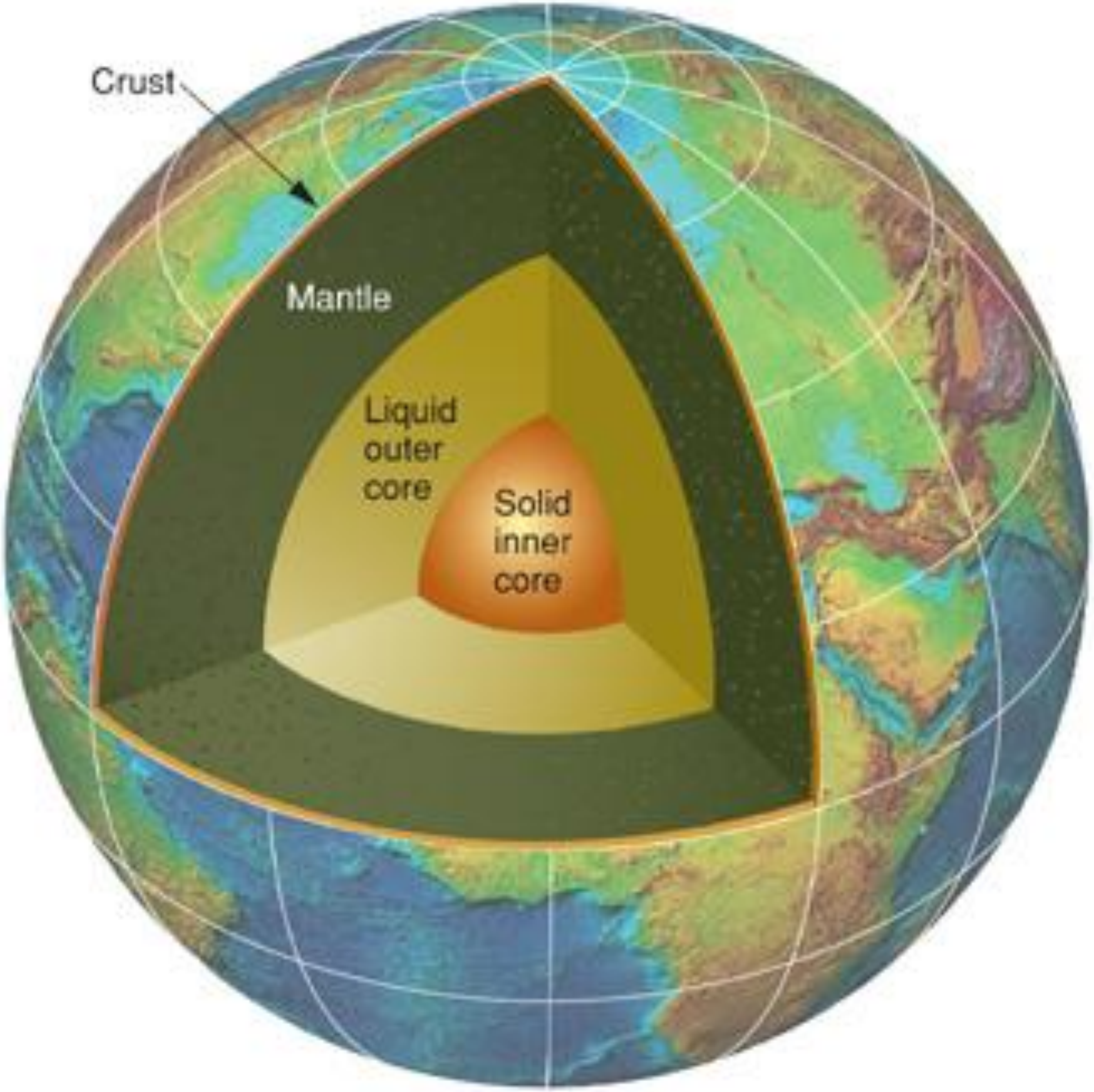
Neutron scattering in Earth Sciences

Martin Dove

The structure of the Earth



Properties under Earth conditions

Changes in structure

Phase changes, including displacive, cation ordering and reconstructive

Changes in properties

Density, elasticity, diffusivity/conductivity, phonon frequencies

What do we want to know?

- Same as in many fields …
- Structure, in absolute sense and also as function of external variables
- Lattice dynamics, in part to understand flexibility, also to use as basis for modelling
- Localised effects, such as motions of water molecules within structures
- Magnetic structures
- … which can be obtained using standard approaches in neutron diffraction and spectroscopy

So what is different?

Sample environment

We might want to go to rather high pressures and temperatures, out of the range of the norm

System complexity

Many crustal minerals do not have simple crystal structures (many atoms in the unit cell, low symmetry)

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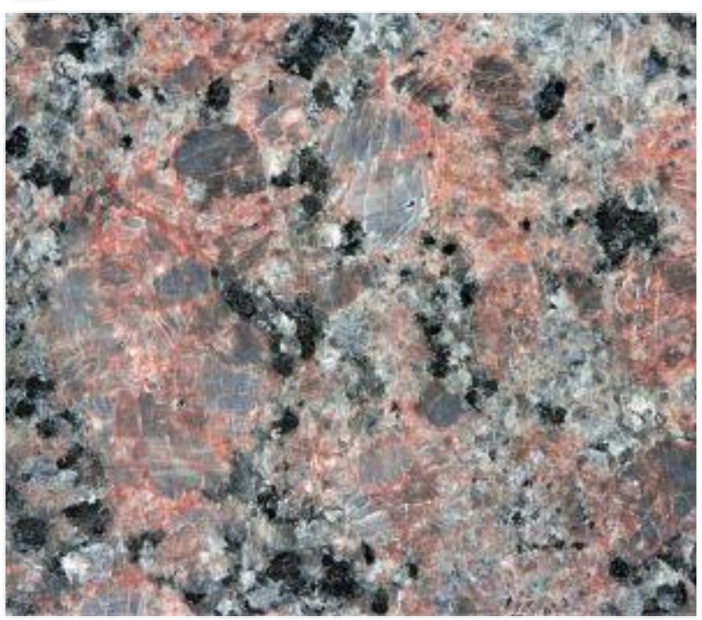
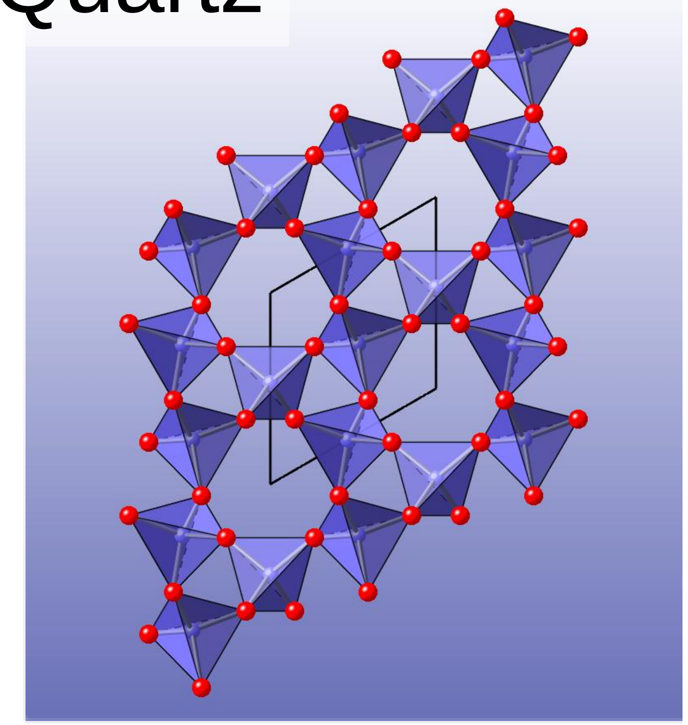
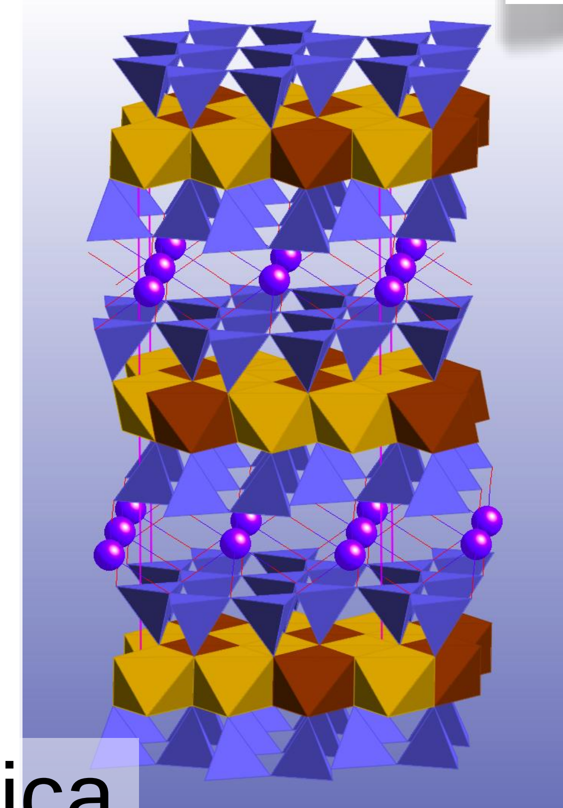
Constituents of granite



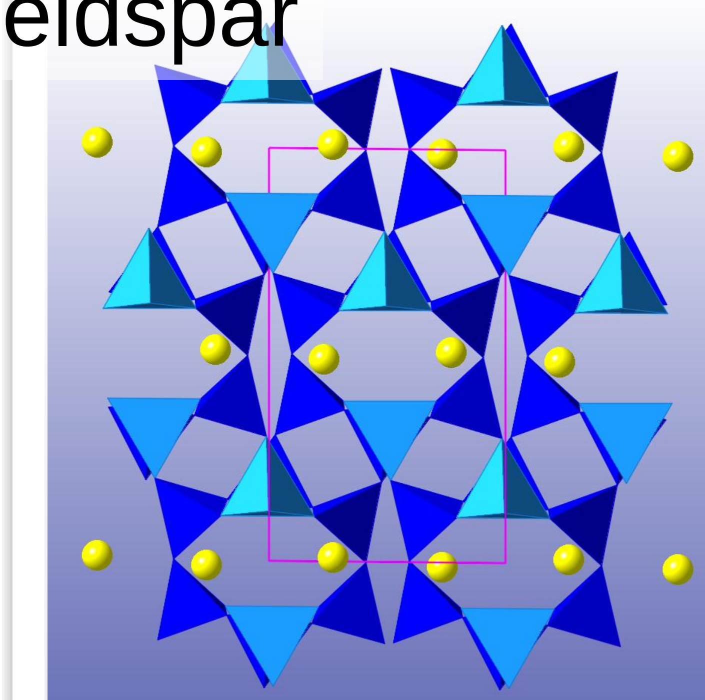
Quartz





Mica

Feldspar



So what is different?

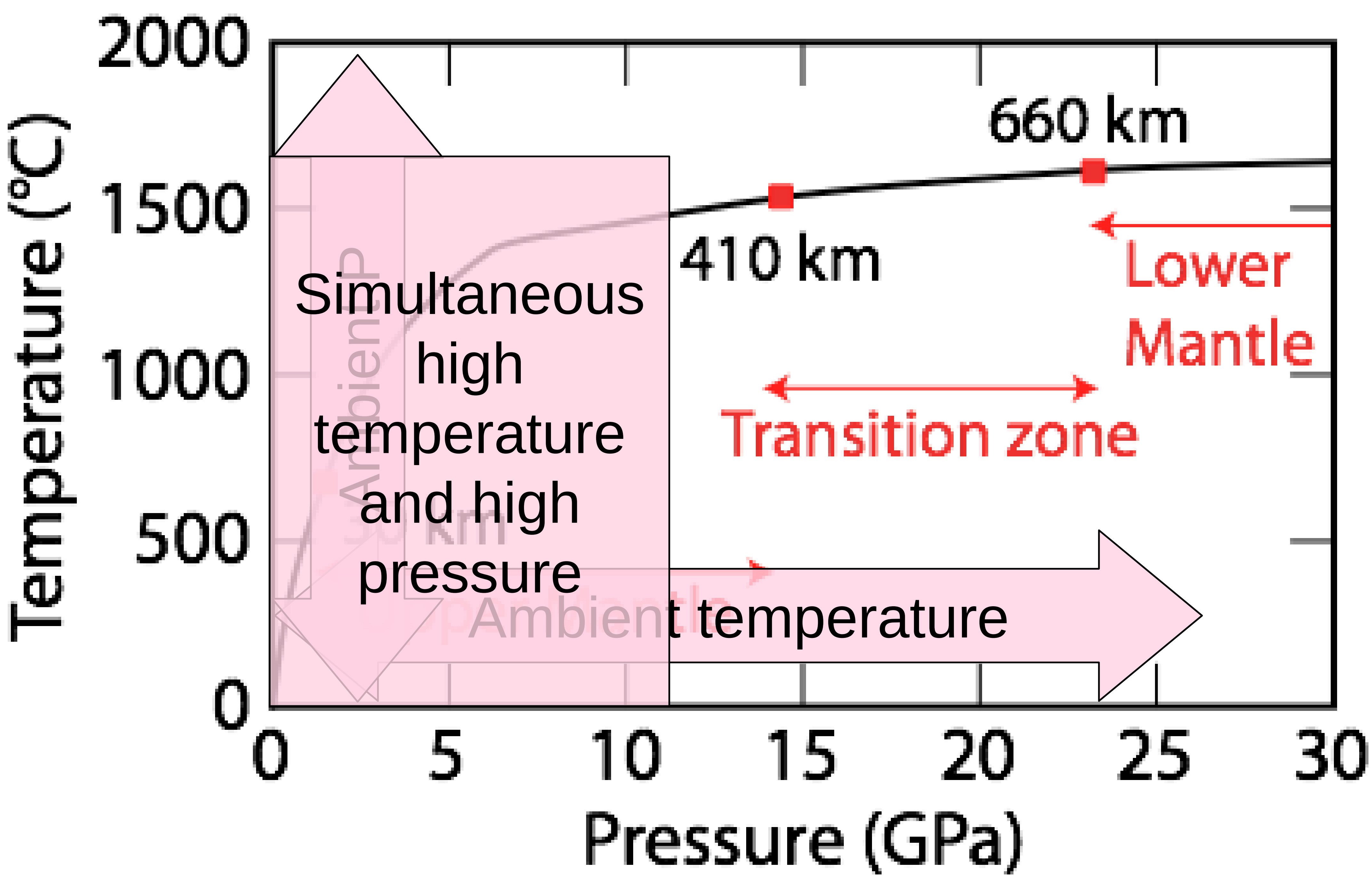
Sample environment

We might want to go to rather high pressures and temperatures, out of the range of the norm

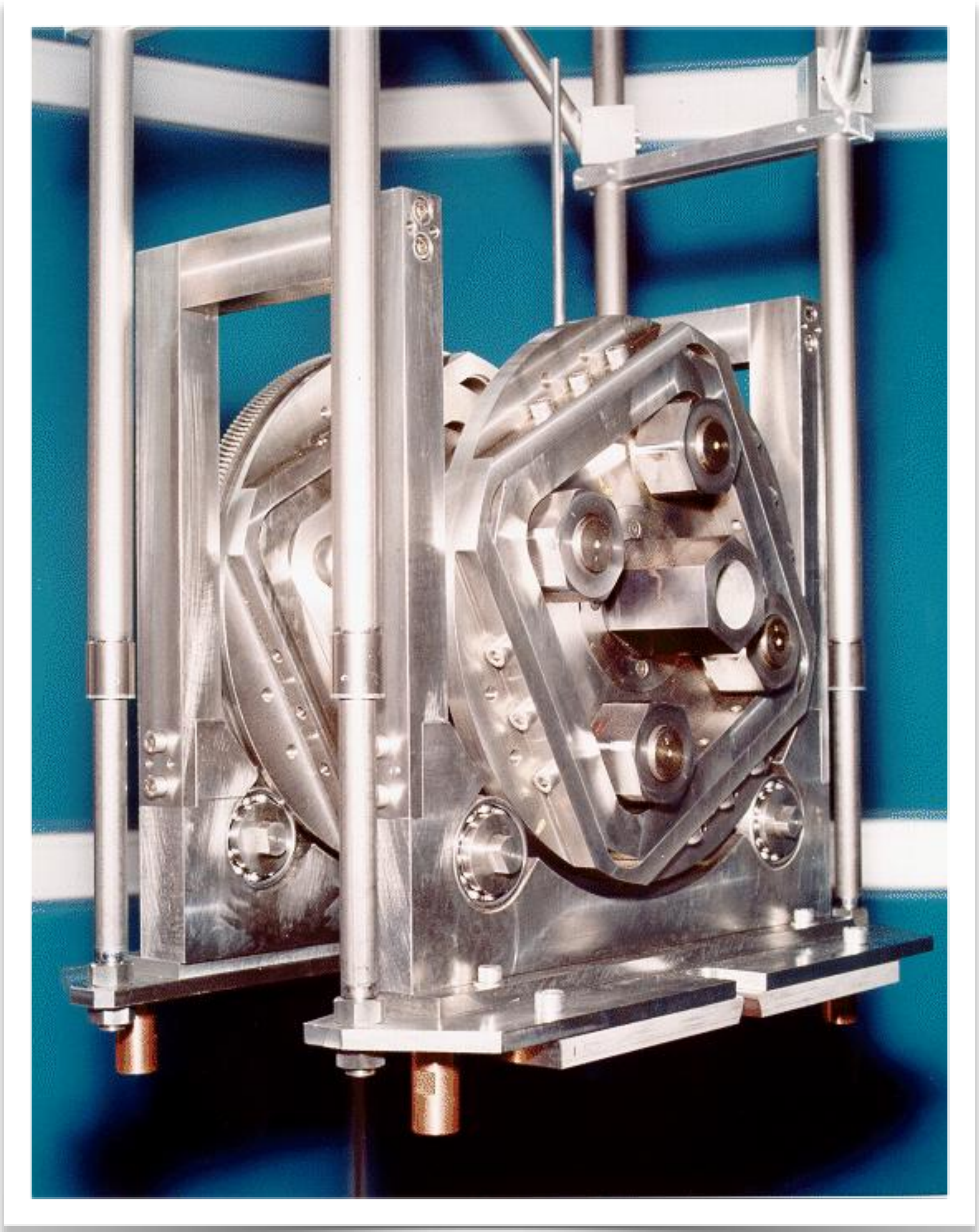
System complexity

Many crustal minerals do not have simple crystal structures (many atoms in the unit cell, low symmetry)

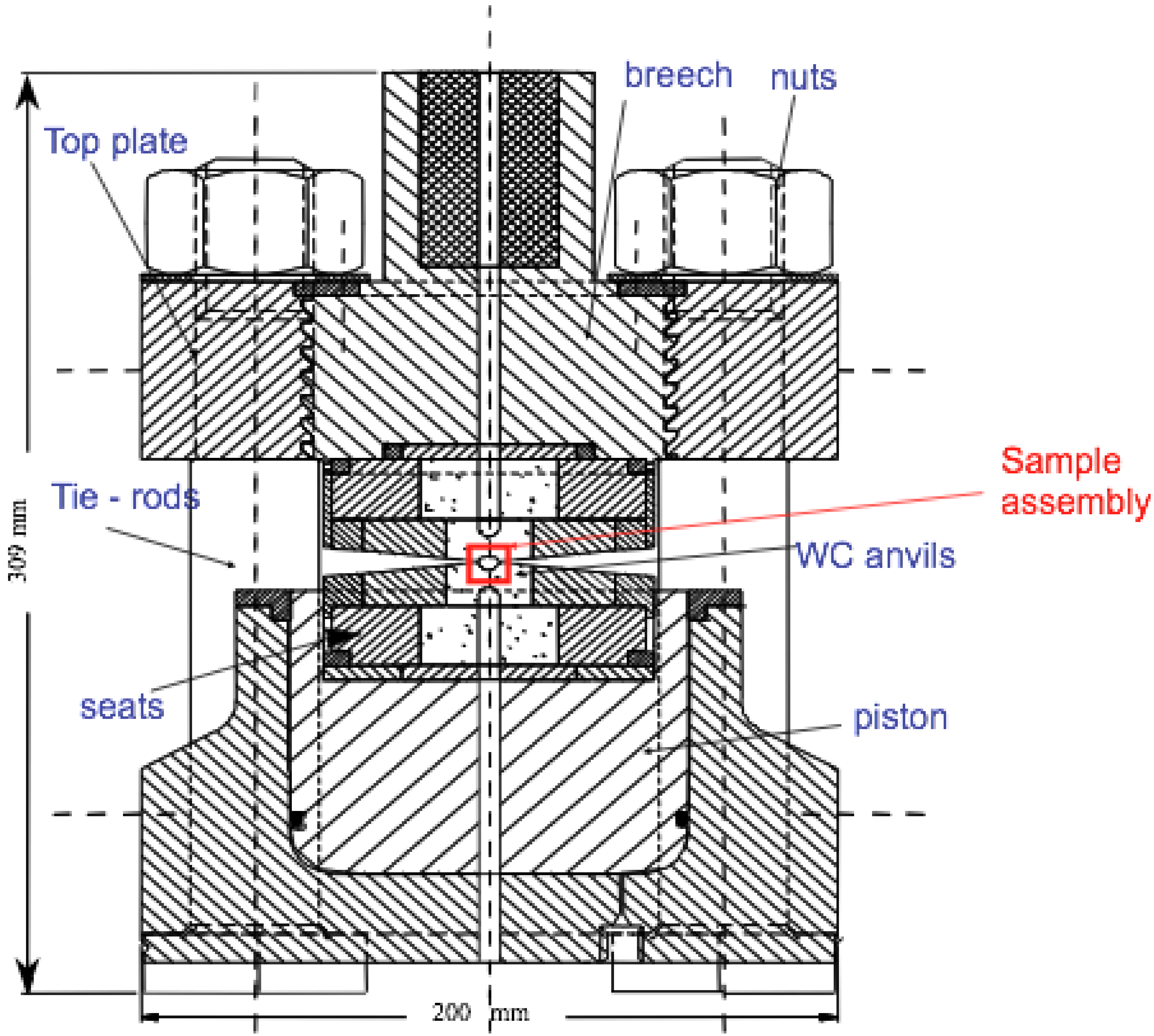
Earth temperature/pressure profile



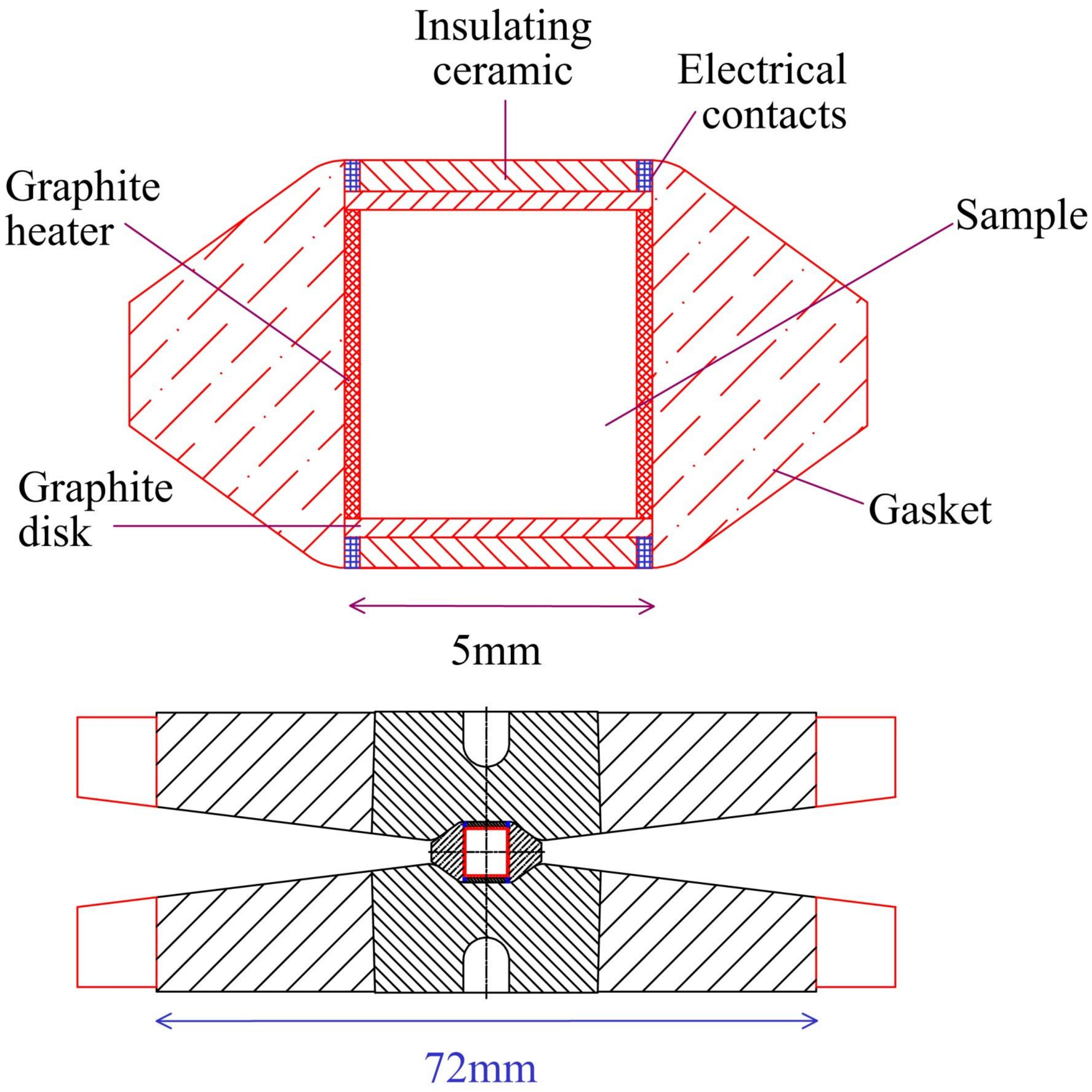
Paris-Edinburgh cell



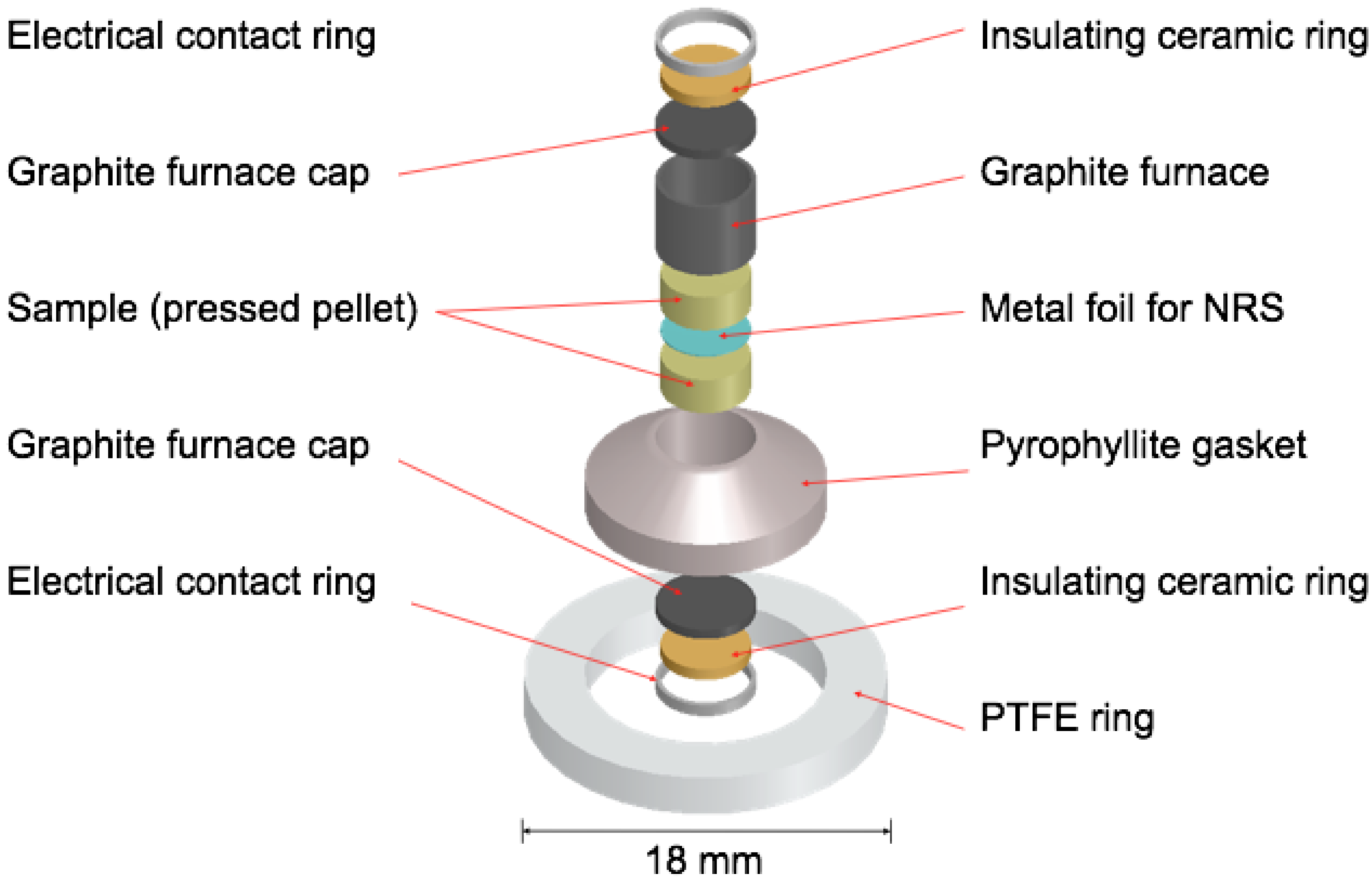
PE cell with internal microfurnace



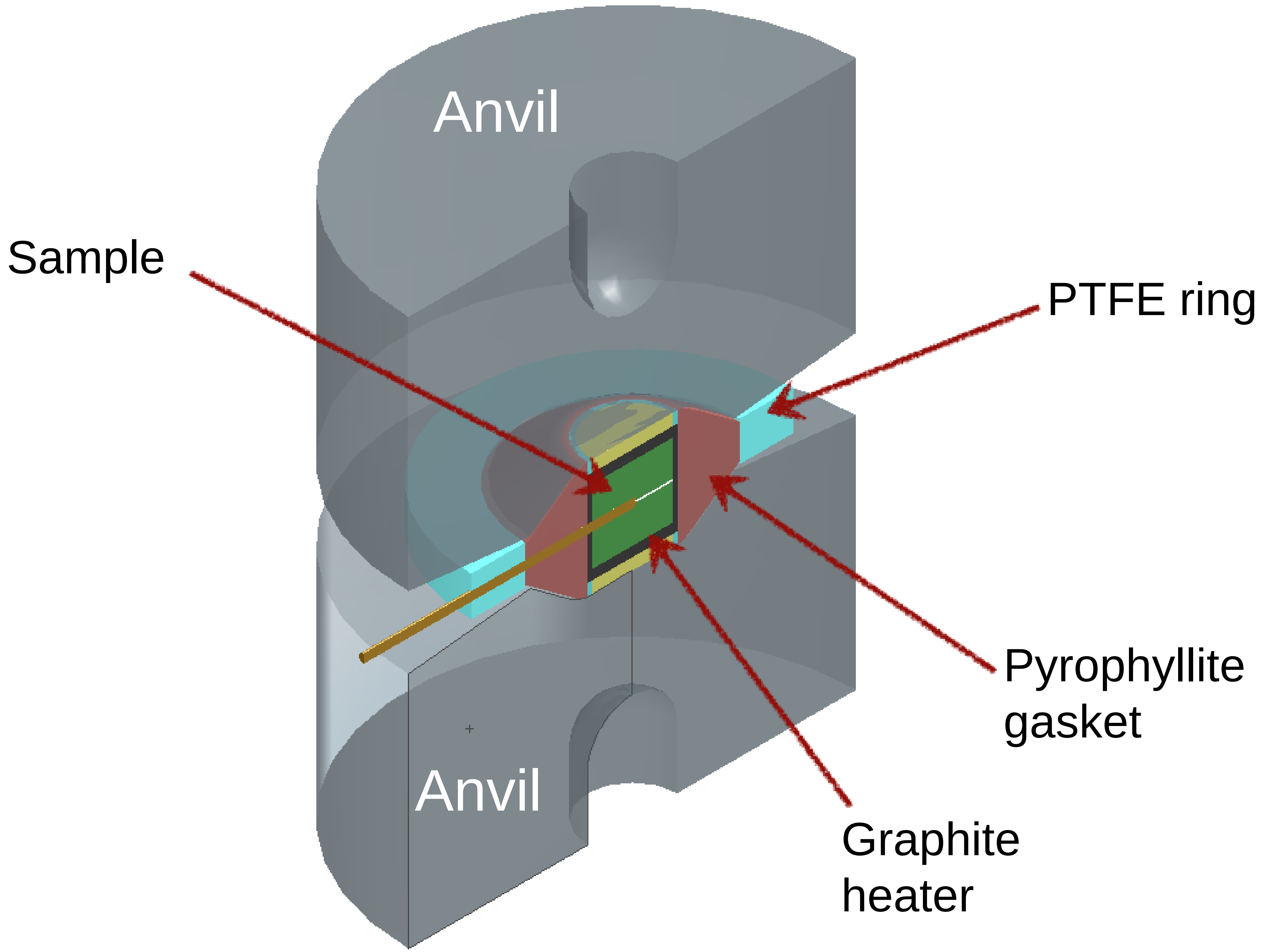
Internal heating – plan diagram



Internal heating – exploded view

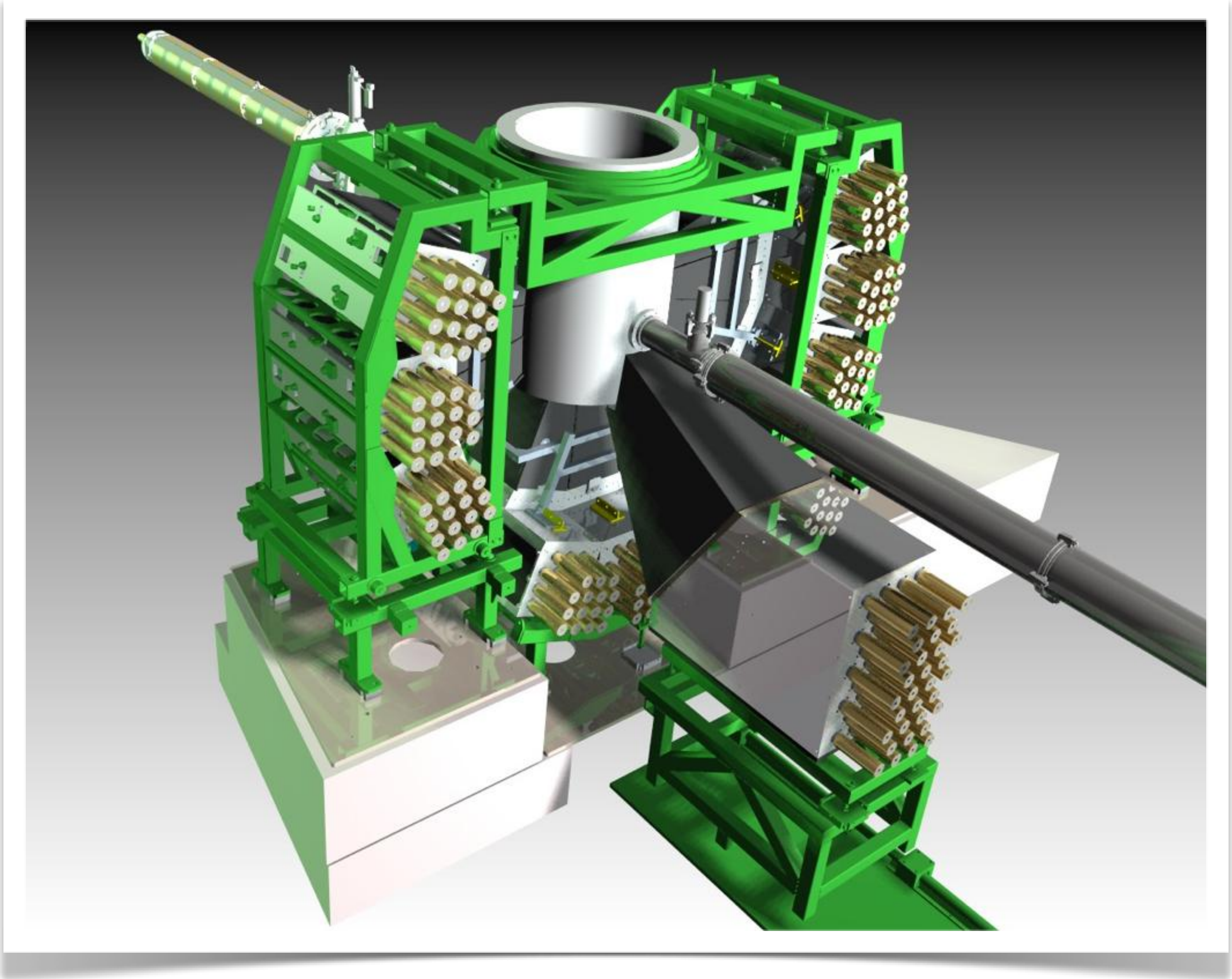


Assembly

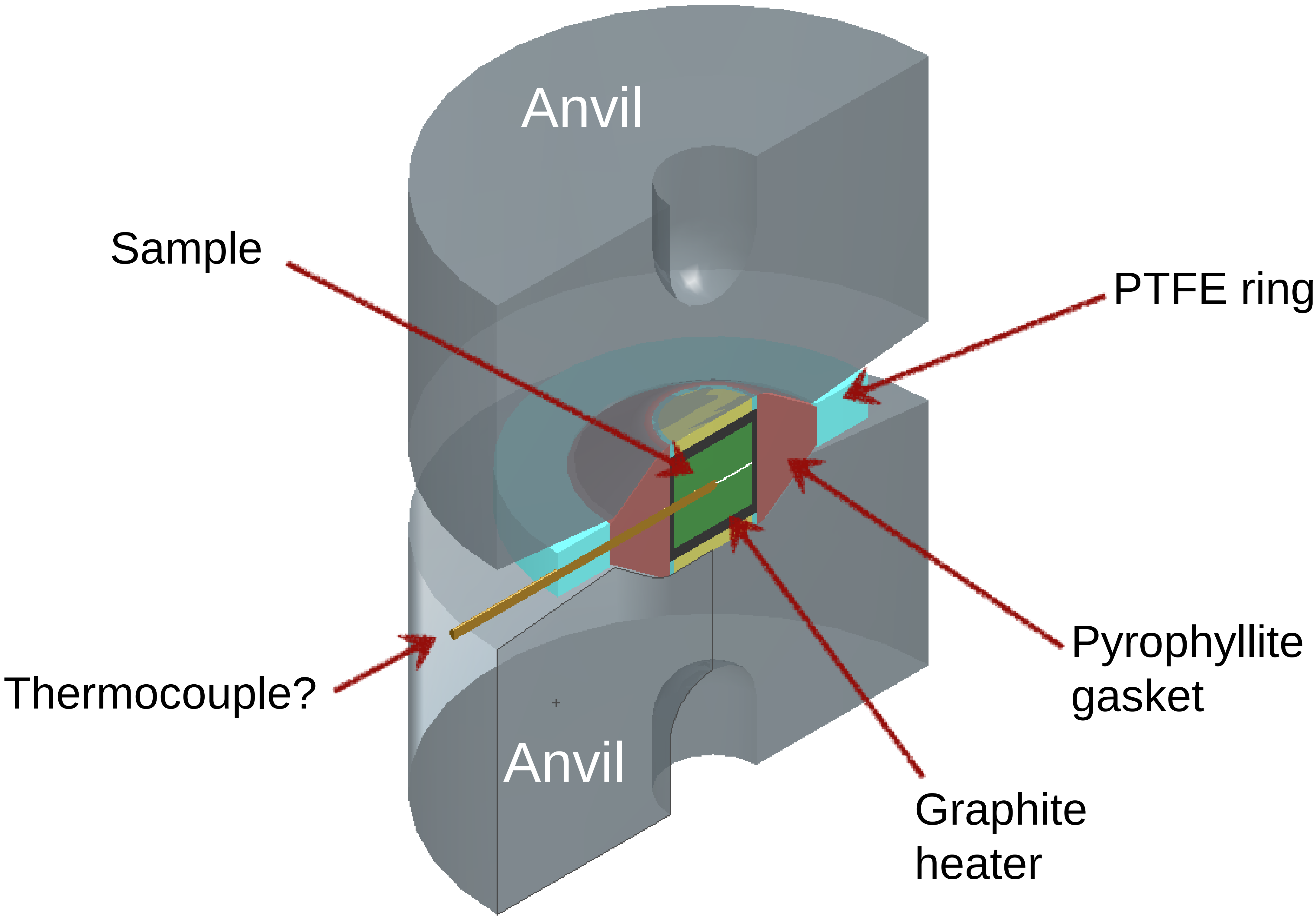


Anvil
Sample
PTFE ring
Pyrophyllite gasket
Graphite heater
Anvil

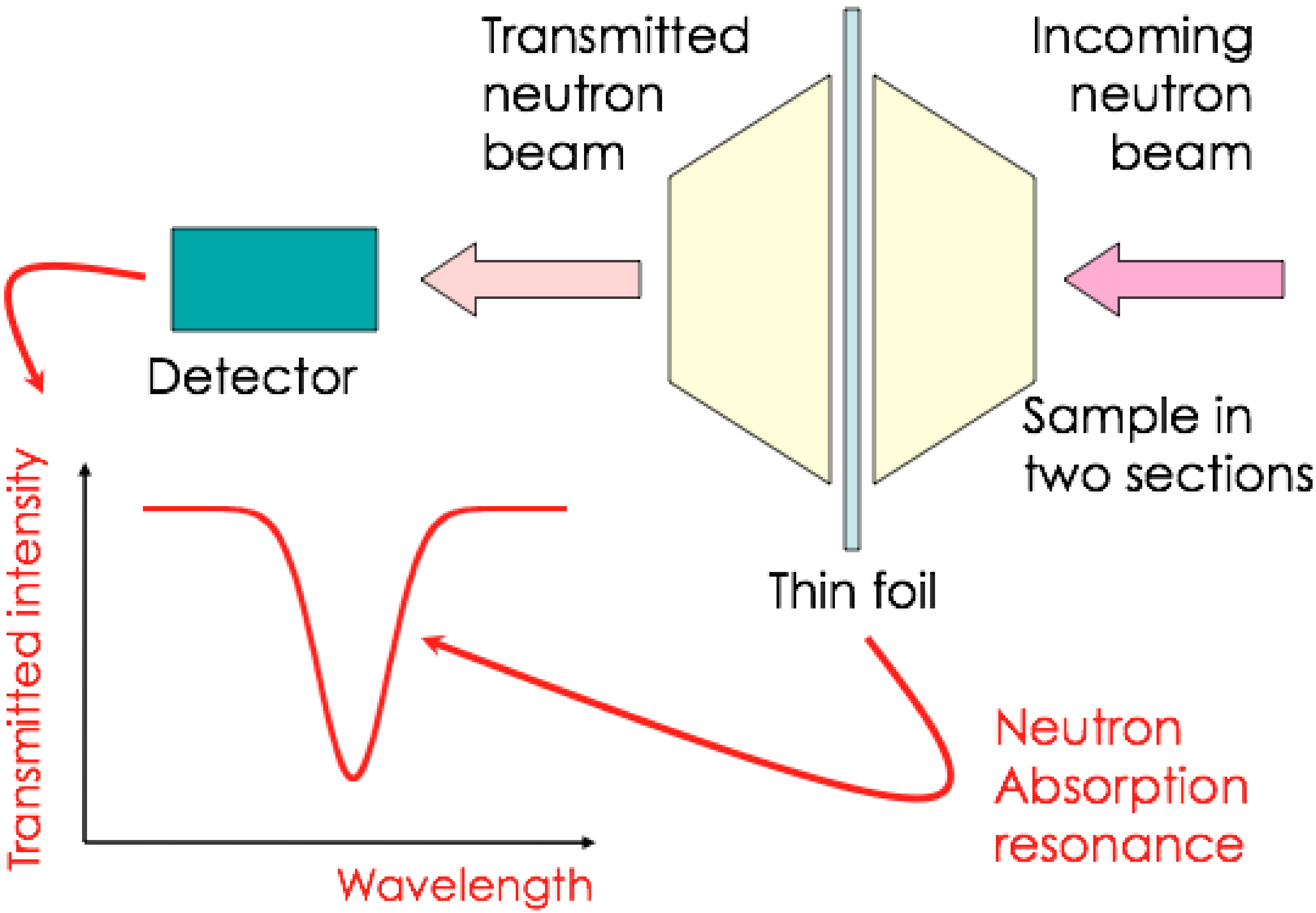
High-pressure diffraction @ ISIS



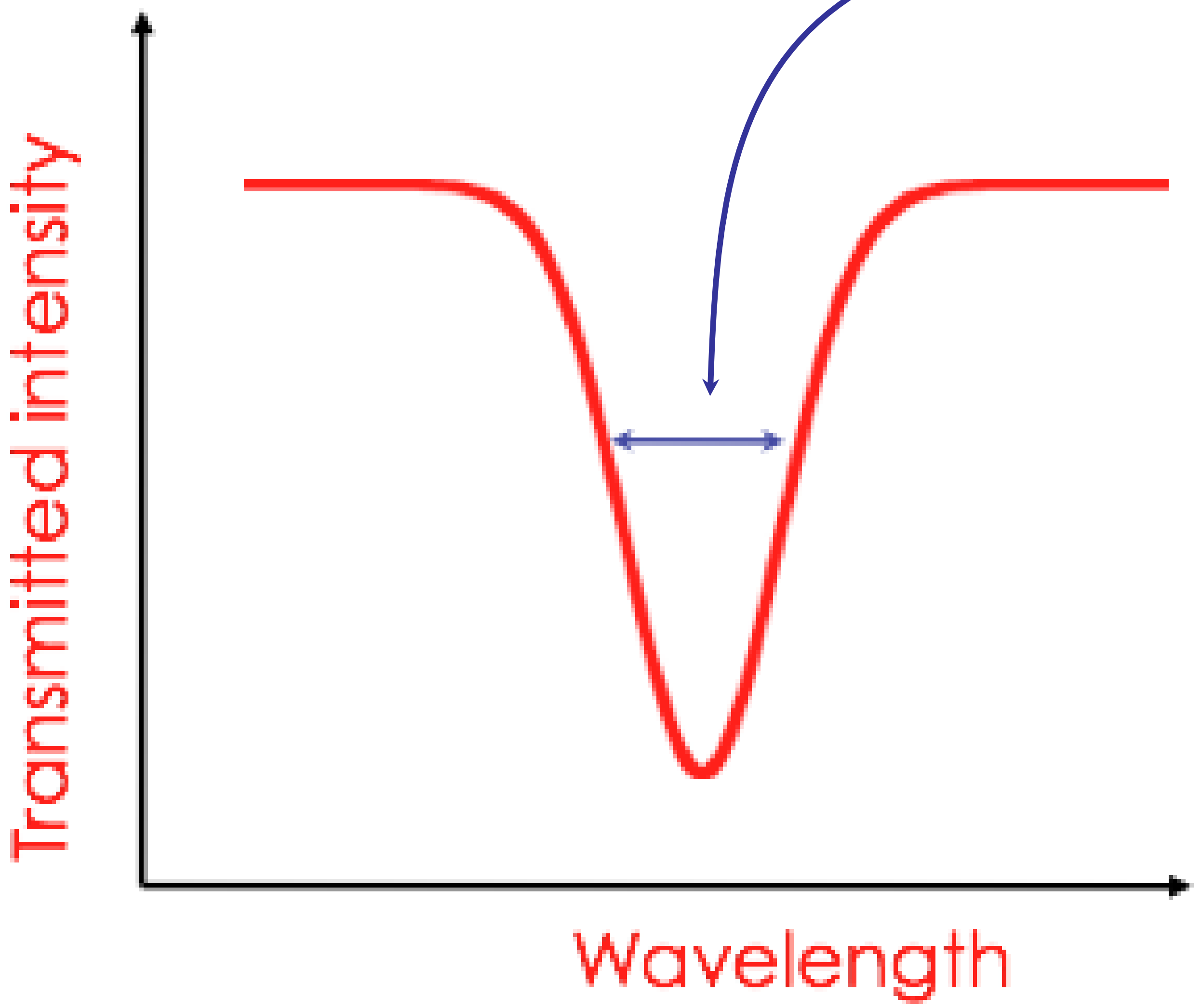
Assembly


Anvil
Sample
PTFE ring
Pyrophyllite gasket
Thermocouple?
Anvil
Graphite heater

Temperature measurement by radiography



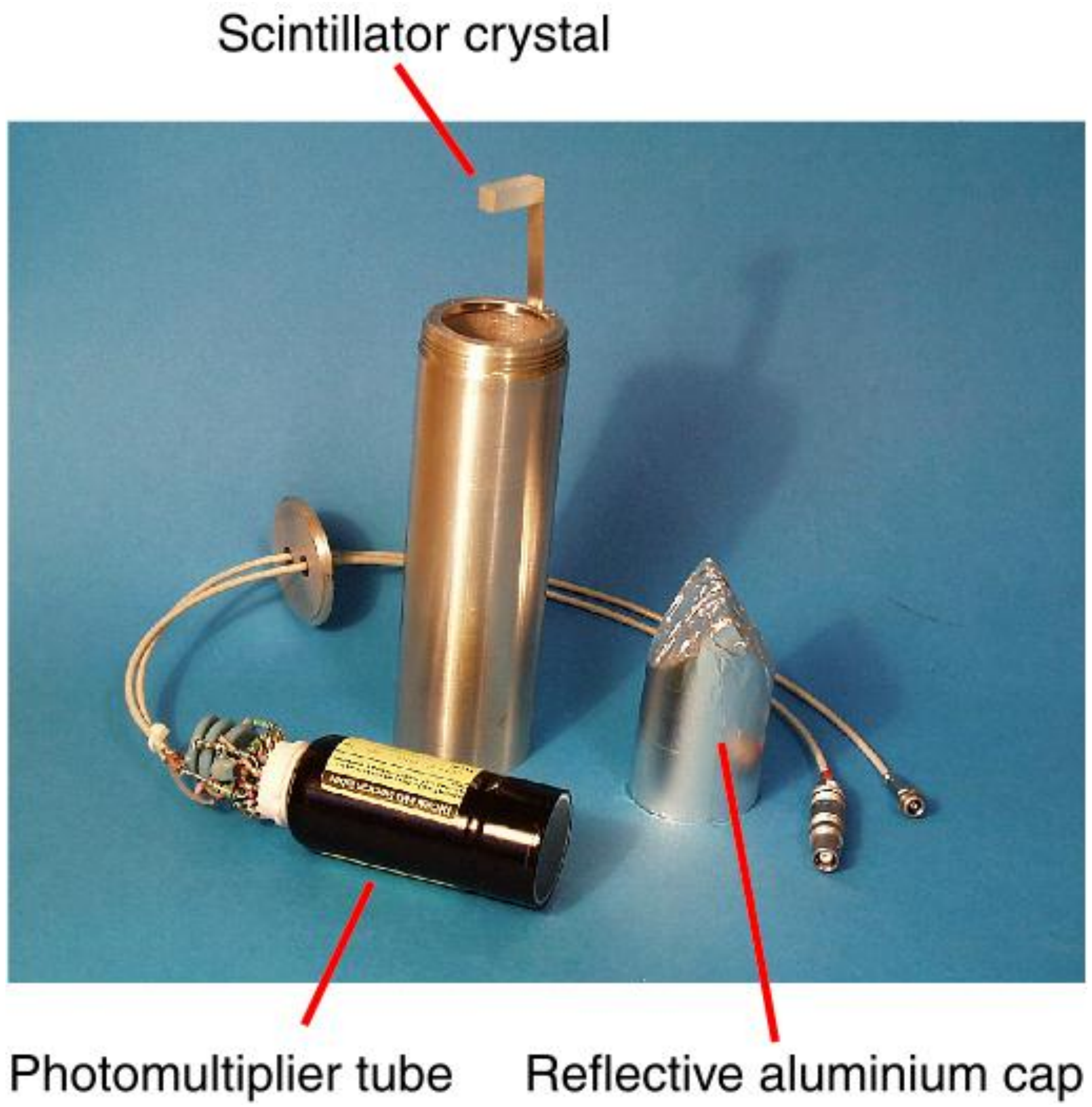
Radiography principal



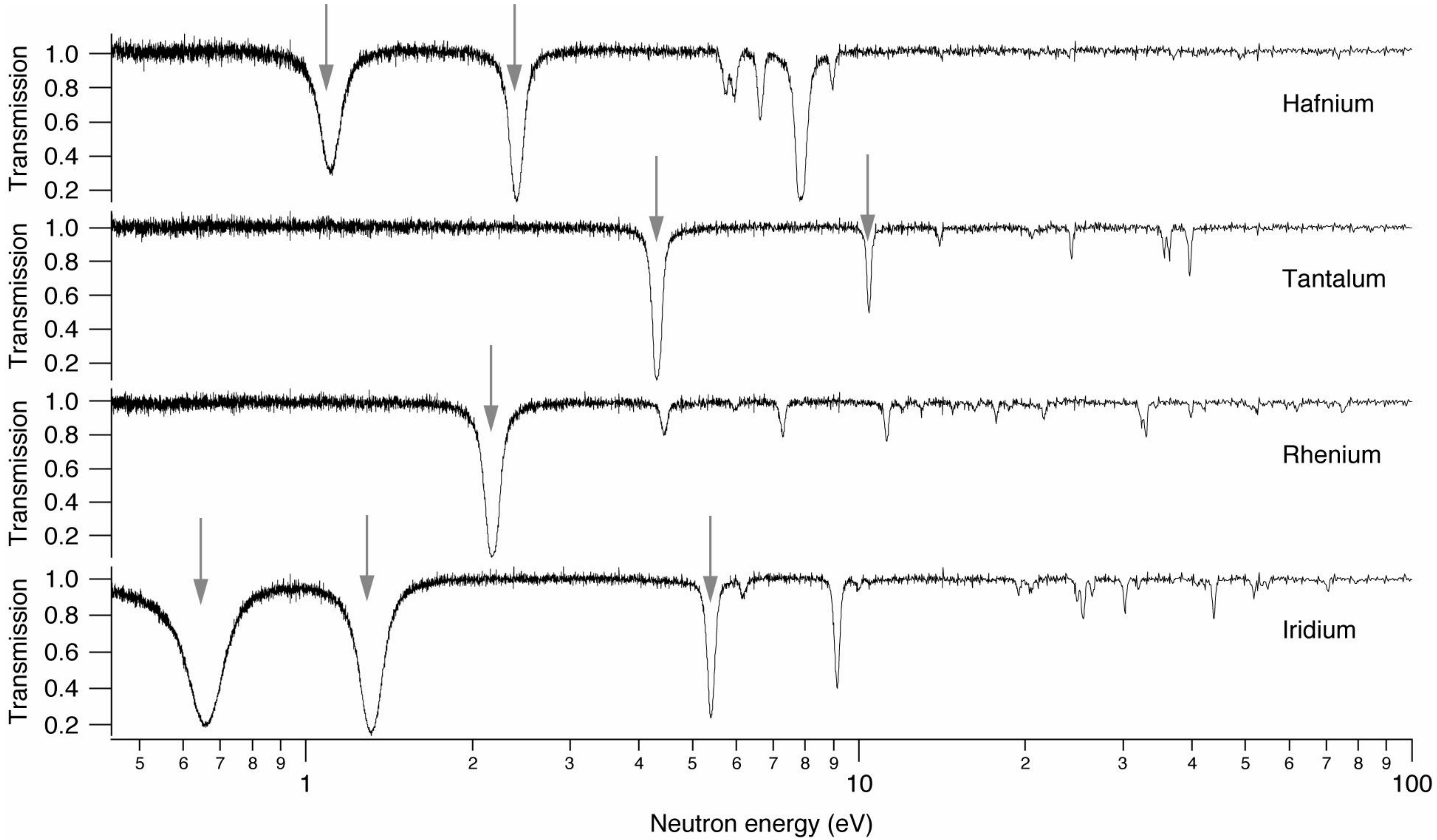
Width of resonance line increases with temperature due to Doppler effect

Width of resonance line can be used to calibrate temperature

Simple detector assembly



Example resonances



Theoretical basis

Energy transfer function
(the Doppler broadening functi

Breit-Wigner lineshape

Total cross-section: $$\sigma_{tot}(E) = \int_{-\infty}^{\infty} \sigma_{BW}(E')S(E-E')dE'$$

Transmitted signal: $$Tr(E) = \exp(-\mu\sigma_{tot}(E))$$

Area density of
absorbing nuclei

Detected signal: $$I(E) = \int_{-\infty}^{\infty} P(E')\varepsilon(E')R(E')Tr(E-E')dE'$$

Pulse source
function

Detector efficiency

Instrument
resolution function

Theoretical basis

Measured signal

$$I(E)=\int_{-\infty}^{+\infty}P(E')\varepsilon(E')R(E')T(E-E')\,\mathrm{d}E'$$

Pulse source function

Detector efficiency

Resolution function

Transmitted signal

$$T(E)=\exp\left(-\mu\sigma(E)\right)$$

Foil thickness x number of atoms

Absorption cross section

$$\sigma(E)=\int_{-\infty}^{+\infty}\sigma_{\mathrm{BW}}(E')S(E',E)\,\mathrm{d}E'$$

Breit-Wigner lineshape

Energy transfer function
(Doppler broadening function)

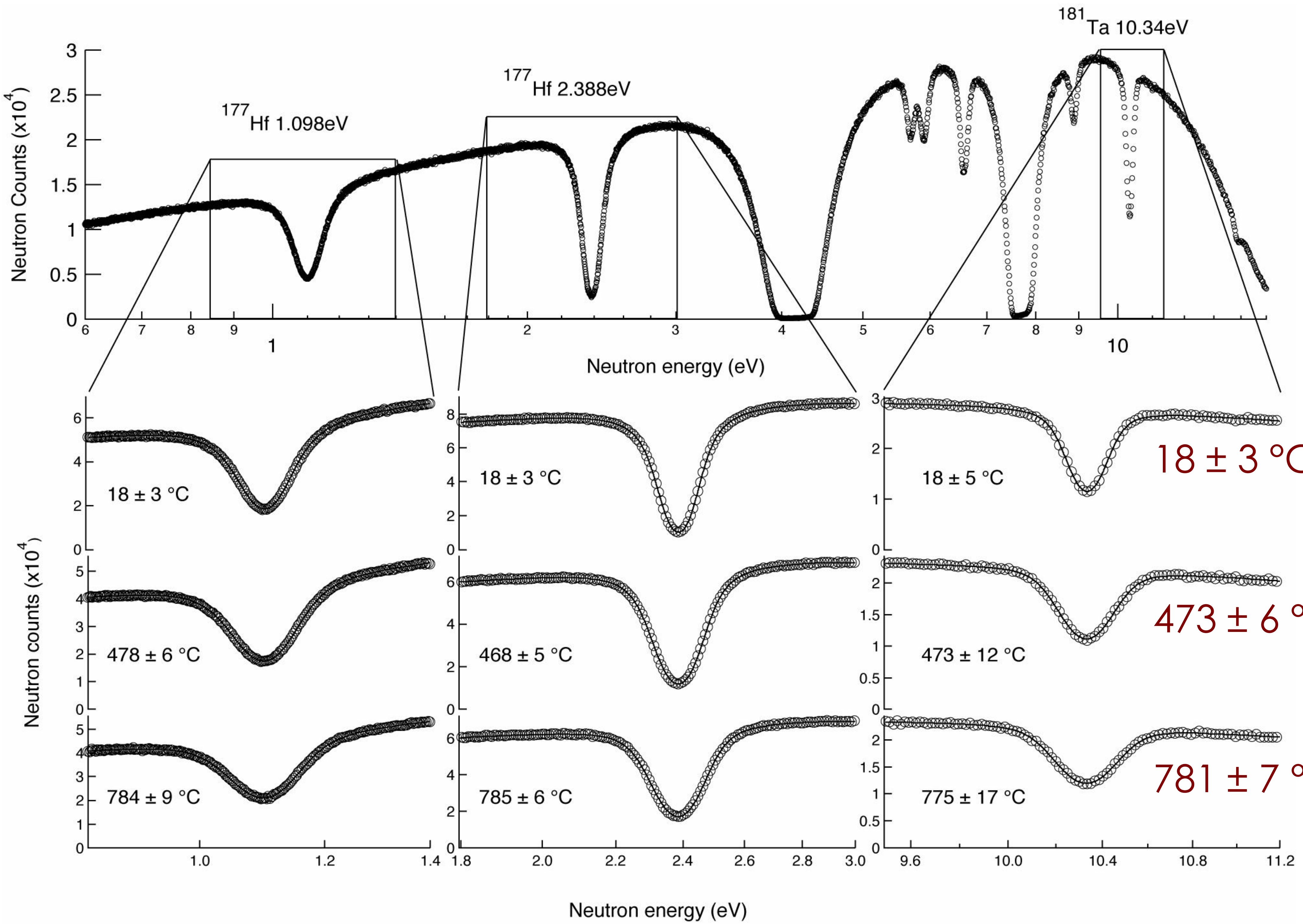
Energy transfer function

$$S(E') = \frac{1}{\Delta\sqrt{\pi}} \exp\left(-(E' - E)^2 / \Delta^2\right)$$

$$\Delta = \sqrt{\frac{4mME_{\mathrm{R}}k_{\mathrm{B}}T}{(M+m)^2}}$$

Temperature of absorbing atoms = sample temperature

Example of application

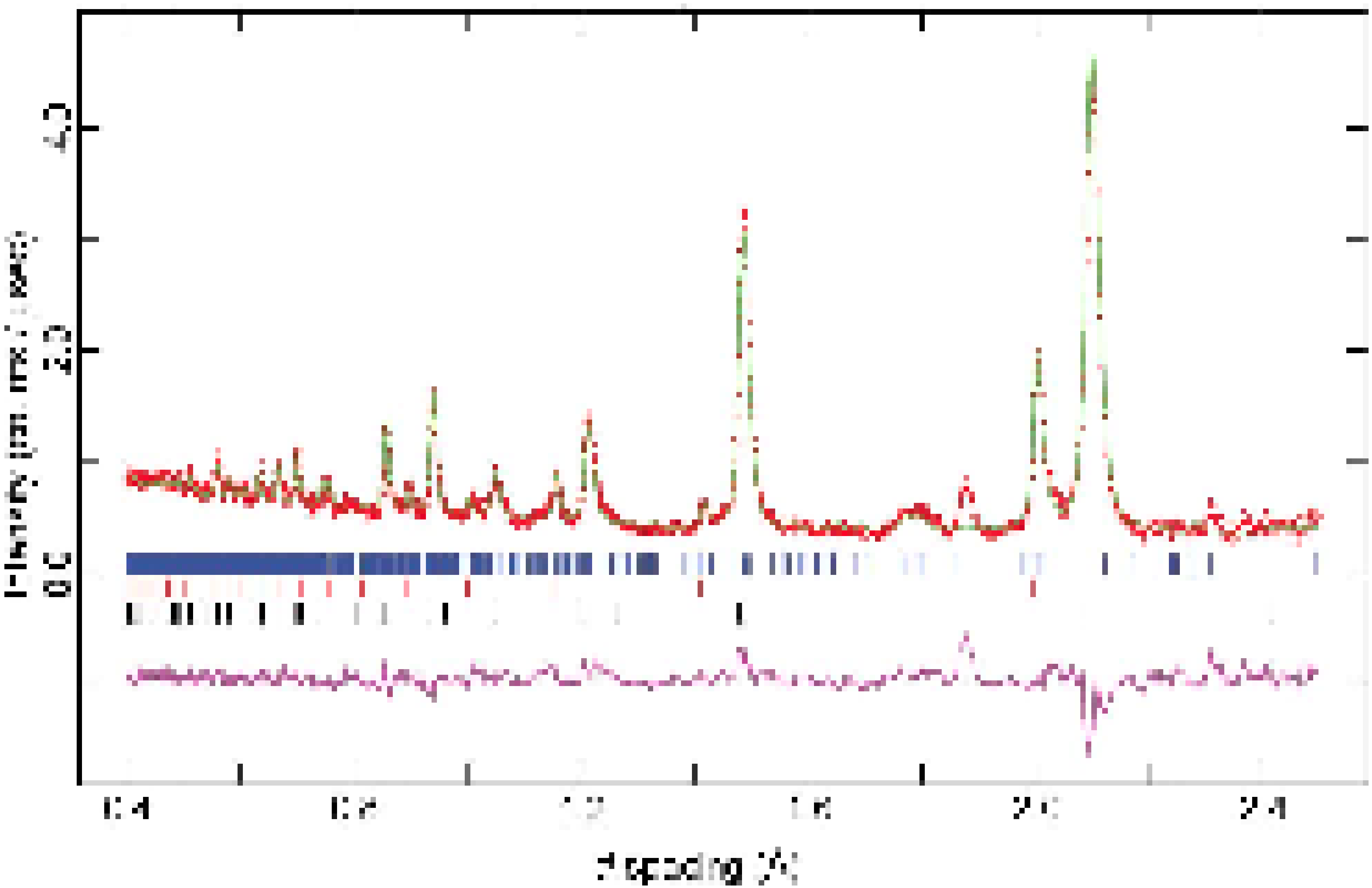


18 ± 3 °C

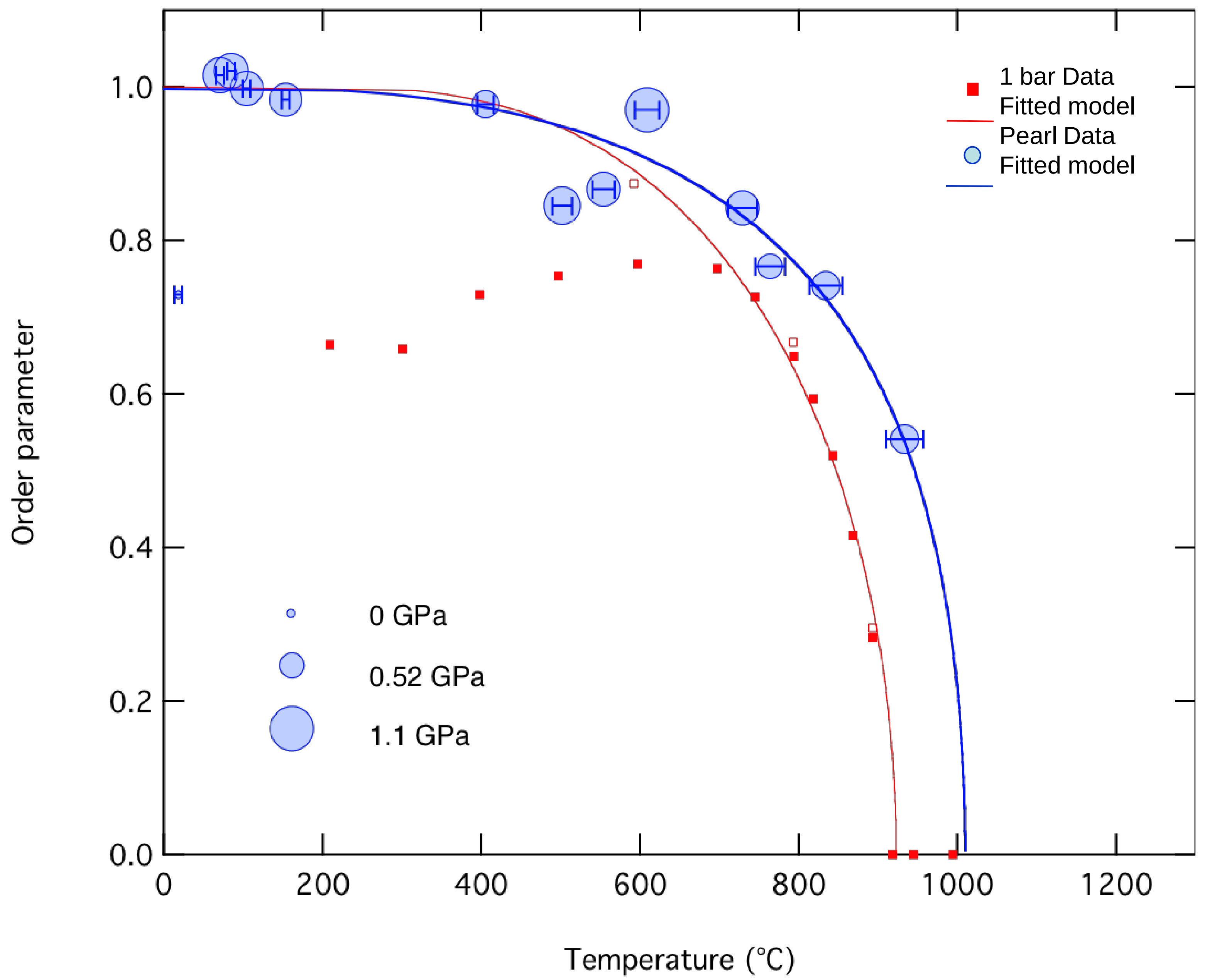
473 ± 6 °C

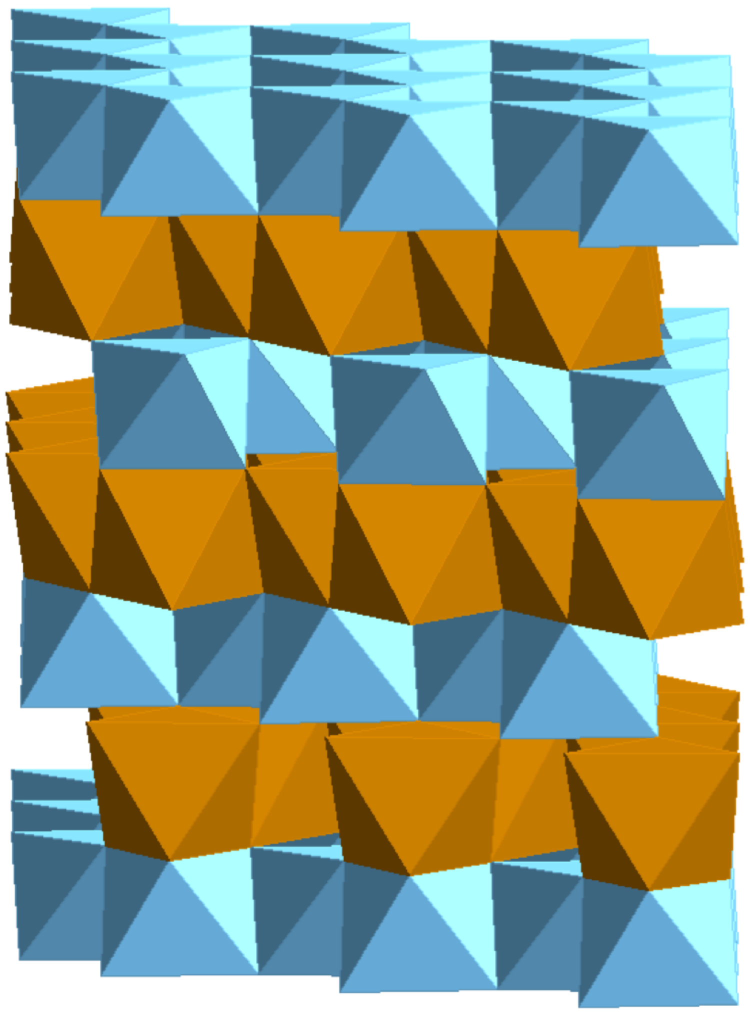
781 ± 7 °C

Example of diffraction data: $Mg_{0.7}Fe_{0.3}O$ at 621 K and 9.82 GPa



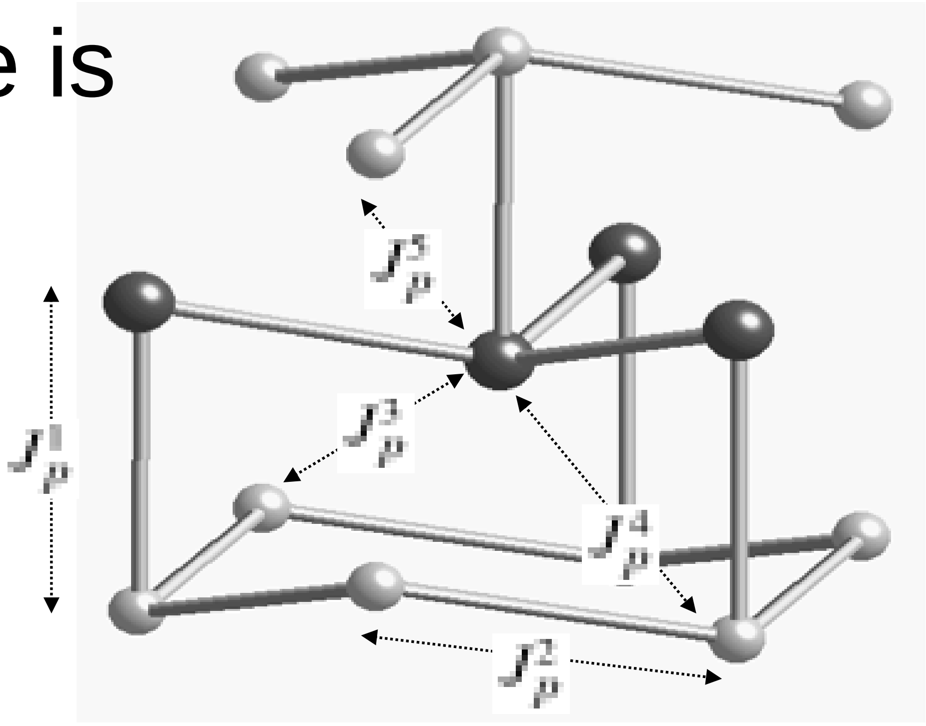
Pressure dependence of Fe/Ti ordering in $Fe(Fe_{0.35}Ti_{0.65})O_3$





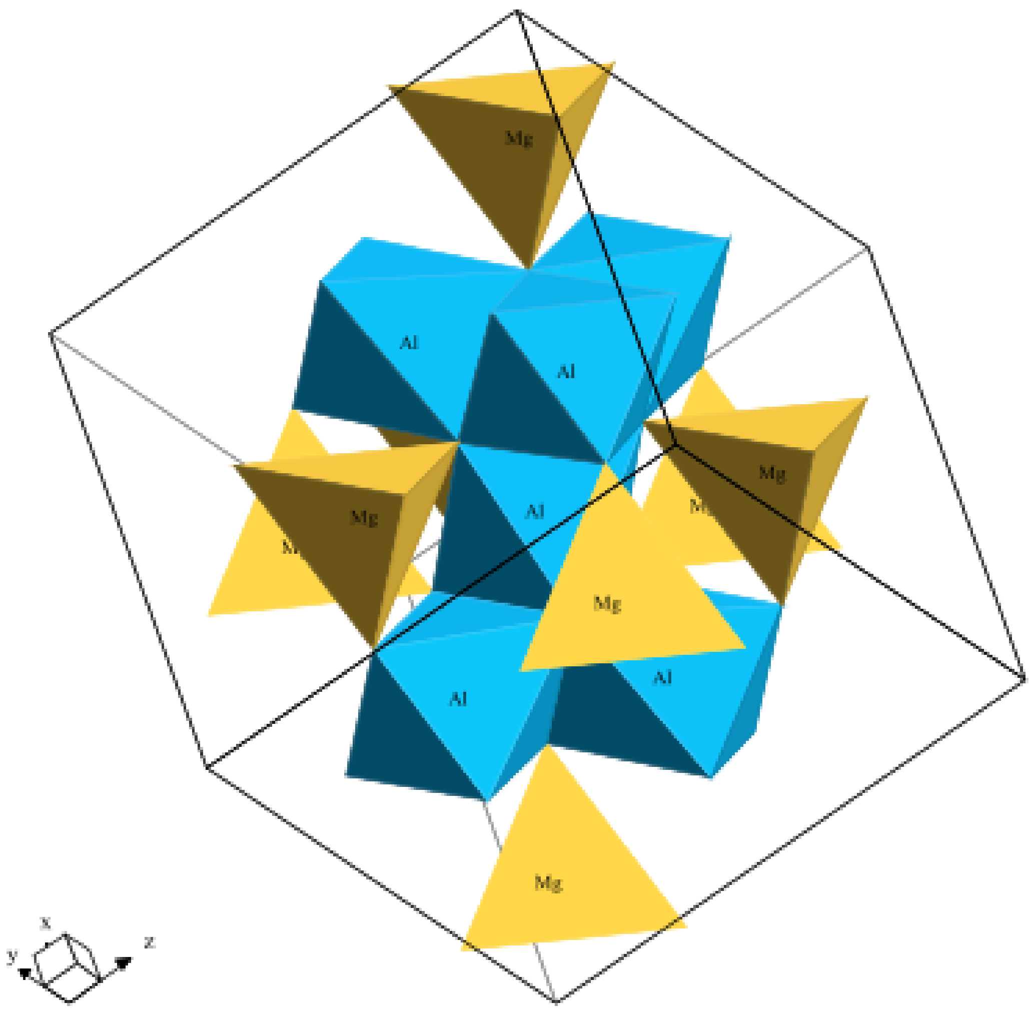
Pressure dependence of Fe/Ti ordering in $Fe(Fe_{0.35}Ti_{0.65})O_3$

- Increase in T_c cannot be accounted for by conventional strain effects
- Increase in T_c must therefore come from increased internal energy of ordering, i.e. increased cation interaction as structure is squeezed

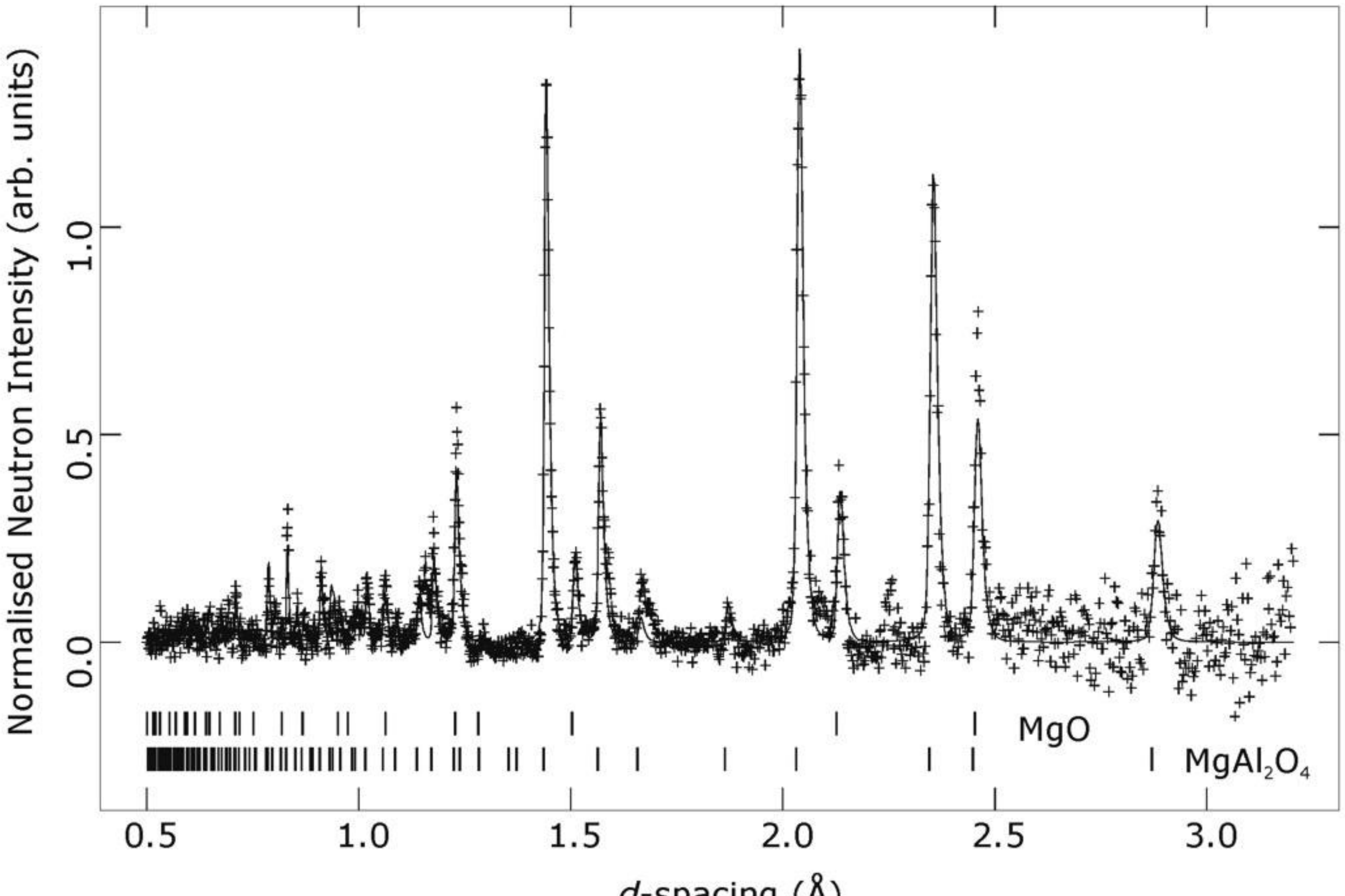


Influence of pressure on Mg/Al order-disorder in spinel, $MgAl_2O_4$

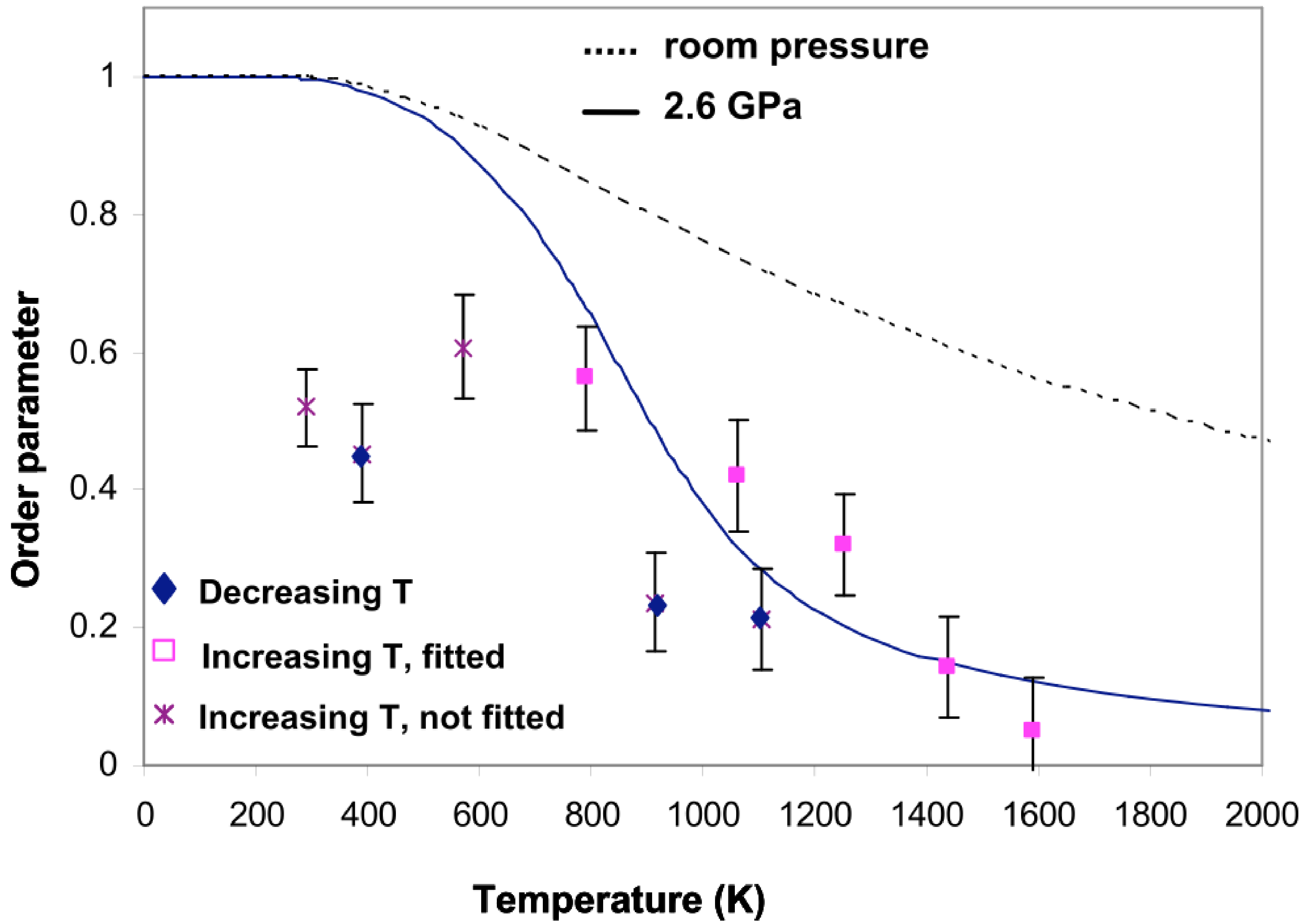
- Determine the pressure-dependence of the kinetics of order-disorder in minerals
- Probe the pressure dependence of the equilibrium high-T order-disorder properties: first neutron measurements of these phenomena at real Earth interior conditions



Diffraction pattern from $MgAl_2O_4$, at 1600 K and 3.2 GPa



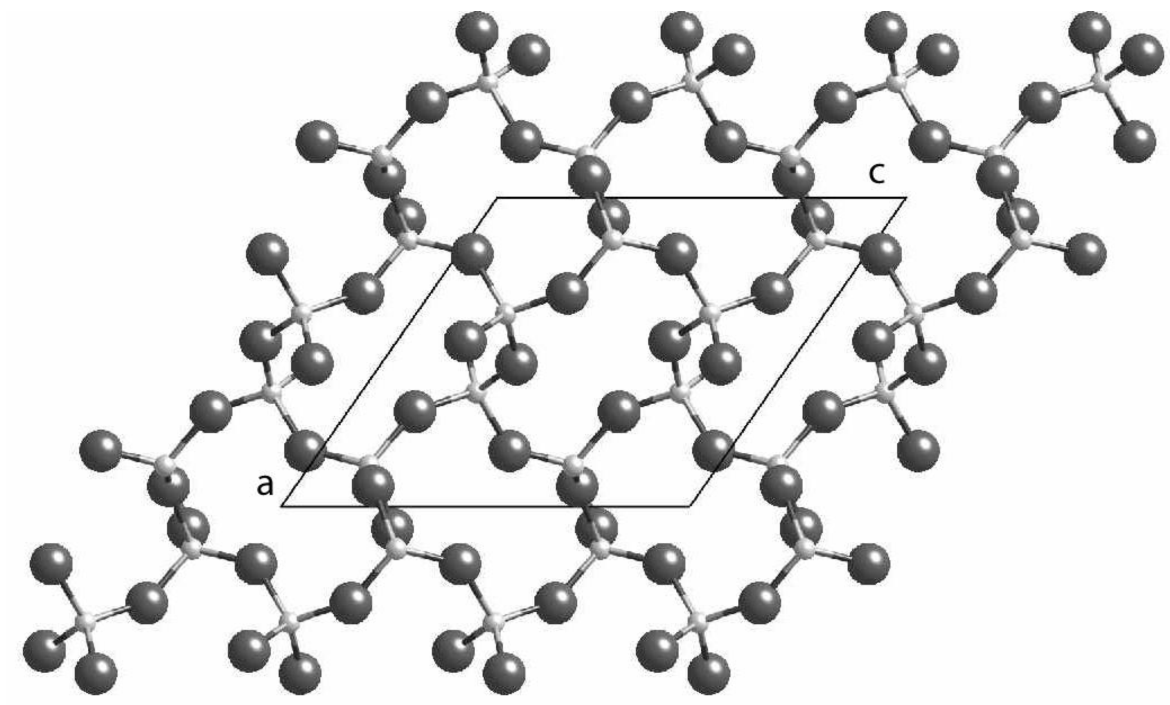
Variation of order as a function of pressure

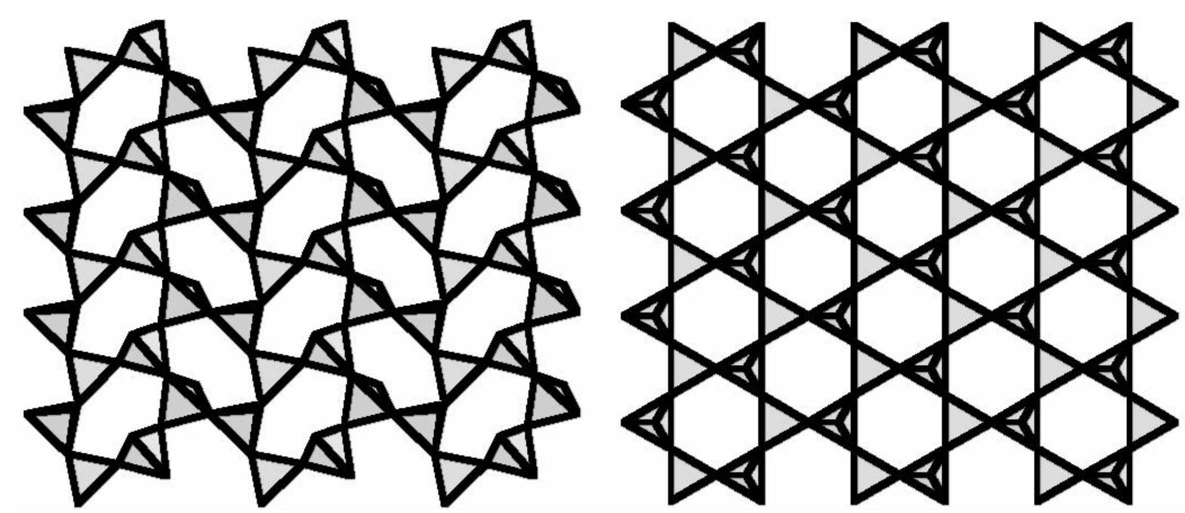


- Pressure significantly modifies the degree of order
- More disordered with pressure: effect of changing local interactions between Al and Mg neighbours

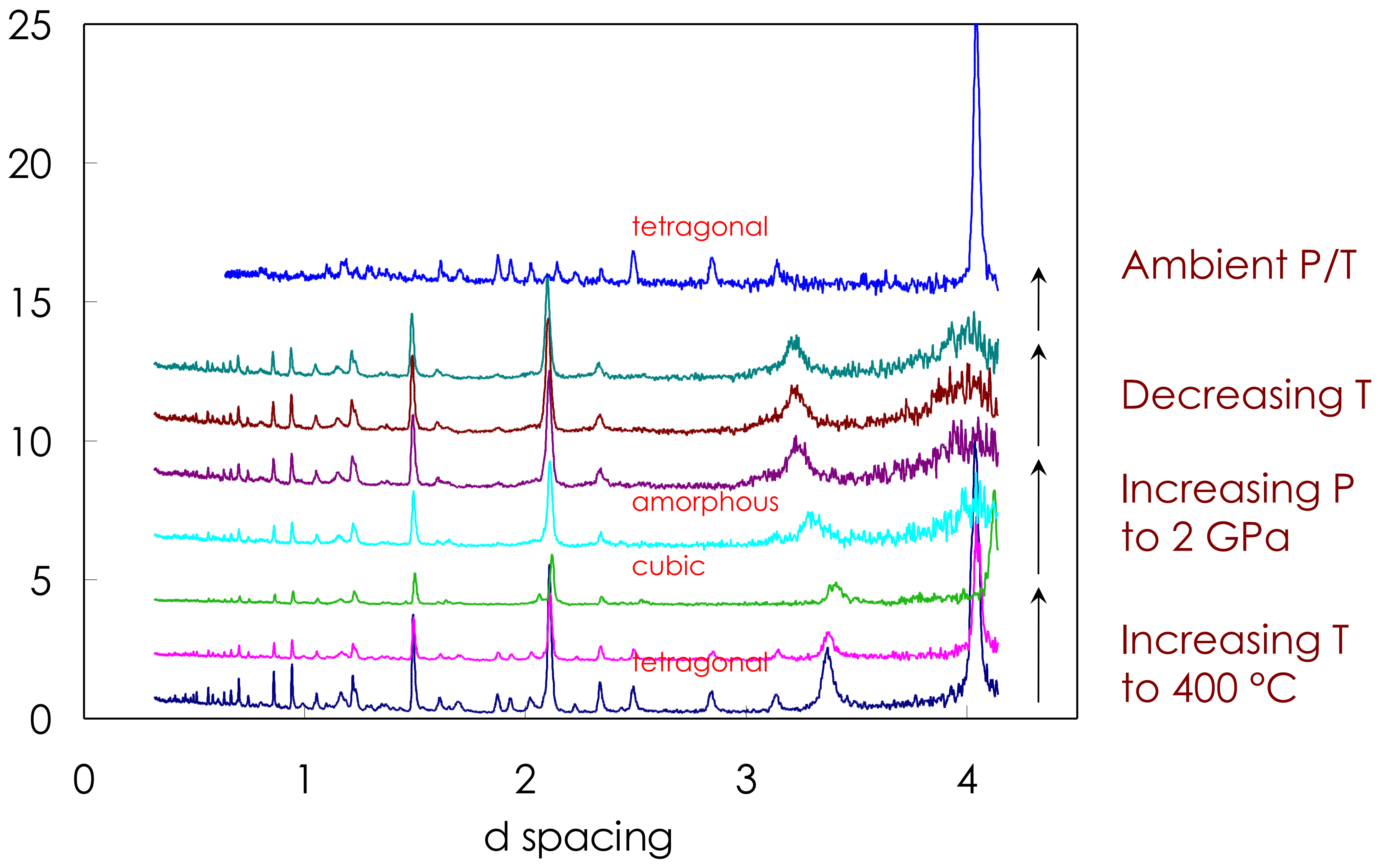
High-pressure displacive phase transition in cristobalite, SiO_2

- Stable above ca 1.5 GPa
- Although it is the lowest-symmetry phase, it is derived from cubic β rather than tetragonal α
- Structure identified using simulations

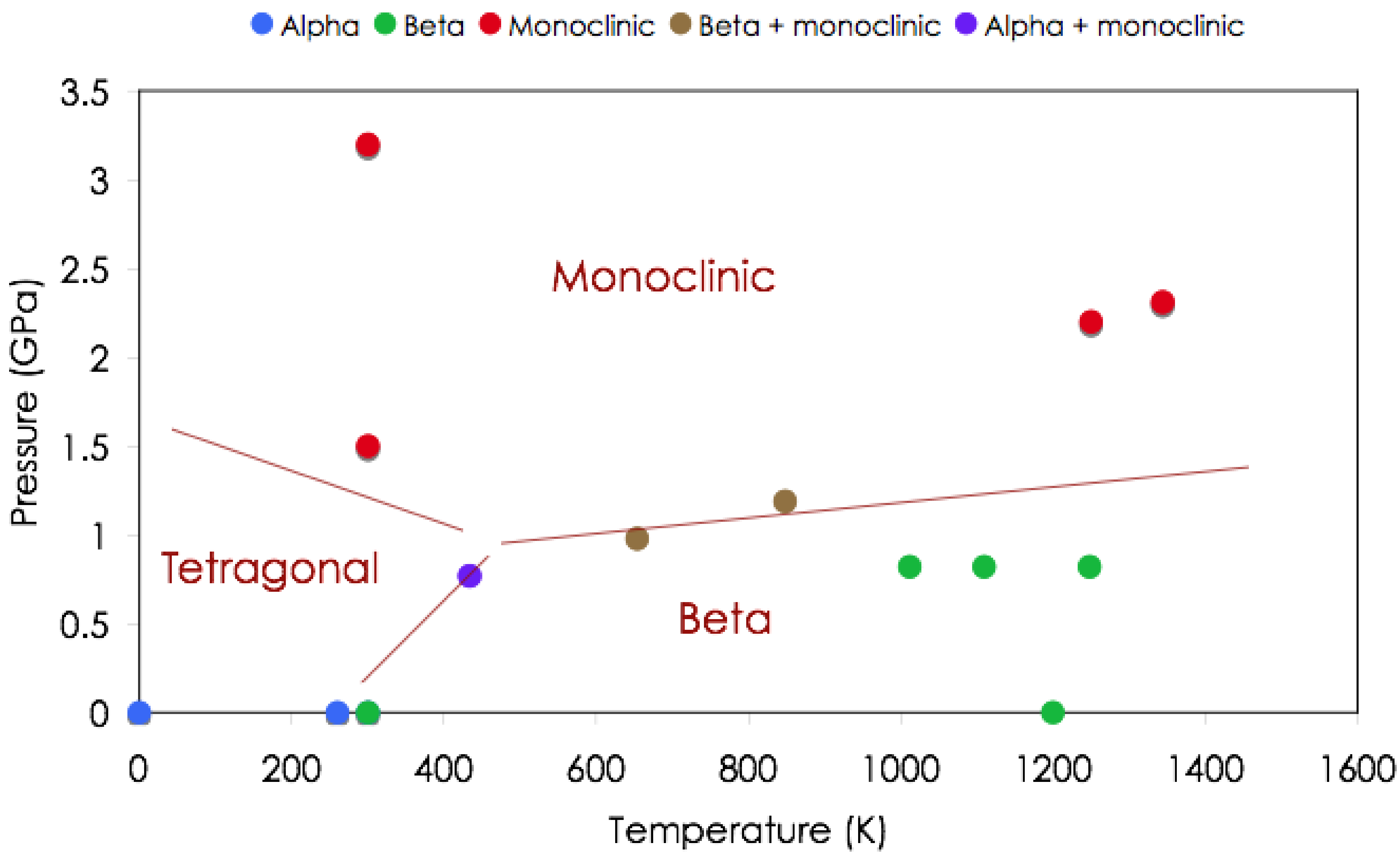




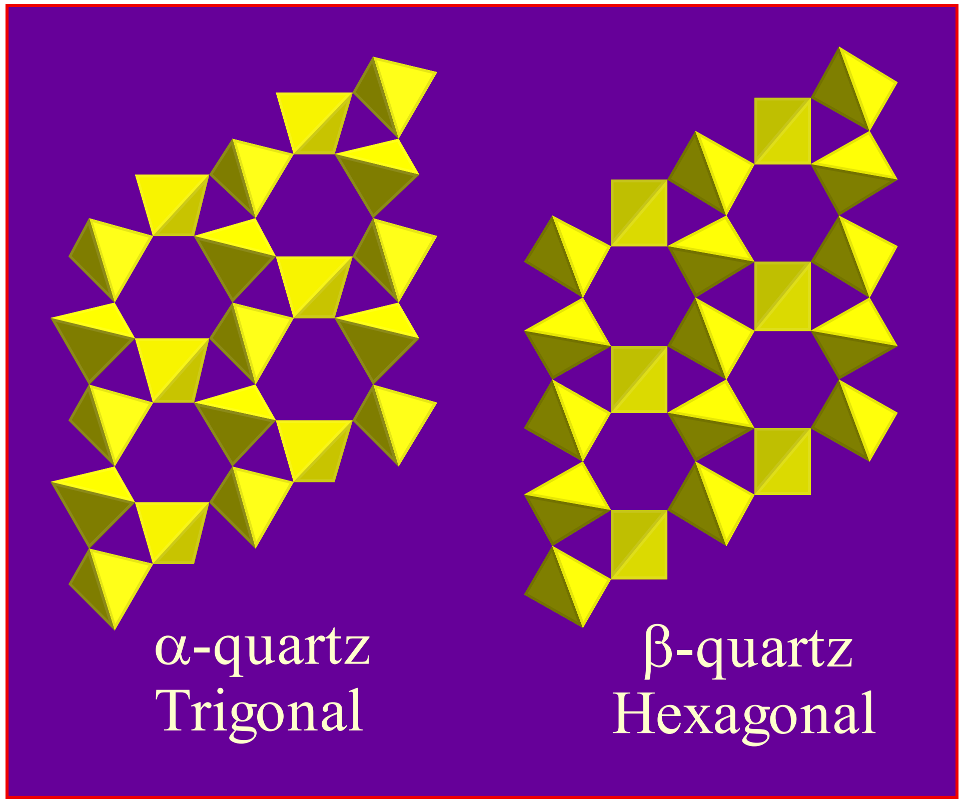
Effects of varying pressure and temperature



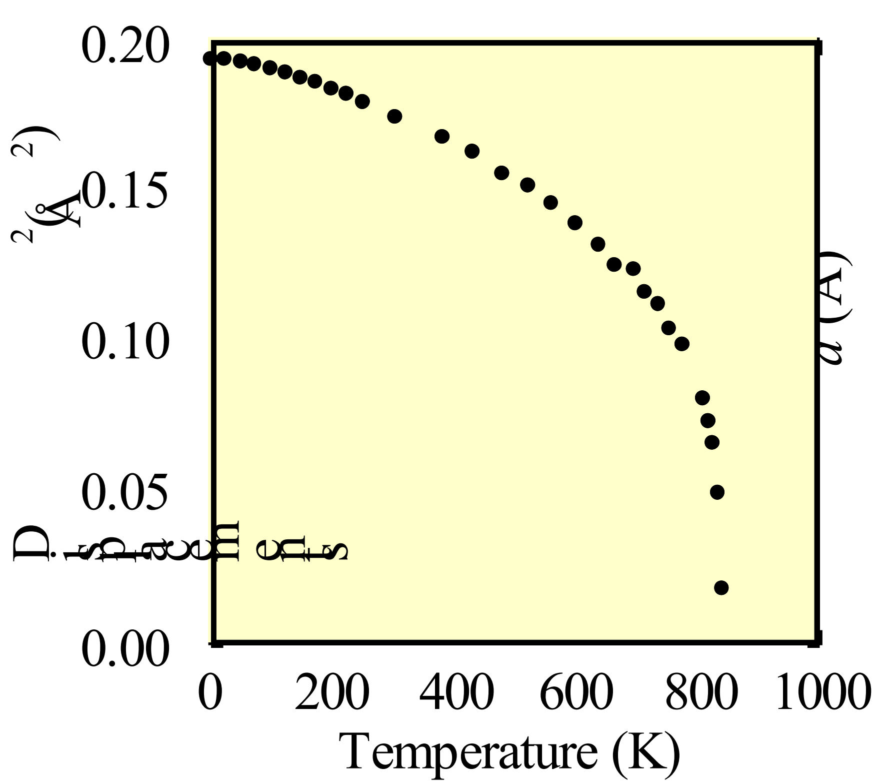
Phase diagram

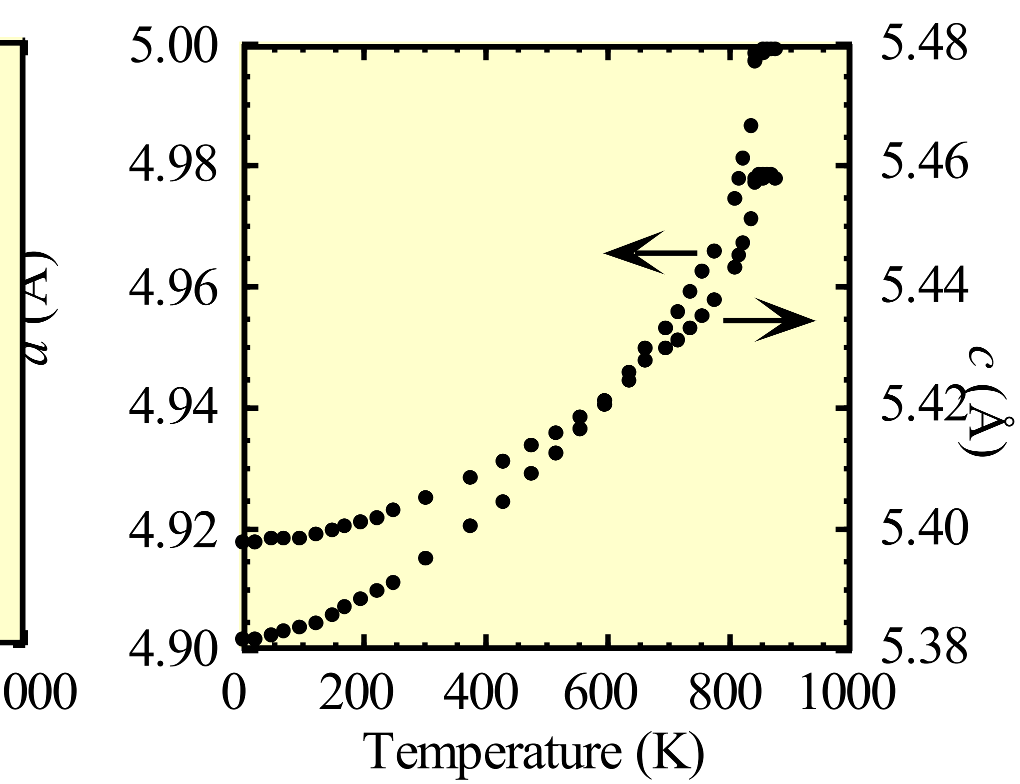


High-temperature displacive phase transition in quartz, SiO_2

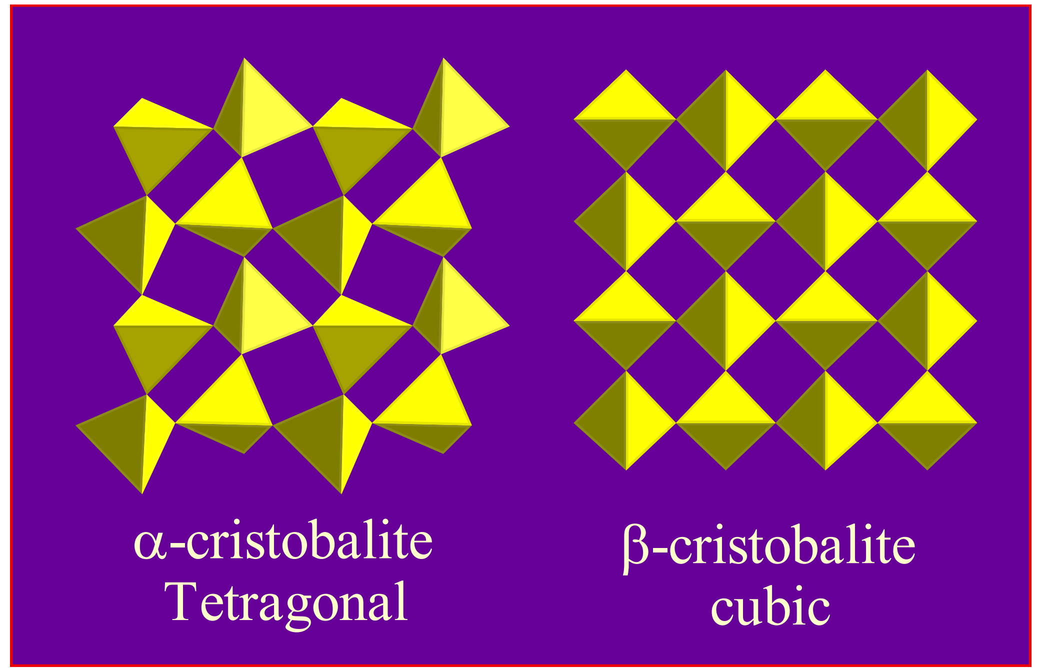


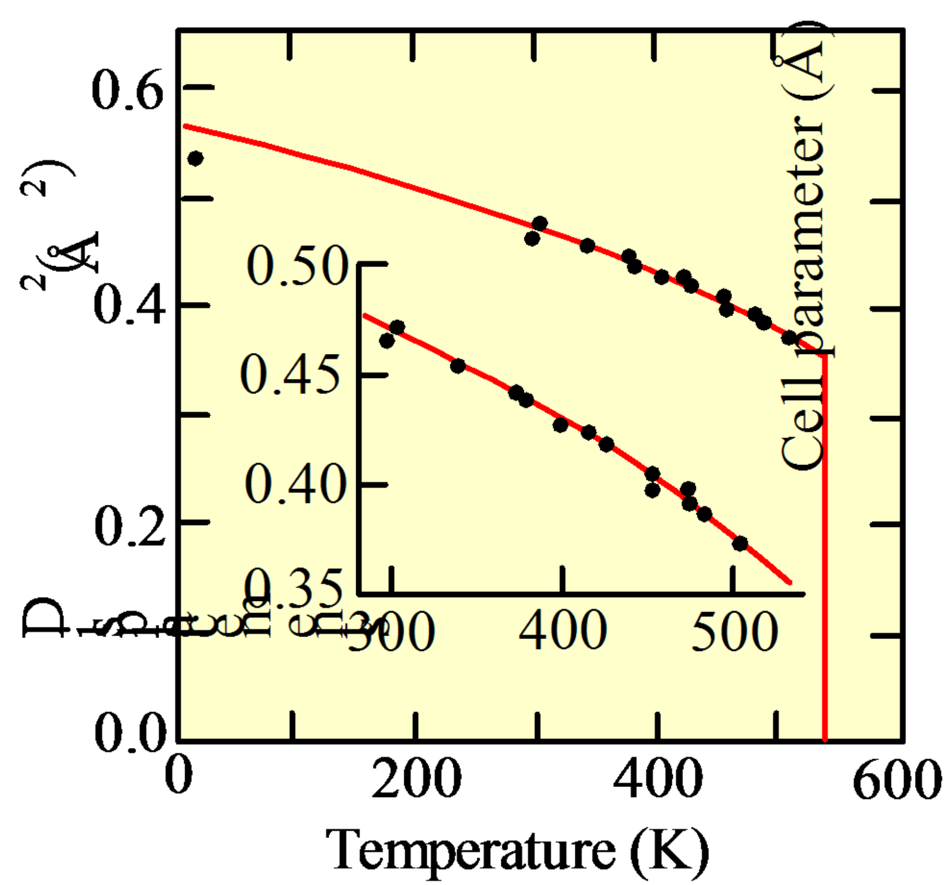
Small displacements of atoms that change the symmetry

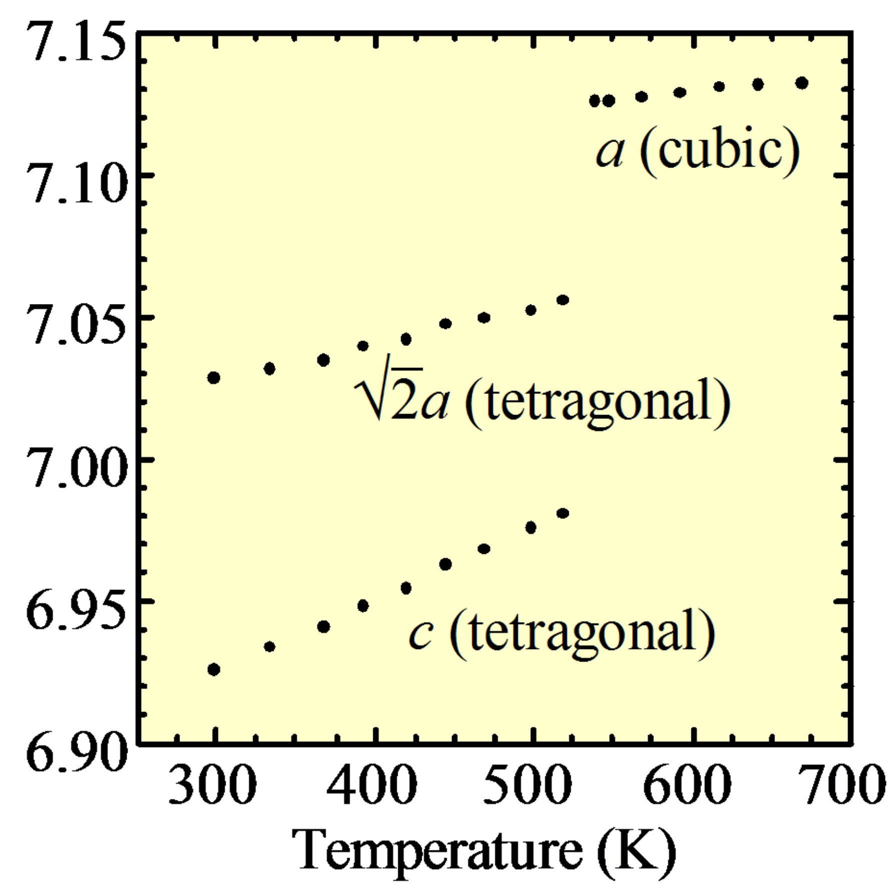




High-temperature displacive phase transition in cristobalite, SiO_2



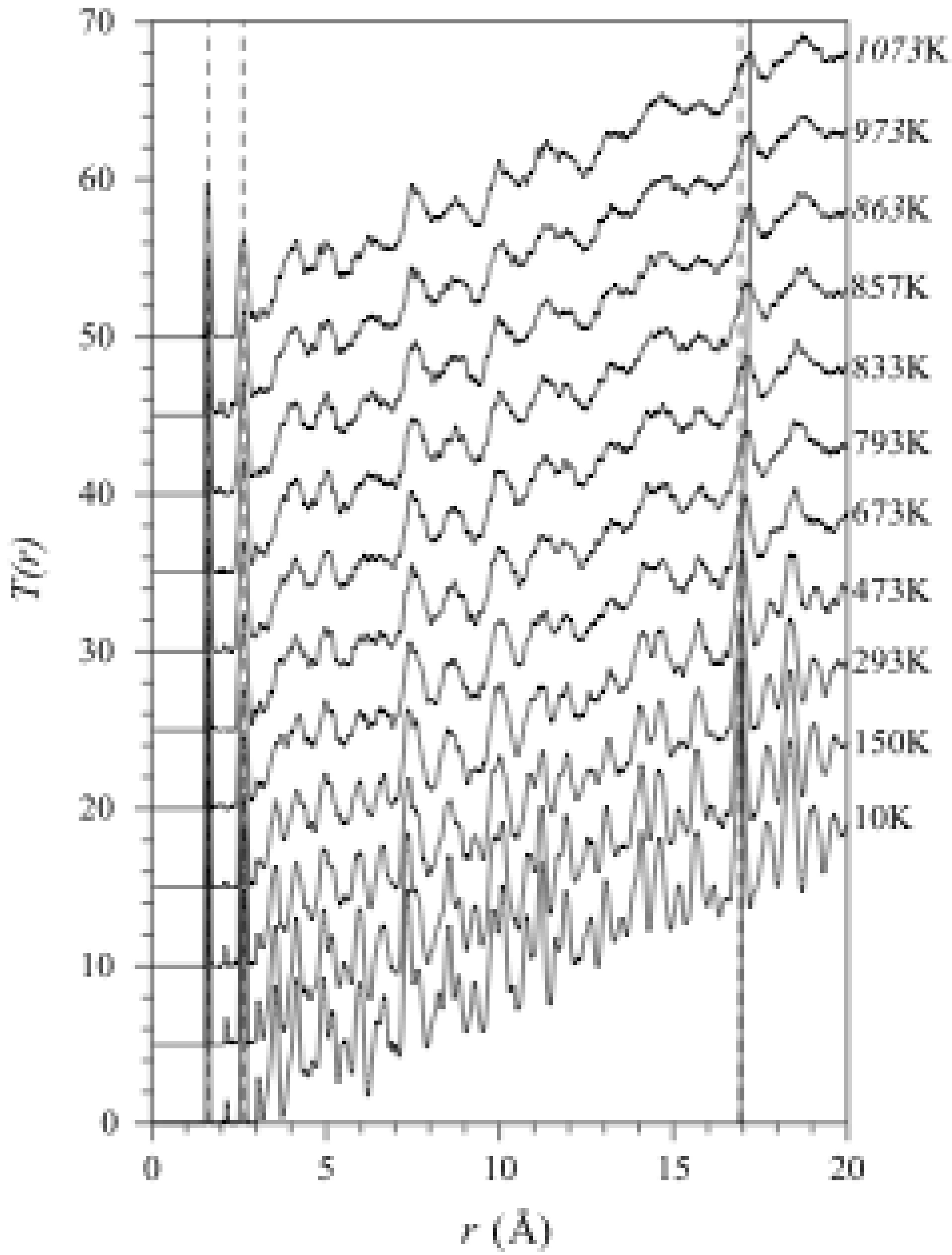




What do high-temperature phases look like?

- The challenge is that the local structure is unlikely to be exactly reflected in the average structure
- Local structure can be probed using total scattering – the same approach that is used to study amorphous materials and liquids
- We use the Reverse Monte Carlo method to build large atomic models consistent with the Bragg scattering, total scattering, and pair distribution function data

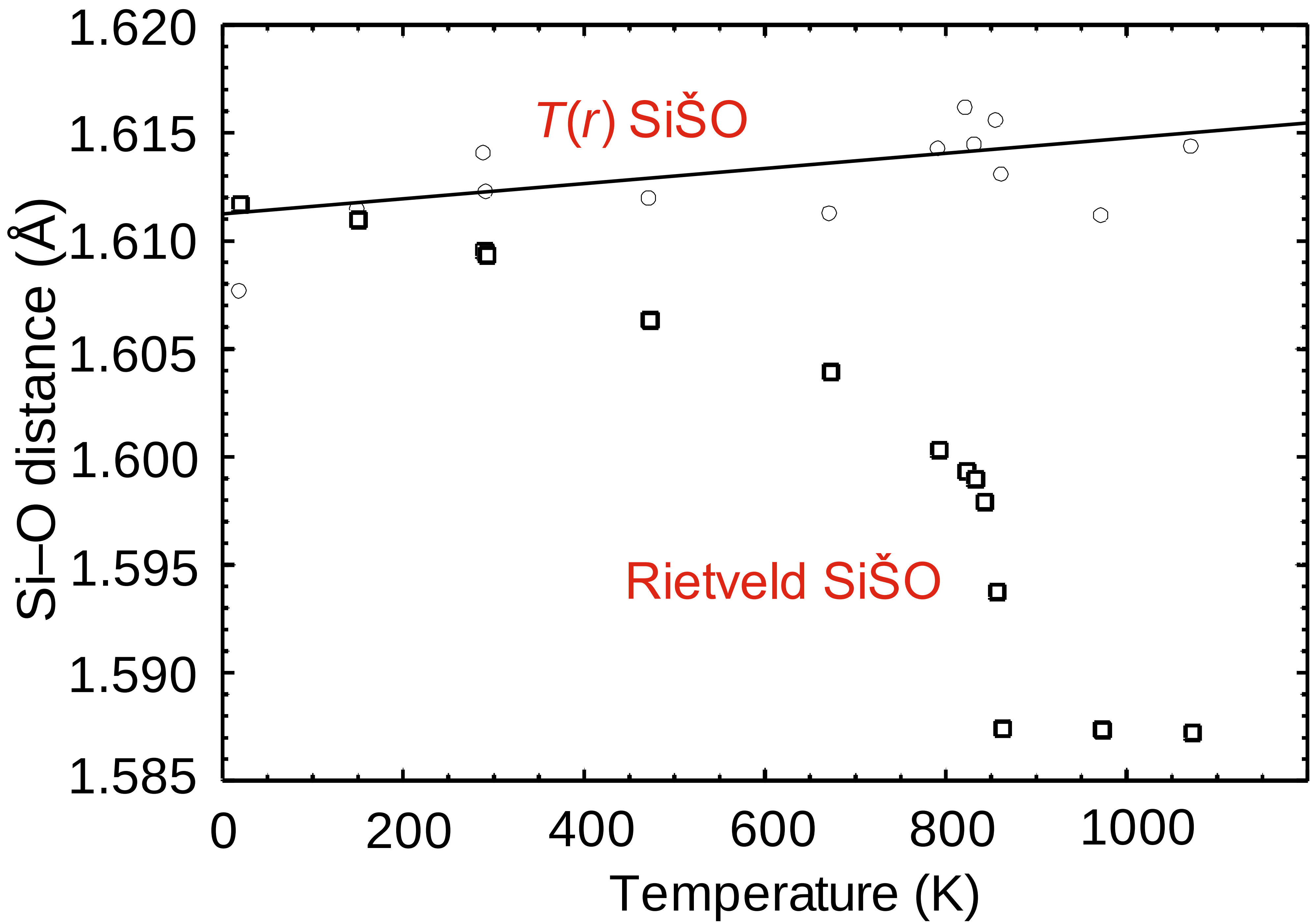
PDF in quartz



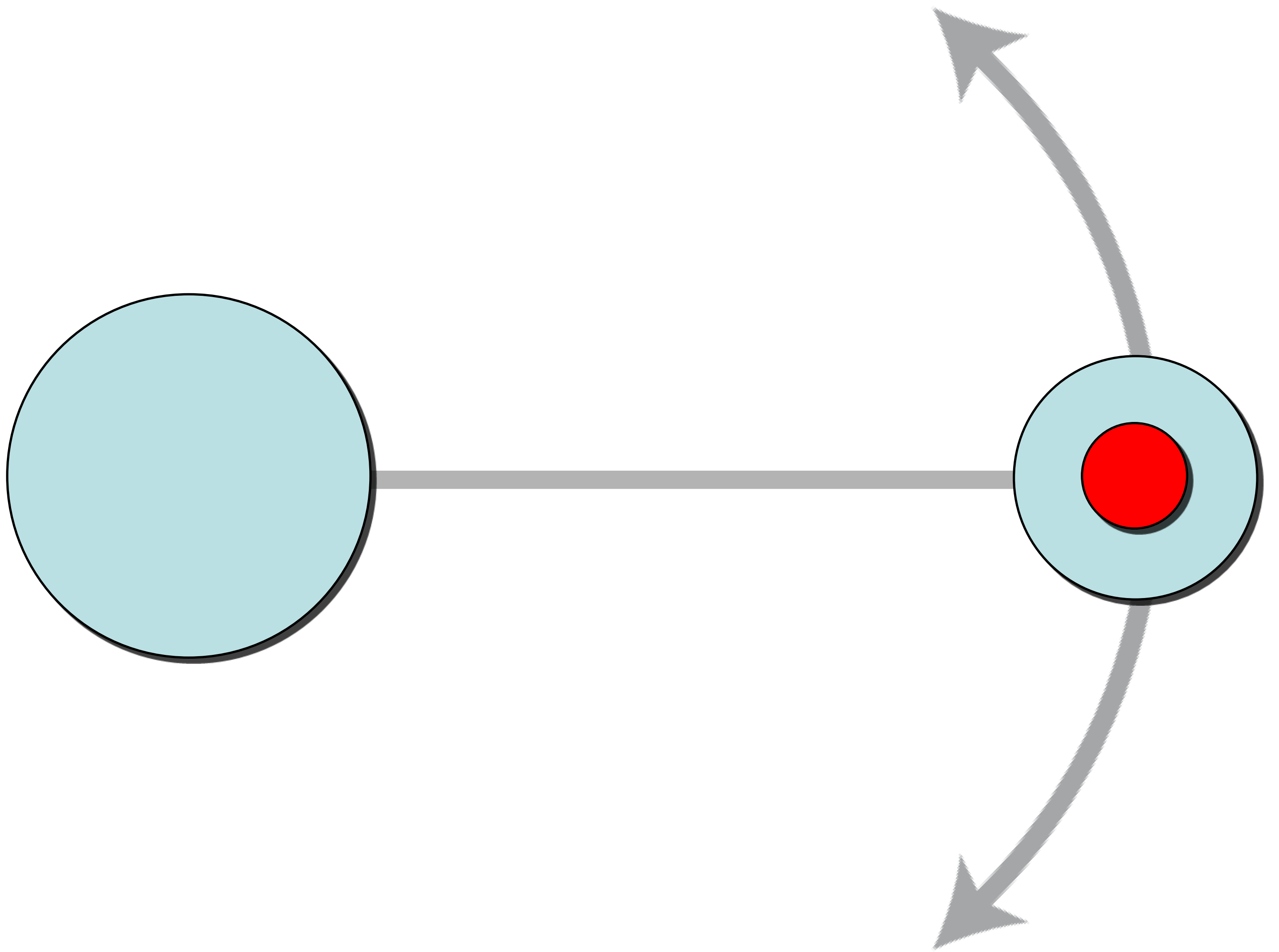
Increasing temperature shows broadening of interatomic correlations

Suggests increase in disorder on heating

Bond lengths



Thermal motion and interatomic distances



Apparent shortening of bond increases with temperature

Reverse Monte Carlo modelling

Generate initial configuration of atoms

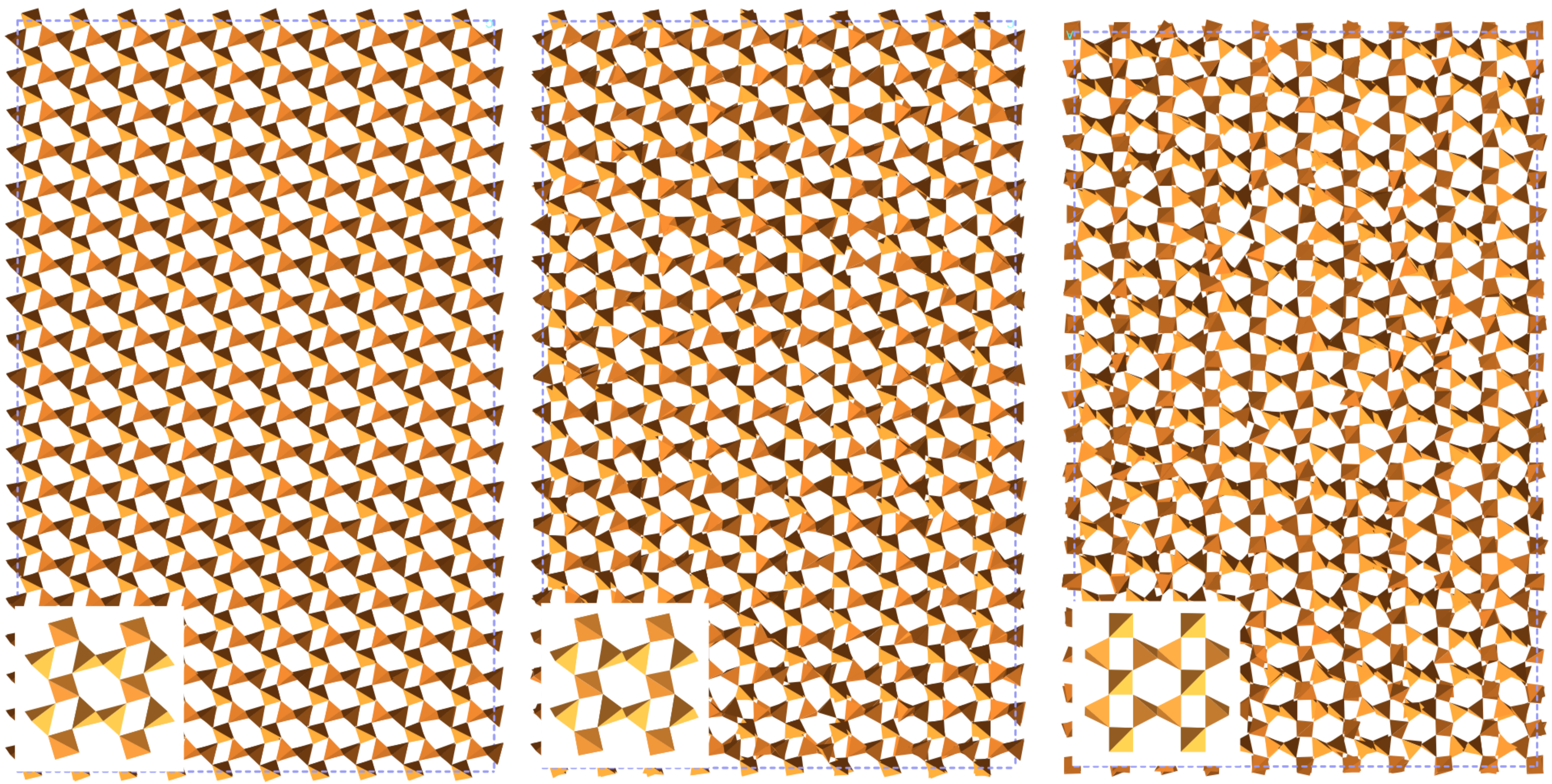
Move one randomly-selected atom by a small random vector

Compute new experimental functions and compare with data

Only reject change if comparison is worse and with some probability

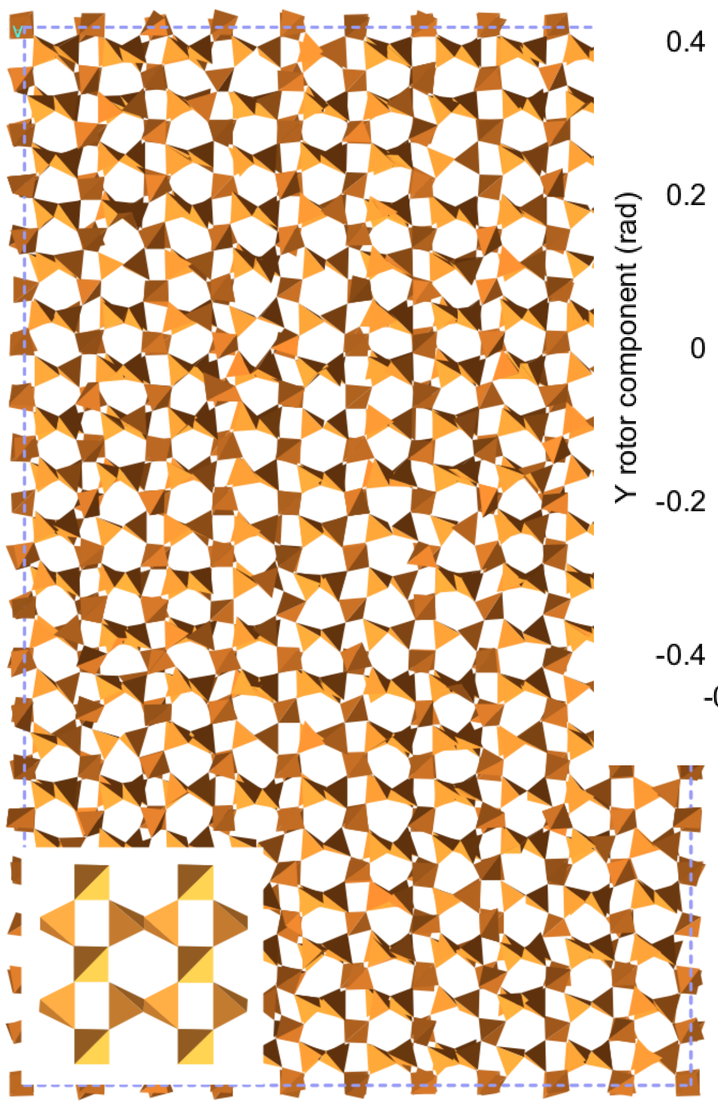
Atomic configurations of quartz

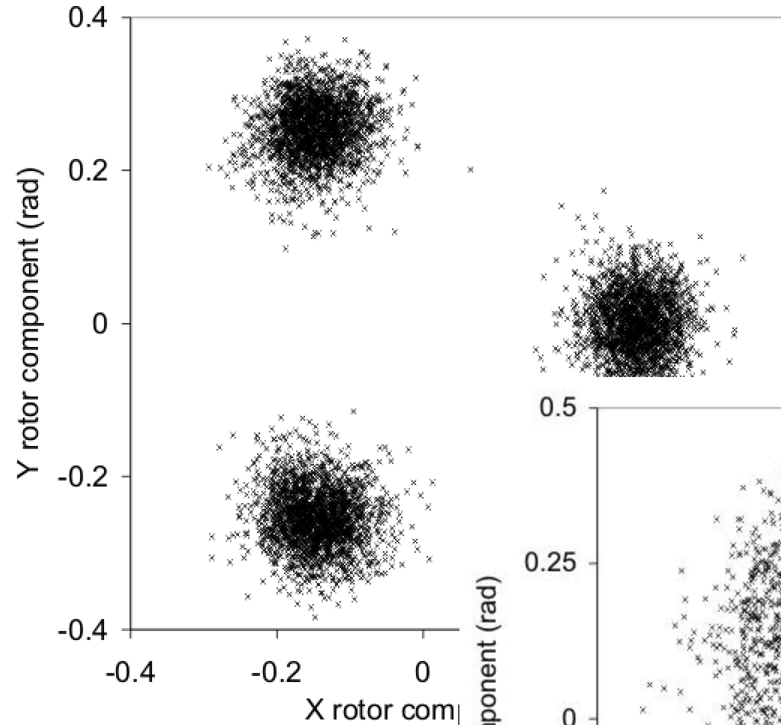
20 K, 〈　　793 K, 〈　　1073 K, ®

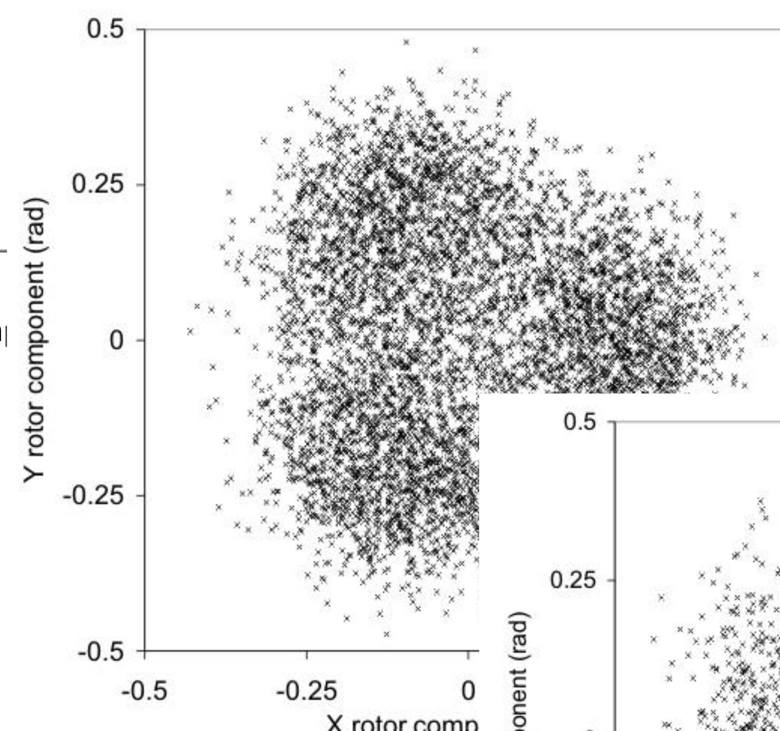


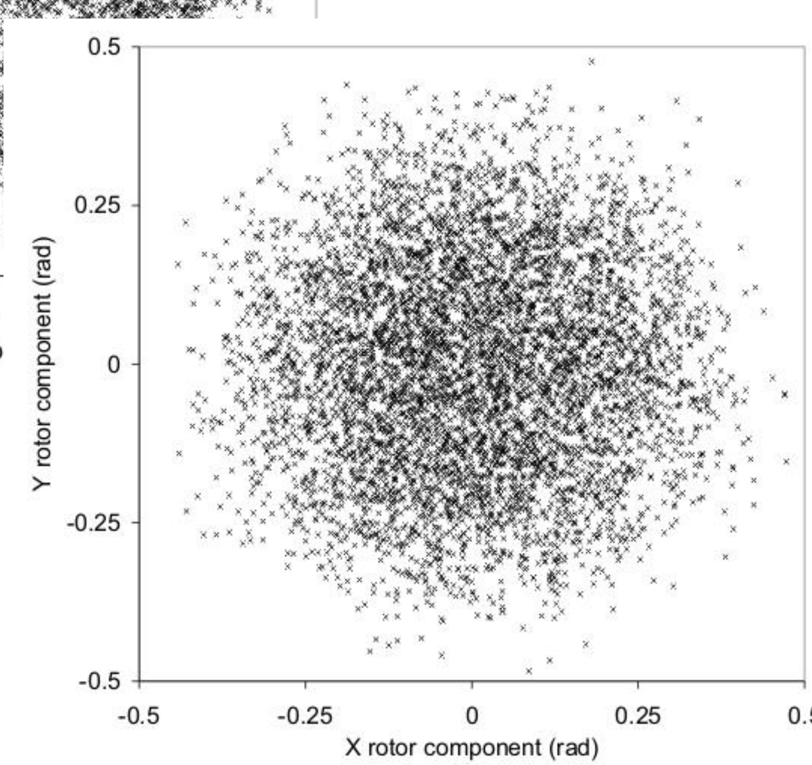
Onset of disorder observed on heating

Orientational disorder of SiO_4 tetrahedra in quartz





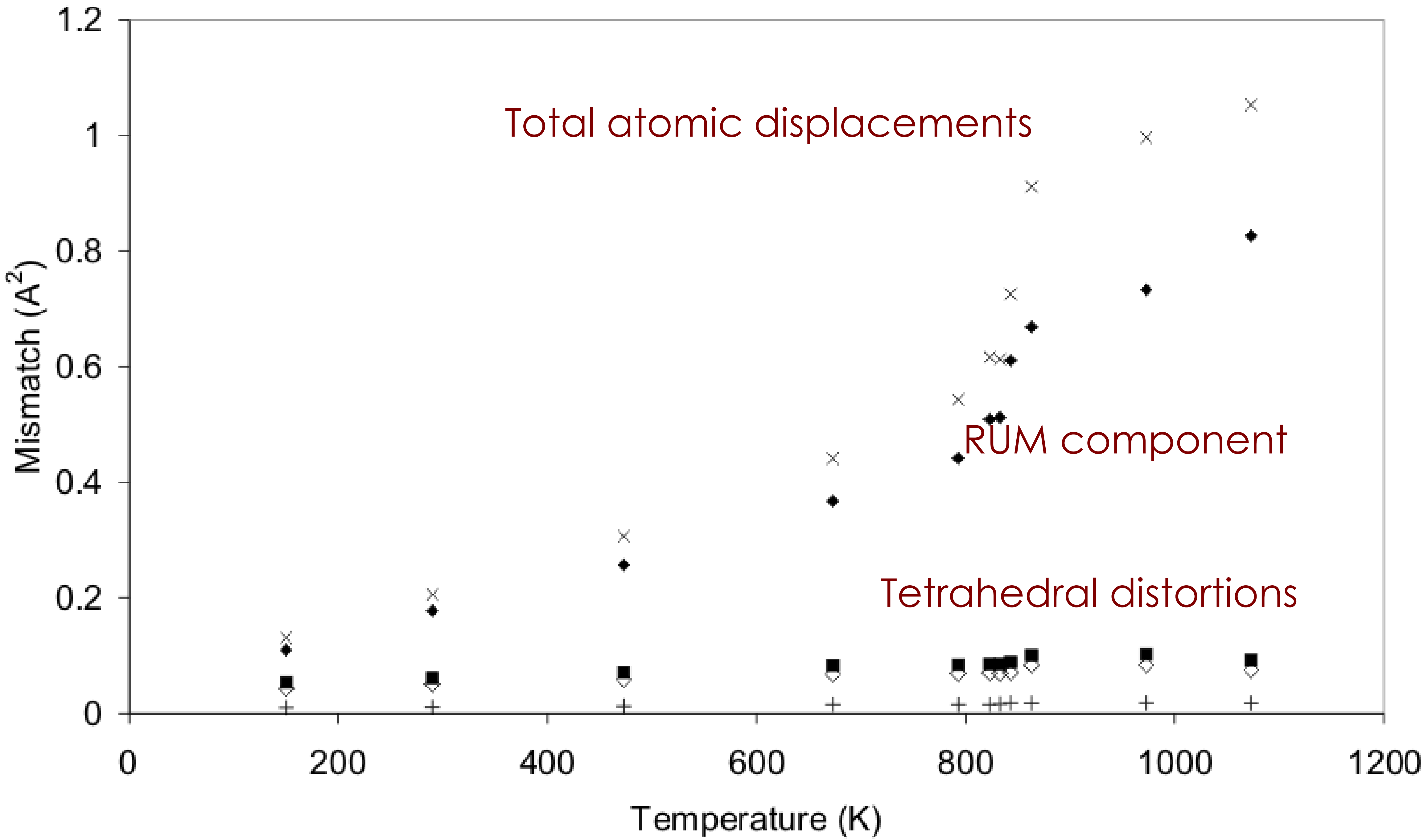




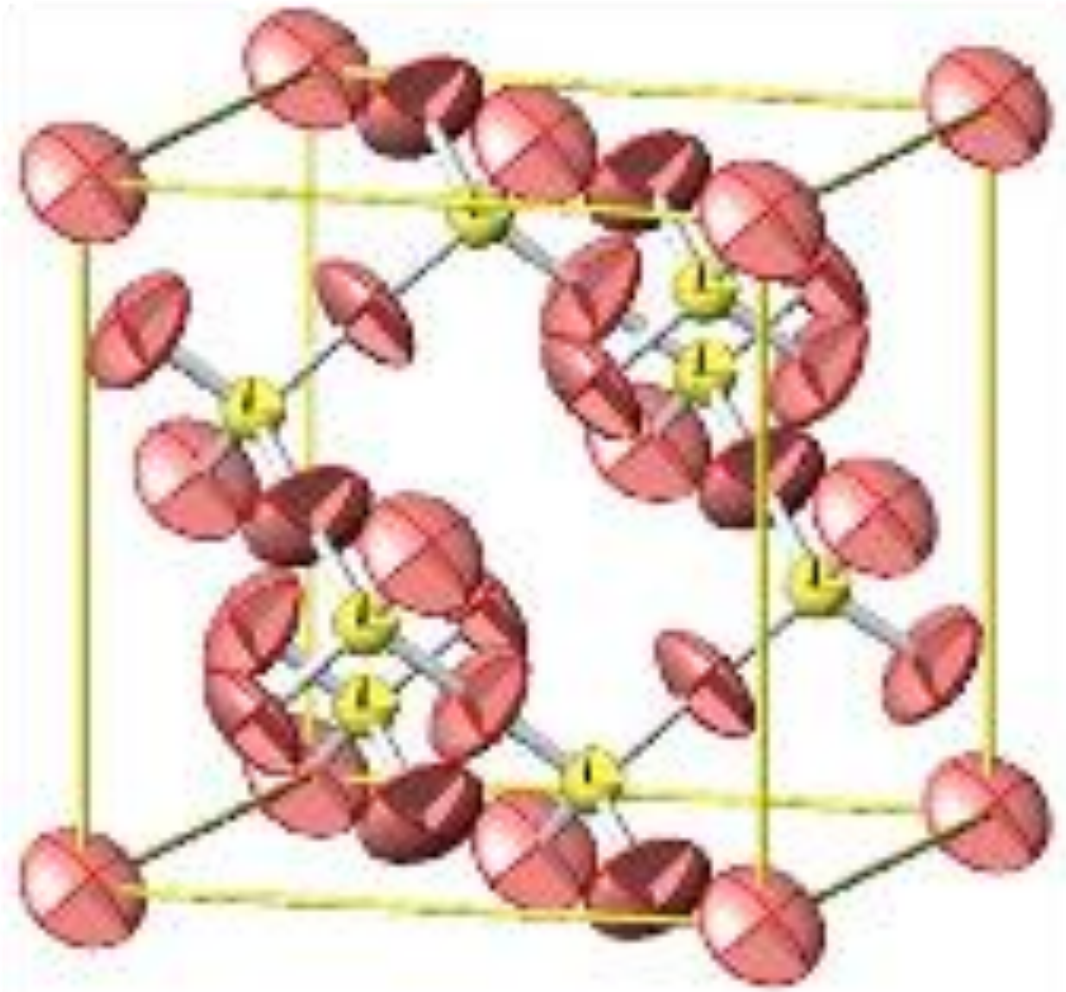
Distribution of SiO_4 orientations

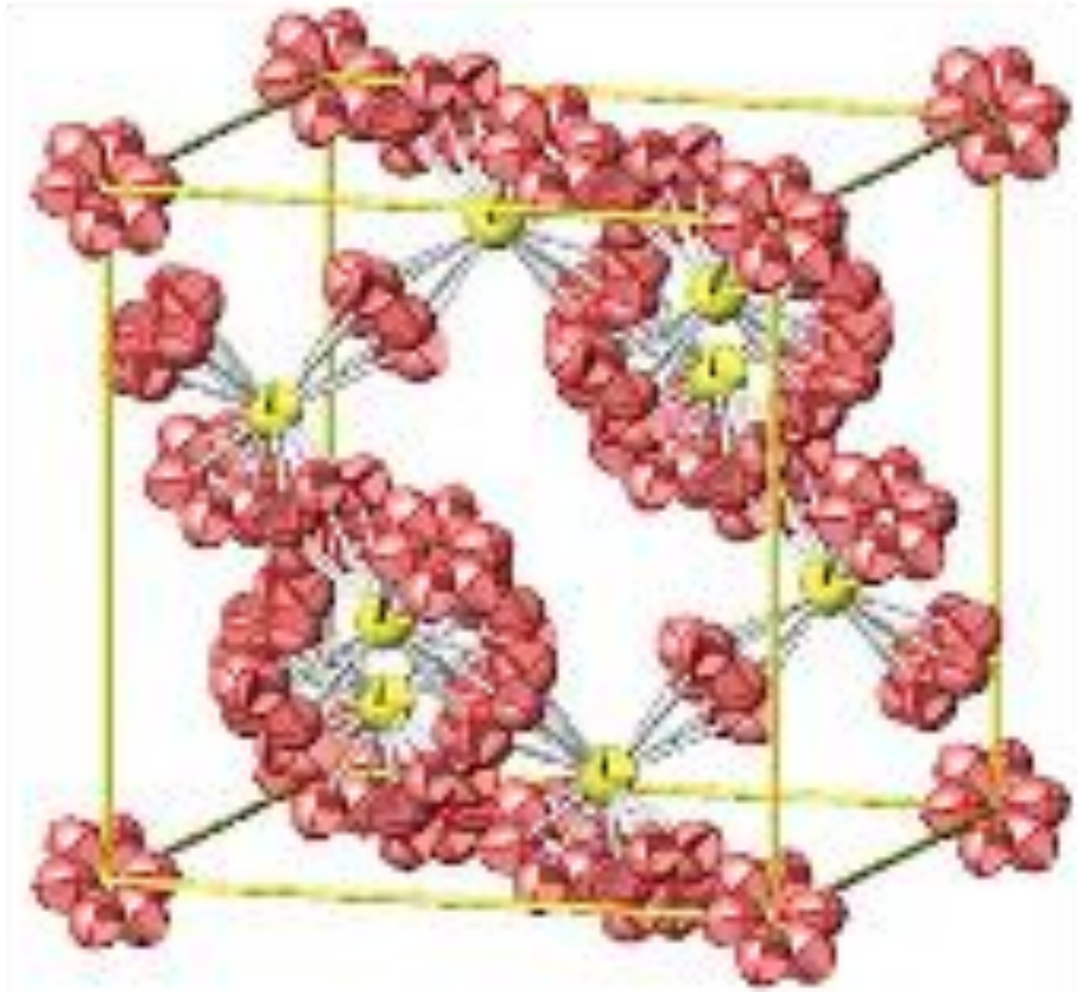
Heating

Rigid unit motions of SiO_4 tetrahedra in quartz



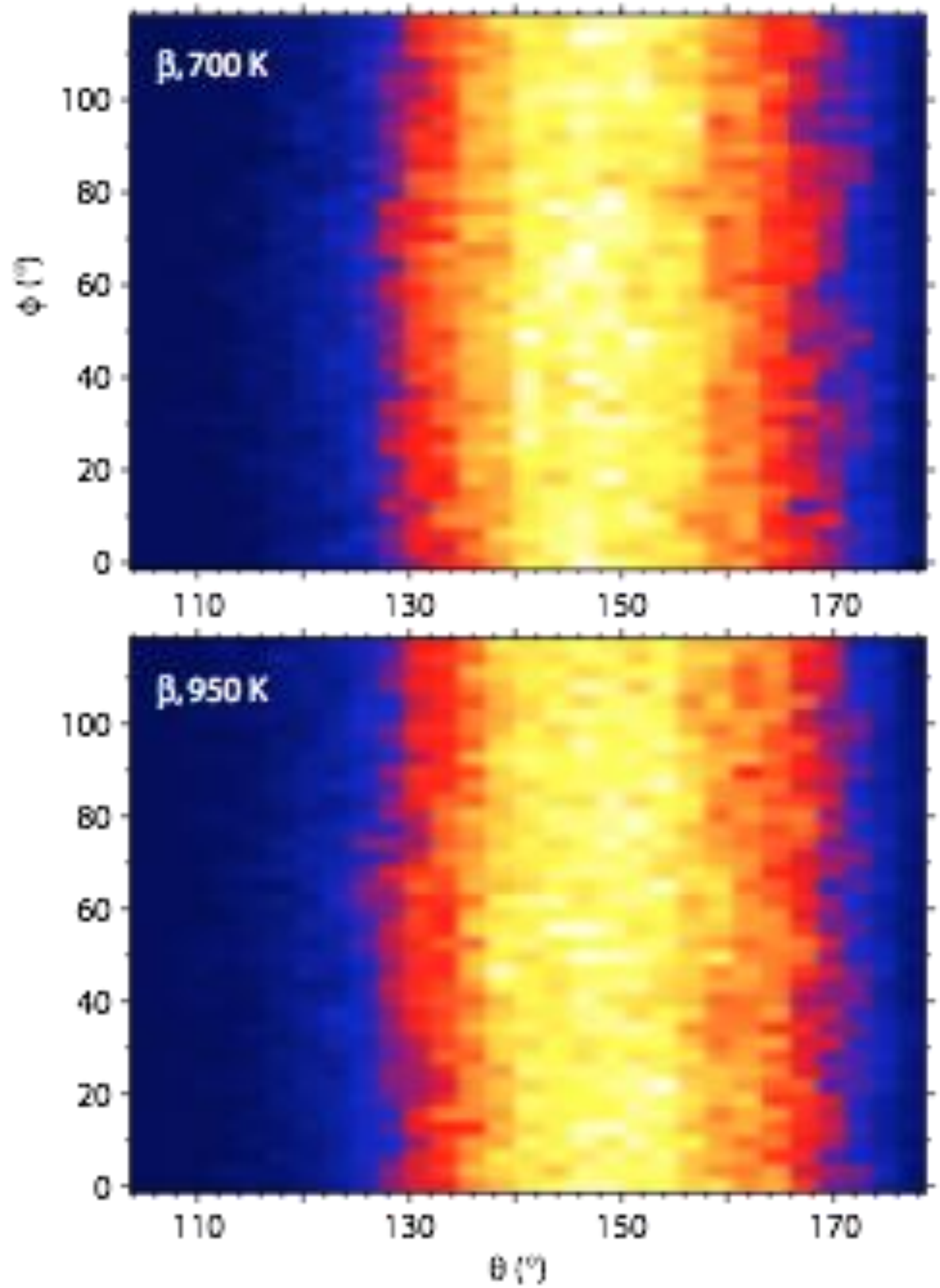
Disorder in ®-cristobalite

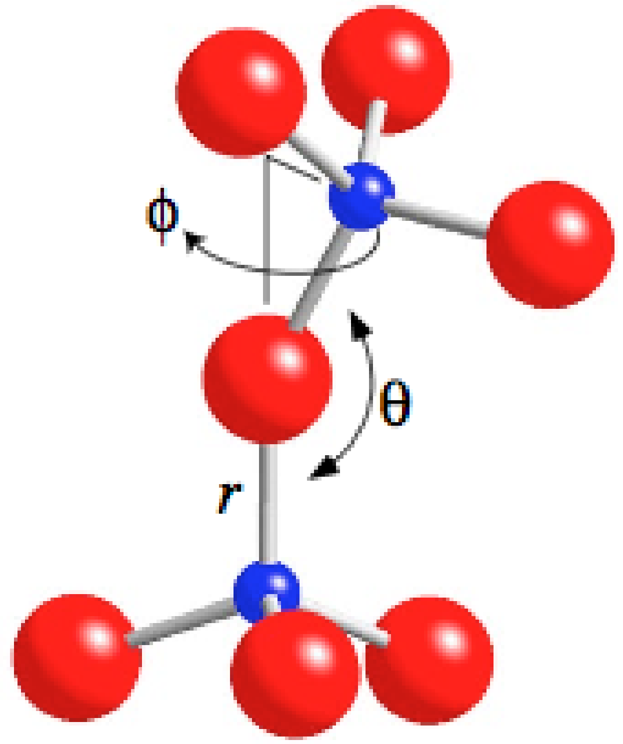




Single pancake site or six sites for oxygen atoms?

Orientations of Si–O bonds



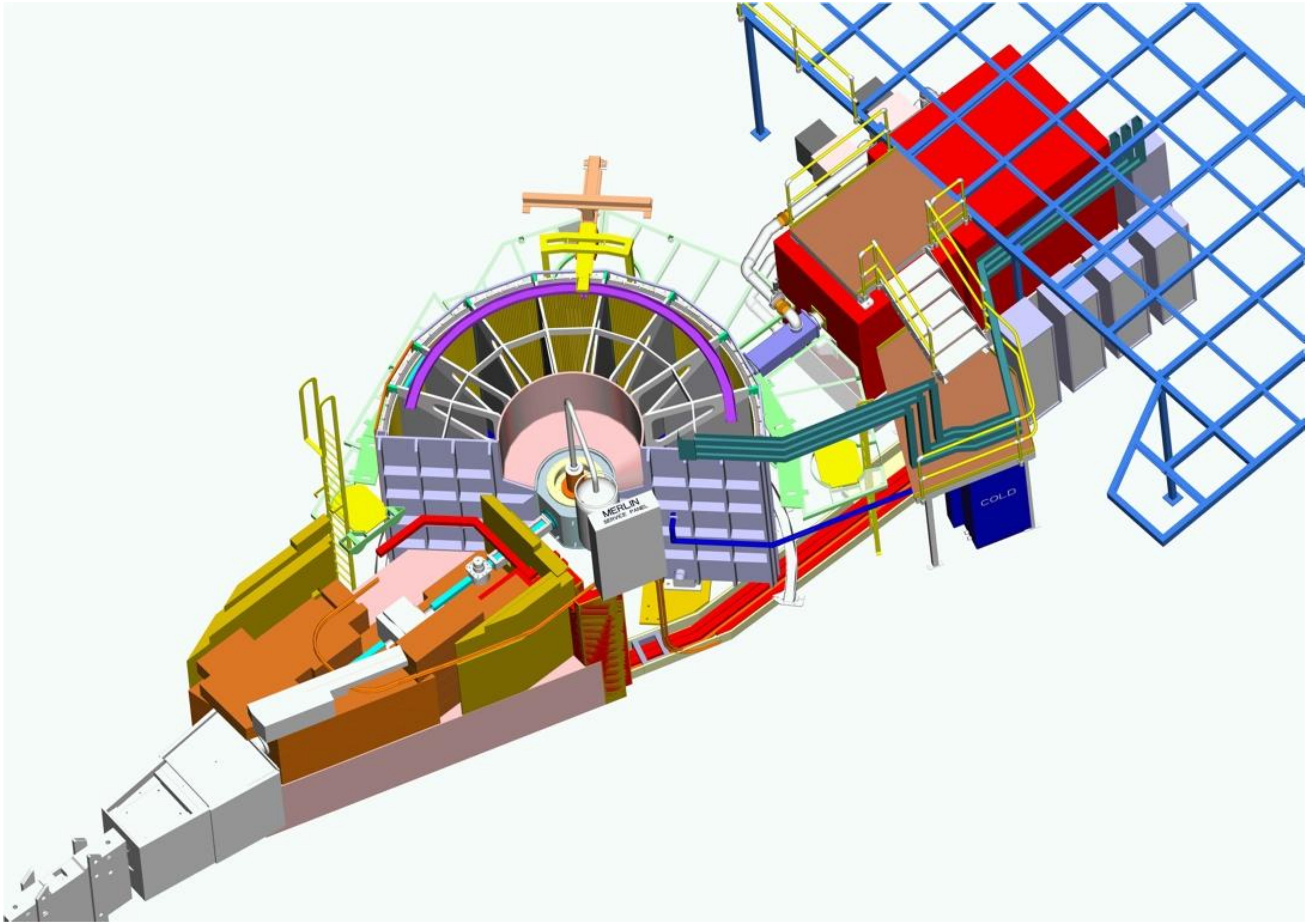


- No obvious special orientations of Si–O bonds
- Suggesting no well-defined domains

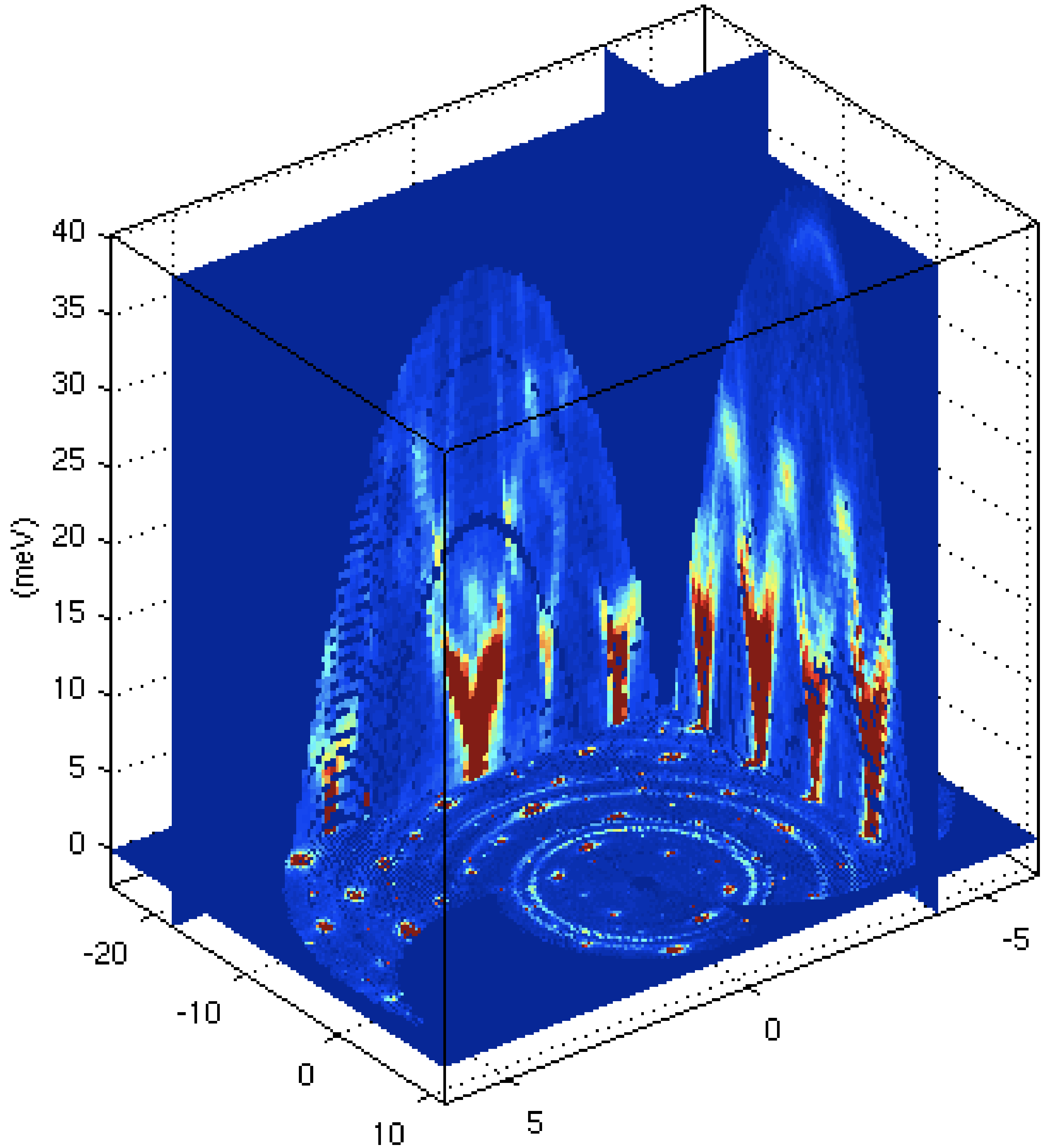
Phonon dispersion curves

- Dispersion curves have an important role in enabling the construction of accurate models of interatomic forces
- Atomistic simulation plays an important role in mineral sciences because of the access it gives to extreme temperatures and pressures
- New instrumentation at ISIS and ILL will give new capabilities

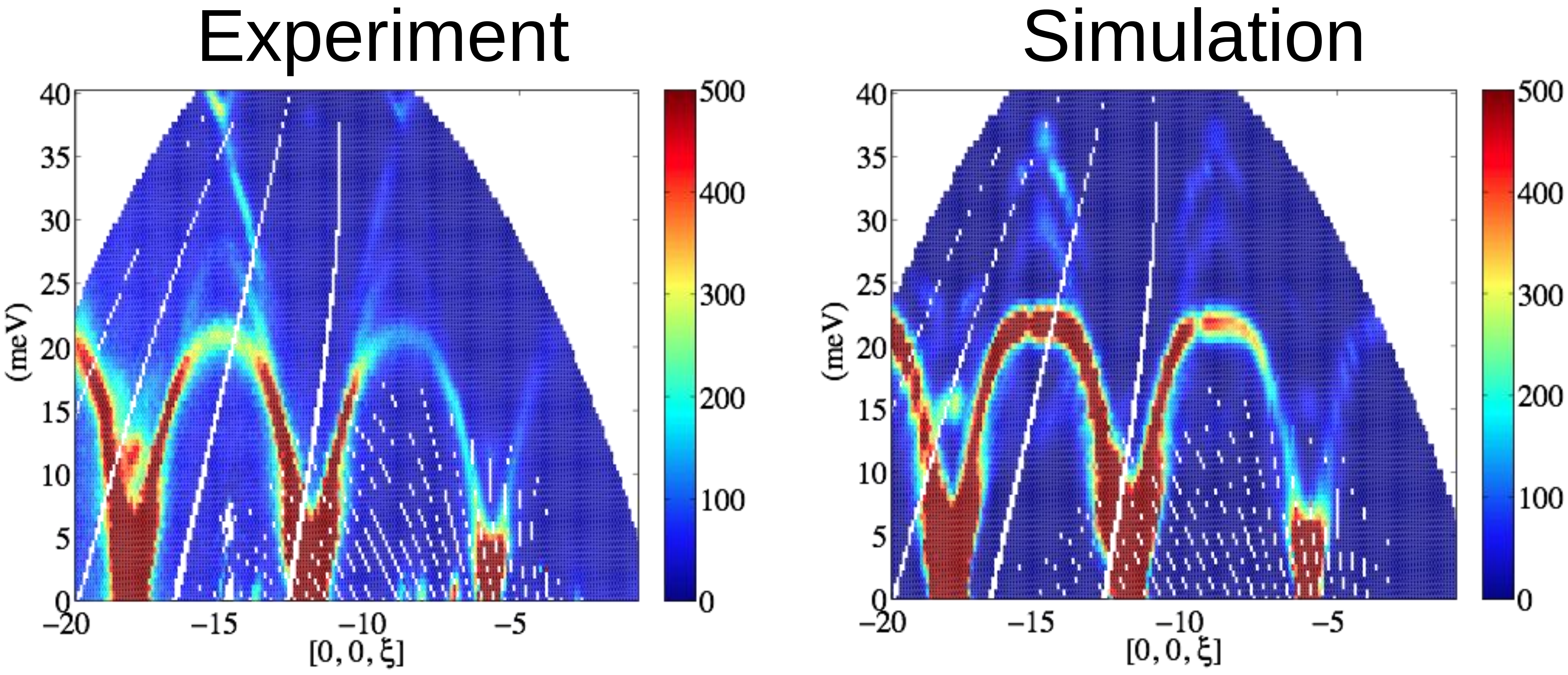
MERLIN spectrometer at ISIS



Phonon dispersion curves in calcite, $CaCO_3$, measured on MERLIN

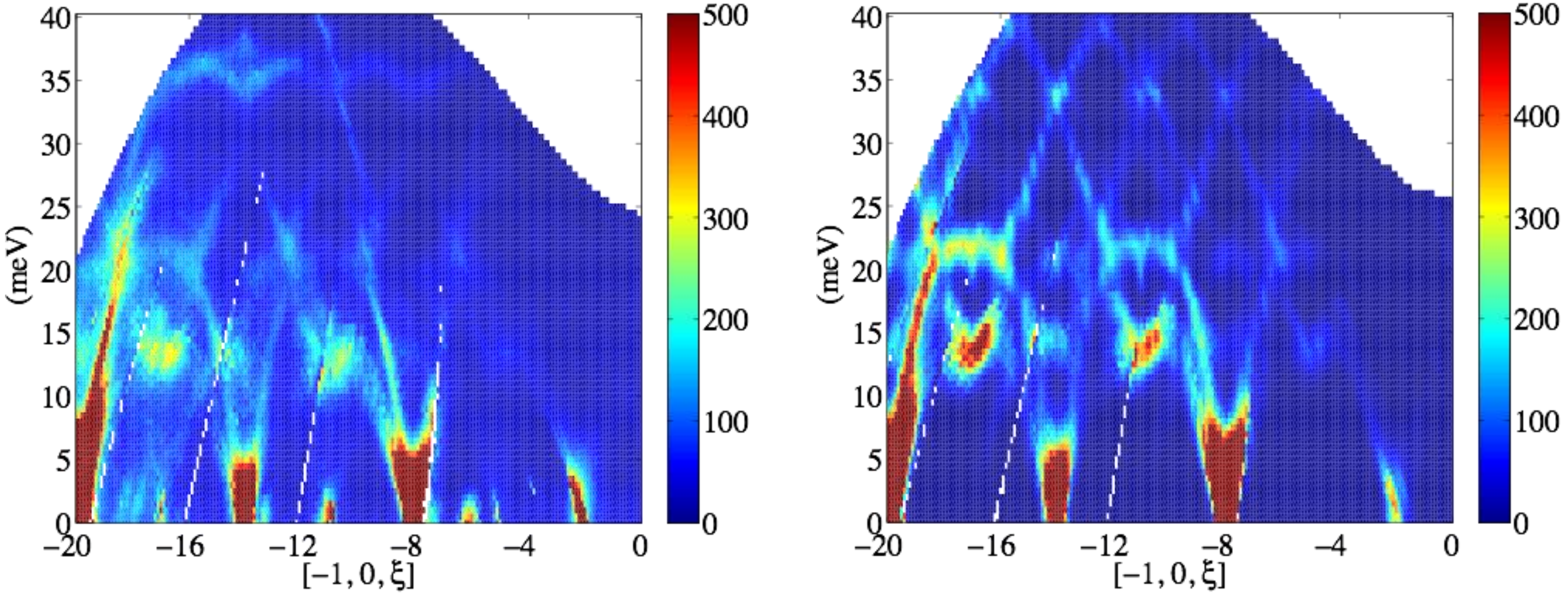


Calculated and measured of phonon scattering in calcite



Calculated and measured of phonon scattering in calcite

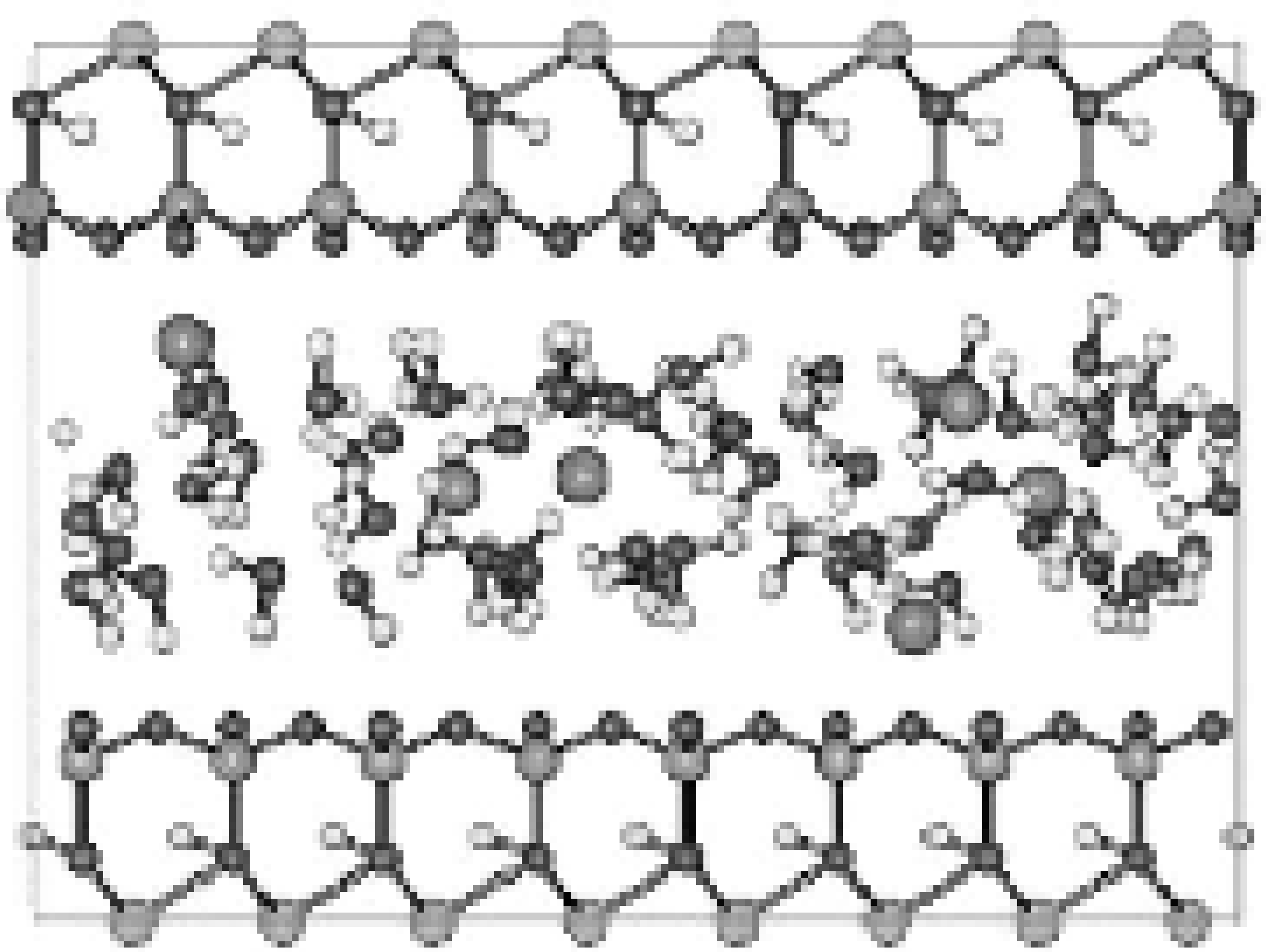
Experiment Simulation



Water in minerals

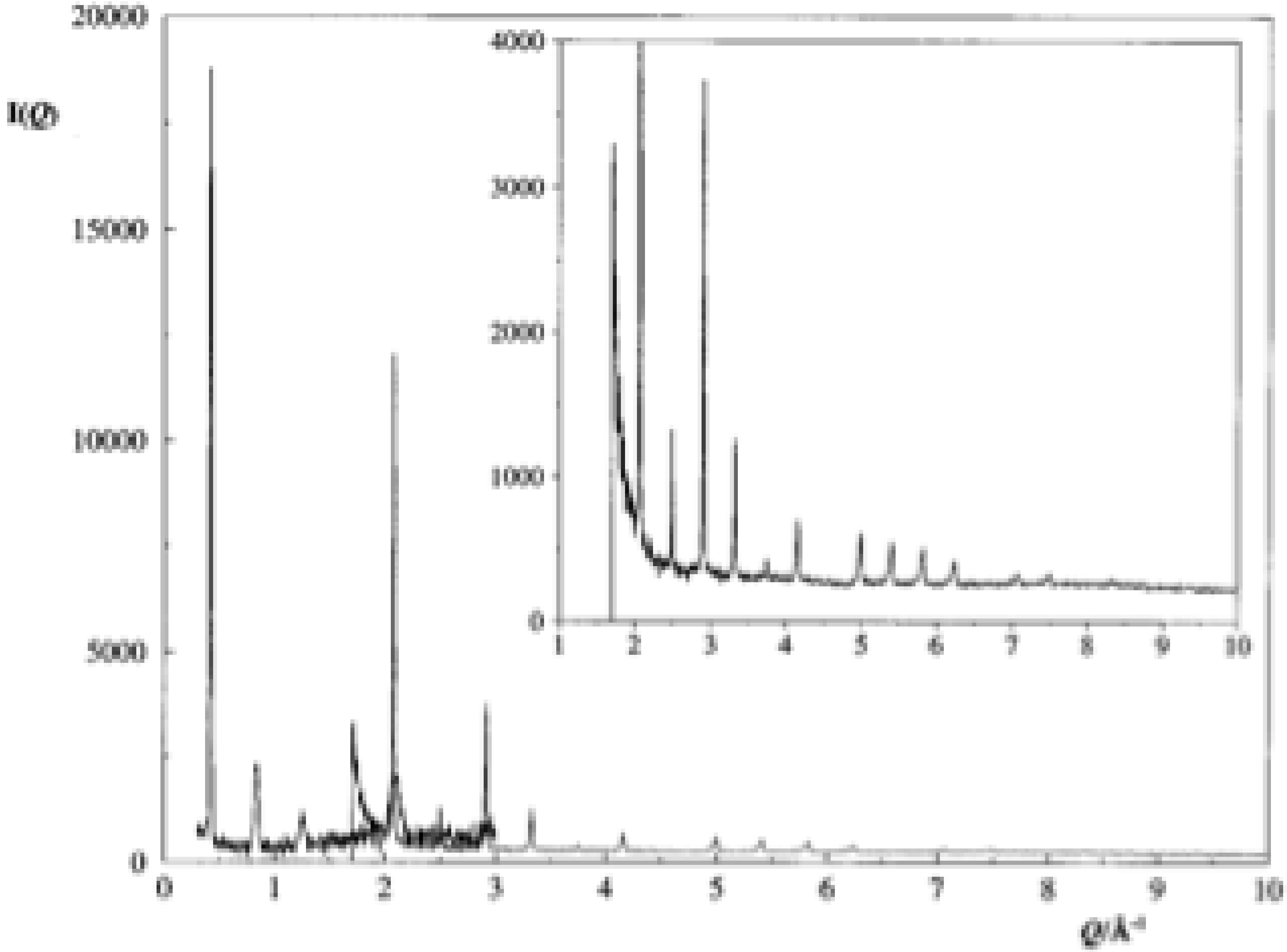
- Some minerals, such as clays and zeolites, contain significant quantities of water in pores and between atomic layers
- Water is the grease of the Earth – it is what enables the convection of minerals in the inner Earth that drives plate tectonics
- Neutrons are particularly good for the study of hydrogen and hence water
- Incoherent scattering is a probe of individual hydrogen atoms and hence dynamics of water molecules

Water in clays

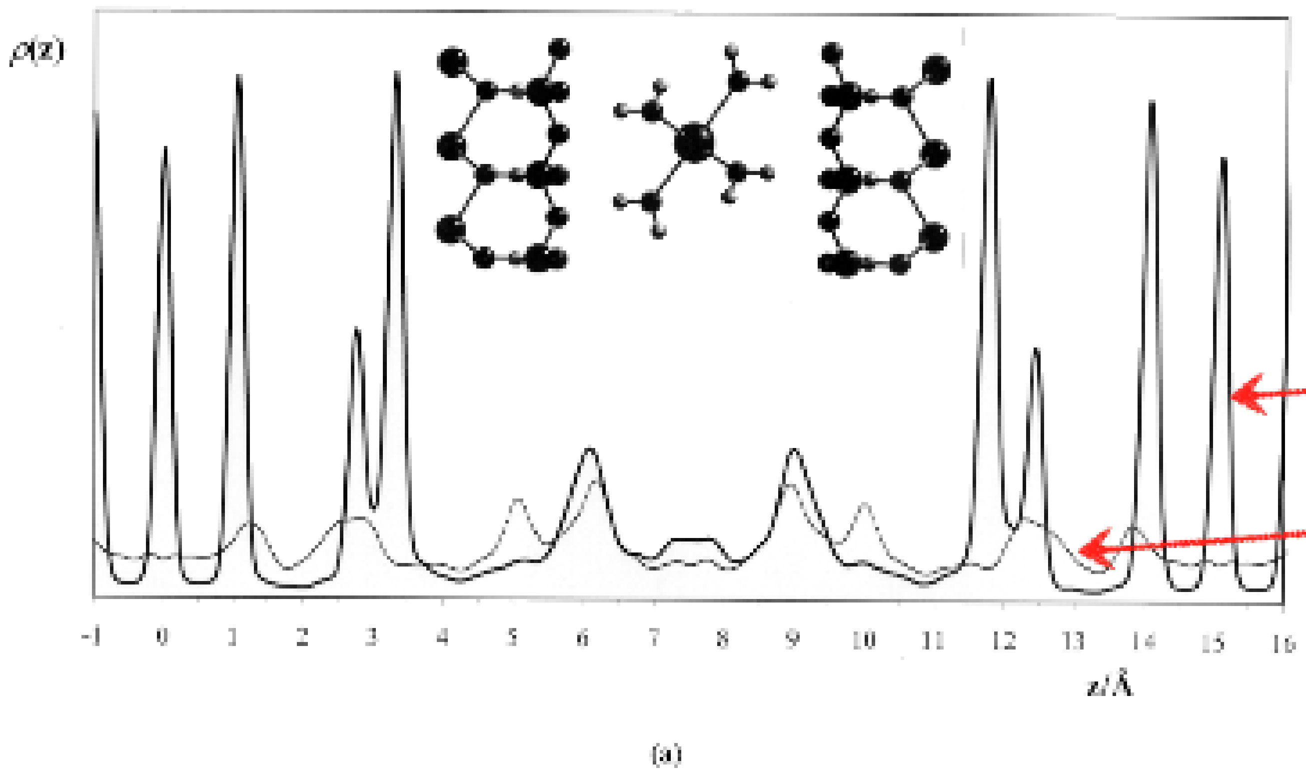


Water molecules and cations are found within the space between tightly-bound oxide layers

00ℓ diffraction from clays



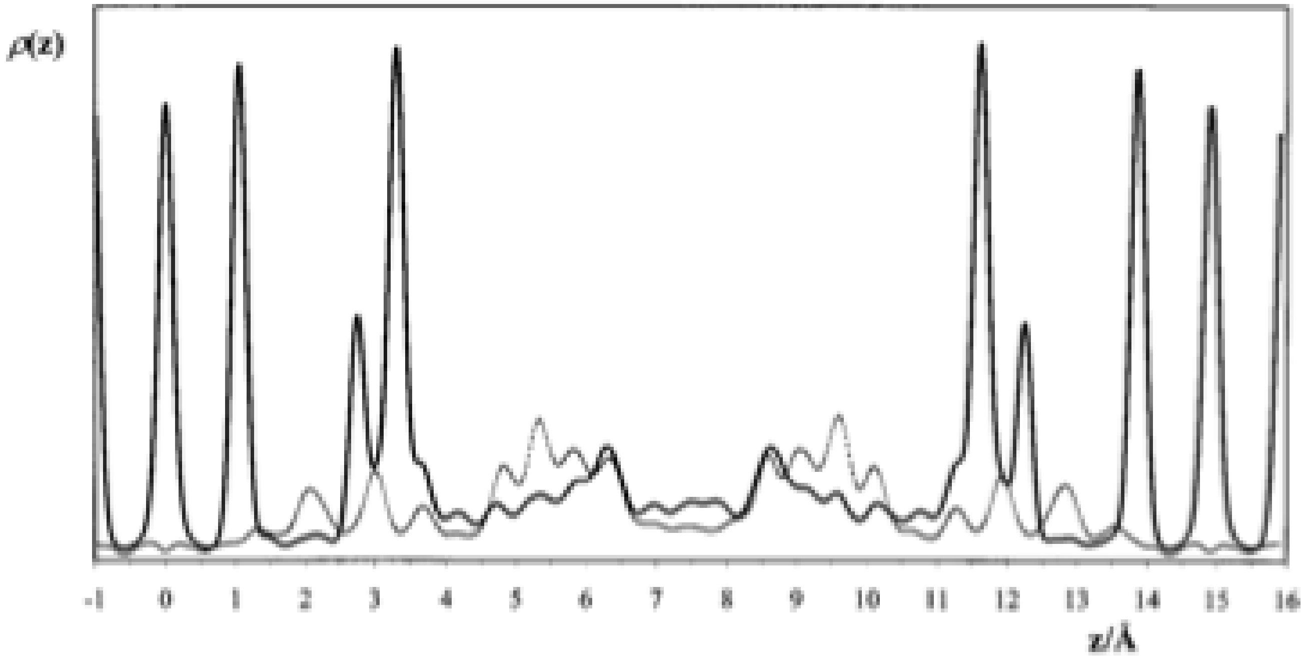
Structure of water within clay interlayer space



Surface conditions

Other atoms

Hydrogen



Depth of 10 km

Outlook for neutrons in Earth Sciences

- Instrumentation is excellent
- Range of techniques is unrivalled
- Sensitivity of light elements and hydrogen is not matched by other techniques (such as synchrotron radiation)
- Ability to control sample environment is much easier than with other probes
- Ability to match computer simulation and neutron scattering is excellent

However …

- The small volumes required for very high pressures and much less problematic for synchrotron radiation sources
- The community of advocates and those with experience is small (sub-critical), and neutron scattering has often suffered through appearing to have a skills barrier
- Much of what is being done is not challenging (typically powder diffraction)

Acknowledgements

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