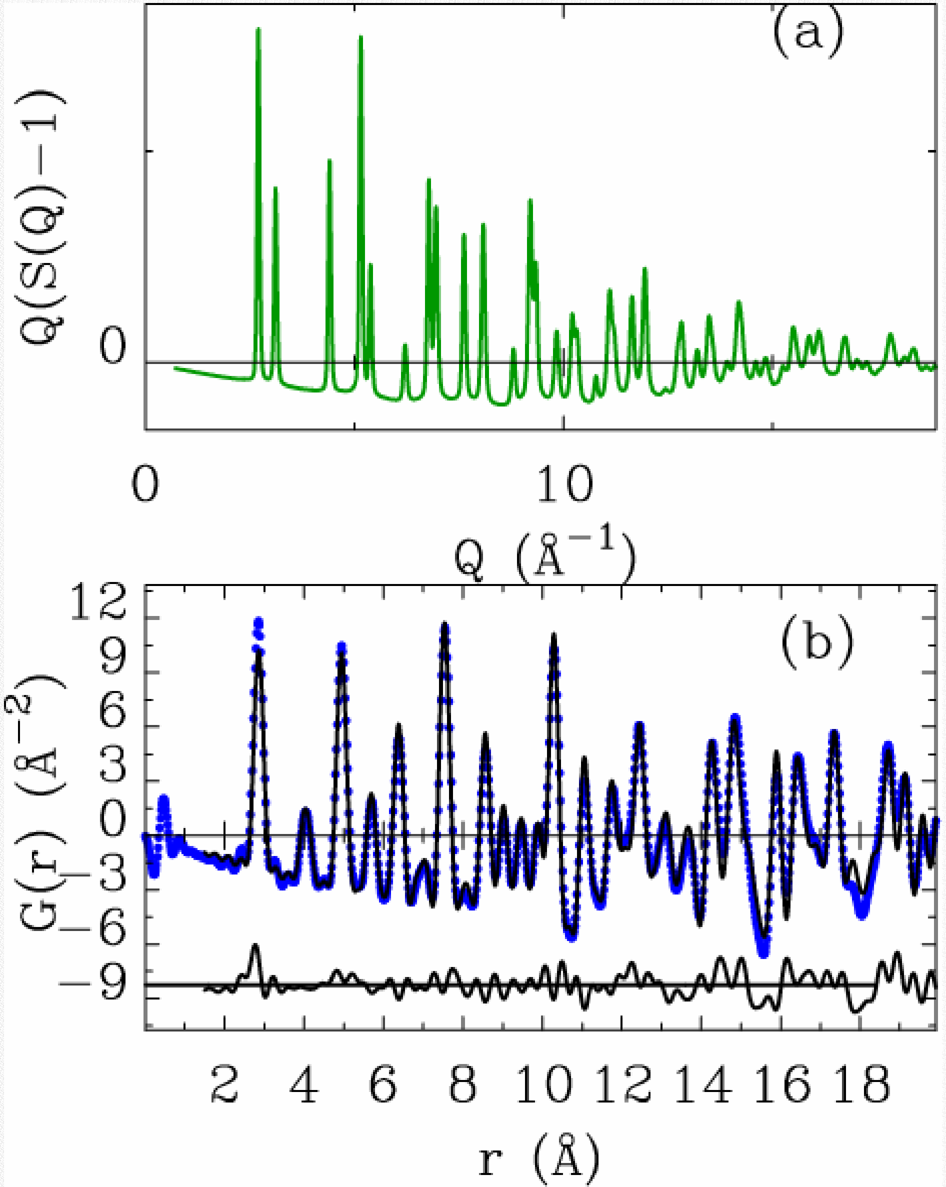




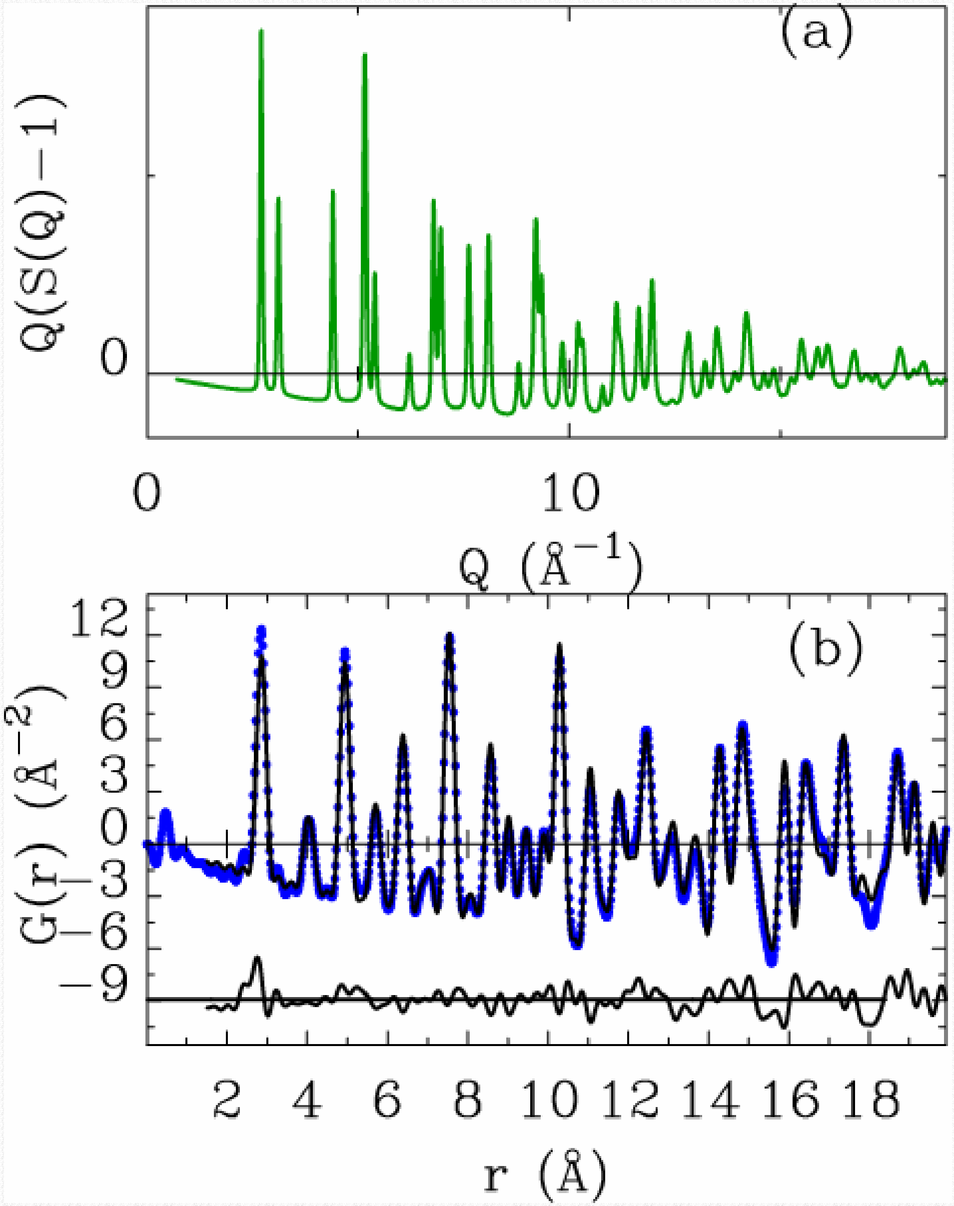
Ambient P,
inside DAC



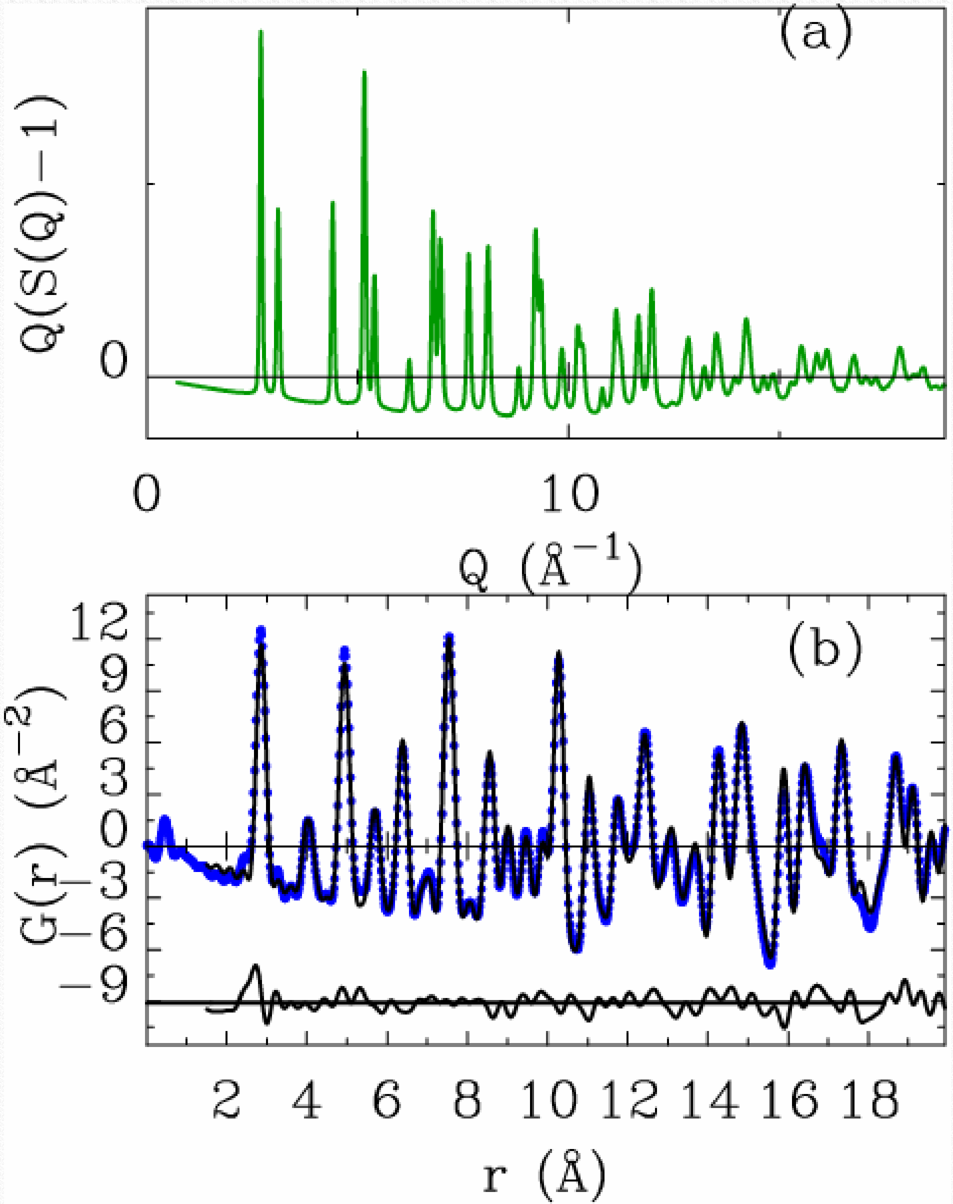
6.38 GPa



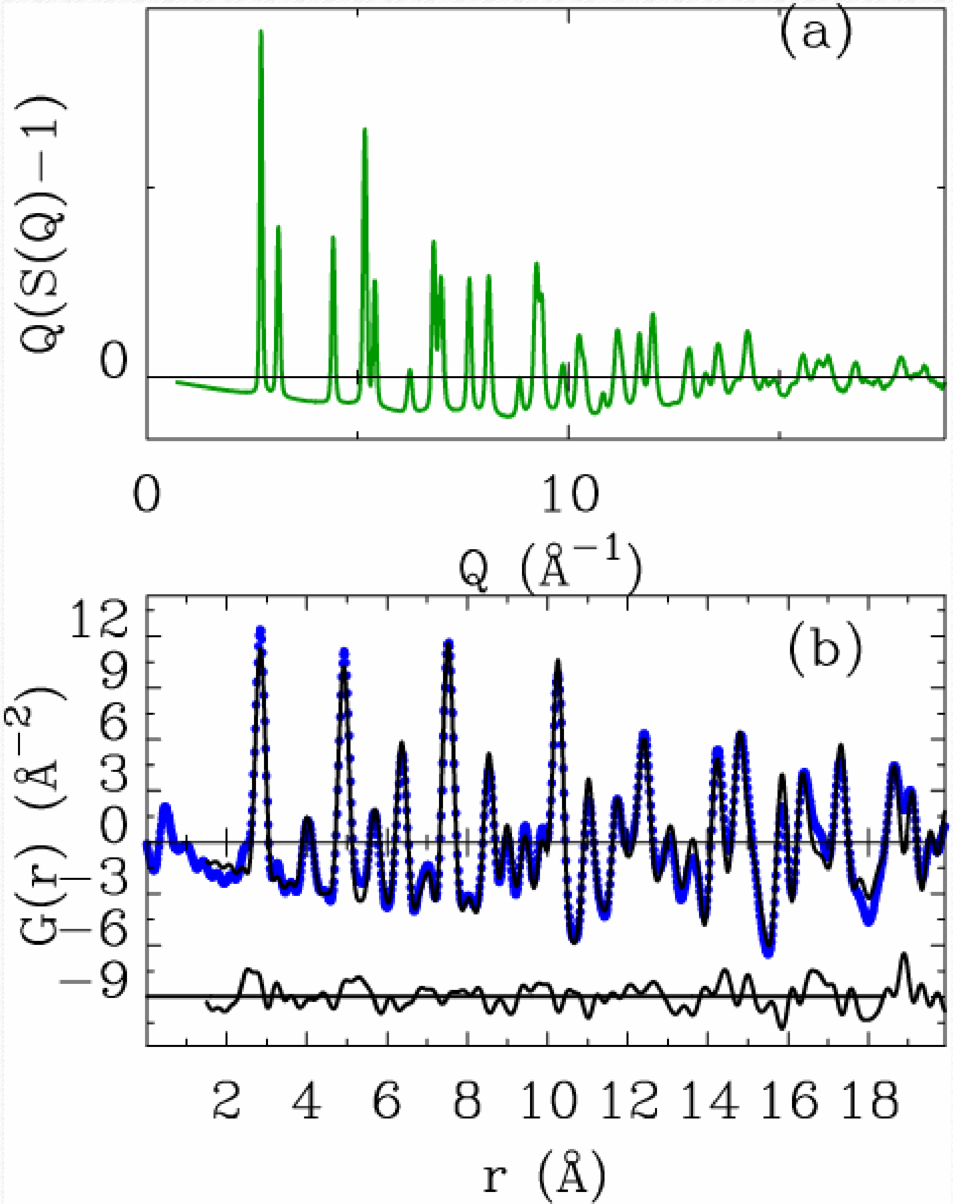
7.50 GPa



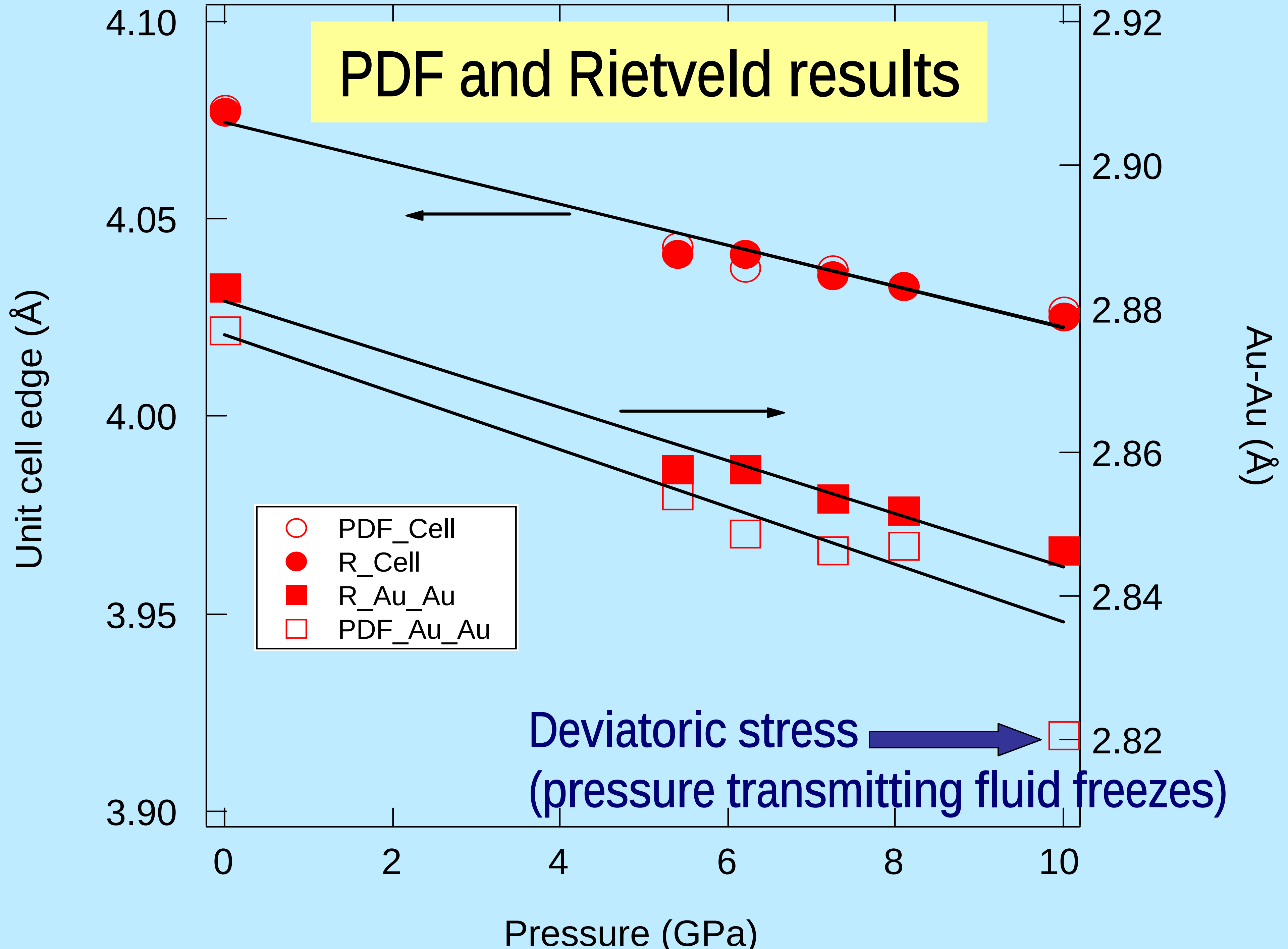
8.50 GPa



10.50 GPa - deviatoric stress



PDF and Rietveld results



Conclusions

- Protocols for collection of reliable diffraction data at HP established
  - Large volume and DAC
  - High energy, slits, quiet detectors
  - Couple to synthesis efforts for making practical materials
- Protocols for studying (quantitative) short range order-disorder (and time resolved?) at HP now being explored
  - Encouraging results
  - Experiment requiring high energy (100keV capable), focused undulator beams