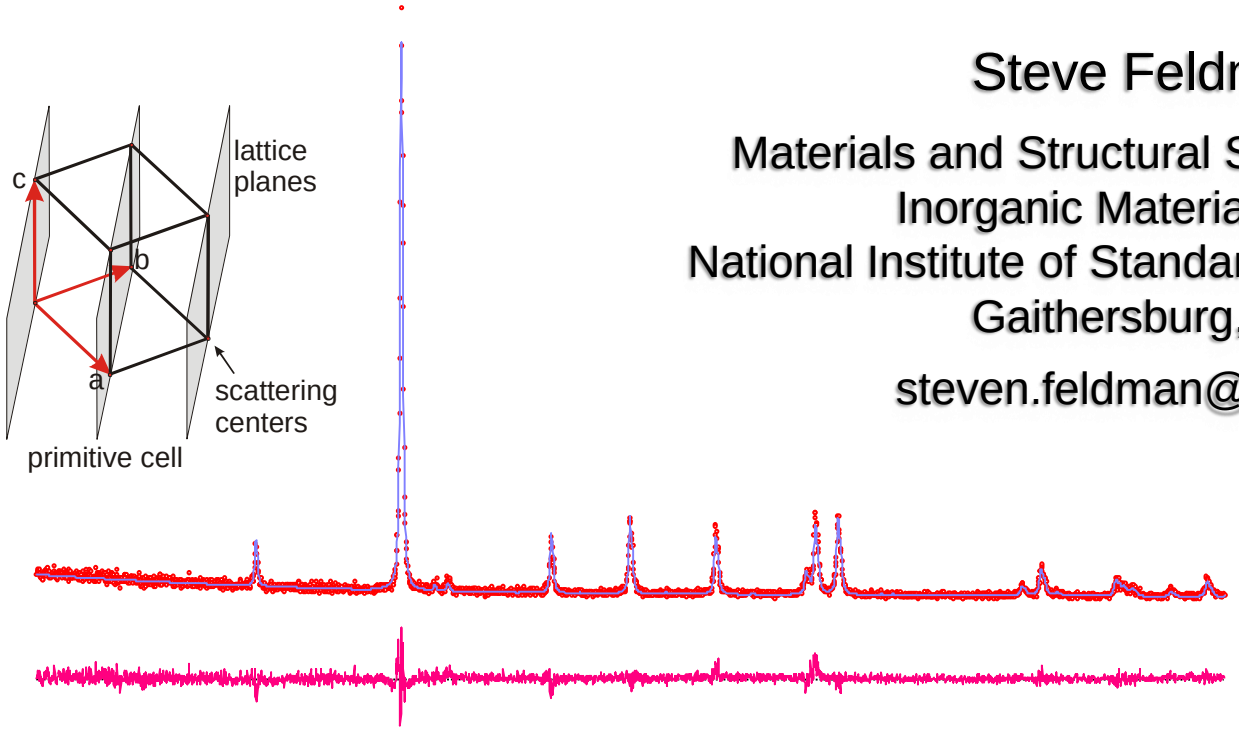
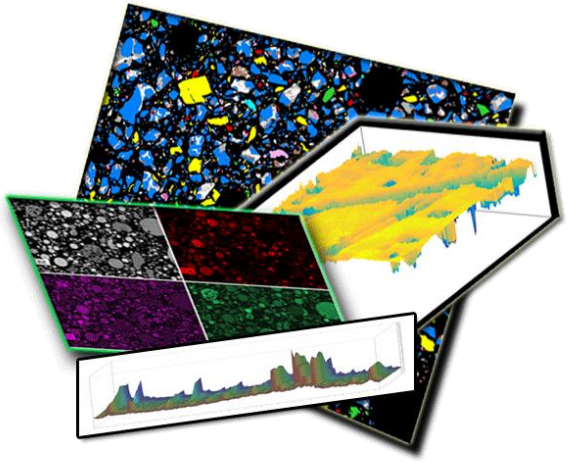
X-Ray Powder Diffraction and Rietveld Analysis with Applications to Cementitious Materials – I



Steve Feldman

Materials and Structural Systems Division
Inorganic Materials Group
National Institute of Standards and Technology
Gaithersburg, MD

steven.feldman@nist.gov

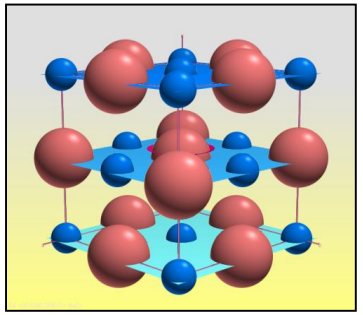


NIST
National Institute of Standards and Technology
U.S. Department of Commerce

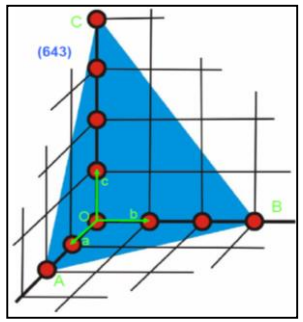
engineering laboratory

Scope

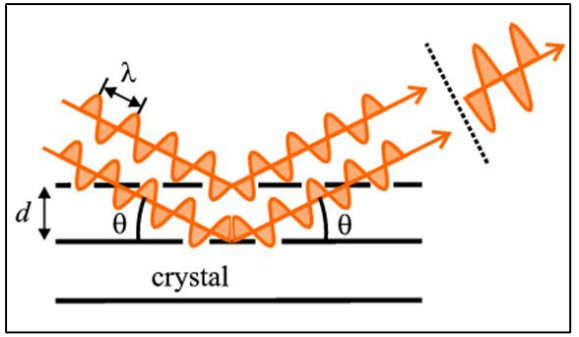
1. Background and scope of modern powder diffraction (XRPD)
   - ✓ What are we measuring and how do we interpret the data?
   - ✓ Types of applications with examples
2. XRD instrumentation
3. XRD theory and introduction to crystallography
4. Qualitative analysis: phase identification
5. Optimizing data collection and mitigating potential sources of error
6. Quantitative phase analysis
   - ✓ Traditional XRD methods
   - ✓ Special challenges with cement materials
   - ✓ Introduction to the 'Rietveld' method
7. Additional examples and refinement strategies



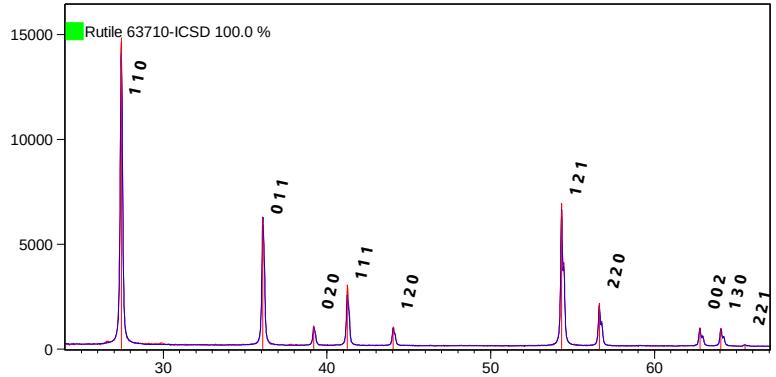
Unit cell



Lattice plane



Powder diffraction



Diffraction pattern with Indexed Peaks

1. Background and Scope of Modern Powder Diffraction

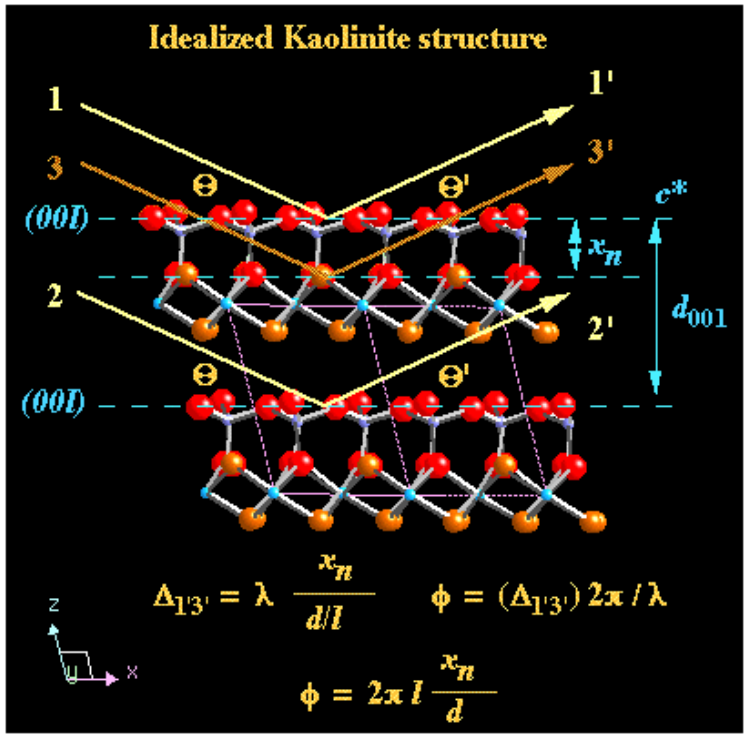
What does it tell us?

Applications and examples

Background and scope of XRPD

Types of powder *x-ray diffraction* applications:

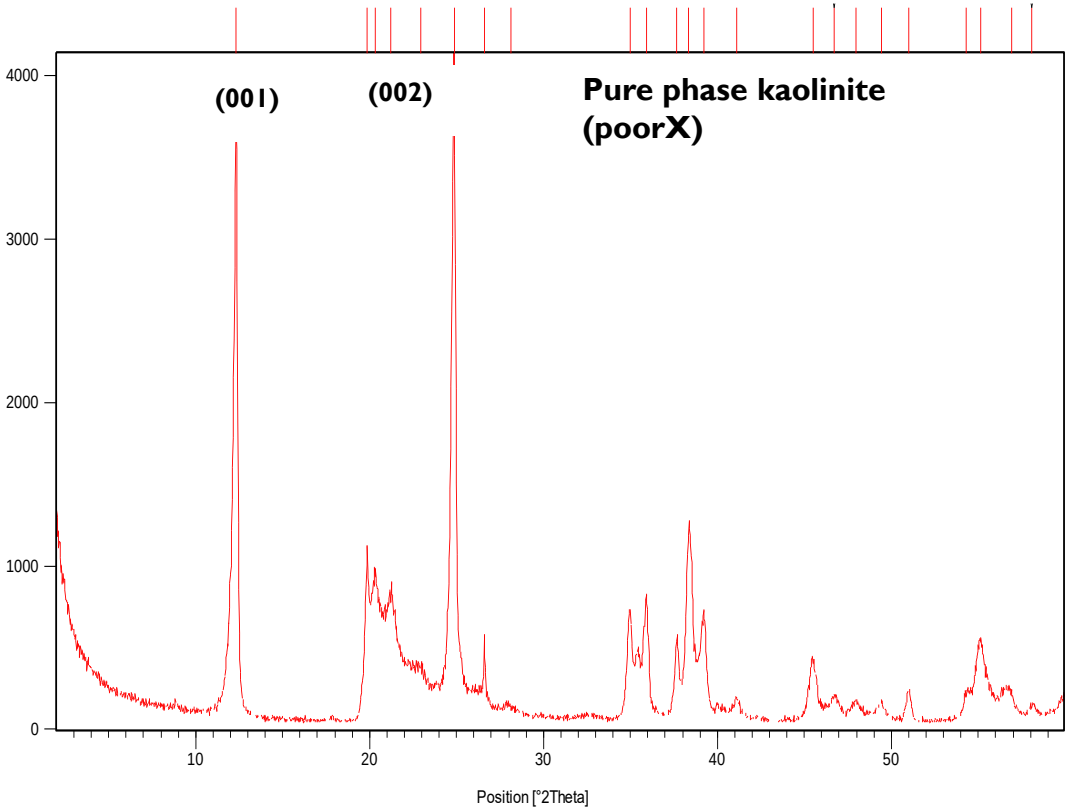
- ✓ Phase identification *
- ✓ Quantitative analysis *
- ✓ Size/strain (line profile) analysis
- ✓ Crystallographic analysis
  - Lattice parameters, site occupancy, etc.
- ✓ Percent crystallinity
- ✓ Non-ambient (*in situ*) analysis
- ✓ Residual stress
- ✓ Texture
- ✓ Reflectivity
- ✓ Microdiffraction (~1-50μ spot size)

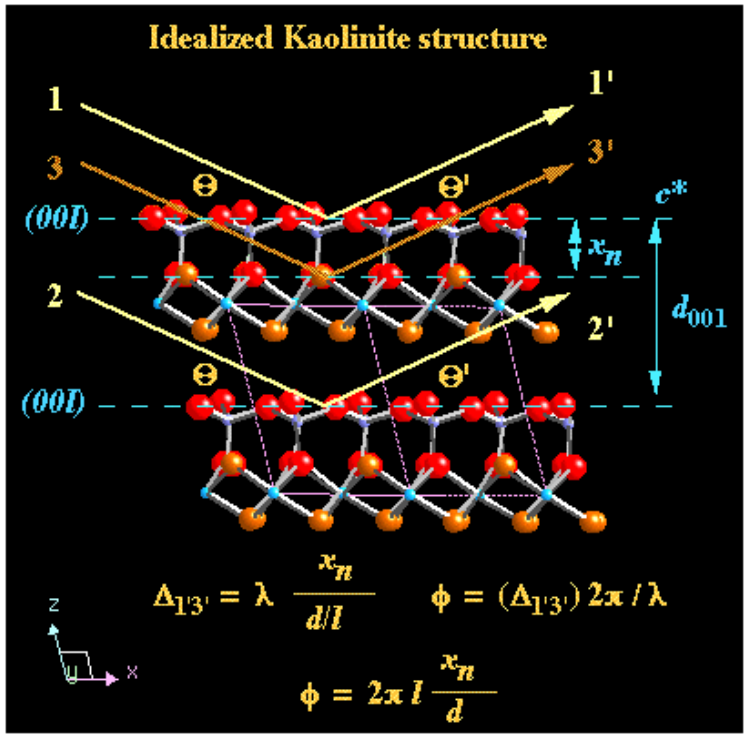


Background and scope of XRPD

Information content of a powder XRD scan

XRD patterns are unique ‘fingerprints’ of the crystal structure of materials that can be used to determine *phase composition* of mixtures.



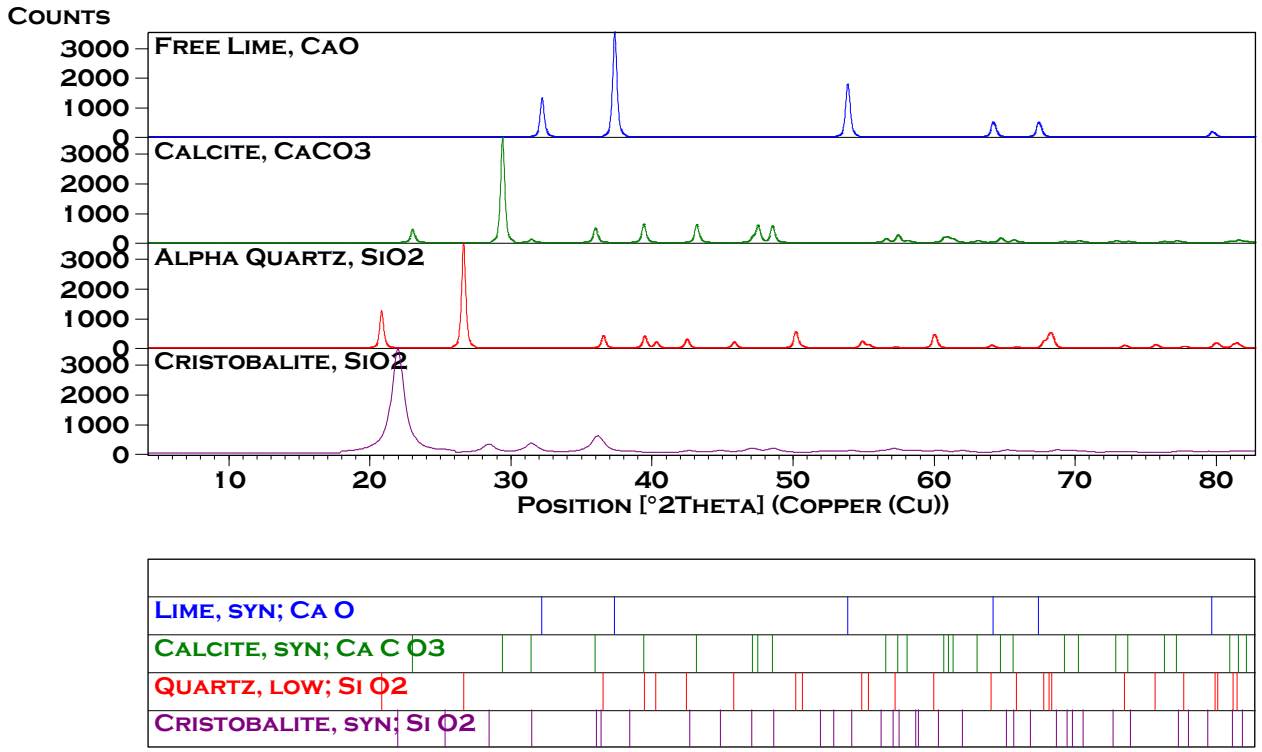


Typically there are many peaks, even for a single phase!

Background and scope of XRPD

Information content of a powder XRD scan

XRD patterns are unique ‘fingerprints’ of the crystal structure of materials that can be used to determine *phase composition* of mixtures.

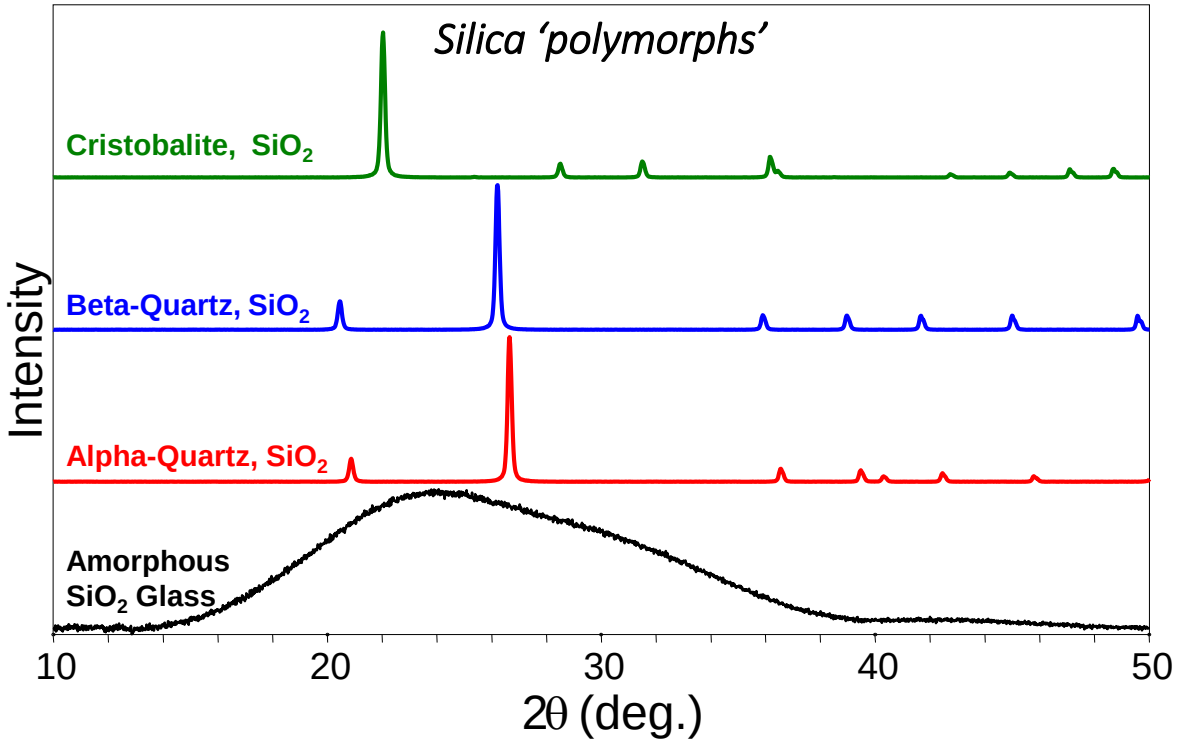


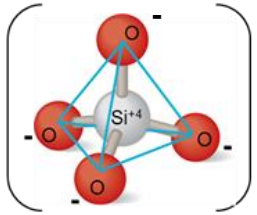
Different minerals/materials have unique peak positions (‘fingerprints’) and peak shapes as influenced by the crystal structure and crystallite size or degree of order-disorder.

Background and scope of XRPD

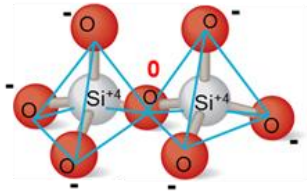
Information content of a powder XRD scan

Silica 'polymorphs': All 4 chemically identical forms of SiO_2 with different x-tal structures (*e.g.,* order-disorder) giving rise to different diffraction patterns.

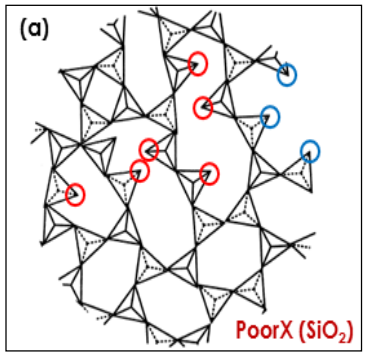


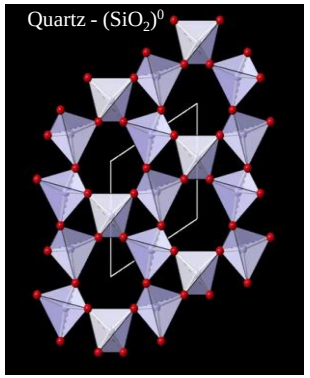


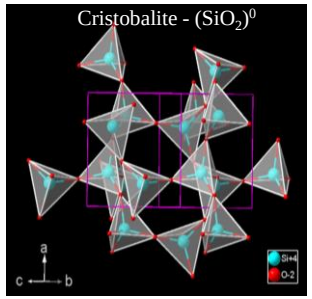
Si tetrahedron



Point-shared dimer







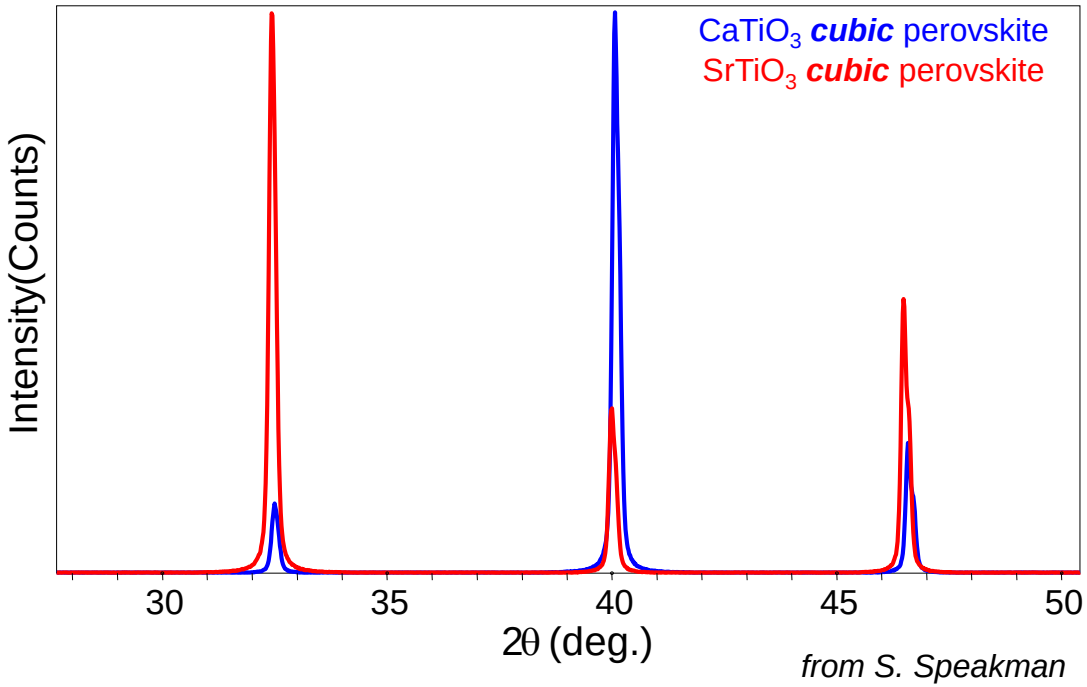
The Si and O atoms in amorphous glass does not have long-range atomic order and therefore produce only broad scattering features (no peaks).

Background and scope of XRPD

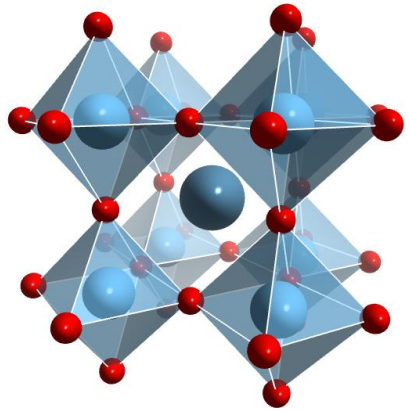
Information content of a powder XRD scan

XRD patterns are unique ‘fingerprints’ of the crystal structure of materials that can be used to determine *phase composition* of mixtures.

Perovskite ‘isomorphs’ (ABO3 structure)



from S. Speakman



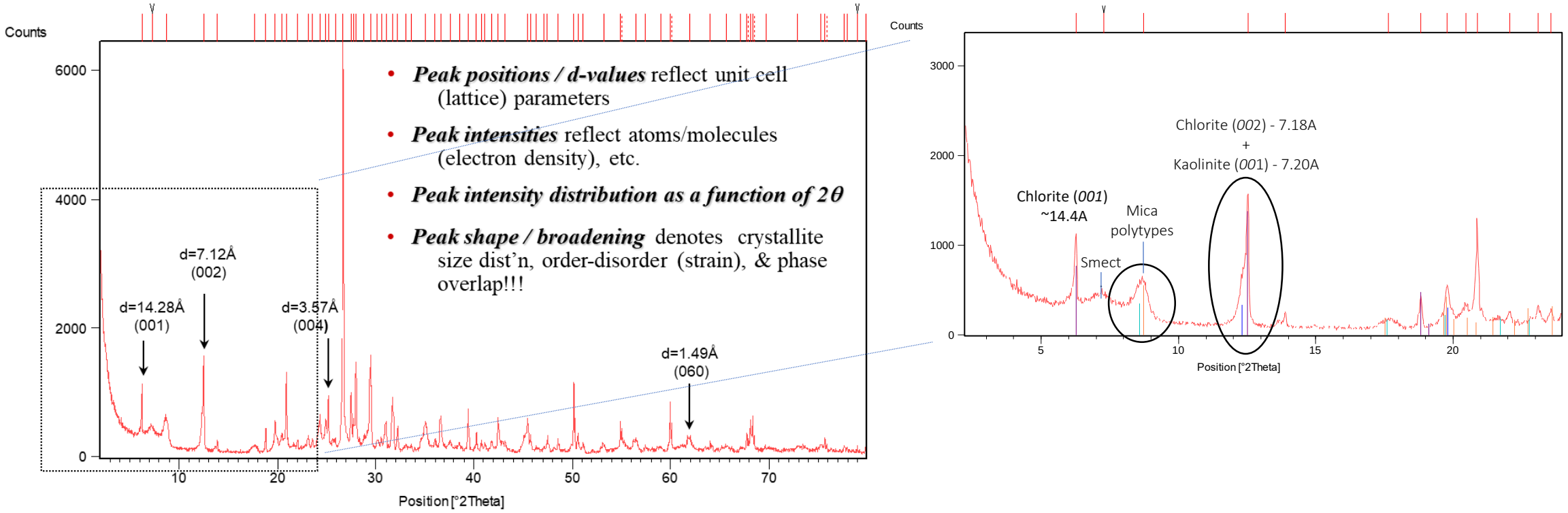
- The cubic phases of $CaTiO_3$ and $SrTiO_3$ have identical crystal structures, with the A cation replaced by Ca or Sr respectively
- Differences in electron density scatter X-rays proportionally to Z therefore giving differences in peak intensity.

XRD can discern between isostructural compounds as well as between polymorphs

Background and scope of XRPD

Information content of a powder XRD scan

Complex polycrystalline mineral mixture with complex, overlapping peaks

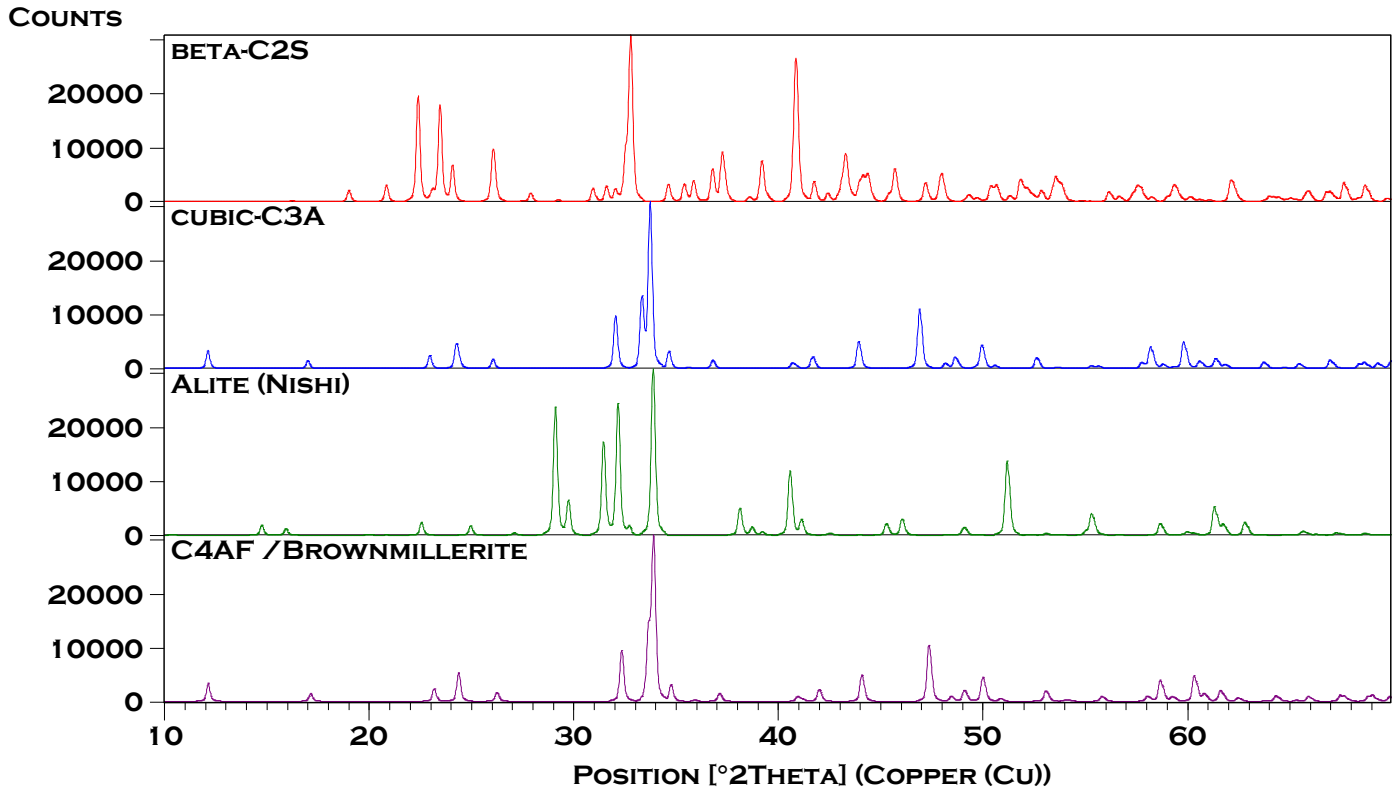


Background and scope of XRPD

Information content of a powder XRD scan

Diffraction patterns of the major clinker phases

…Clinker/cement phases can be very complicated!!

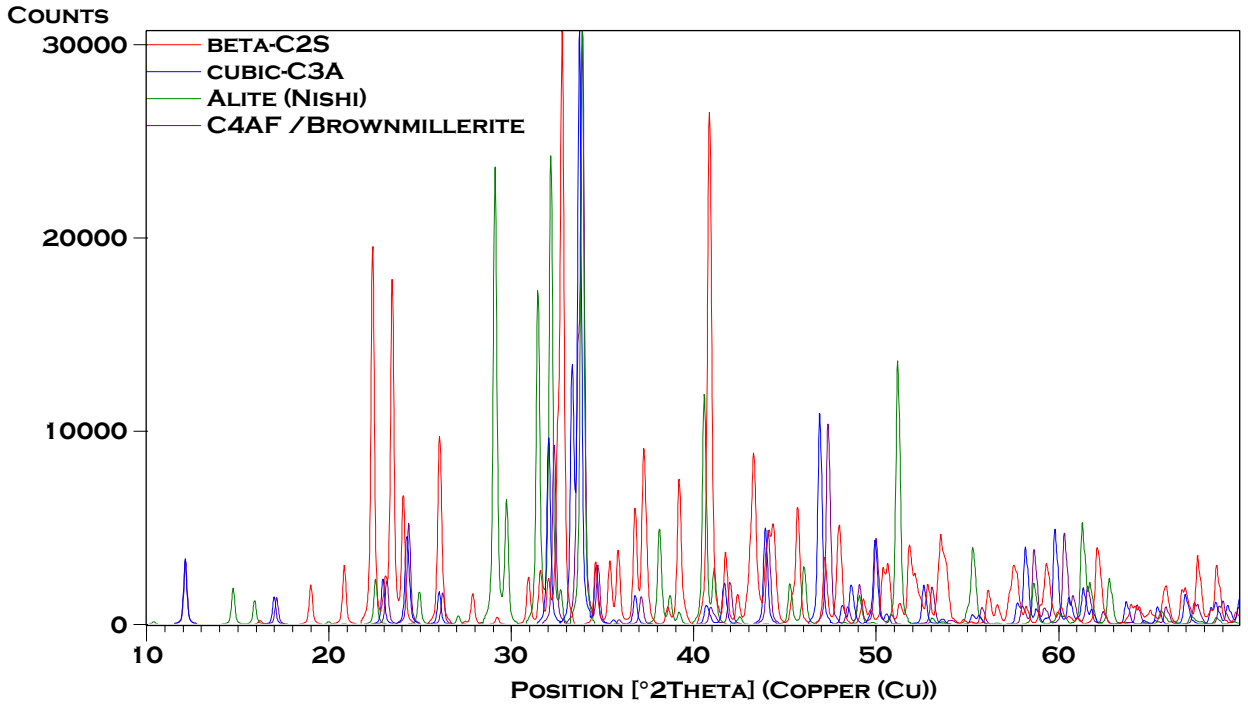


Background and scope of XRPD

Information content of a powder XRD scan

Severe peak overlap among the major clinker phases

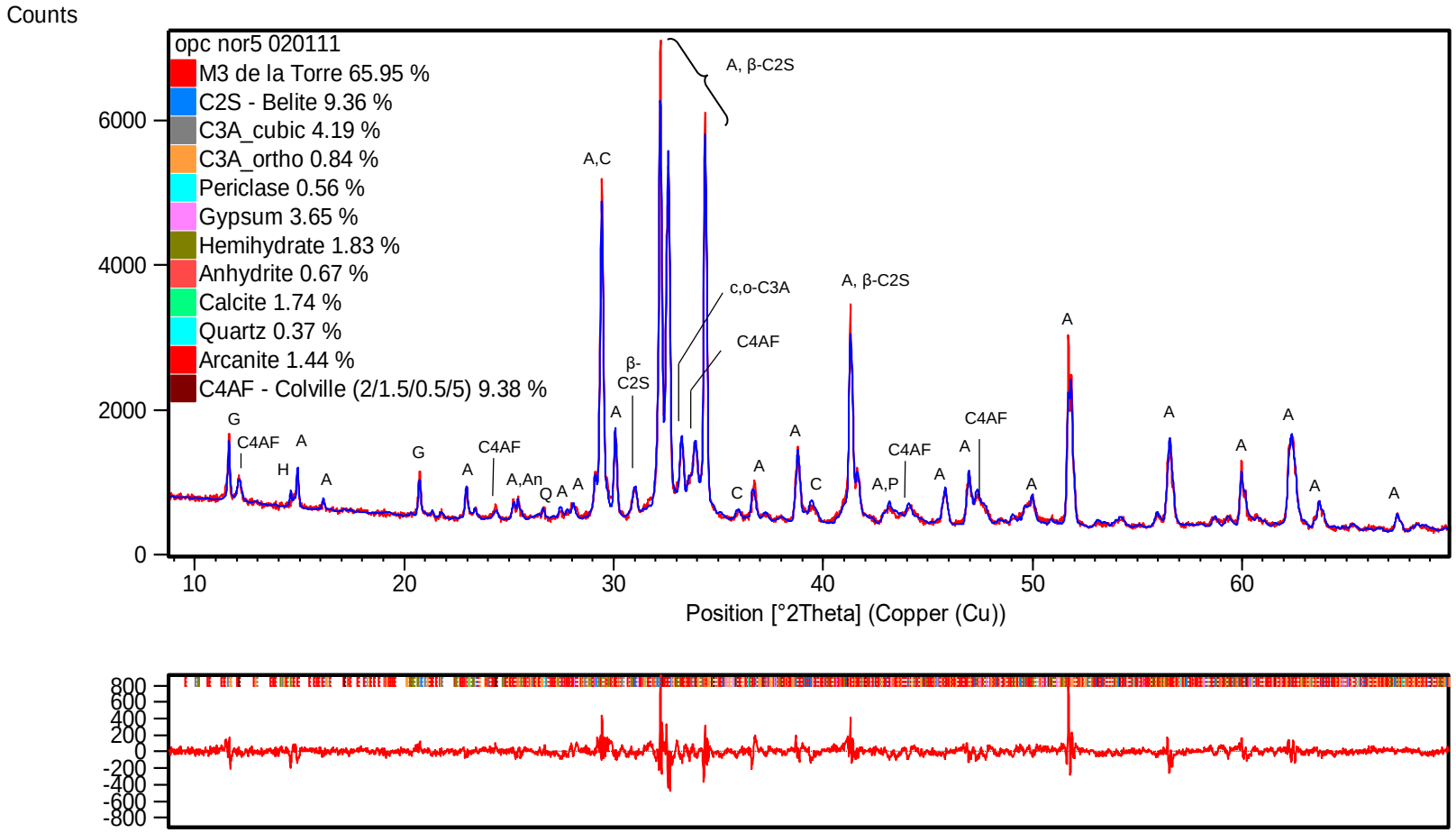
Or course, peak overlap can become a real problem!!



Background and scope of XRPD

Information content of a powder XRD scan

Phase composition and Rietveld Refinement of a Type II cement

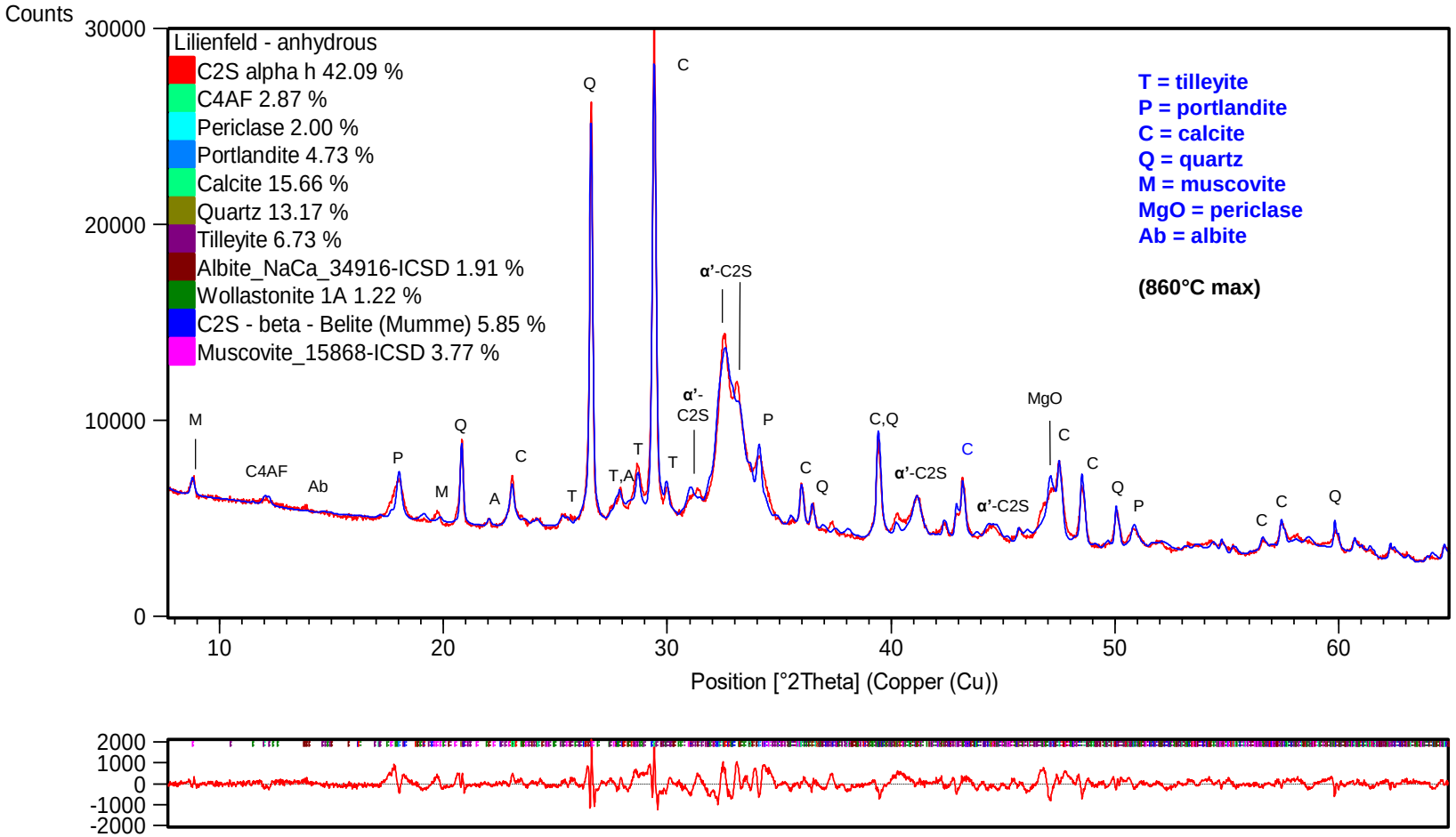


Complex mineralogy and peak overlap

Background and scope of XRPD

Phase composition and Rietveld refinement of a ‘Roman Cement’

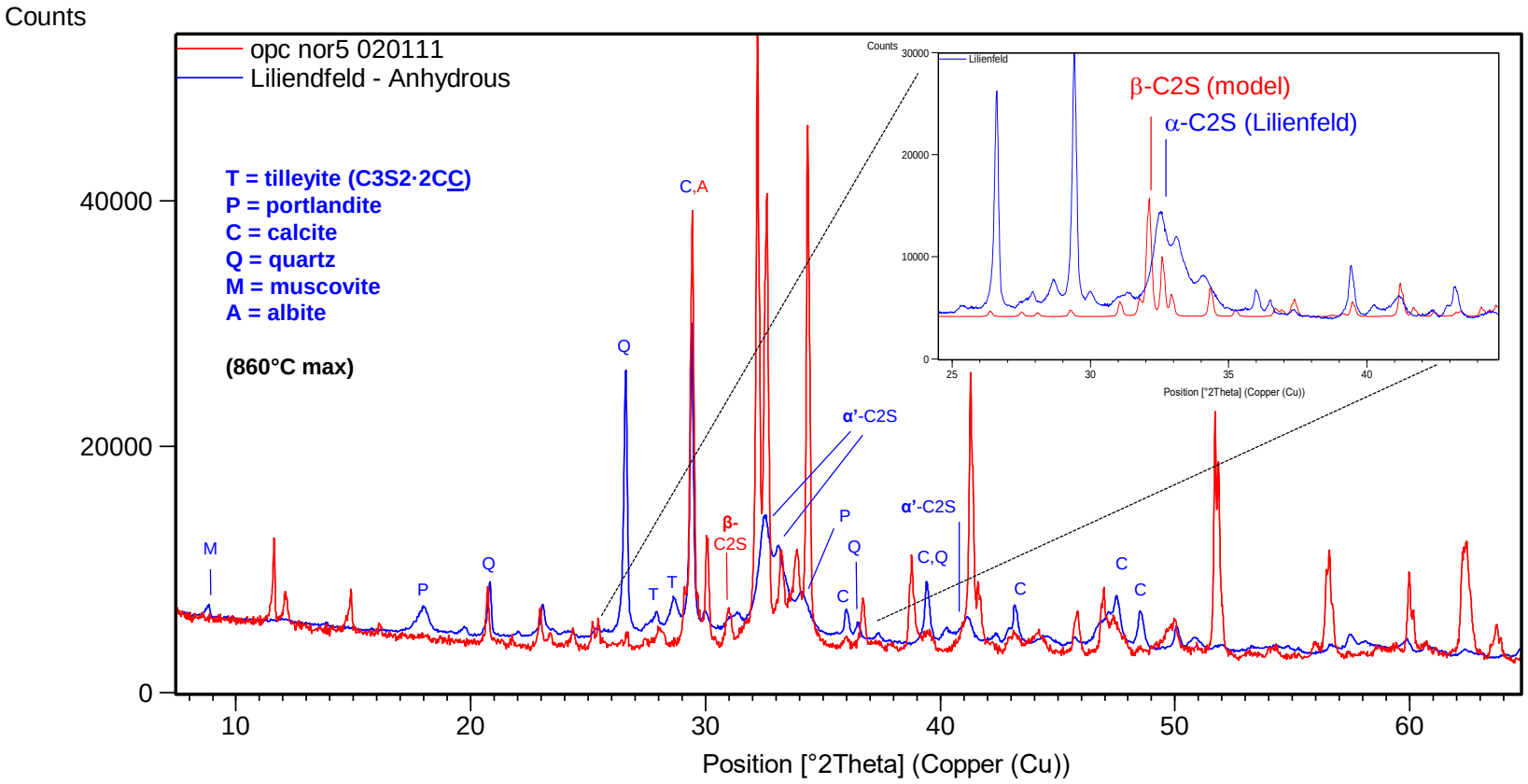
Low temperature ‘clinkering’: α’-C2S and carbonated silicates w/ no C3S



Background and scope of XRPD

Phase composition and Rietveld refinement of a ‘Roman Cement’

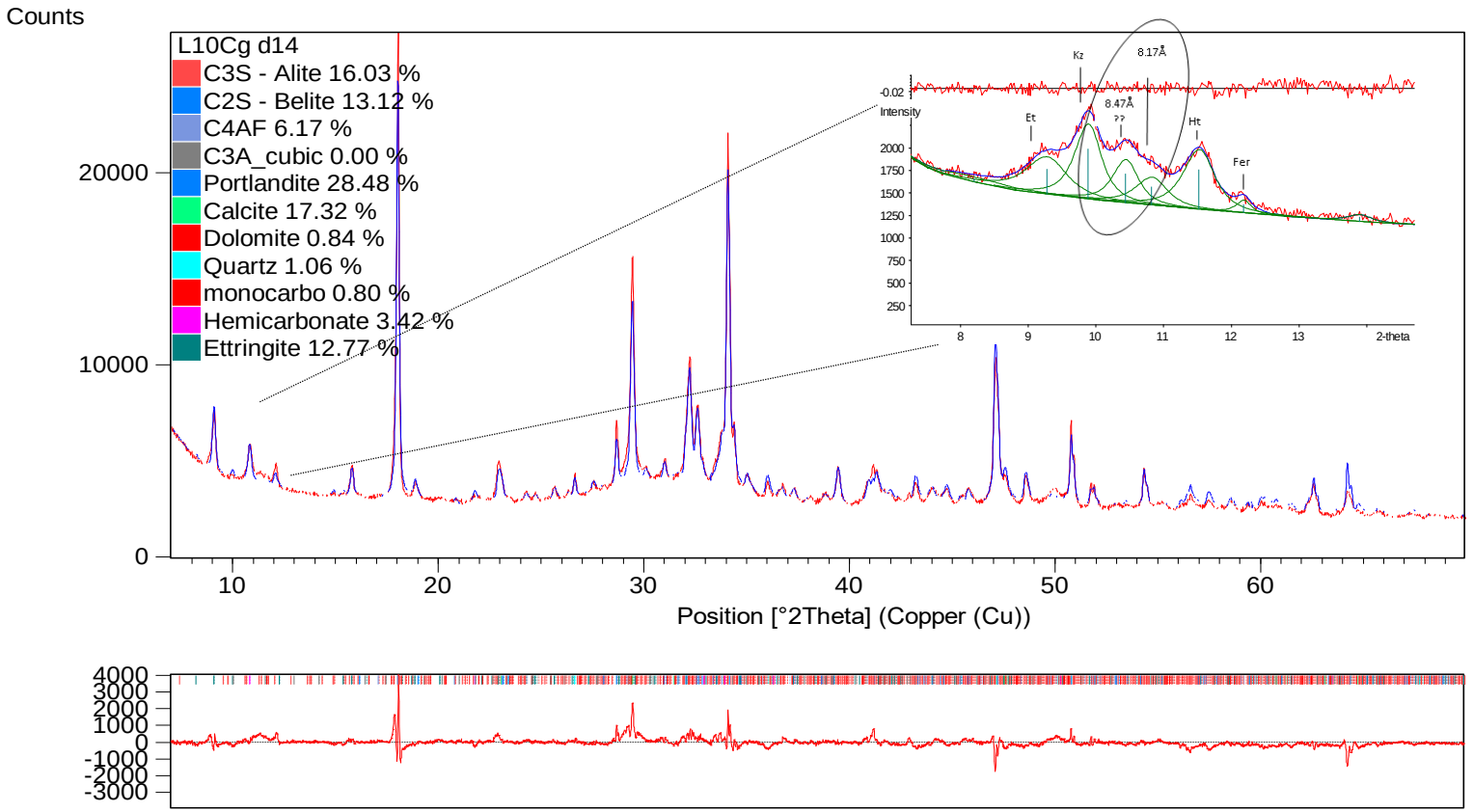
Low temperature ‘clinkering’: α’-C2S and carbonated silicates w/ no C3S



Background and scope of XRPD

Phase composition and Rietveld refinement of a hydrating cement

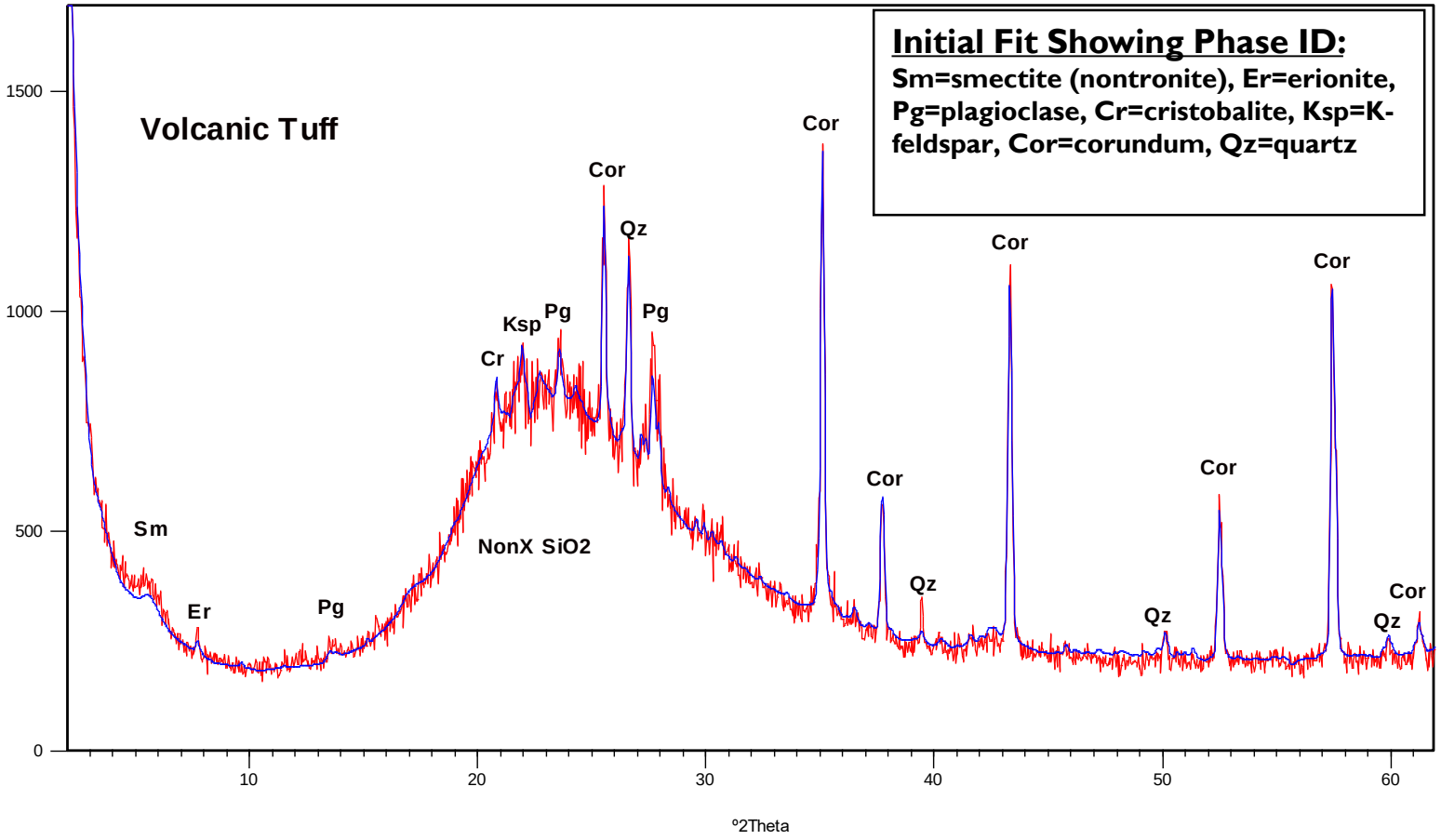
Paste Hydration Products: ‘Type II’ OPC



Background and scope of XRPD

Noncrystalline analysis: Pozzolanic material

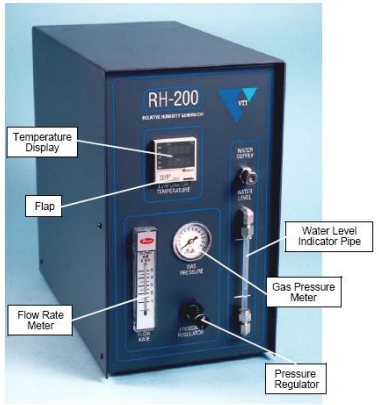
With known amount of an internal (corundum) standard

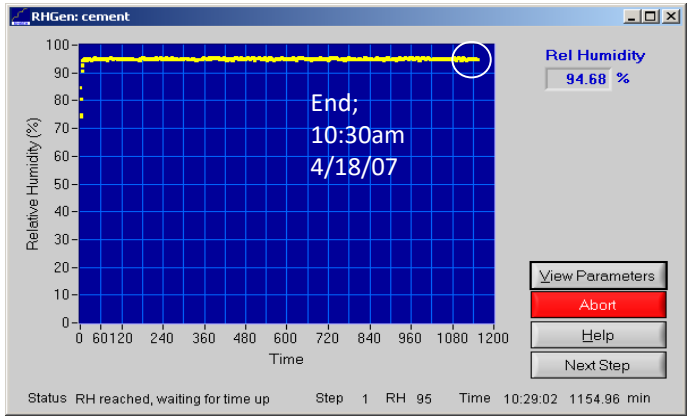


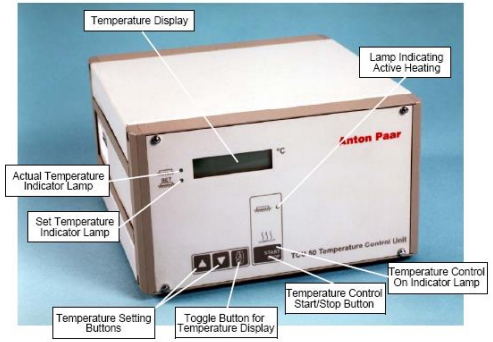
Background and scope of XRPD

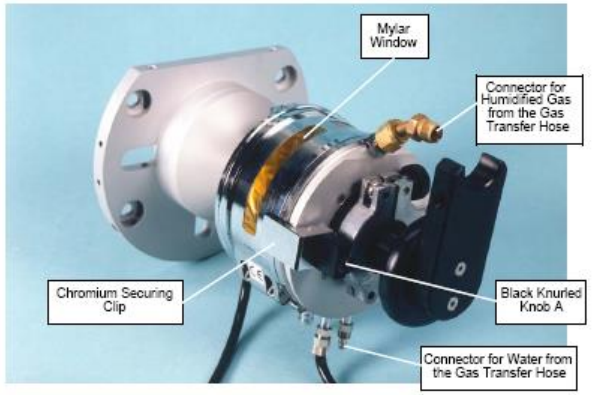
Non-Ambient / *In Situ* Analysis

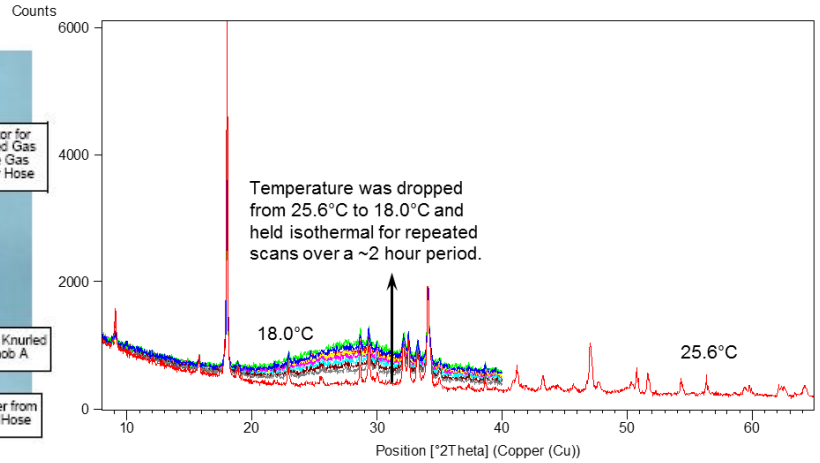
High temperature or humidity control in air or purge gases







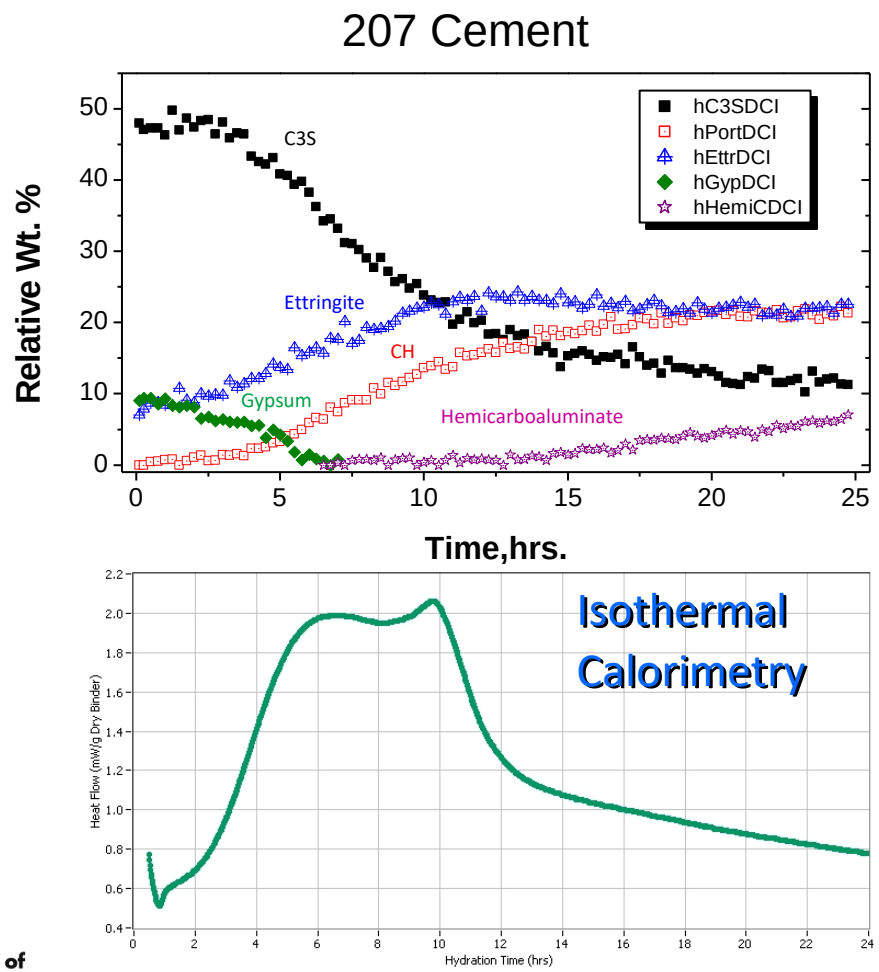




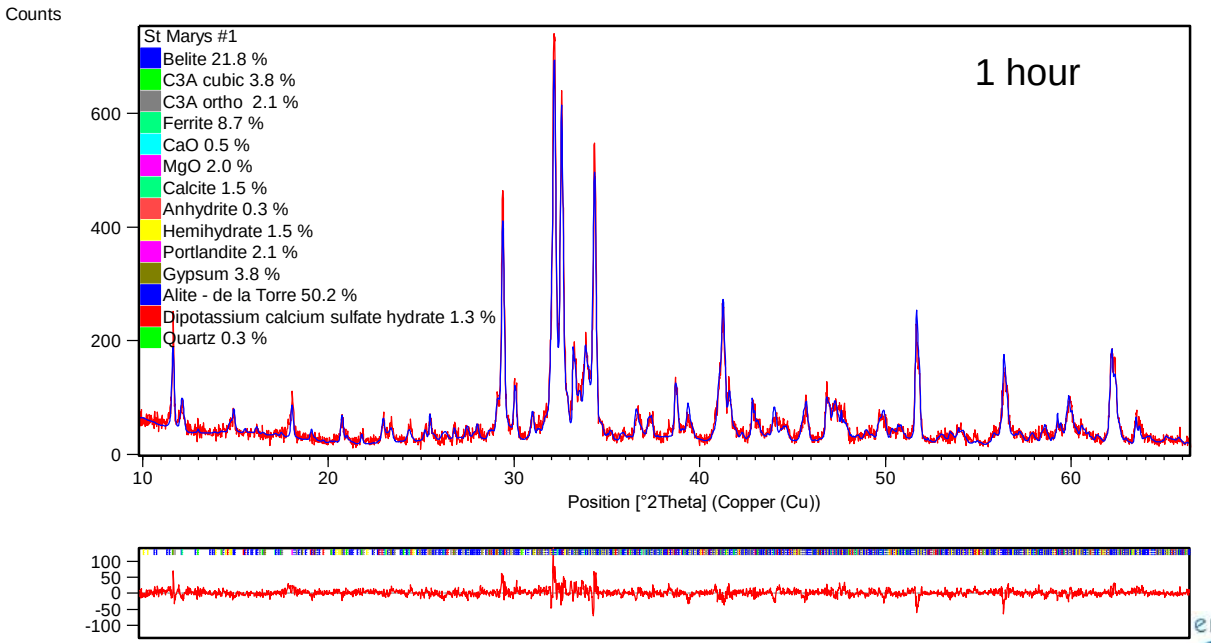
Background and scope of XRPD

Non-Ambient / In Situ Analysis

High temperature or humidity control in air or purge gases



- Humidity chamber (reflection)
- Rietveld refinement (100 scans in 24 hours)



NIST National Institute of Standards and Technology U.S. Department of Commerce

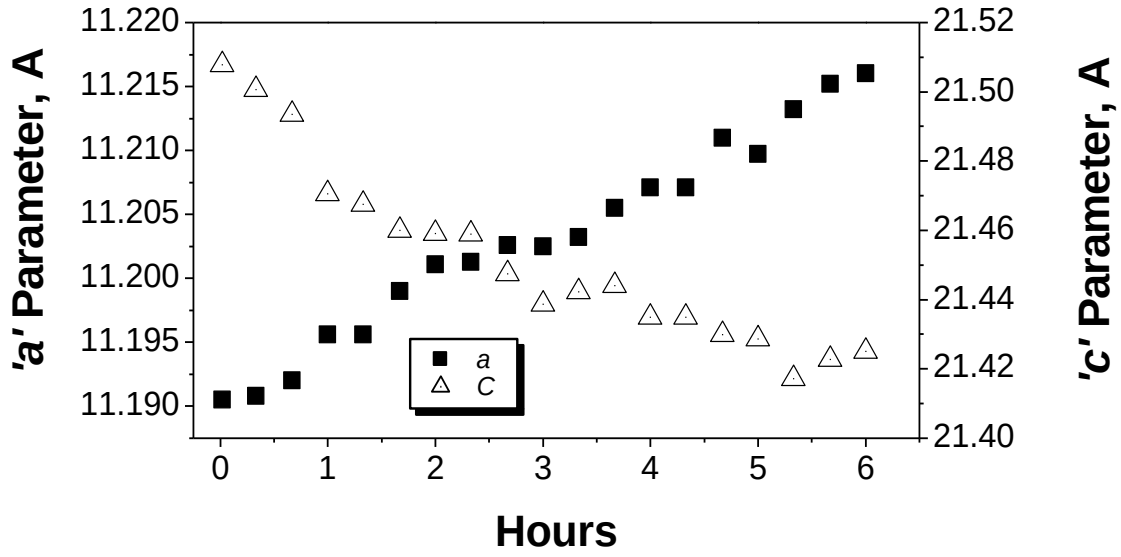
engineering laboratory

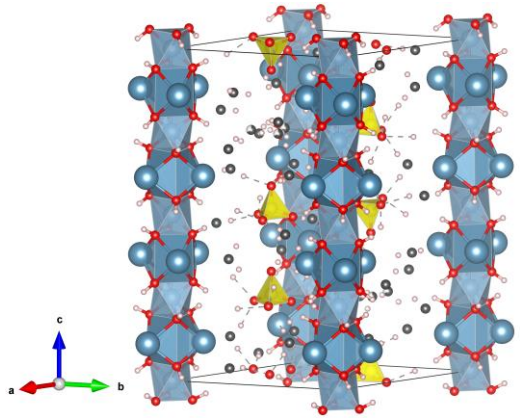
Background and scope of XRPD

Non-Ambient / In Situ Analysis

High temperature or humidity control in air or purge gases

Change in ettringite *a* and *c* lattice parameters during early cement paste hydration





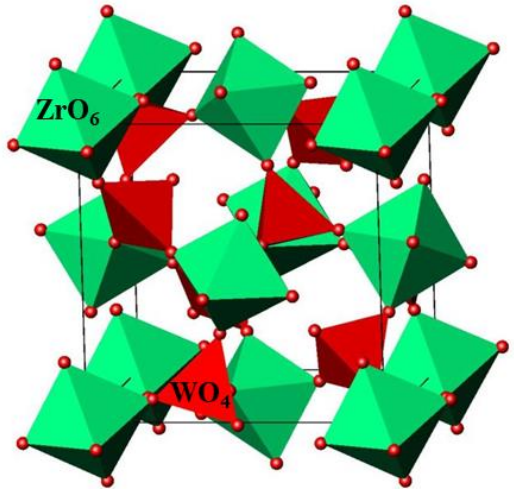
Ettringite

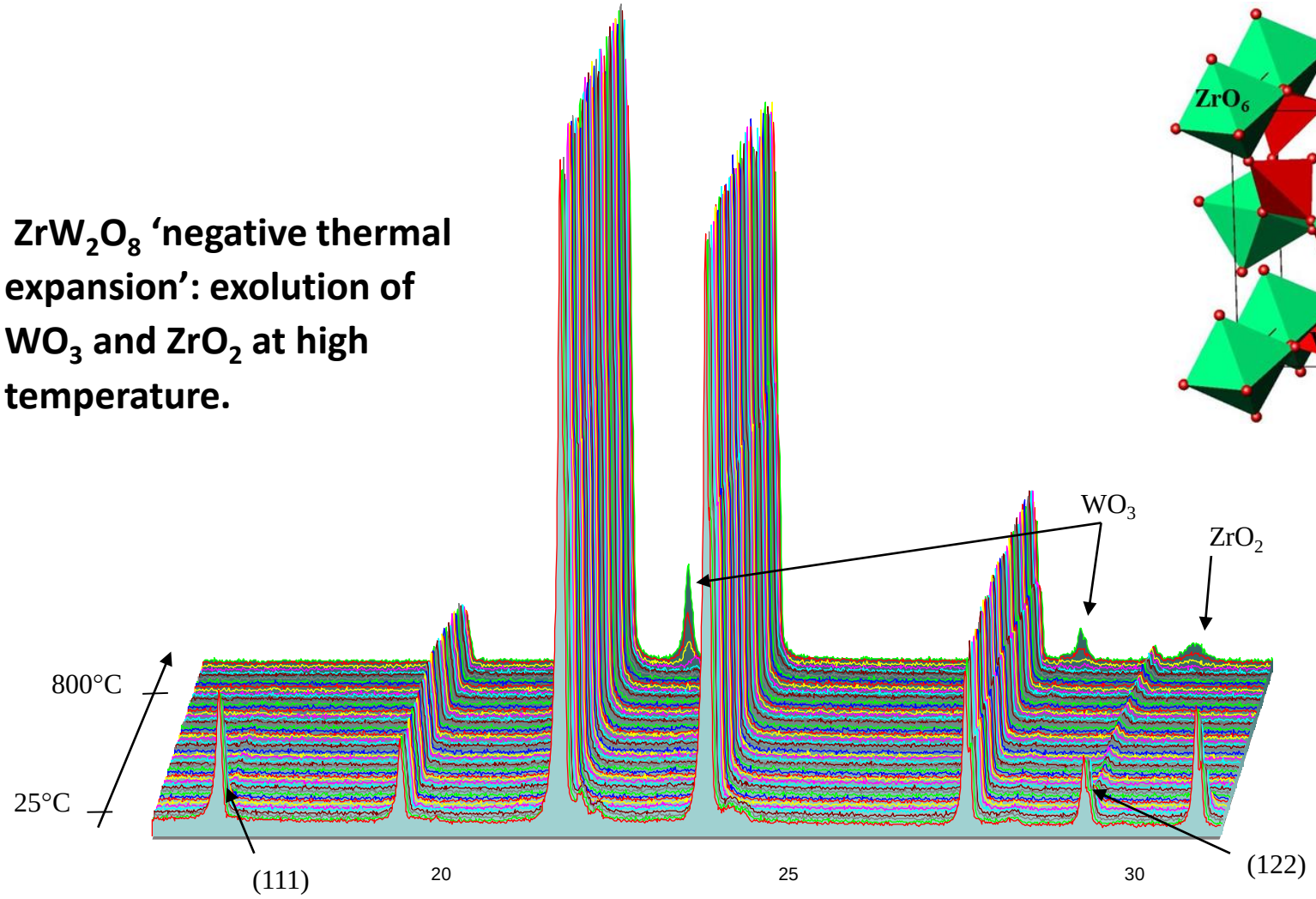
$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$

Background and scope of XRPD

Non-Ambient / In Situ Analysis

ZrW_2O_8 'negative thermal expansion': exolution of WO_3 and ZrO_2 at high temperature.





Background and scope of XRPD

Calculation of unit cell (lattice) parameters by empirical measurement of d-spacings, e.g.,

High temperature or humidity control in air or purge gases

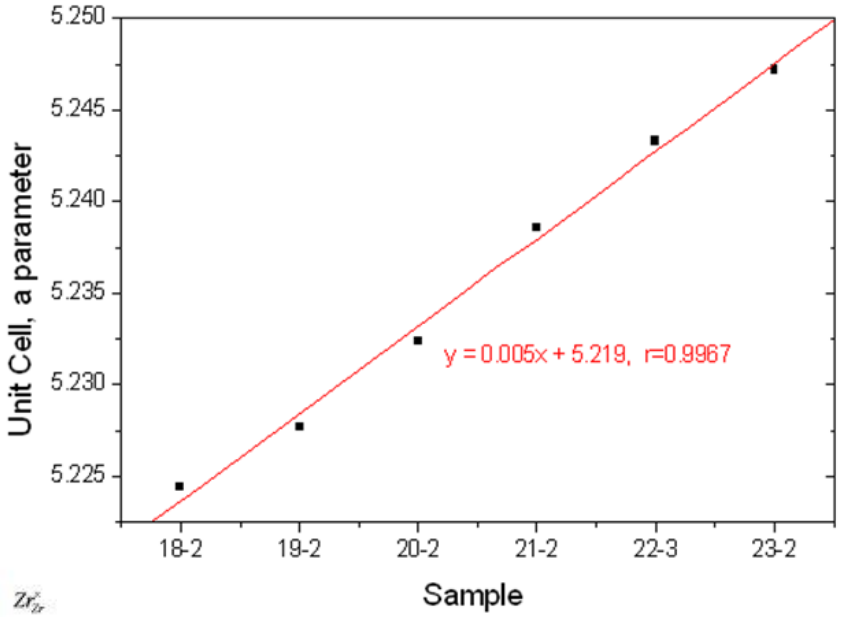
Cubic planar spacings: $$d = \sqrt{\frac{a^2}{h^2 + k^2 + l^2}}$$

Hexagonal planar spacings: $$d = \sqrt{\frac{1}{(h^2 + k^2 + hk)\frac{4}{3a^2} + \frac{l^2}{c^2}}}$$

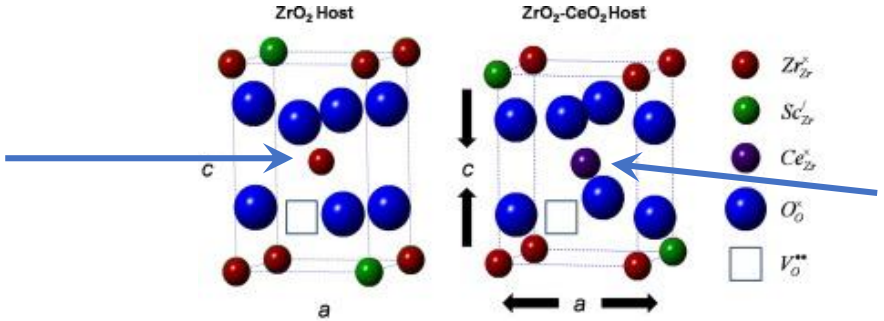
Cubic interplanar angles: $$\cos\phi = \frac{hh' + kk' + ll'}{\sqrt{h^2 + k^2 + l^2}\sqrt{h'^2 + k'^2 + l'^2}}$$

Hexagonal interplanar angles: $$\cos\phi = d_{hkl} d_{h'k'l'} \left\{ \left[hh' + kk' + \tfrac{1}{2}(hk' + kh') \right] \frac{4}{3a^2} + \frac{ll'}{c^2} \right\}$$

Effect of site occupancy on unit cell 'a' parameter in Ce-doped zirconias



Increasing Ce content

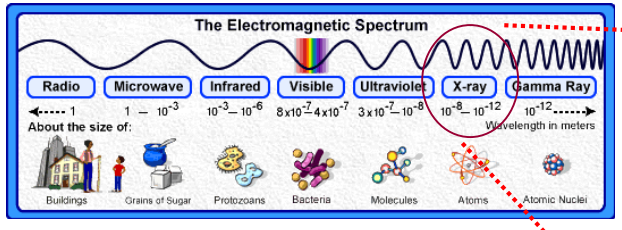


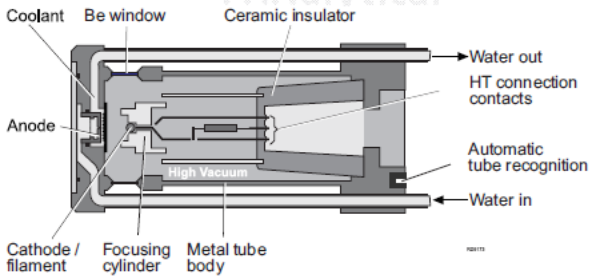
Addition of 1 mol.% CeO_2 in ZrO_2 host-lattice increases tendency to form high-symmetry, high-conductivity phases

2) XRD Instrumentation

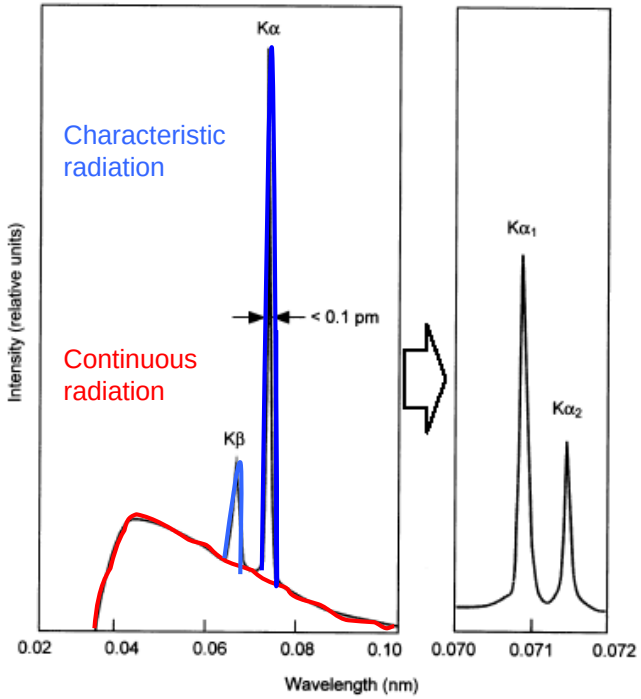
XRD Instrumentation

Generation of x-rays



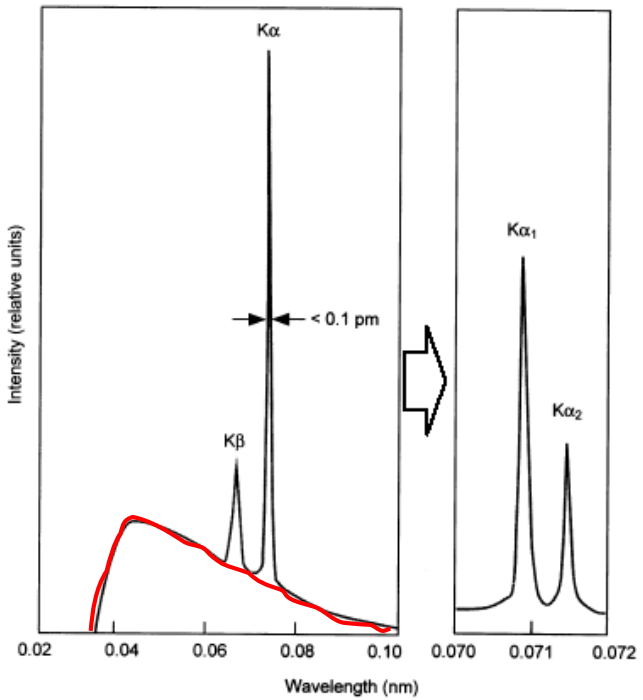


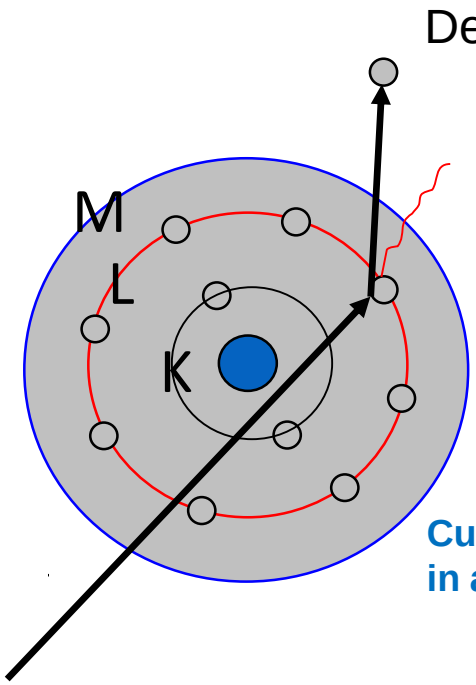
Signal emitted from tube



XRD Instrumentation

Generation of x-rays





Decelerated electron

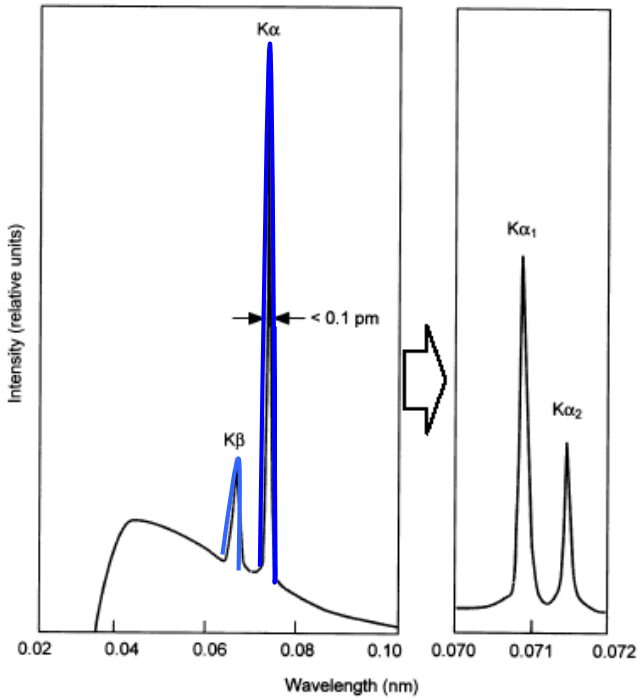
Background ('braking') radiation (Bremsstrahlun)

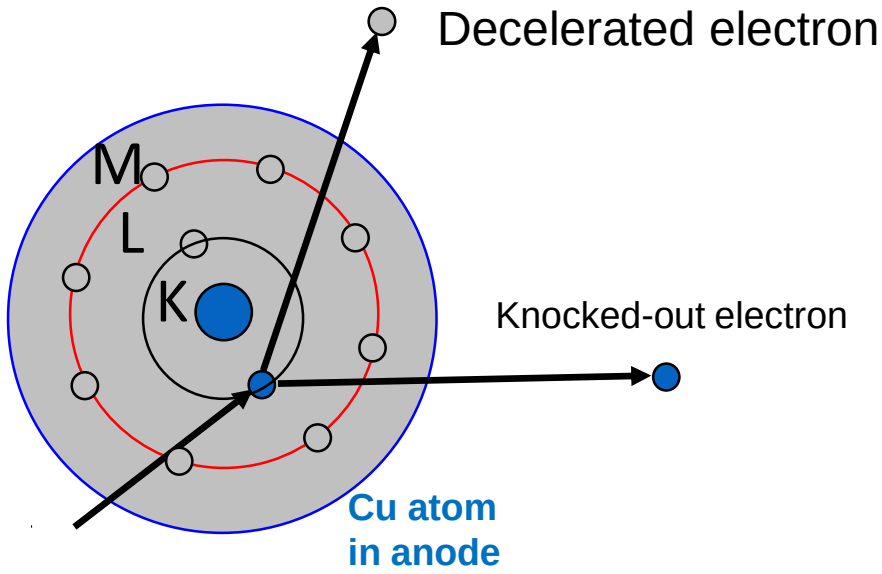
Cu atom in anode

Continuous radiation: Caused by deceleration of electrons emitted from the filament when passing the positively-charged nuclei in the anode, or when colliding with electrons of the anode atoms.

XRD Instrumentation

Generation of x-rays



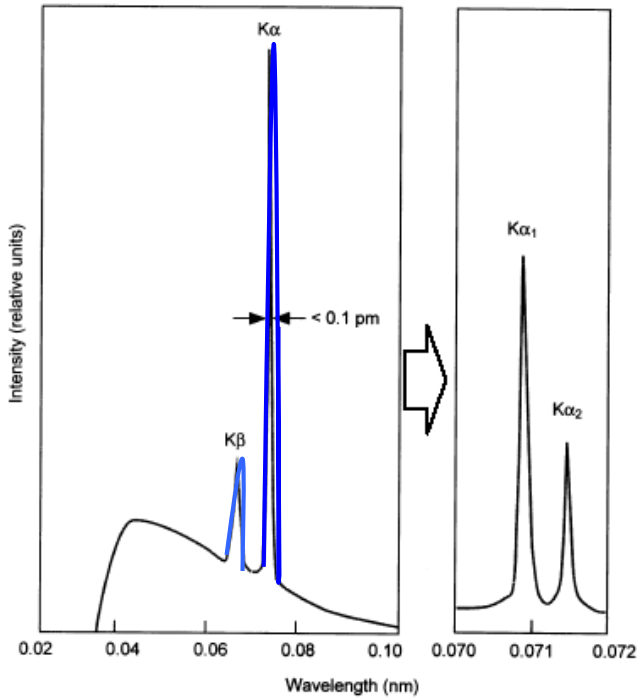


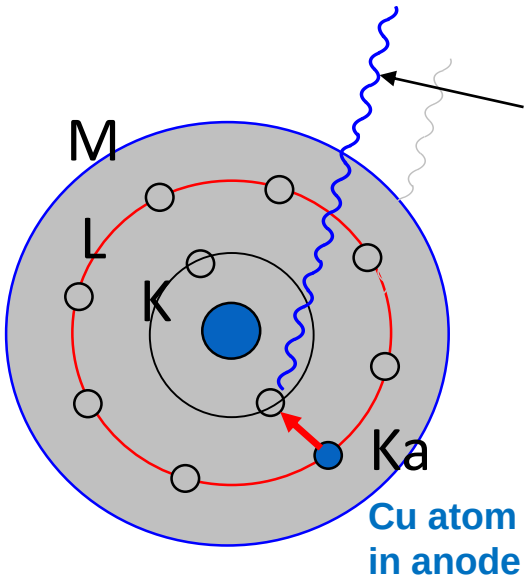
Characteristic radiation:

1) incident electrons have sufficient energy to eject electrons out of the inner shell of the target (anode) metal, and then…

XRD Instrumentation

Generation of x-rays





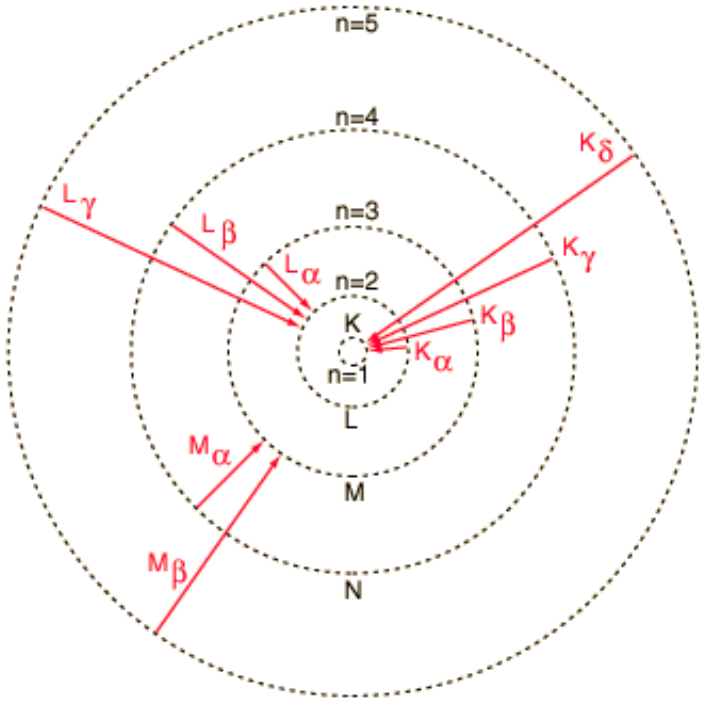
Characteristic radiation:

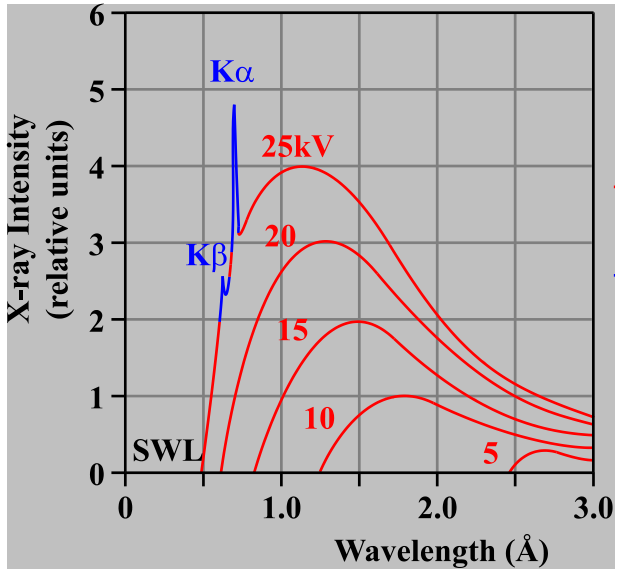
2) electrons from a higher energy shells drop down to fill the vacancy, emitting x-ray photons with precise energies that are 'characteristic' of the electron energy levels of the target metal atoms AND the specific orbital shell energy.

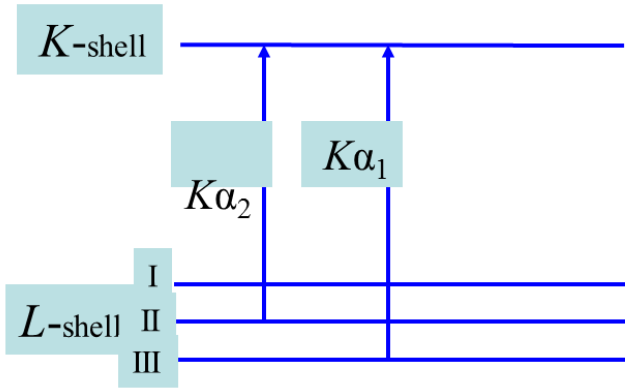
XRD Instrumentation

Kα1, Kα2, and Kβ are the primary wavelengths of interest

- Characteristic radiation is only emitted above certain threshold energy levels
- Kα radiation comprises two wavelengths: $K\alpha_1$ and $K\alpha_2$. The wavelengths correspond to the transitions from the L-shell to the K-shell.



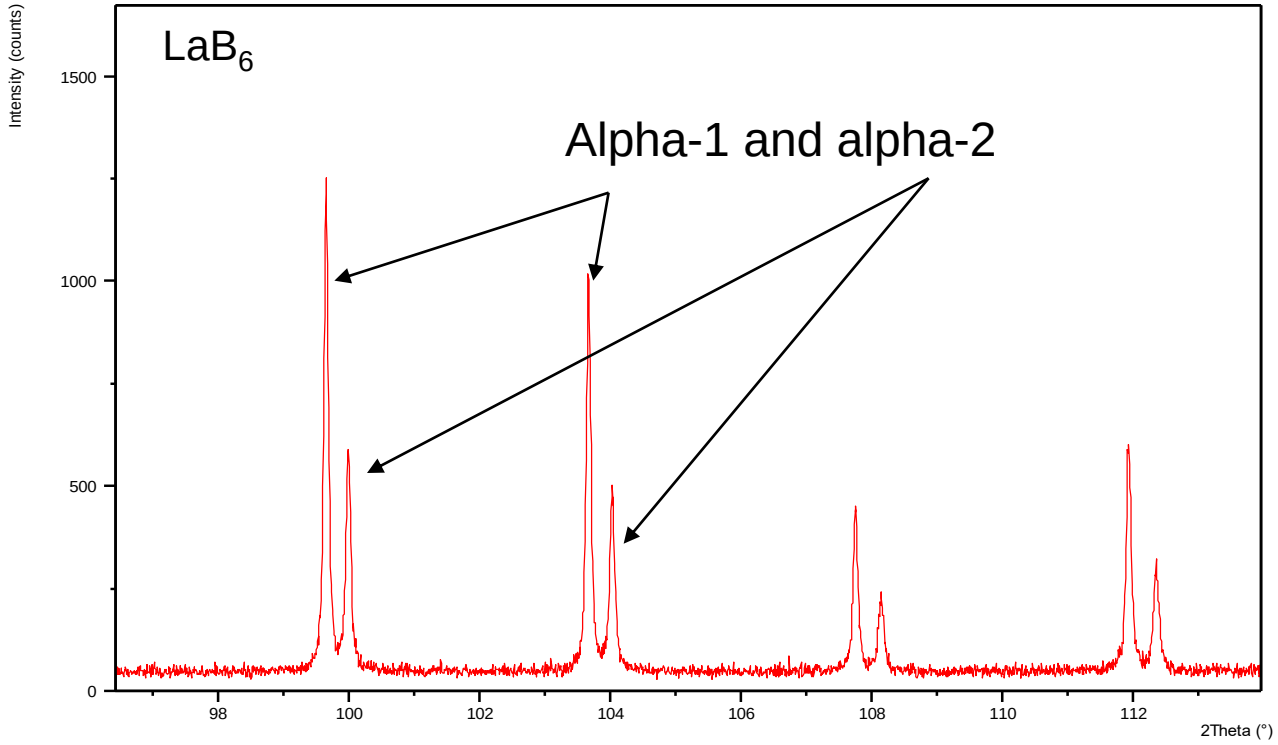




XRD Instrumentation

Kα1, Kα2, and Kβ are the primary wavelengths of interest

Two peaks for each crystalline reflection!!!



XRD Instrumentation

Kα1, Kα2, and Kβ are the primary wavelengths of interest

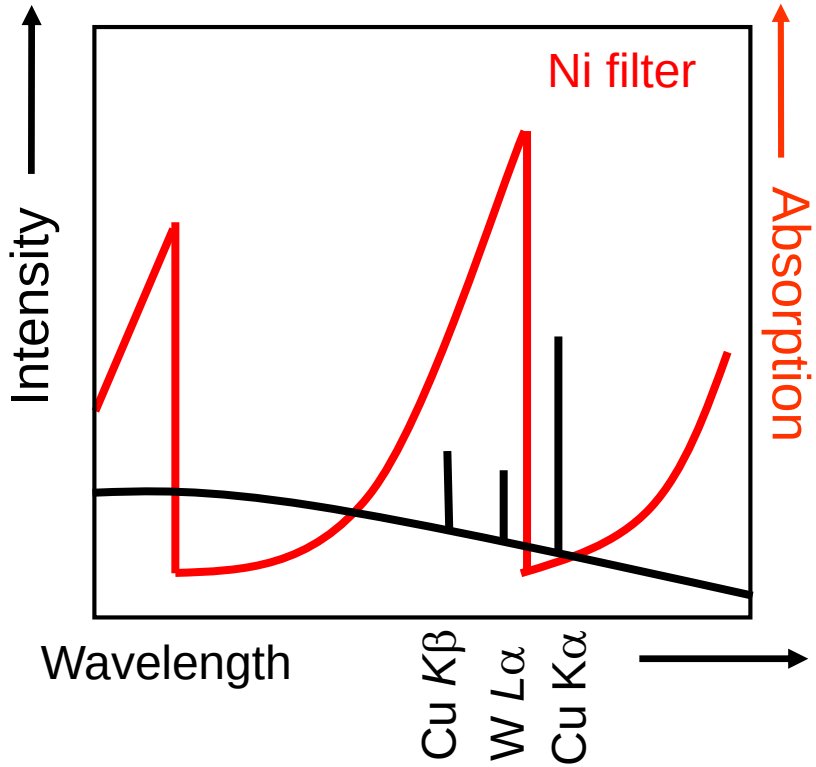
Kα1 and Kα2 peaks are acceptable: Kβ is not

FIX: Use filter material * with an absorption edge in between the Kα and Kβ line

e.g.,

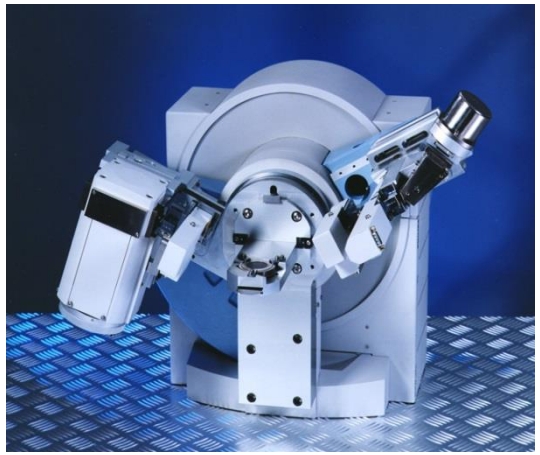
Ni filter for Cu-radiation

* or a monocrhomater or an energy dispersive detector



XRD Instrumentation

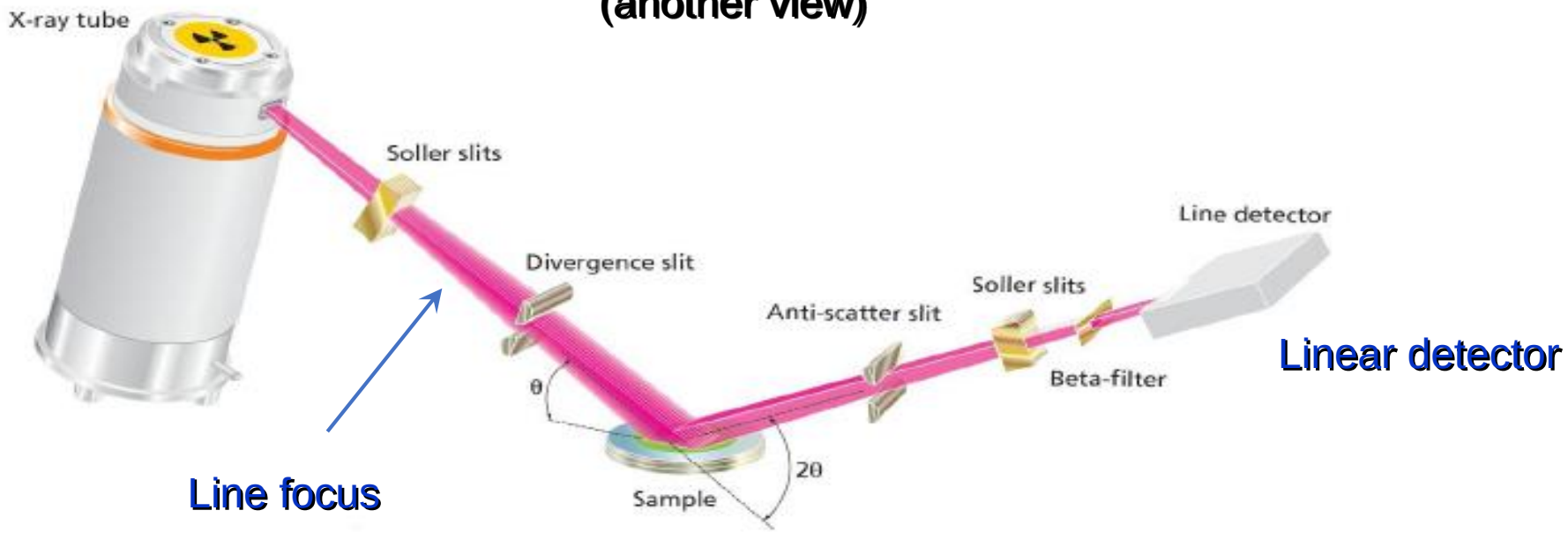
Conventional ‘reflection’ geometry and focusing optics



XRD Instrumentation

Conventional ‘reflection’ geometry and focusing optics

Focusing (Bragg-Brentano) Optics
(another view)



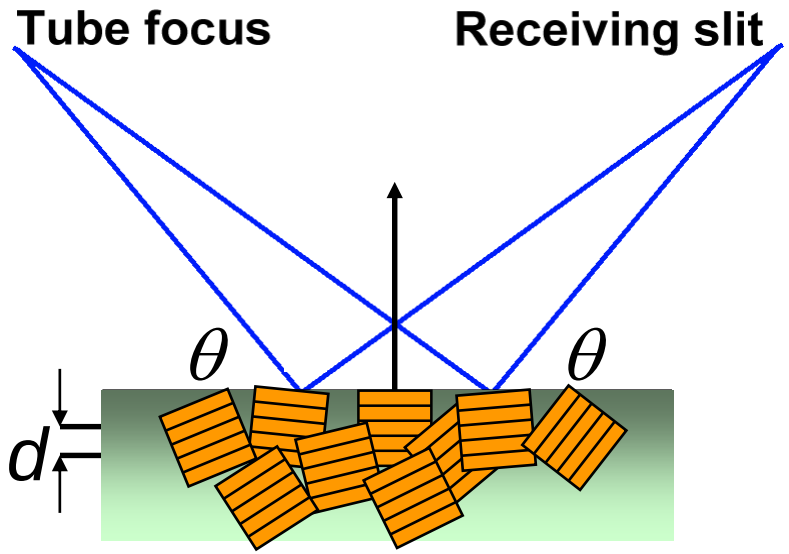
Line focus

Linear detector

XRD Instrumentation

Conventional ‘reflection’ geometry and focusing optics

- ✓ Sample surface bisects incident and scattered beams
- ✓ Scattered beams focus at the same distance as the tube focus in receiving slit



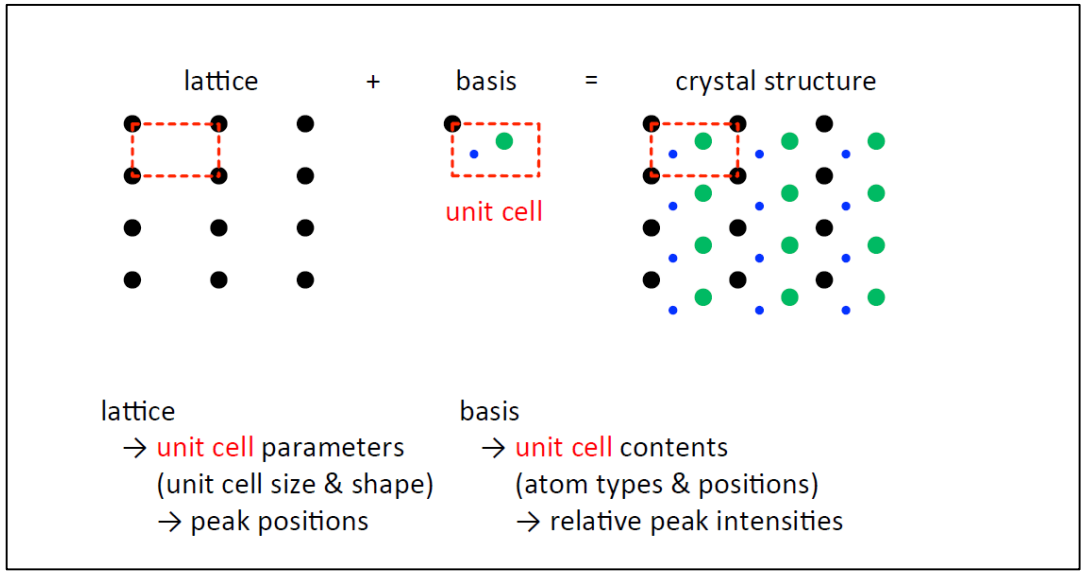
$$\lambda = 2\, d \sin(\theta)$$

3) X-Ray Diffraction Theory and Introduction to Crystallography

XRD Theory and Basic Crystallography

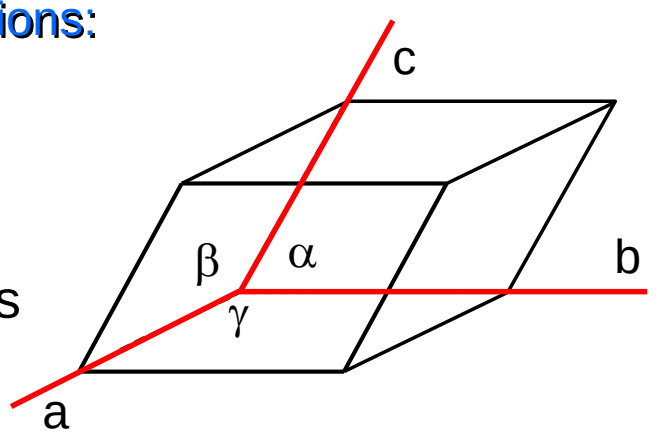
Crystalline materials: orderly, periodic array of atoms, each describing an identical environment

The *unit cell* is the basic repeating unit that defines a crystal.



Unit cell dimensions:

a b c - sides
α β γ - angles

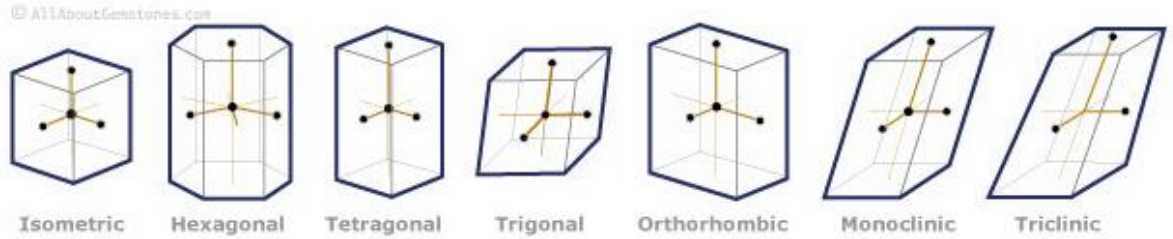


The unit cell describes at least one repeating unit that can be used to construct the structure.

XRD Theory and Basic Crystallography

Crystalline materials: orderly, periodic array of atoms, each describing an identical environment

The 7 Types of Unit Cells:



The 7 Crystal Systems:

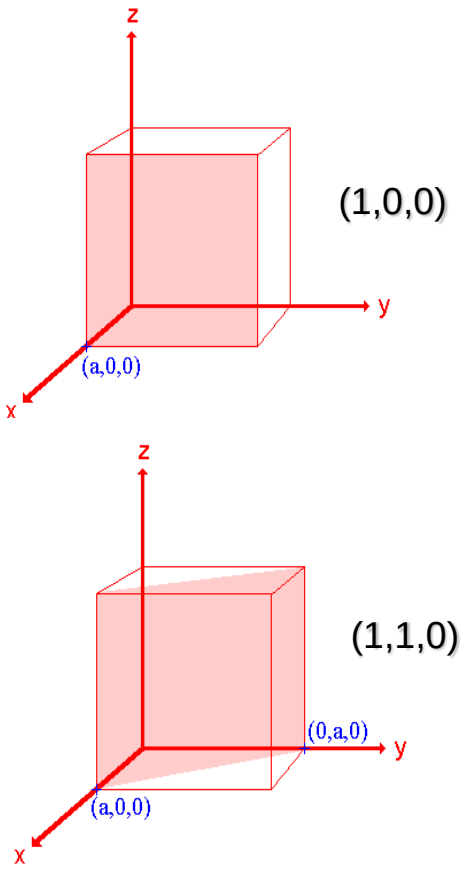
Increasing Symmetry →

Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma \neq \beta$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Trigonal	$a = b = c$	$\alpha = \beta = \gamma < 120°, \neq 90°$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$

XRD Theory and Basic Crystallography

Crystalline materials: orderly, periodic array of atoms, each describing an identical environment

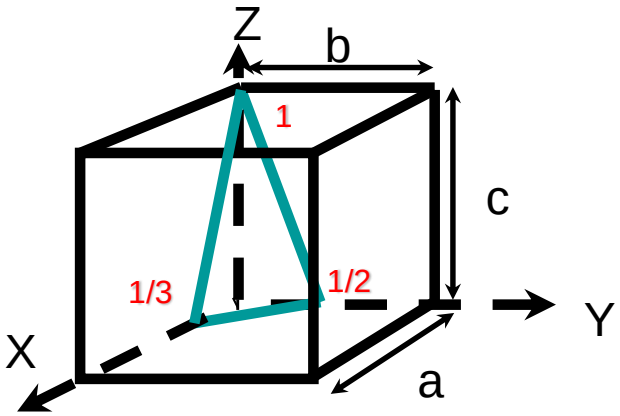
Miller Indices



To find the Miller Indices:

- Find intercepts on a, b, c axes (*e.g.,* 1/3, 1/2,1)
- Take reciprocals (3 2 1)

All lattice planes can be indexed in the same way



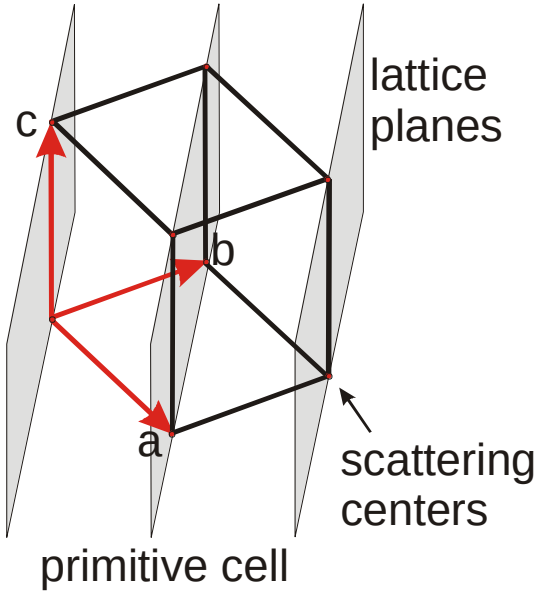
The (321) plane is shown with intercepts at a/3, b/2, c

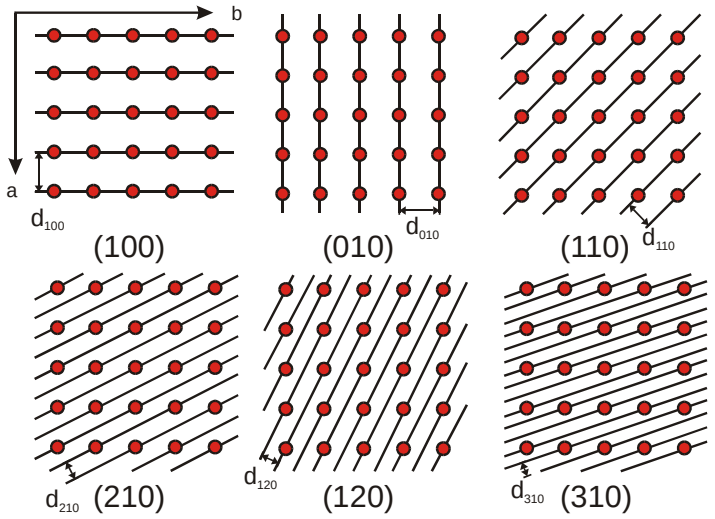
e.g., 1/3, 1/2, 1

XRD Theory and Basic Crystallography

Crystalline materials: orderly, periodic array of atoms, each describing an identical environment

Interaction of x-rays with *different planes* of atoms produce a unique diffraction pattern, which contains information about the atomic arrangement within the crystal.



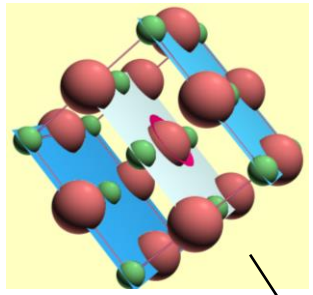


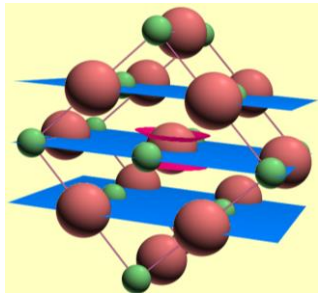
The unit cell parameters determine i) the peak positions and ii) the peak intensity results from the effect of atom type (electron density).

XRD Theory and Basic Crystallography

Crystalline materials: orderly, periodic array of atoms, each describing an identical environment

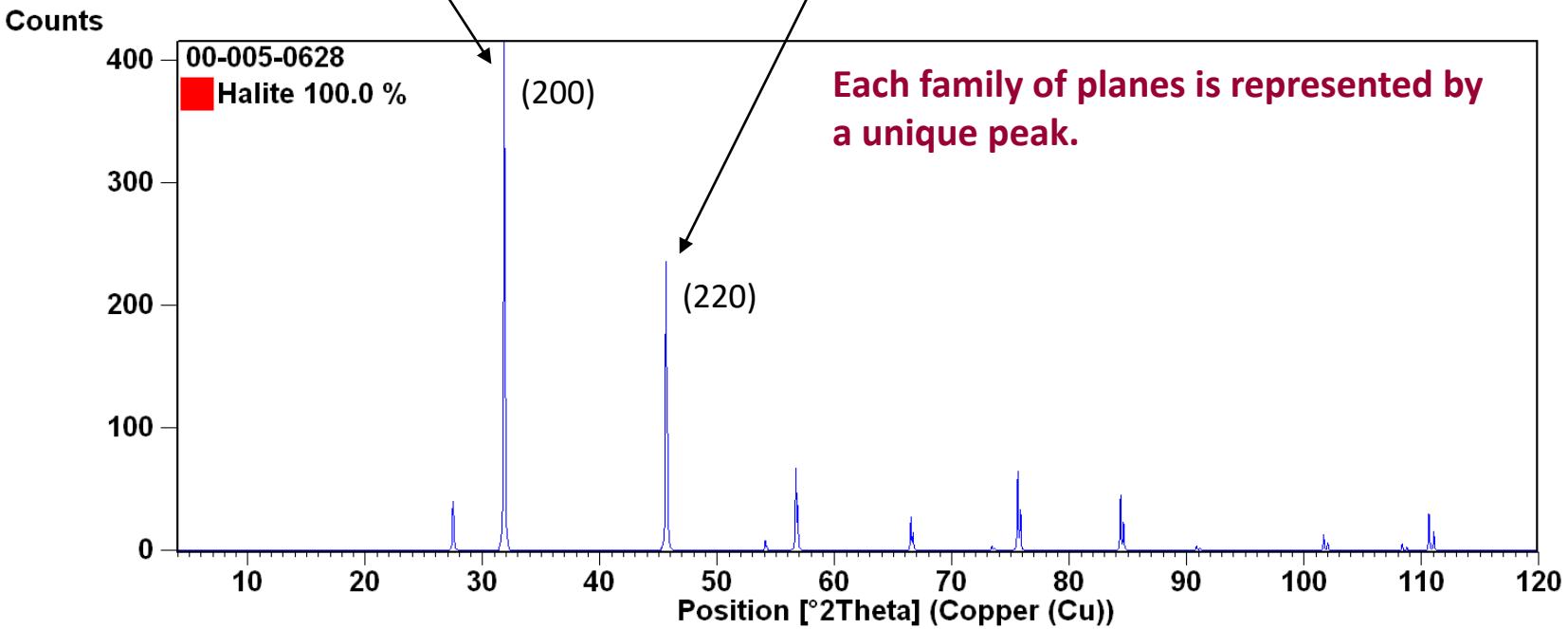
The (200) planes of atoms in NaCl





The (220) planes of atoms in NaCl

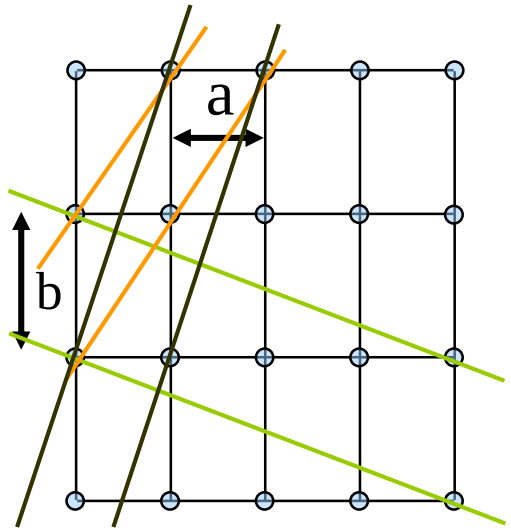
Halite



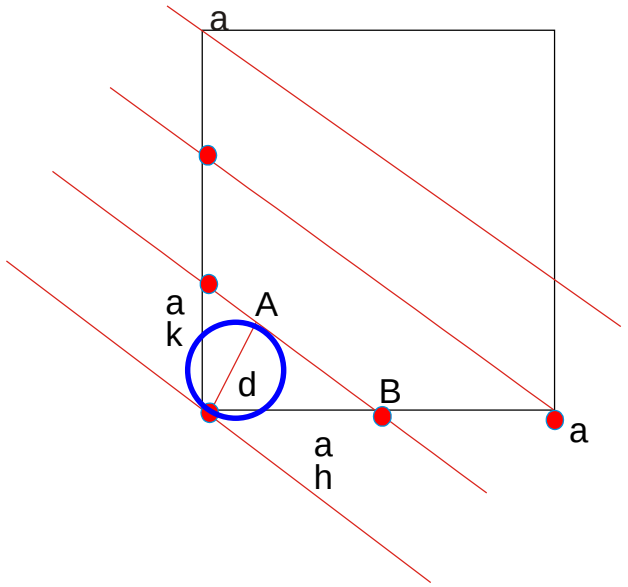
XRD Theory and Basic Crystallography

Crystalline materials: orderly, periodic array of atoms, each describing an identical environment

The position of a diffraction peak in ‘degrees 2θ’ is a product of the crystal lattice interplanar spacing, or *d-spacing,* which can be calculated using the scan angle and x-ray wavelength through the Bragg equation:



Arrays of atoms
in real space



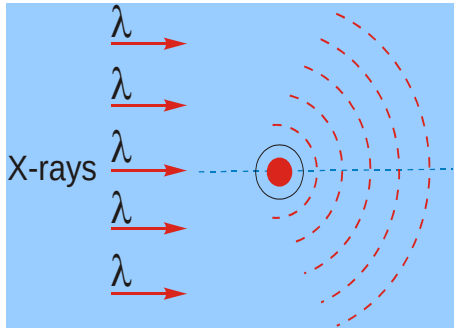
Bragg Equation

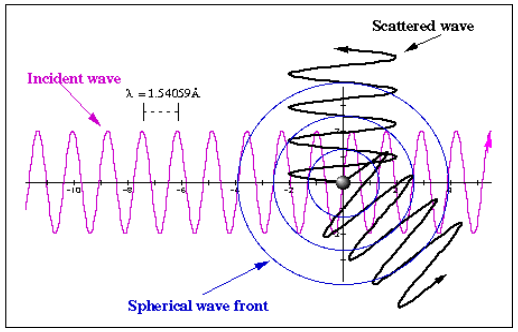
$$n\lambda = 2d \sin \theta$$

XRD Theory and Basic Crystallography

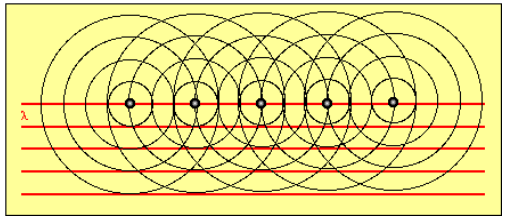
Interaction of x-rays with crystalline material: Scattering

Atoms scatter X-rays and acts as a point source….

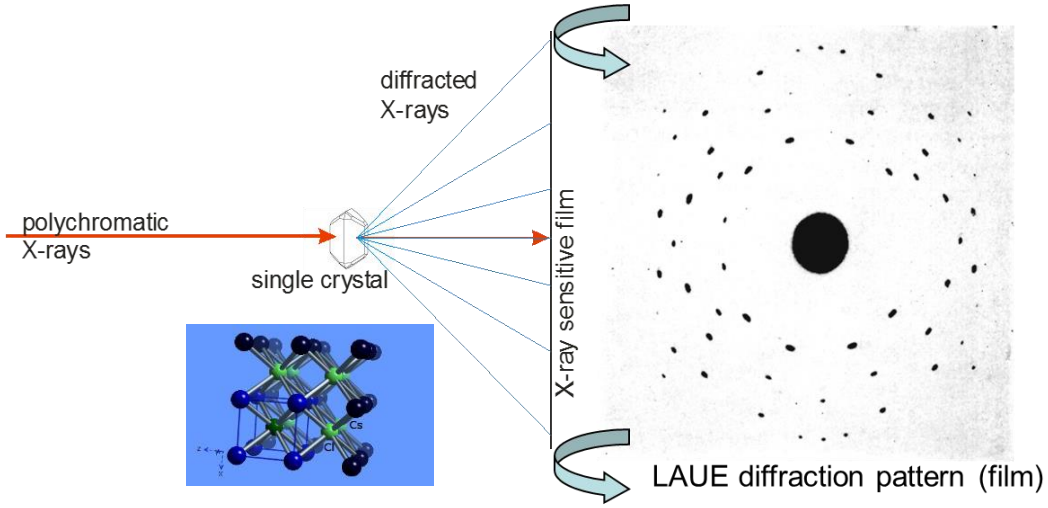




…or when arranged in a regular array.



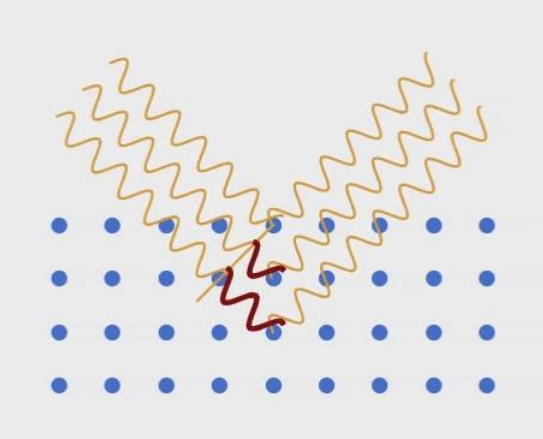
X-rays interact with a crystal and are scattered in different distinct directions as governed by the periodic arramgement of atoms in the structure.

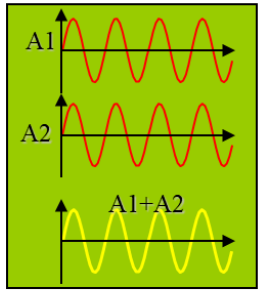


XRD Theory and Basic Crystallography

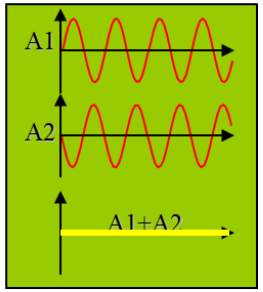
Interaction of x-rays with crystalline material: Diffraction

An array of atoms with incident x-rays of fixed wavelength and their interaction.



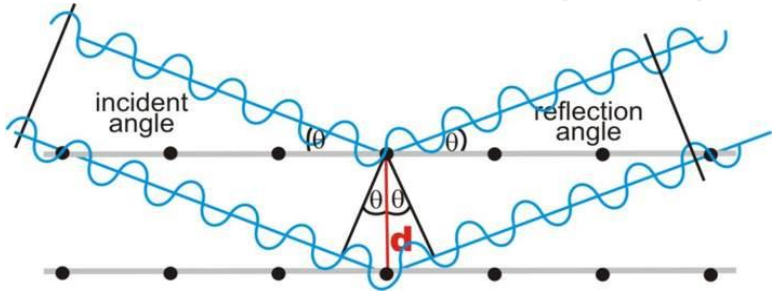


Constructive

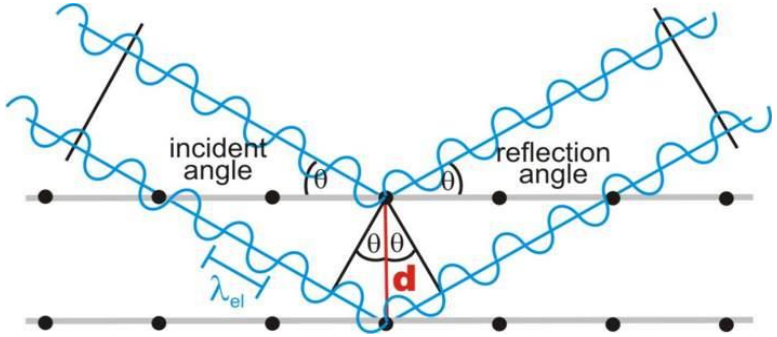


Destructive

Out of phase (destructive)



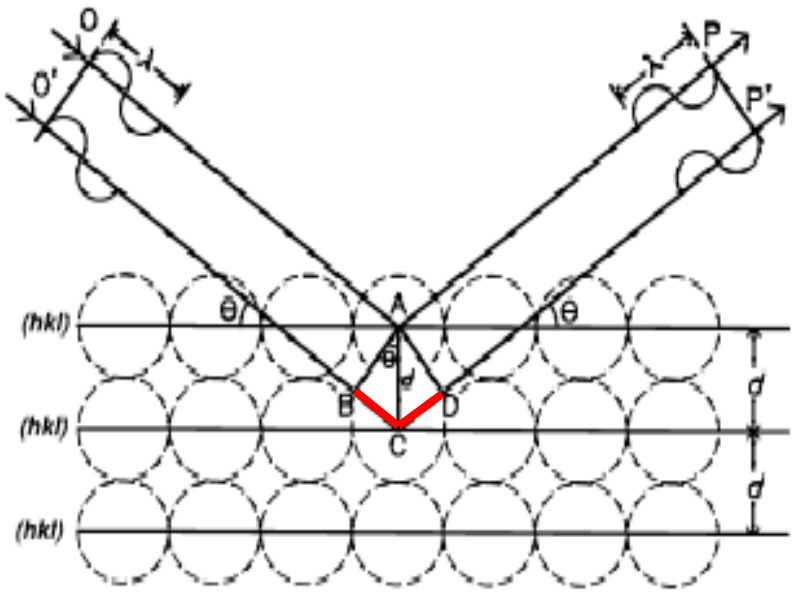
In phase (constructive)



XRD Theory and Basic Crystallography

Interaction of x-rays with crystalline material: Diffraction and the Bragg equation

The condition in which constructive interference occurs:



$n\lambda = 2d \sin \theta$

Bragg Equation

Derivation

1) Incident wave fronts OA and O'C are <u>in phase</u>

2) Scattered waves AP and CP' will be in phase *only* if the extra distance traveled by the longer wave (*i.e.*, BC + CD) equals a <u>whole number of wavelengths</u>.

3) Thus:

$BC + CD = n\lambda$, where n=1,2,3…

or, substituting: $2BC = n\lambda$,

4) From trigonometry:

$\sin \theta = BC/d$, or $BC = d \sin \theta$.

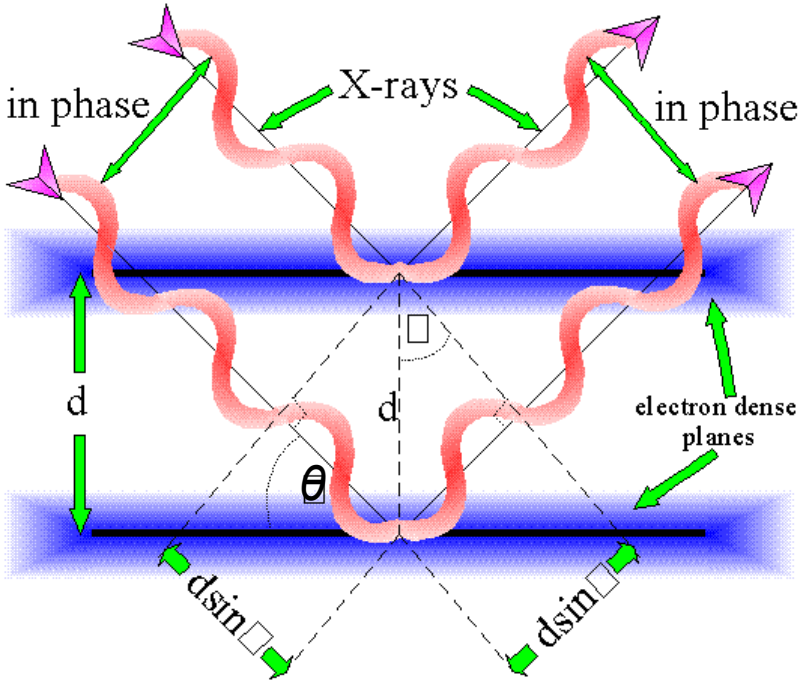
Multiply both sides by 2:

$2BC = 2d \sin \theta$, or

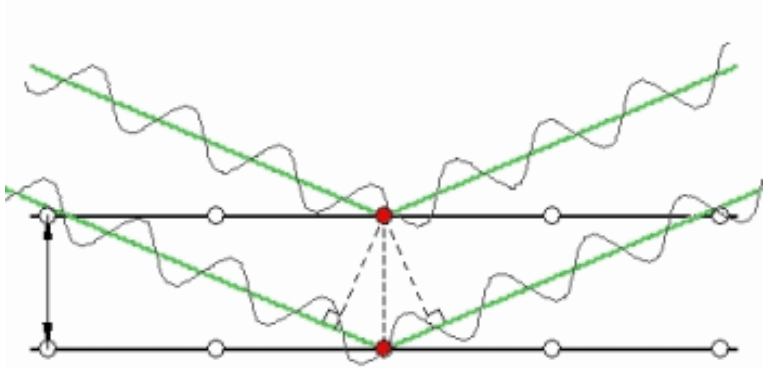
$n\lambda = 2d \sin \theta$

XRD Theory and Basic Crystallography

Interaction of x-rays with crystalline material: Diffraction and the Bragg equation



In plain English, diffraction occurs when the extra distance the 2nd beam travels is one whole number of wavelengths longer than the first.

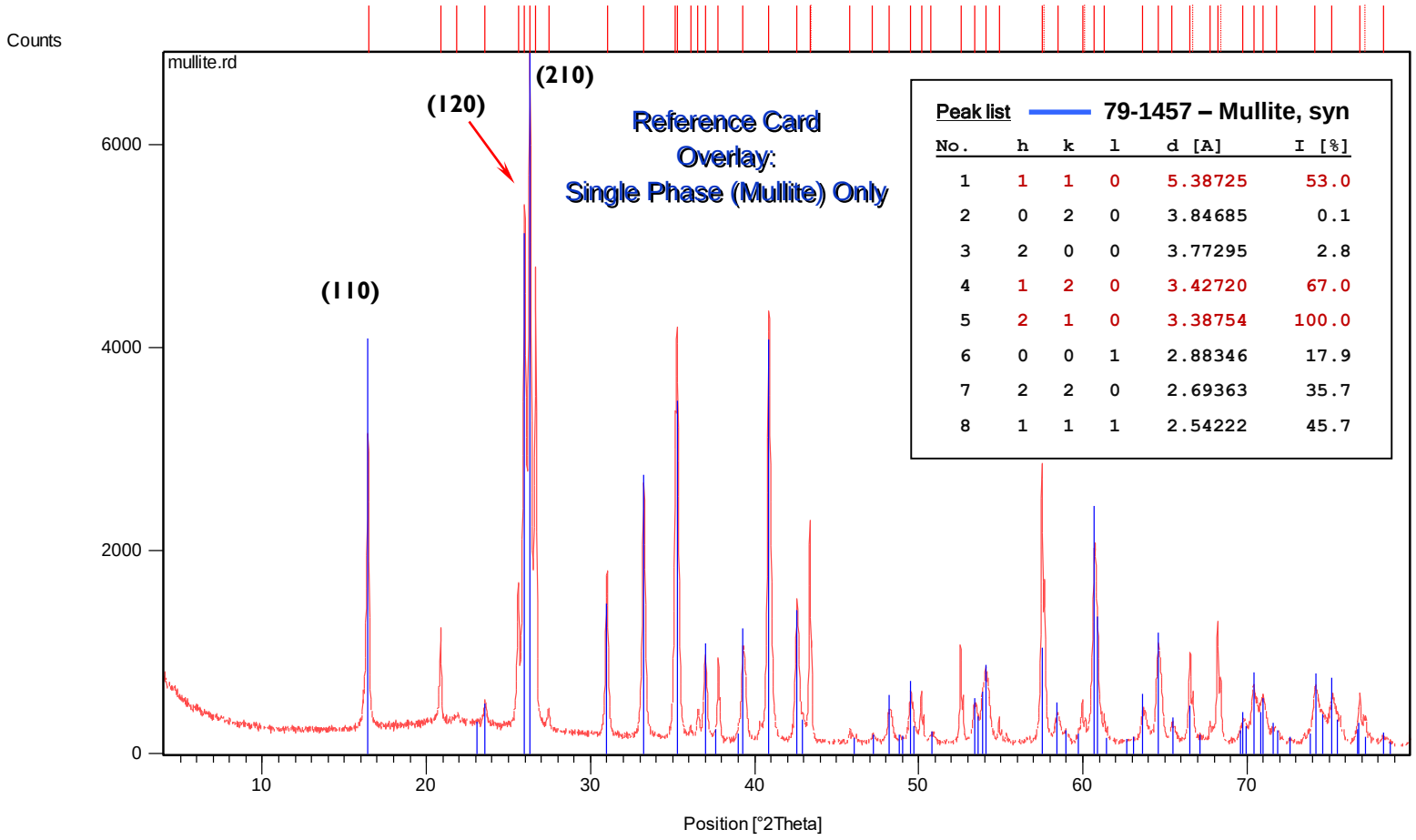


4) Qualitative Analysis: Phase Identification

Overview of phase identification

‘Search-match’ using ‘*d-I pairs*’ from reference databases – *e.g.*, ICDD PDF database

Polycrystalline mixture, showing only the mullite phase with ‘stick overlays’

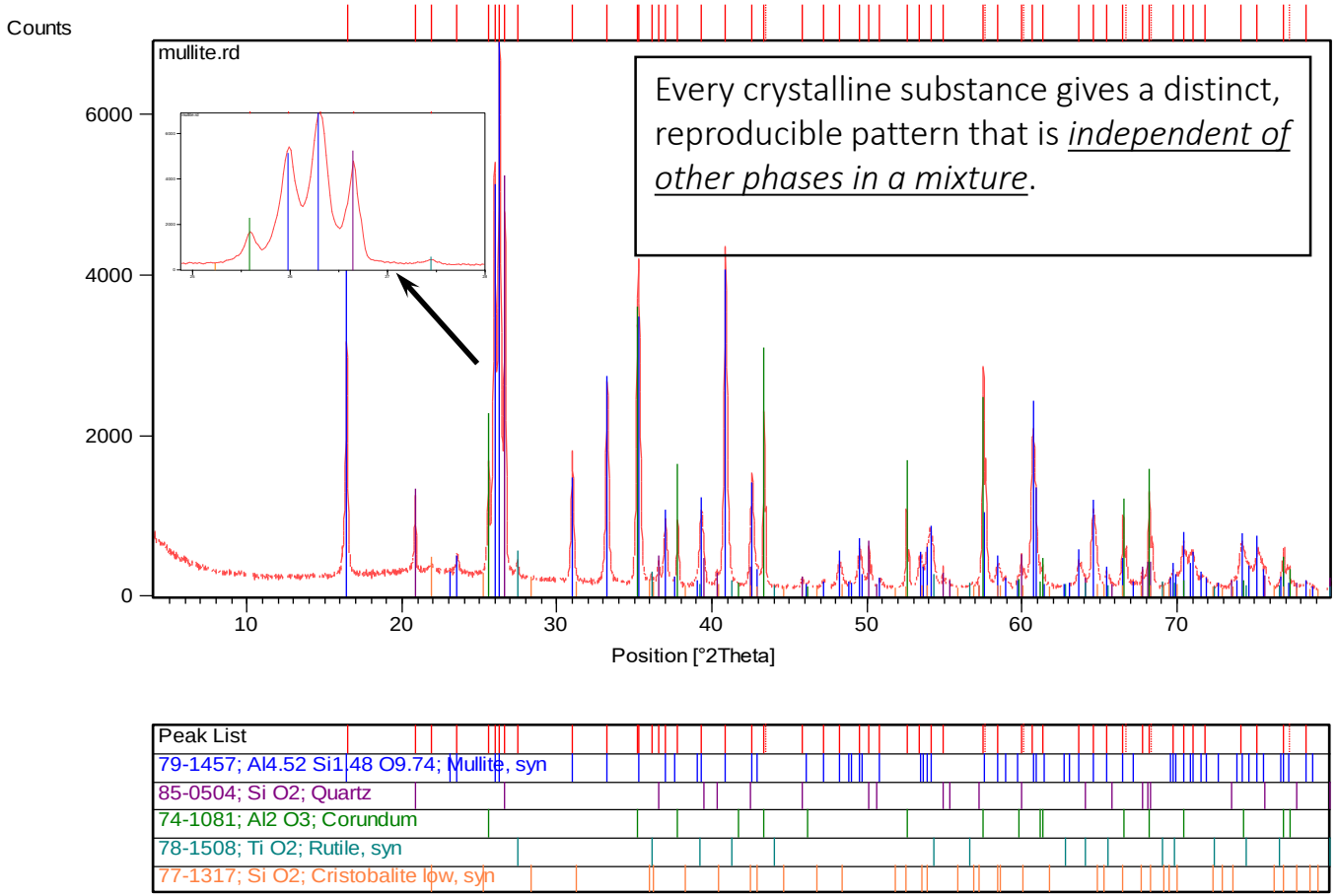


Overview of phase identification

‘Search-match’ using ‘*d-I pairs*’ from reference databases – *e.g.*, ICDD PDF database

Polycrystalline mixture, showing only the mullite phase with ‘stick overlays’

Reference Card Overlay: Complete phase ID



Phase Identification: Online Examples…

~5-Minute Break