Energy, Mining and Environment

Non-ambient Diffraction in the Laboratory Environment

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Accuracy in Powder Diffraction IV, NIST, April 2013

Overview

- Why work in the lab when synchrotron data is better?
  - ‘A bird in the hand….’ (i.e. access!)

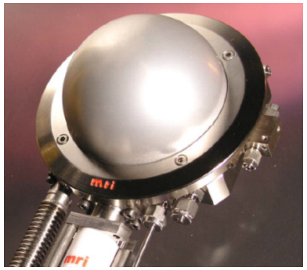
- Commercial stages
  - Some example developments
  - Sample displacement – the old irritant…
- DIY setups
  - Considerations and ‘mind-set’
  - Low temperature capillary – high speed data with mirror optics & PSD
  - High gas pressure – a special case and big headache?
  - Iron ore sintering - high speed data collection using curved PSD

Commercial vendors…

- Some developments…
  - Tensile test stage

Anton-Paar TS 600

  - Dome stages for 2D detectors



mri BTS-BASIC

  - Extremely-low temperature

Oxford Cryosystems Phenix

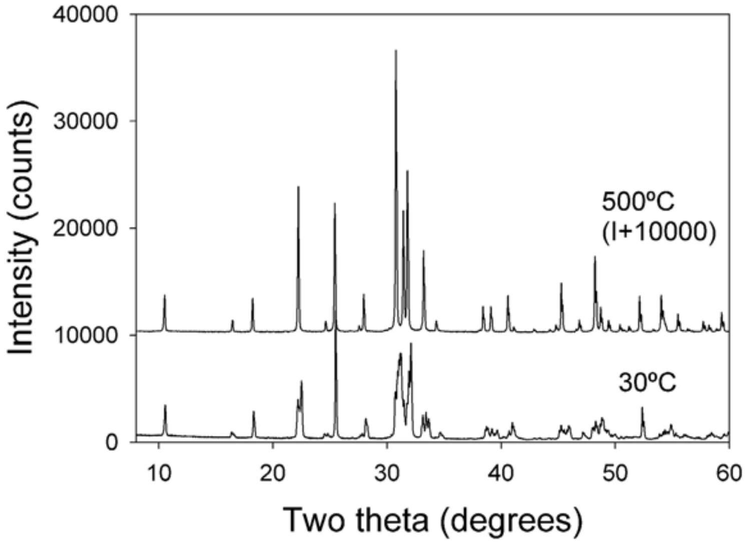
  - Close-cycle coolers → cryogen-free cold stream

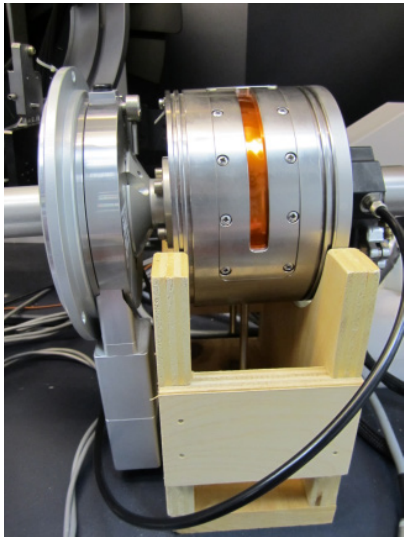
Cryo Industries close cycle cooler

  - Combined XRD-DSC (Rigaku)

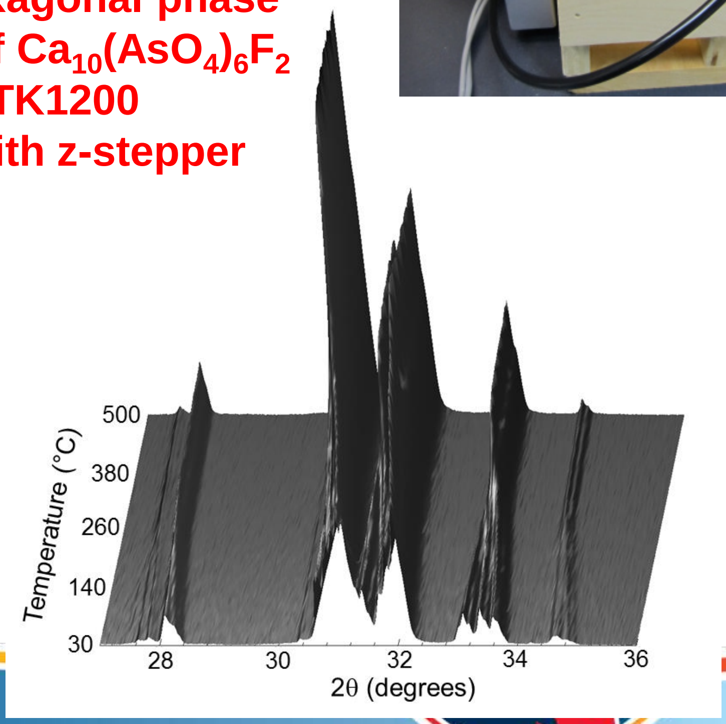
Sample displacement – different approaches

- Z-stepper motor on HTK1200 oven





Triclinic-hexagonal phase transition of $Ca_{10}(AsO_4)_6F_2$ apatite in HTK1200 equipped with z-stepper motor

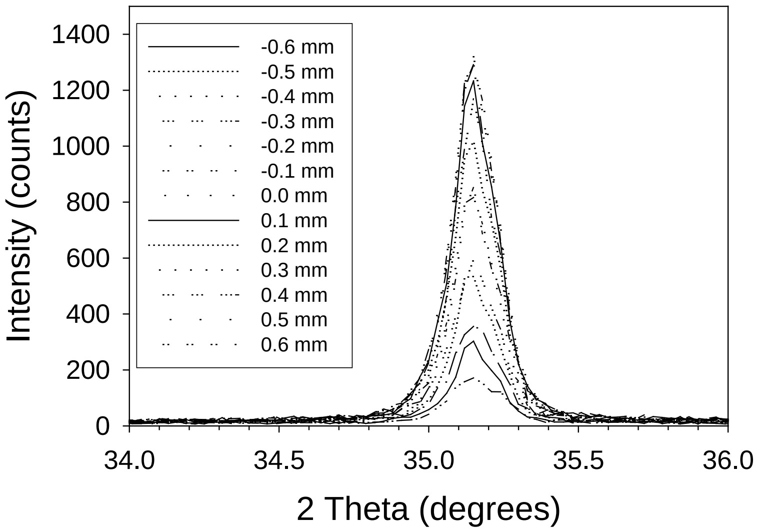


- Has to be properly calibrated

Whitfield *et al*, *J.Appl.Cryst*., 40 (2007), p1019

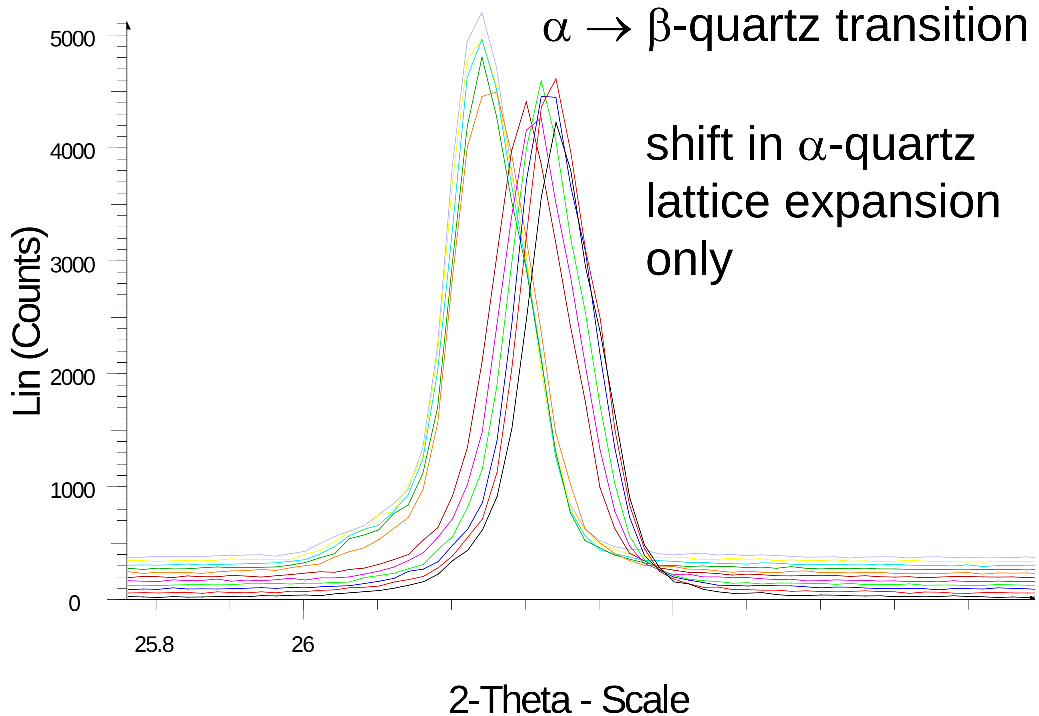
Parallel-beam geometry

- No sample displacement peak shifts



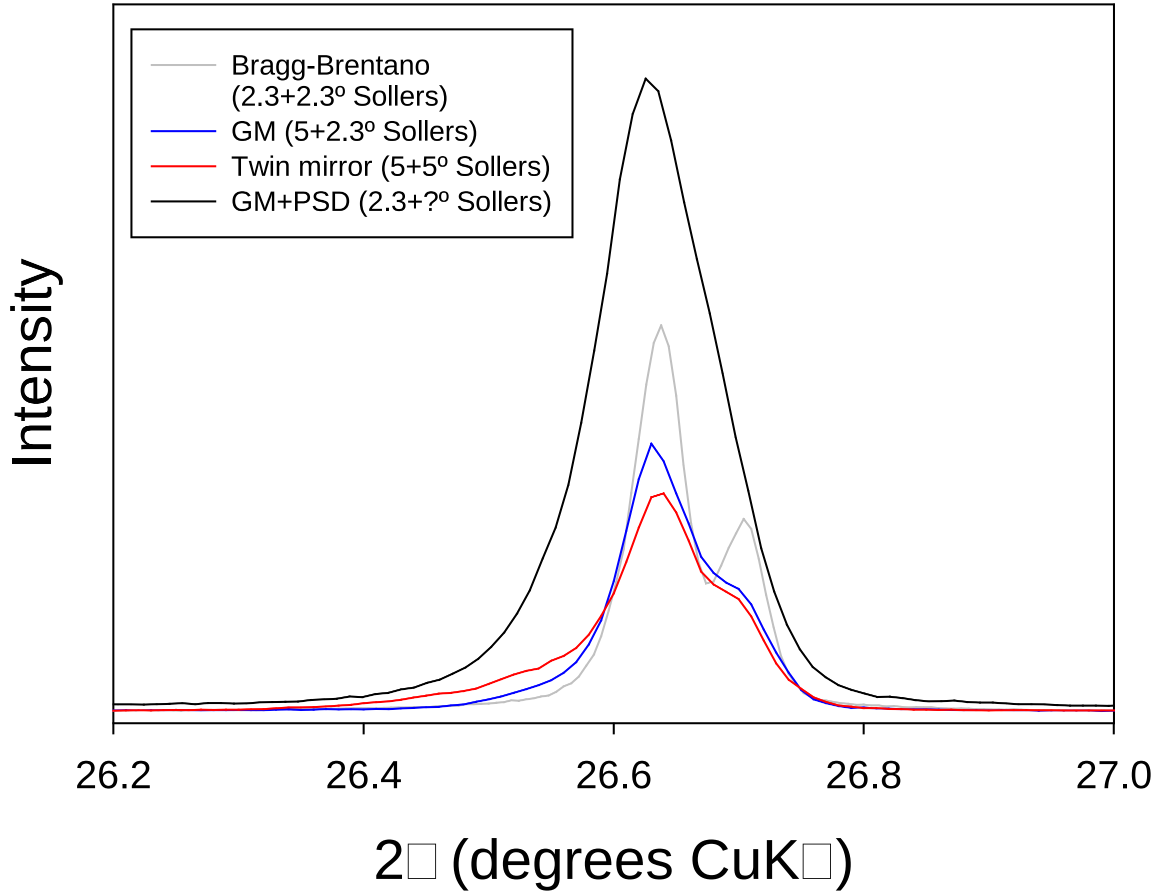
Al_2O_3 104 reflection with displacement (twin mirrors)

Can have confidence that these shifts are real…



Parallel-beam : the down-side

- Lower peak resolution
- Choice of Soller slits a factor….



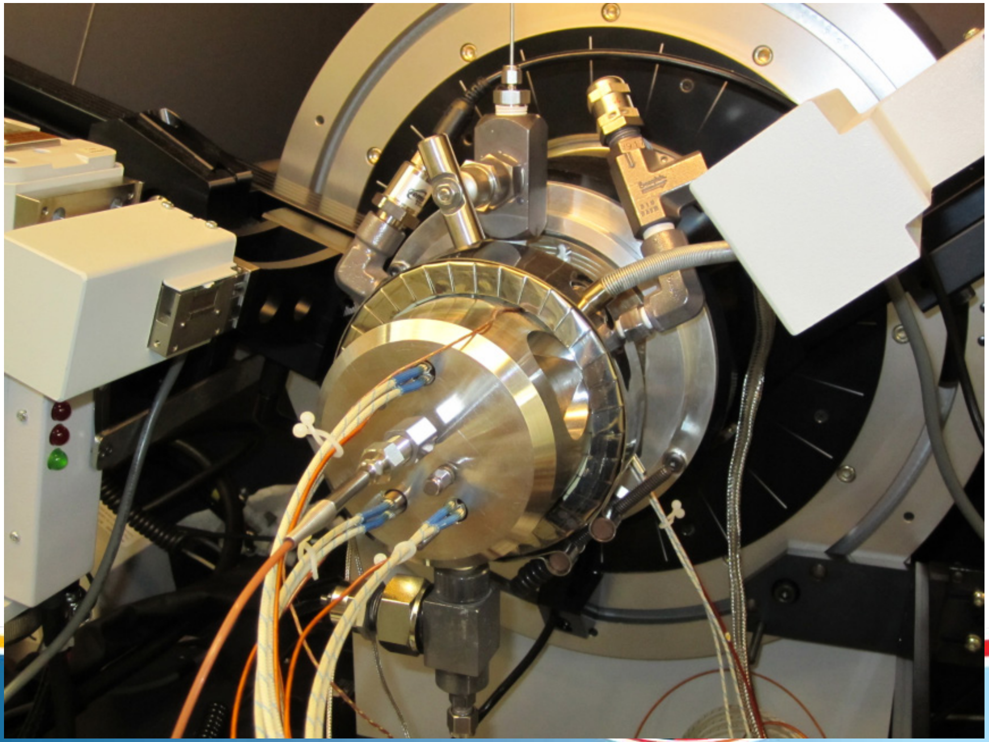
Comparison of the main quartz reflection from different optics

No-one sells what you want? now the fun starts…

- Mind set – it's a complete system, not just a stage
- Some engineering restrictions
  - Size
  - Stage weight (vertical goniometers)
  - Access to pass-throughs
  - θ–θ (don't foul arms!)
  - Door closure

Example where engineering restrictions complicate things:

Bulk (clearance+heat)
Heavy – 10kg
High pressure line pass-through
transducer, thermocouples & heaters



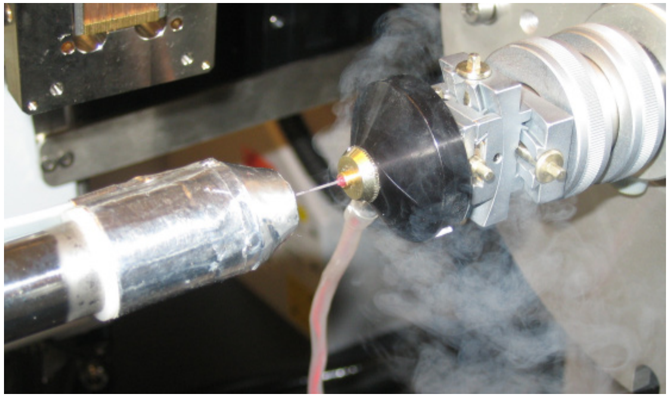
Low temperature capillary work

- System specced and built specifically for rapid low T non-ambient phase studies with large capillaries

  (before Oxford Cryo Compact was available!)

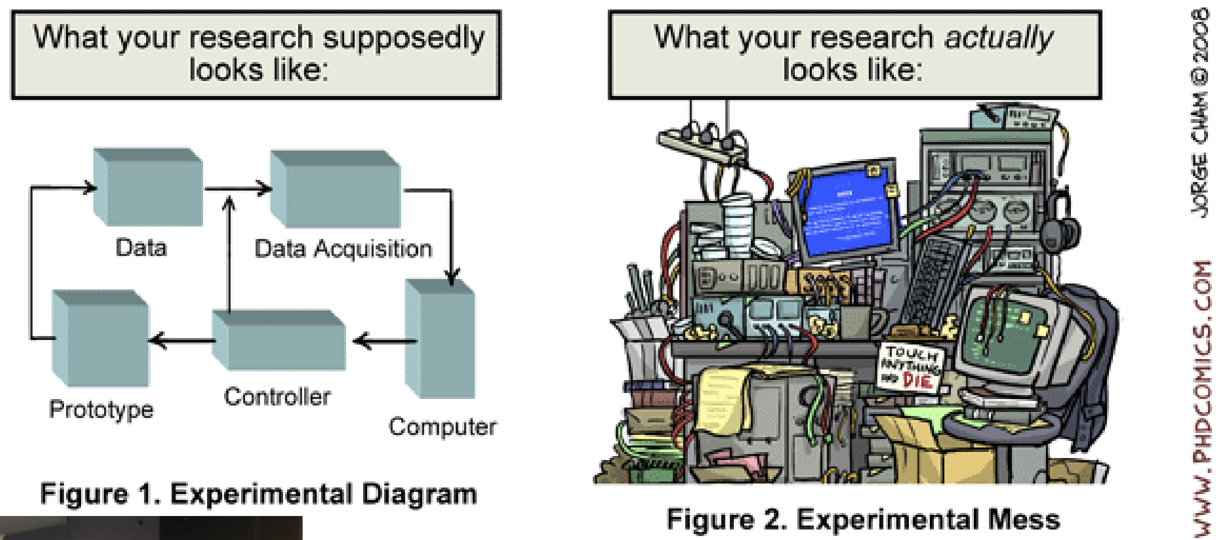
- Laminar flow along capillary axis minimizes LN2 usage without icing (goniometer heat shield needed)

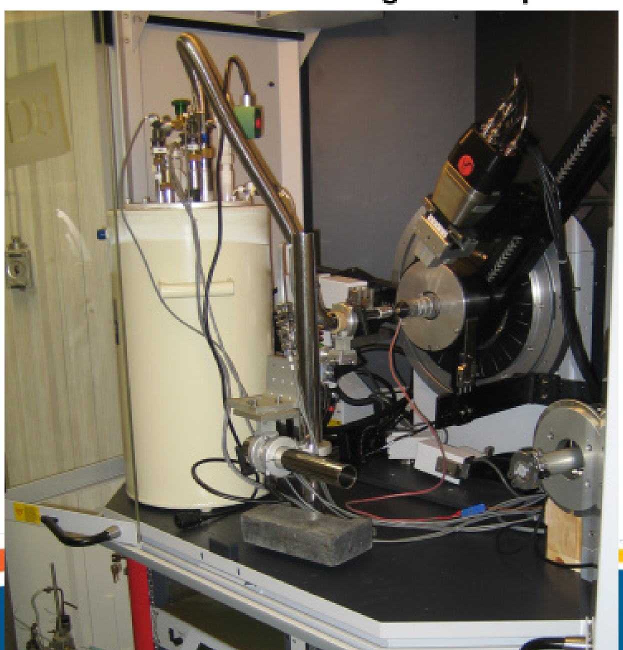
Heat shield on goniometer head

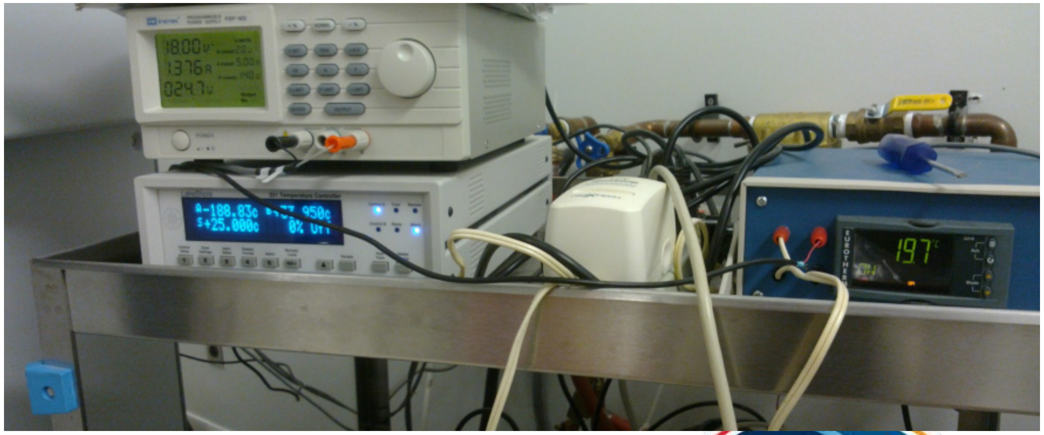


- Vertical goniometer
  - Limited space for nozzle
- Long transfer line not good (if you can get it inside)
  - Put dewar inside the cabinet?

Look familiar?



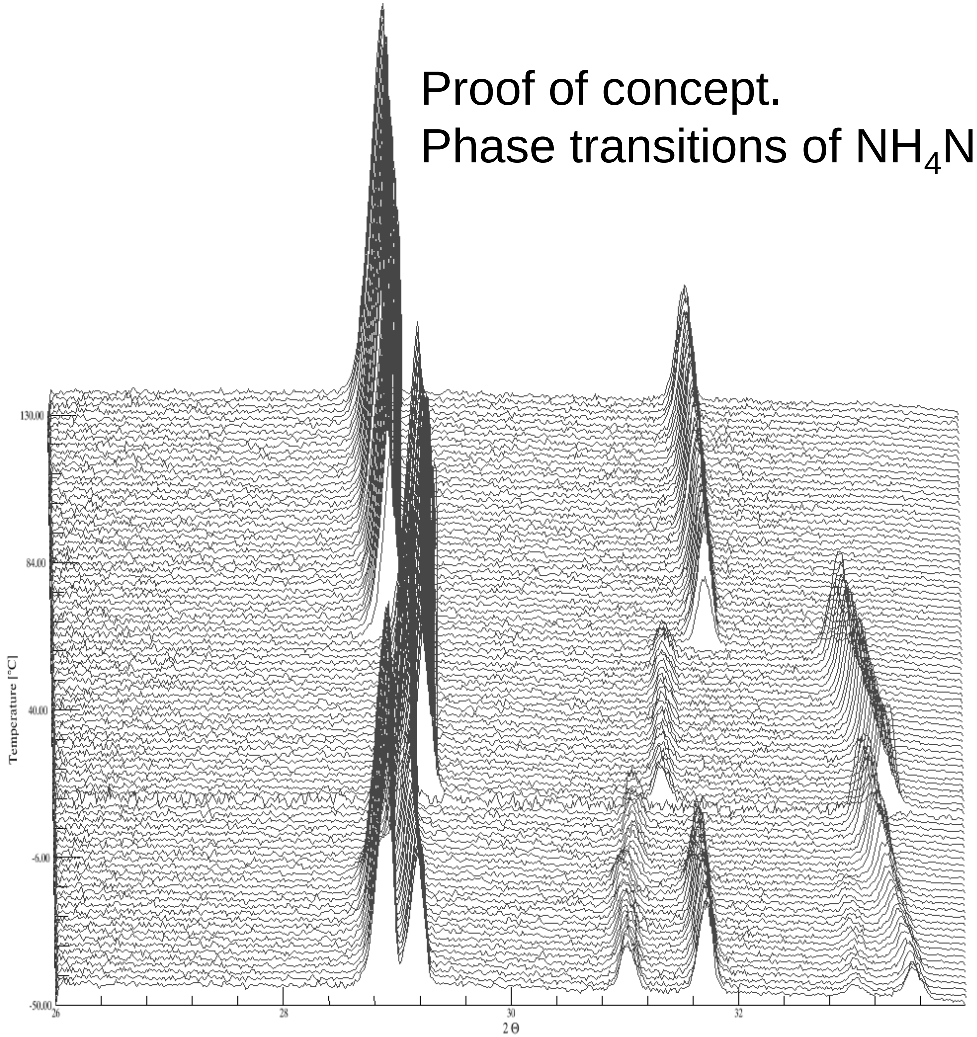




NH_4NO_3 phase transitions

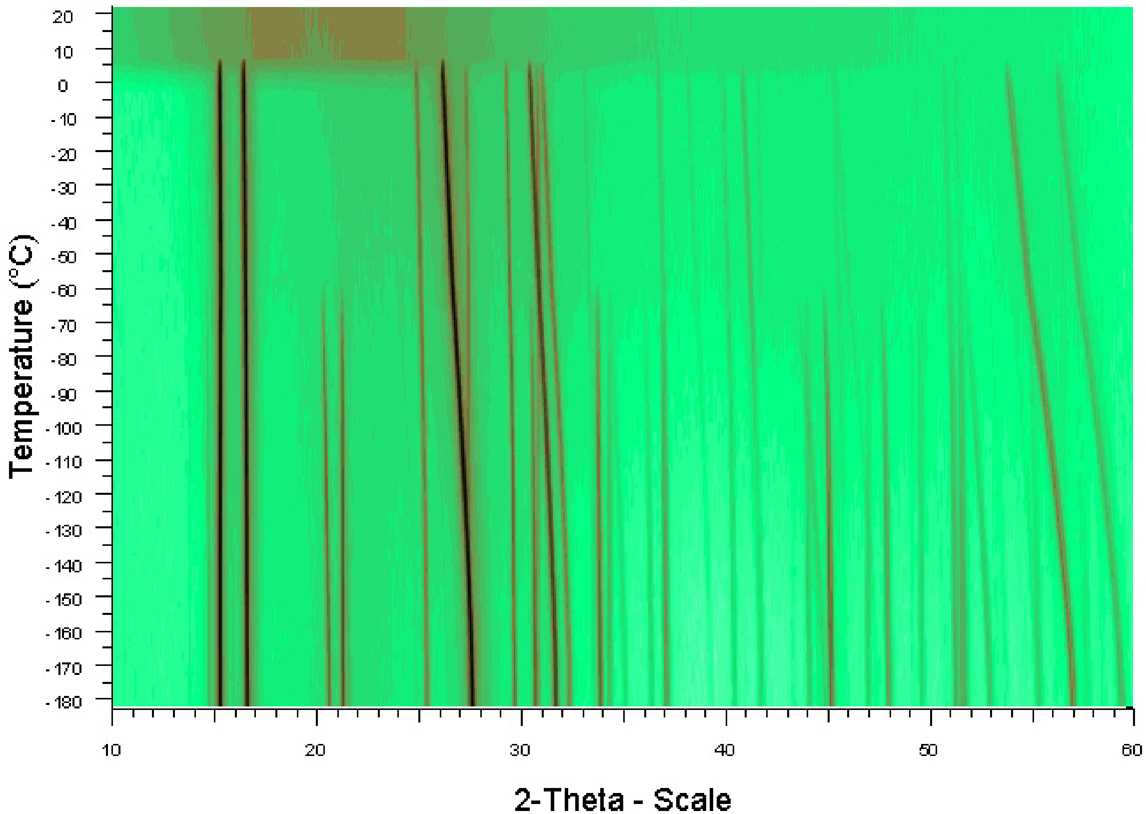
- Focussing mirror optics, cryoflow with linear PSD
- Snapshots, 8° window, 2 second datasets every 2°C
- Continuous temperature ramp (0.1°C/s)

Proof of concept.
Phase transitions of NH_4NO_3



Something more practical….

- Ability to automate complex ramp-soak programs
- 4 minute datasets - shorter than ramp/dwell times
- 48 datasets in ~7 hours



Phase behaviour of the Li-battery electrolyte solvent dimethyl carbonate

Beyond CuKα ...

- Engineering for high pressures often dictates use of higher energies for optimal usage..

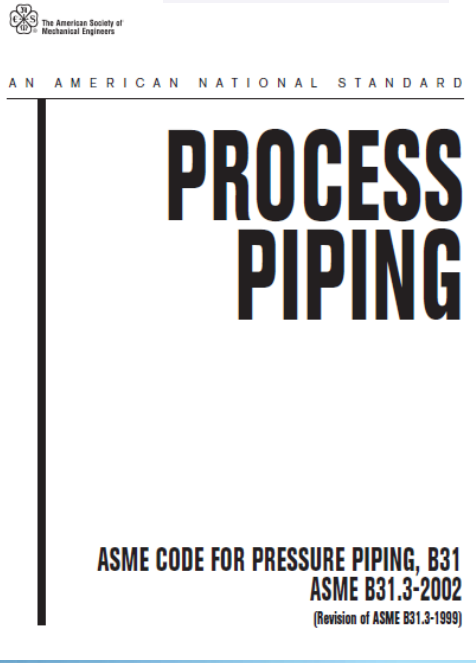
- 1st mainstream company to venture down this route….?
- Anton-Paar HPC-900
  - 100 bar pressure for H_2, etc
  - Requires MoKα
    - – Not a simple add-on

DIY under pressure?

- Home-designed and built pressure vessels?
- Space for sample stage and ancillary stuff limited
- The elephant in the cupboard

  - The pressure codes (ASME in North America) ☹

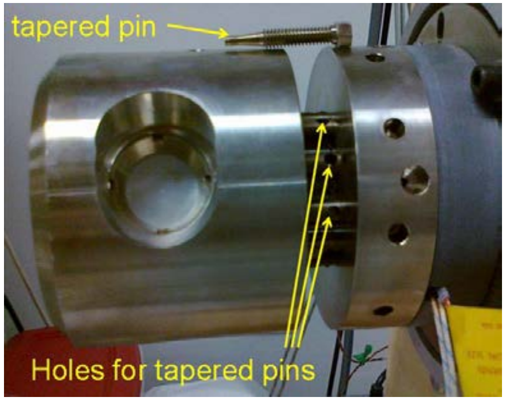
  - Restricts the materials you can use
  - What conditions you can use them under (max stress, temp)
  - Design concepts and validation
  - QC and manufacture



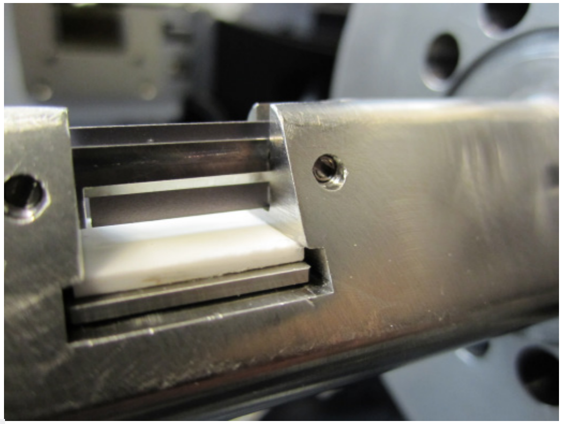
Just one of the ASME pressure codes…

DIY thought process… 300bar, 300°C

- 3 years from concept to delivery
- No modifications – have to think of everything 1st time!



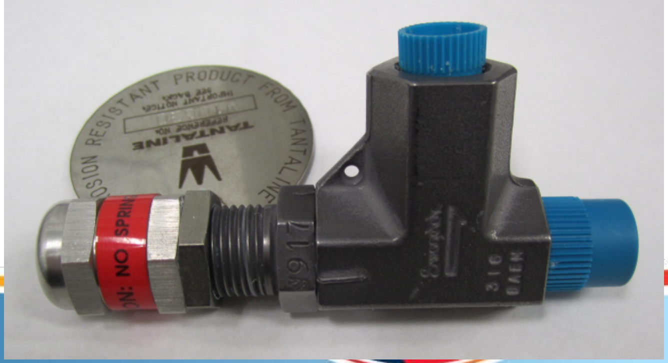
Cover retention . Strong enough but removable using 12 tapered pins



Corrosion-resistant C22 Ni superalloy. Adjustable Ta knife-edge

Heavy-duty! Strong enough at temp with ASME allowables + a bit

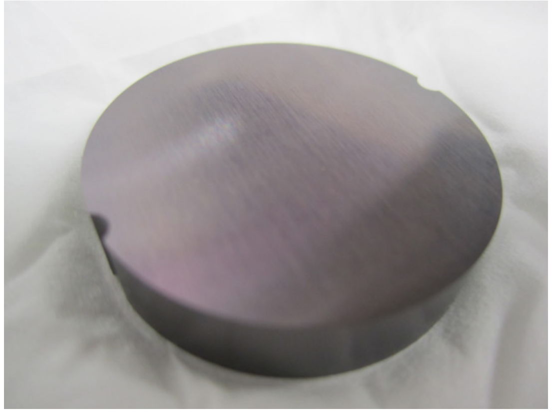
Fittings also need to be corrosion-resistant



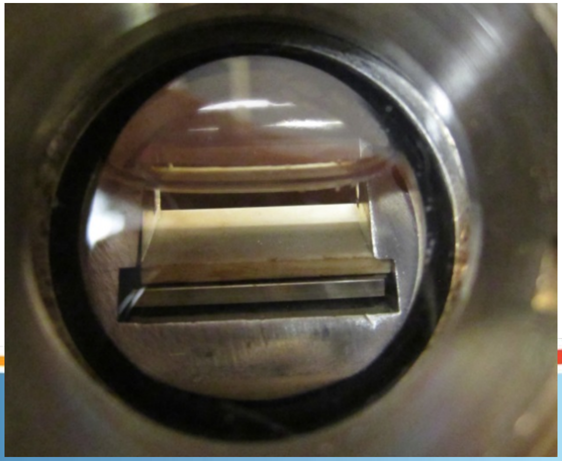
300bar NRC pressure vessel

- Window is the weak-spot
  - Swagelok-type seal (regulator comfort!)
  - Be window material for transmission
  - Be corrosion protection?
  - Strength? (structural grade SR200)
- Windows 6¼ mm thick Be
  - 2μm Ta coating
- Interior flooded with water/steam
- Interior beampath ca. 15 mm
- Penetration is key…..

Ta-coated window. Notches stop window rotating when tightening



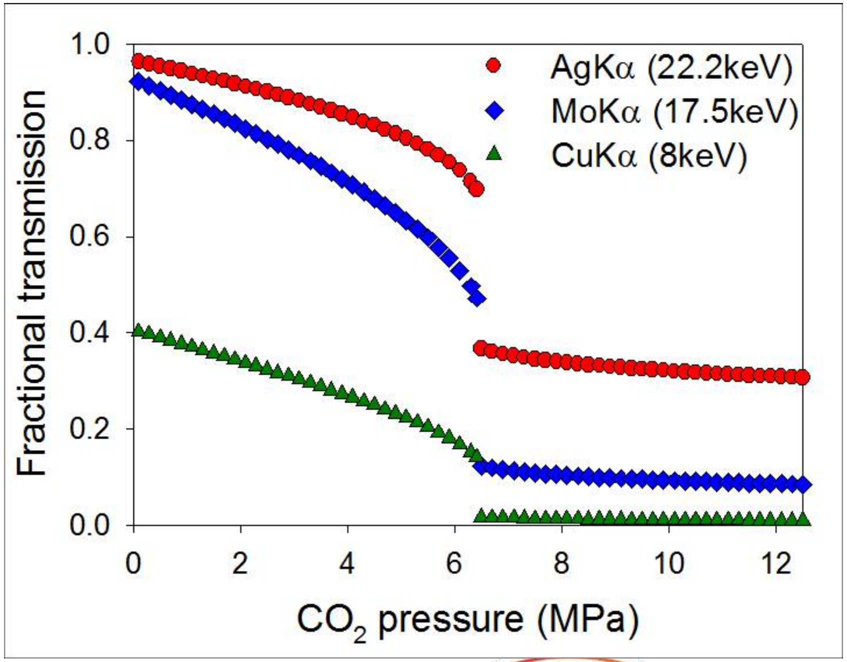
Flooded means flooded..



The exception rather than the rule…

- In this case AgKα (22 keV) needed for increased transmission
- Has consequences….
  - Getting hold of a tube
  - 1.5kW versus 3kW (LFF)
  - Require new PSD optimized for higher energies
  - Pd β-filter effects even worse
- Difference between no signal and some signal
  - Increase in accuracy = ∞ ☺

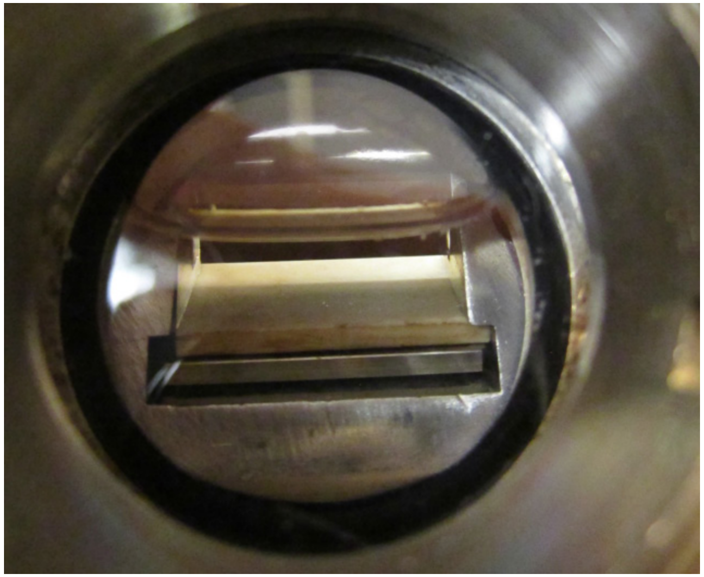
Calculated transmission through the GEN1 pressure stage at different energies

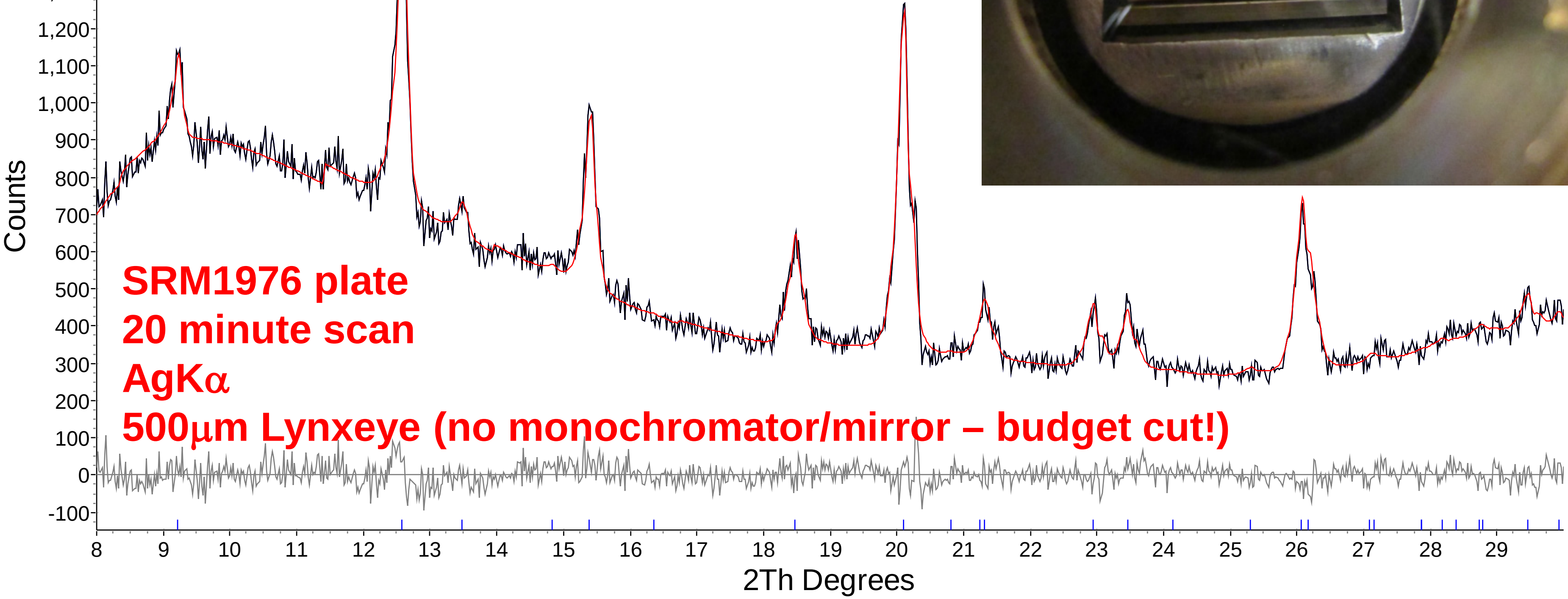


Can you actually see anything?

- Worst case - fully flooded with cold water
- Total beampath
  - 12.5mm Be, 8μm Ta, 15mm water

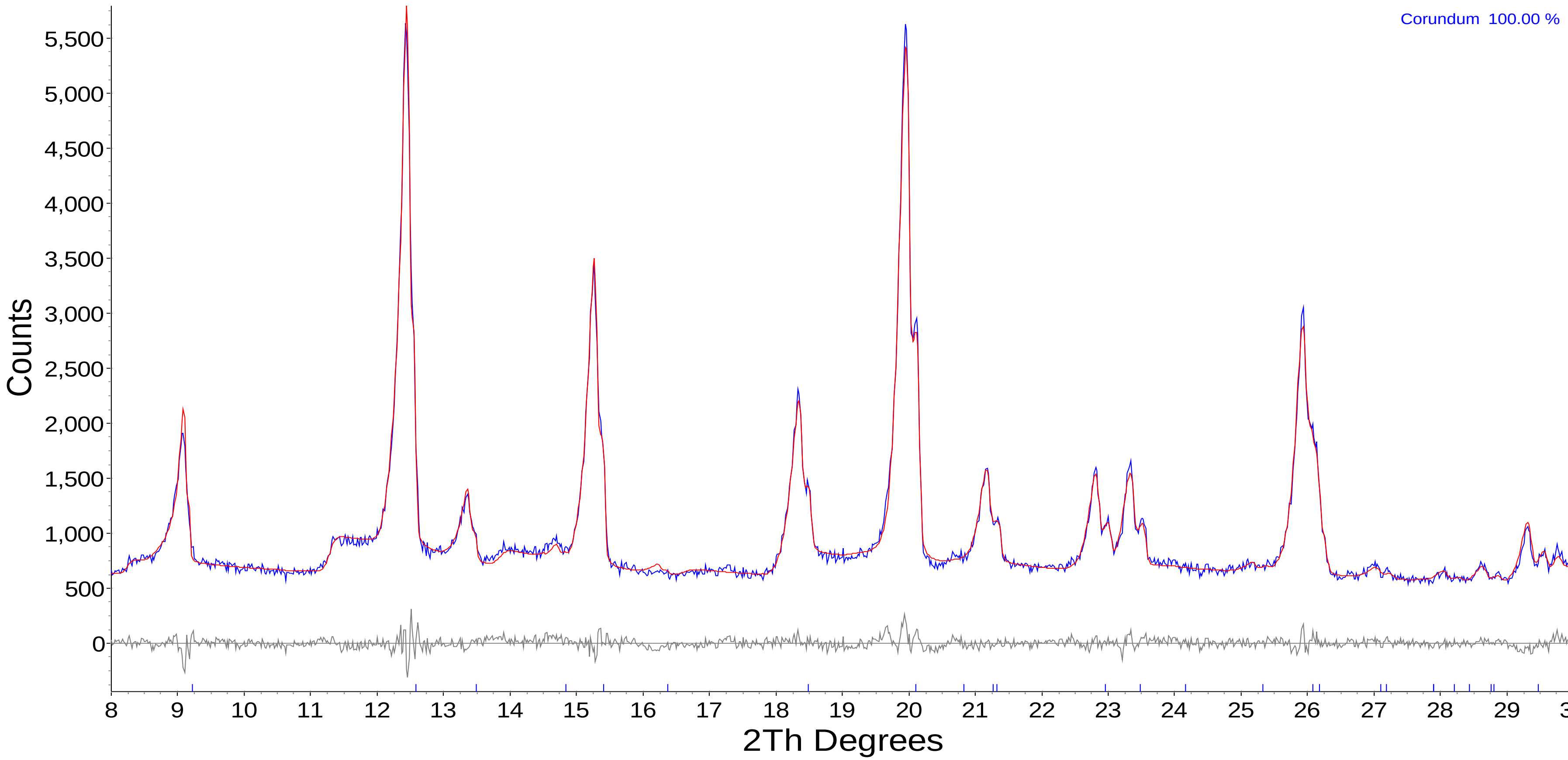
View through
dummy windows





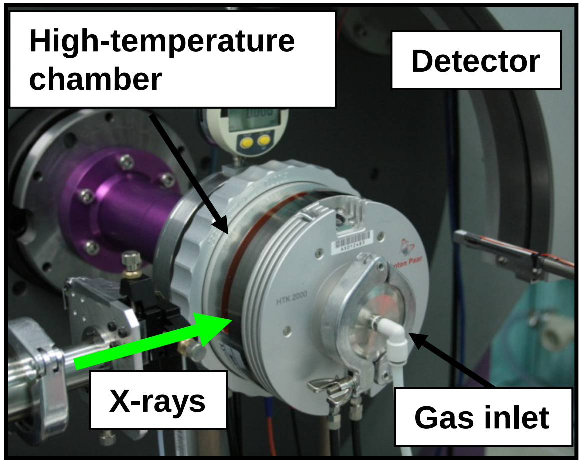
Anything else easy in comparison…

- Autoclave conditions ~190°C
- 161psi steam + 100psi CO_2



Iron Ore Sintering - *In Situ* X-ray Diffraction

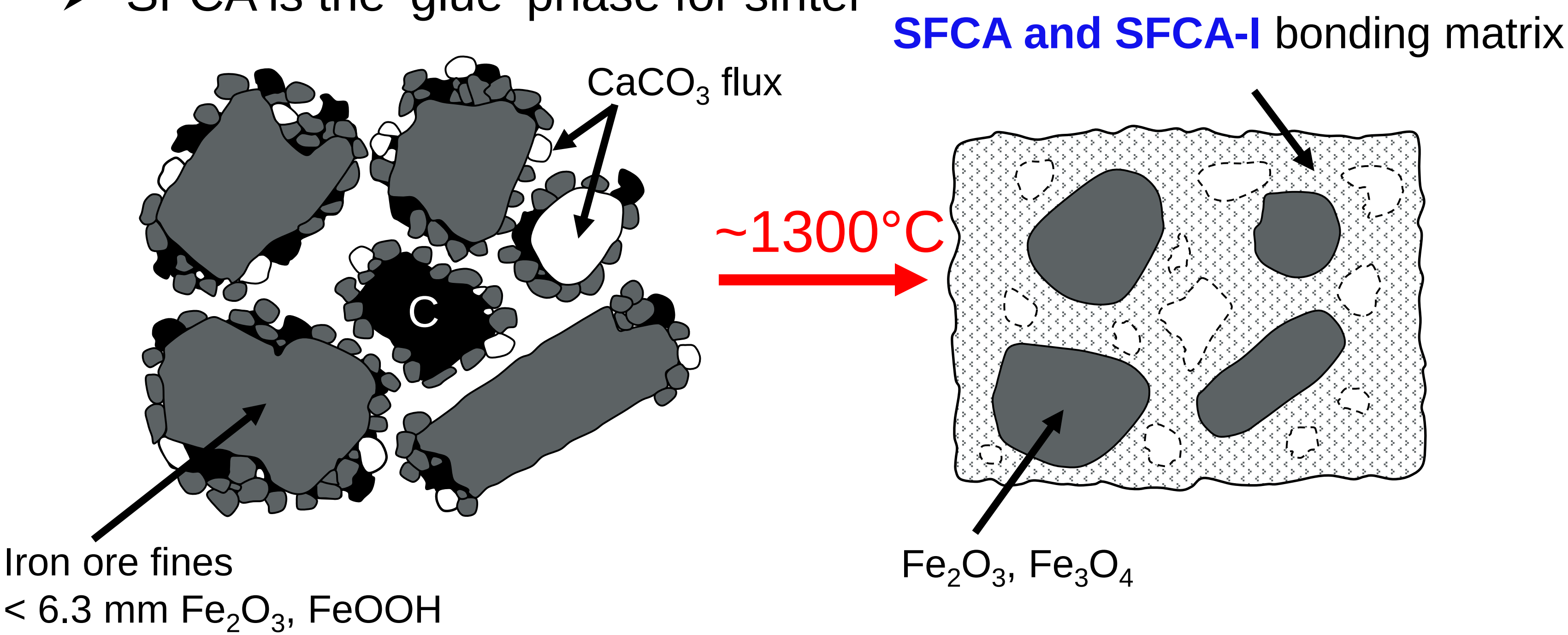
+



Heating Regime 25-1350-25°C
pO_2 = 5 x 10^{-3} atm

Introduction – Industrial Context

- Iron ore sintering = important stage of the steelmaking process
  - SFCA is the 'glue' phase for sinter

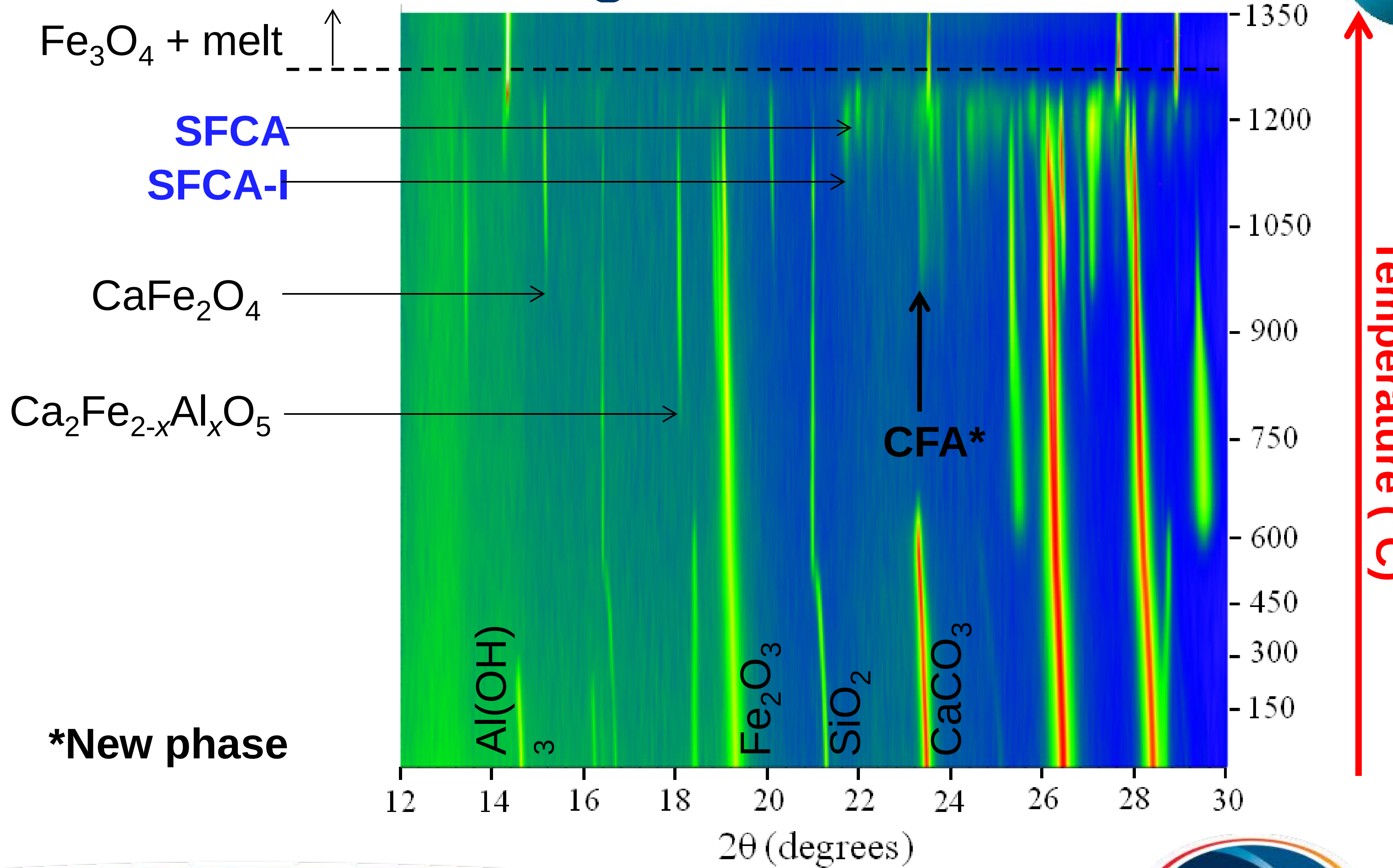


- **SFCA** = Silico-Ferrite of Calcium and Aluminium

  SFCA = $M_{14}O_{20}$, SFCA-I = $M_{20}O_{28}$, M = Fe, Ca, Si, Al

Nathan A.S. Webster *et al*., *Metall. Mat. Trans. B*, 2012, 43, 1344-1357

Results – Heating, 25-1350°C

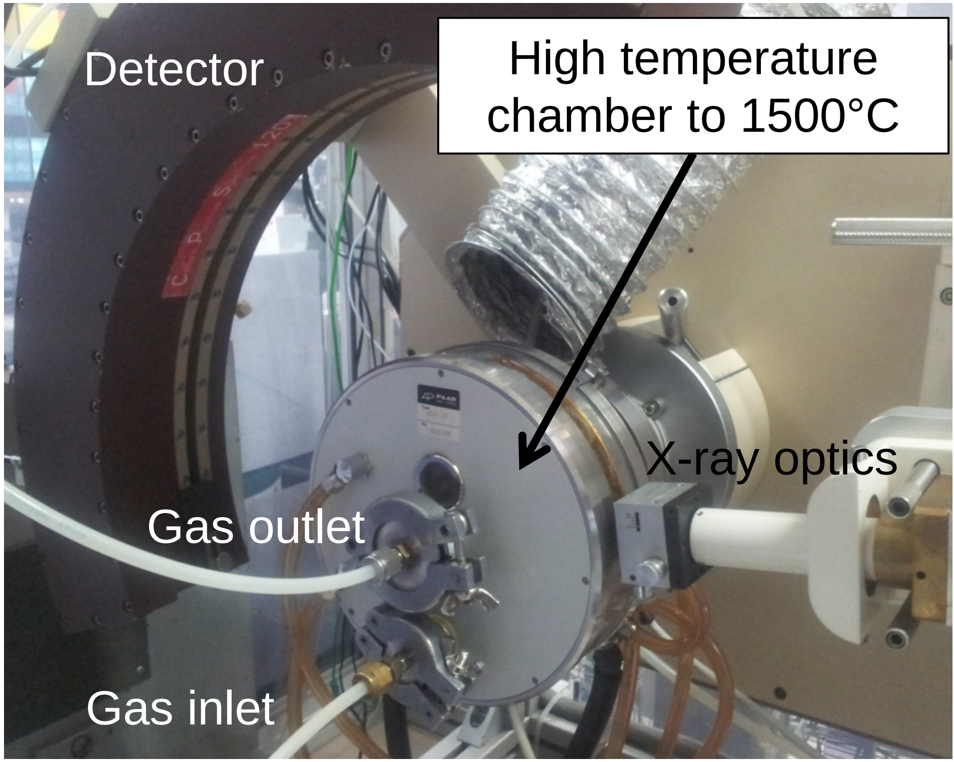


***New phase**

Nathan A.S. Webster *et al*., *Metall. Mat. Trans. B*, 2012, 43, 1344-1357

Iron Ore Sinter Studies
Laboratory Based *in situ* Data Collection

- Beamtime hard to get
  - Waiting time ~ 6 months
- Once phases known from synchrotron experiments – use lab instrumentation
- INEL CPS120
  - Incident beam, multilayer mirror for high intensity
- CoKα

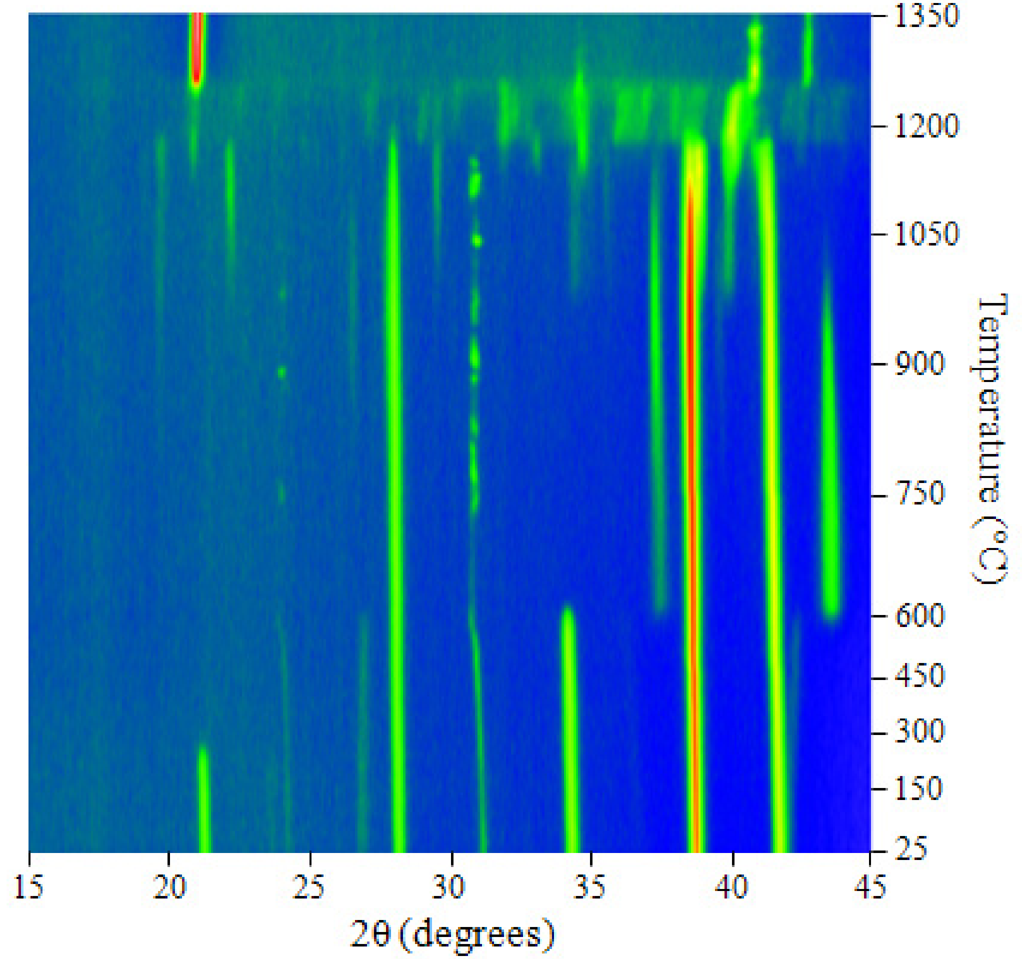


Lab diffractometer setup

Strip heater

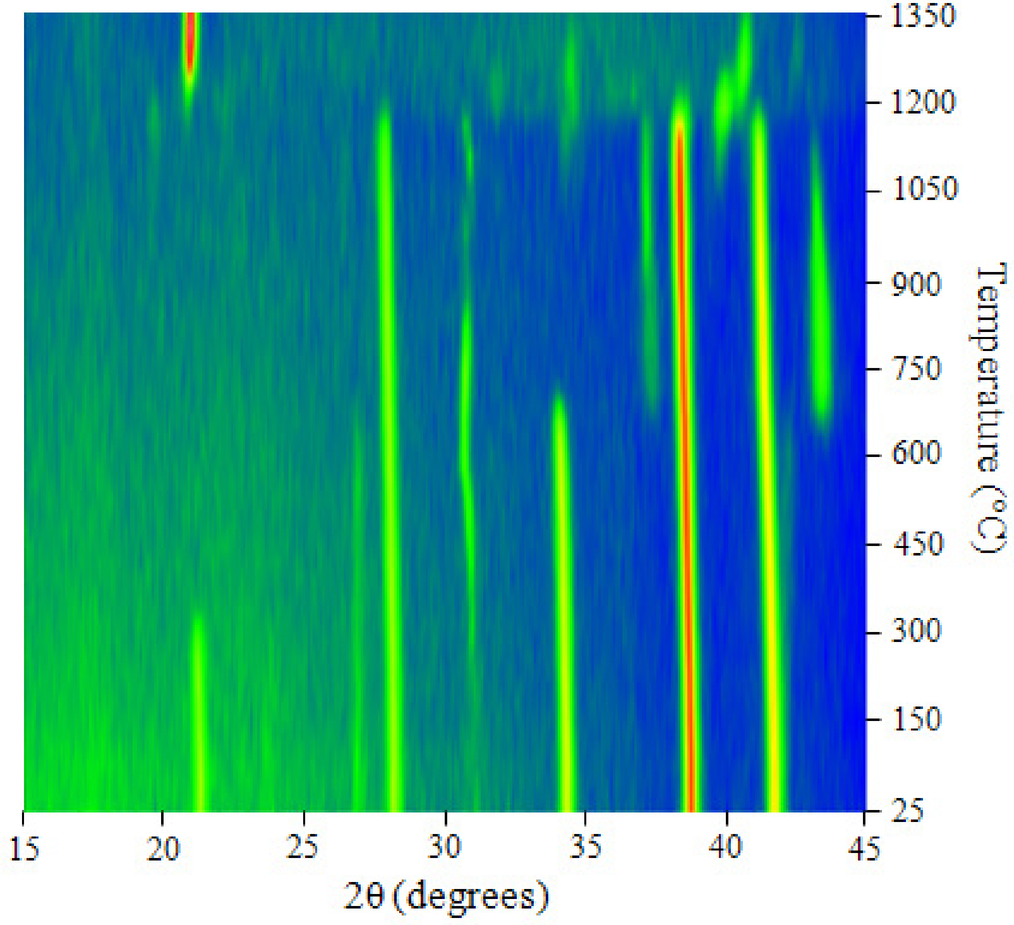
Iron Ore Sinter Studies
Laboratory Based *in situ* Data Collection

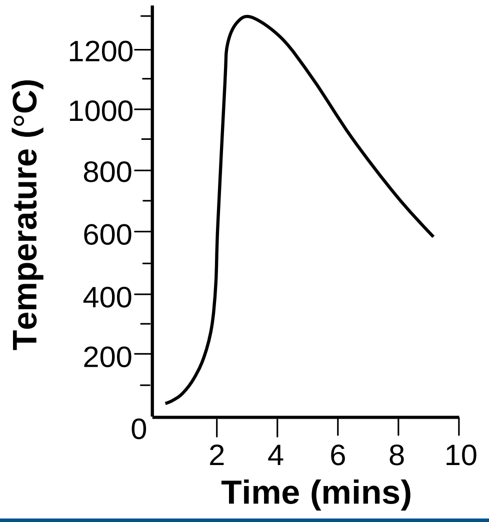
- Heating rate
  - 20°C min^{-1}, 25 → 600°C
  - 10°C min^{-1}, 600 →1350°C
- Data collection time
  - 30 sec for 120° 2θ
- Resolution not as good as synchrotron but most information still visible
- Problem
  - Industry not so interested if conditions not close to real processing conditions



Actual Industrial Heating Rates?
Attempt to Emulate in Laboratory

- Heating rate
  - 200°C min^{-1}, 25 →1350°C
- Data collection time
  - 6 sec for 120° 2θ
- Major and some minor phases still apparent





Typical industrial time-temperature profile

Conclusions

- Lab studies still have a role to play
  - Easy access and the freedom to ‘play’
- Think holistically!
  - In-situ stages don’t work in isolation
  - Source, optics and detector can be changed/tweaked
  - Integration with diffractometer systems desirable but not vital

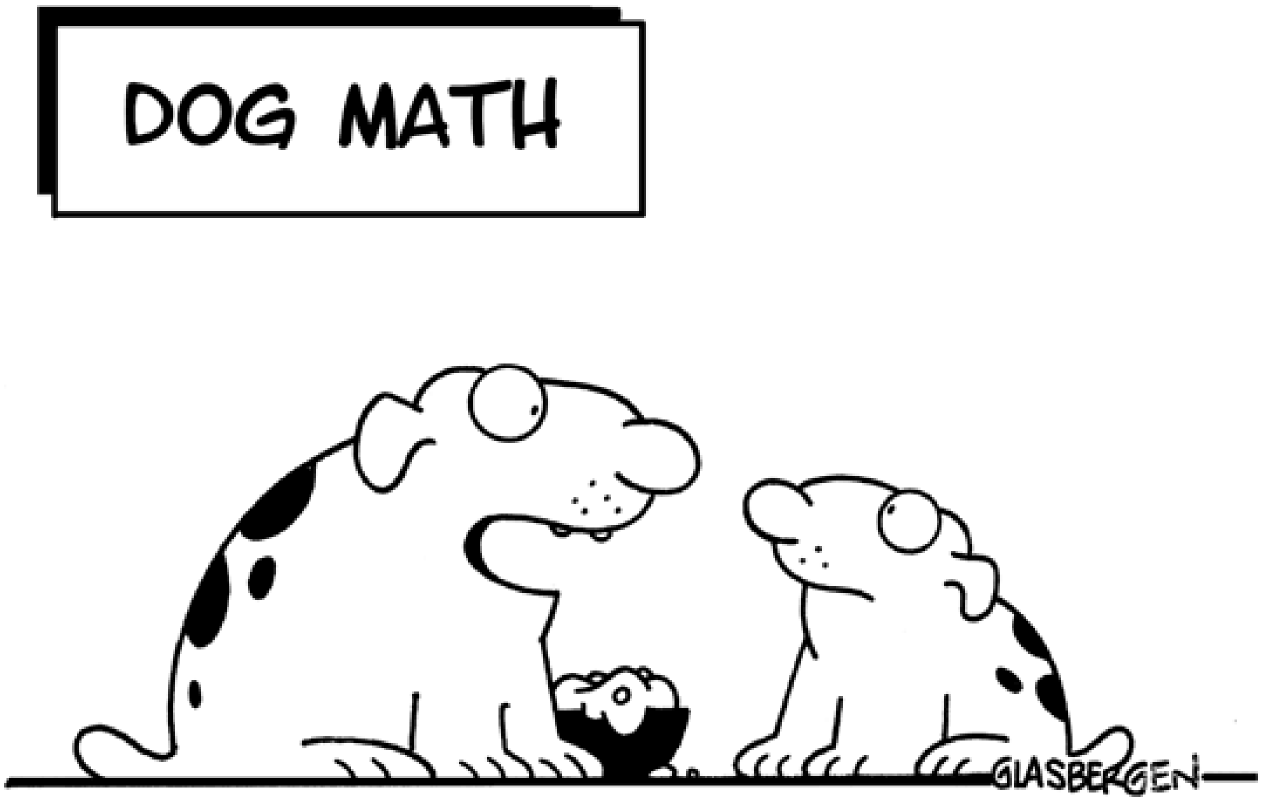
- Think beyond Cu$K\alpha$
- High gas pressure is a real pain (or the regulations are)
  - “abandon hope all ye who pass here!”

Acknowledgements

- Ian Madsen
  - Iron ore sintering study

- Cryo Industries of America
  - Customizing one of their cryo systems for my needs…
- Jim Ross (NRC-DFS) and All-Weld
  - High pressure gas cell

Questions?



“If I have 3 bones and Mr. Jones takes away 2, how many fingers will he have left?”