Methods of High-Pressure Single-Crystal X-ray Diffraction

Ross Angel
Dipartimento di Geoscienze, Universita di Padova

rossjohnangel@gmail.com ***www.rossangel.net***

- ***Technical challenges***
- ***Overview of methods***
- ***Overview of the workshop***

Single crystal and powder

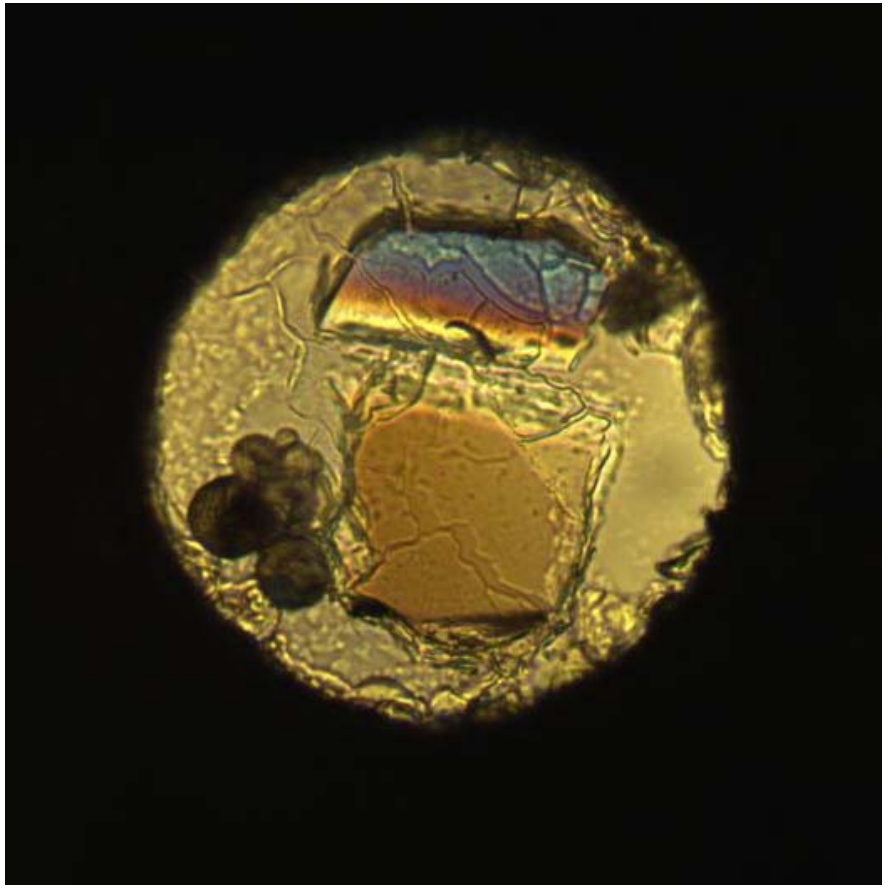
- **Single-crystal data is 3 dimensional not 1 dimensional, intrinsically superior to powder diffraction:**
  - **No peak overlaps**
  - **No resolution problems**
  - **No preferred orientation problems**
  - **No “powder average” problems**
  - **Signal to noise is higher**

- **Single crystal diffraction allows:**
  - **The unambiguous determination of minute structural changes**
  - **The determination of small structural distortions (phase transitions)**
  - **Acentric crystals**
  - **Measurement of diffuse scattering and incommensurate structures**
  - **Reliable displacement parameters**

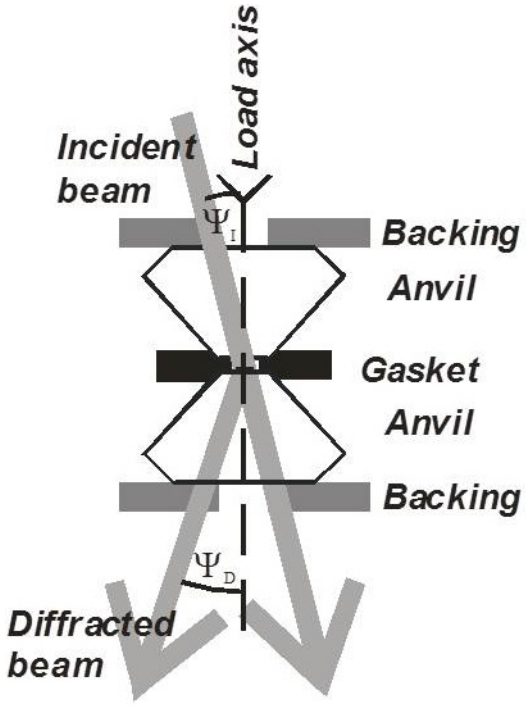
- **“A bad single crystal is better than a good powder” (McMahon)**

Aim of the workshop is to show you 'how'

The Diamond Anvil Cell



Diamond-anvil geometry

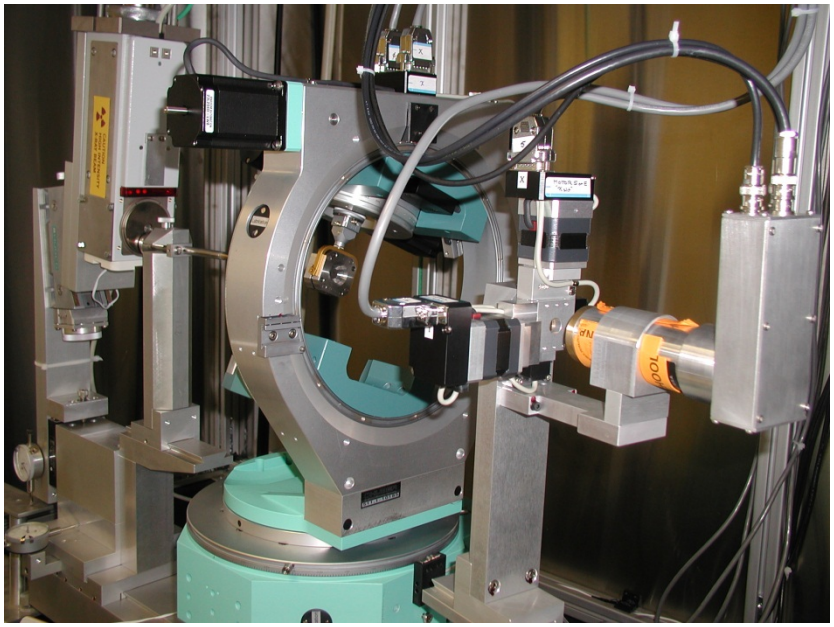


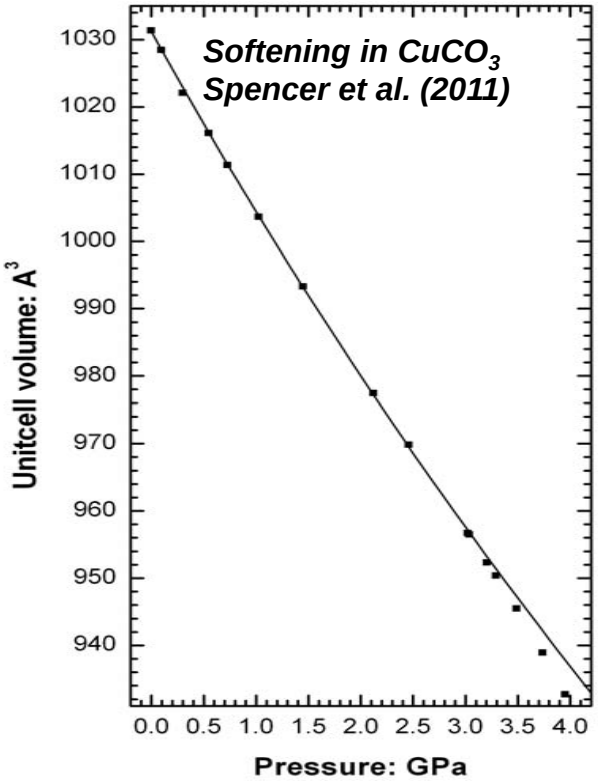
Transmission mode

Ronald : today

Cell parameters at high pressure

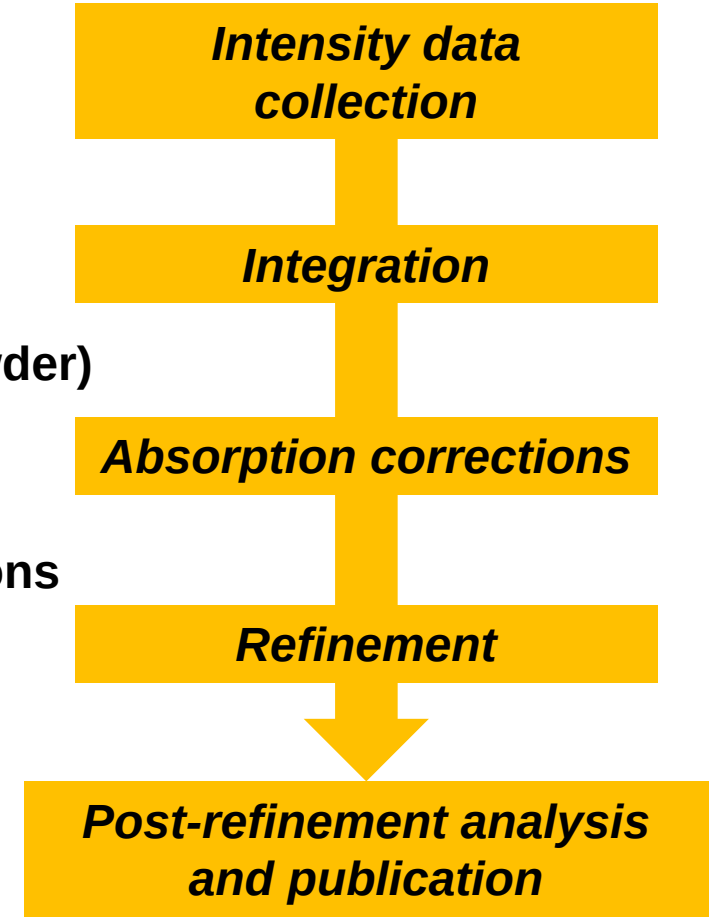
Precise diffraction angle data to measure small changes in cell parameters at high pressures:





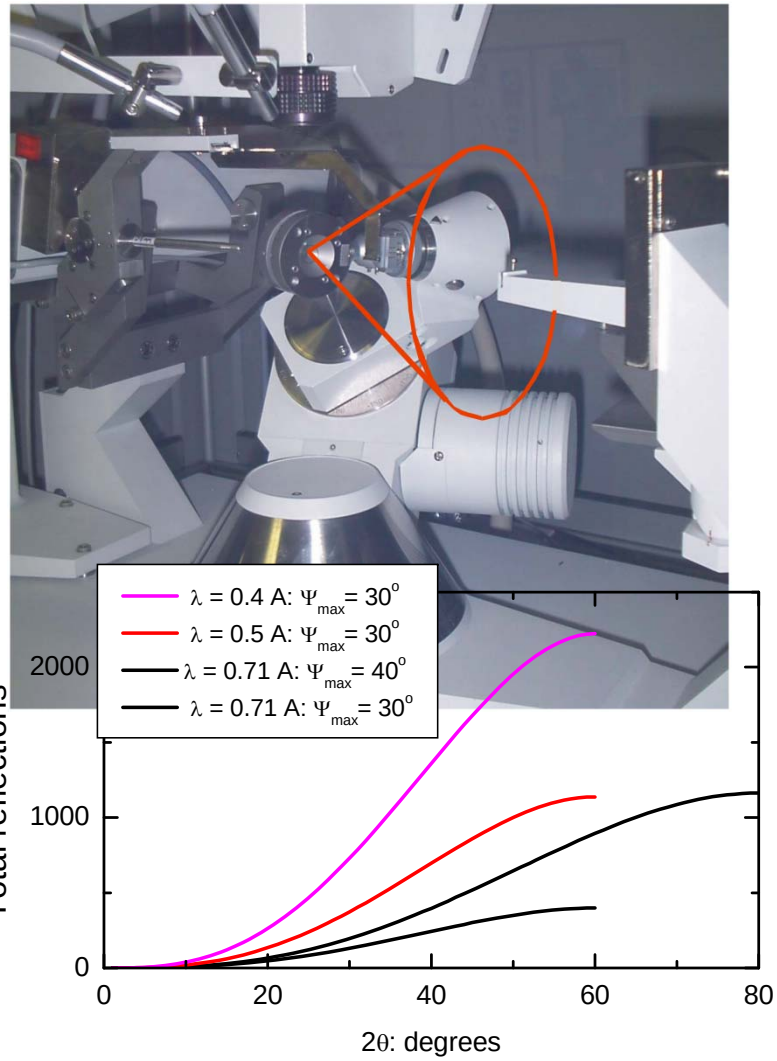
Determining structures at high pressure

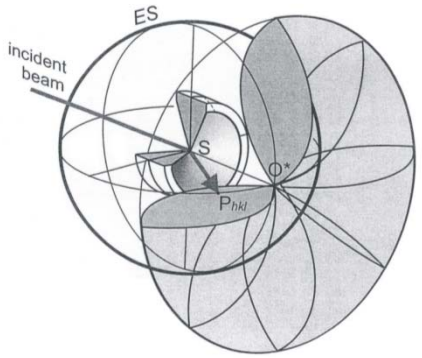
- Workflow is similar to crystals in air



- But there are challenges:
  - Limited access
  - Low signal (but higher than powder)
  - Background scattering
  - Absorption by cell components
  - Maintaining hydrostatic conditions

Limited access





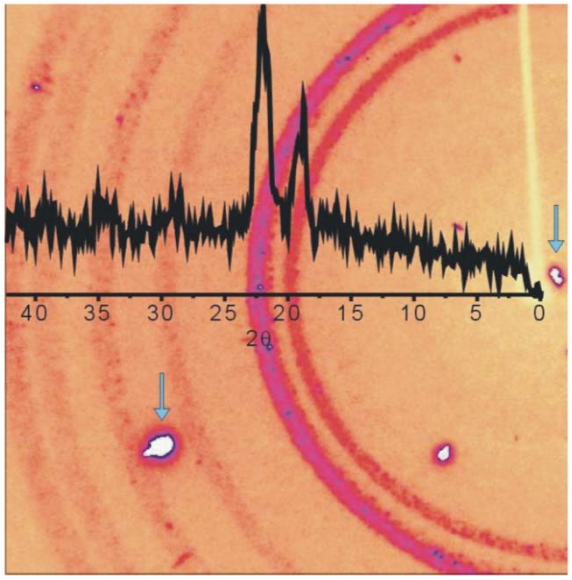
Miletich, RiM volume

Fewer reflections means:

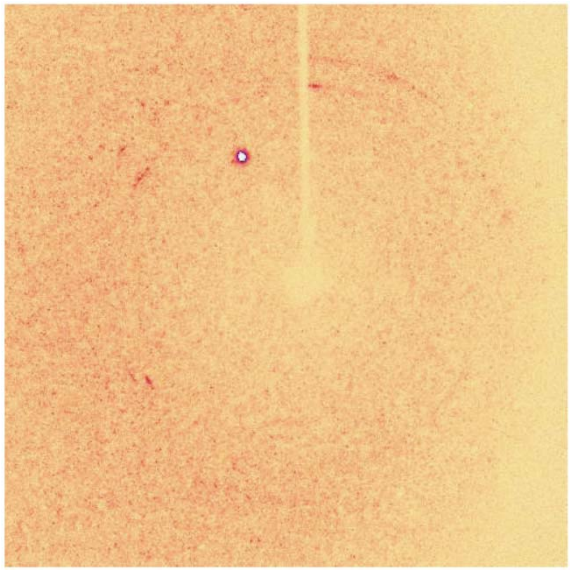
- ***more sensitivity to individual data***
- ***higher chance of systematic error***
- ***higher influence of random error***
- ***less resolution***

Reducing background

Everything you see is background!



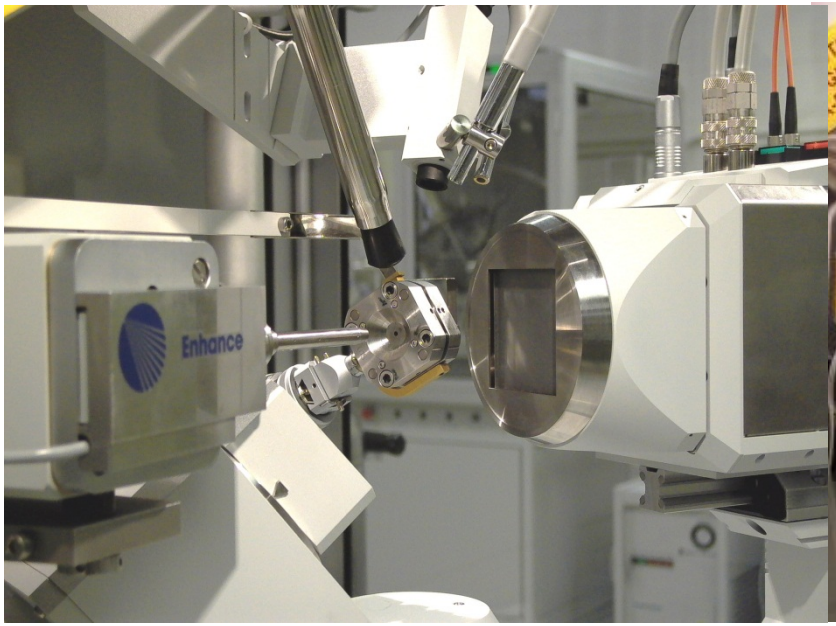
Conventional DAC with Be seats, steel gasket



DAC with steel seats and rhenium gasket

Determining structures at high pressure

- ***Because of the challenges:***
  - ***Optimise the data collection***

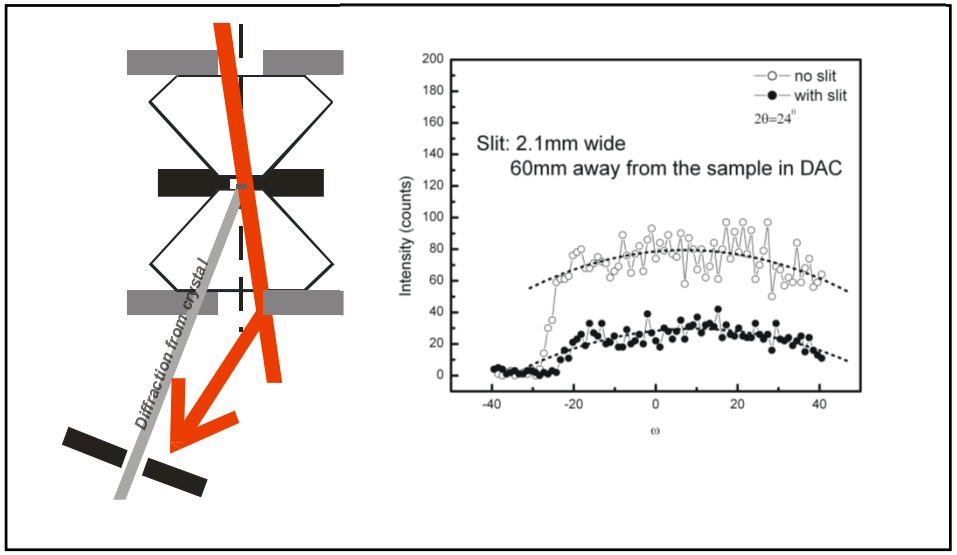


Clivia: today

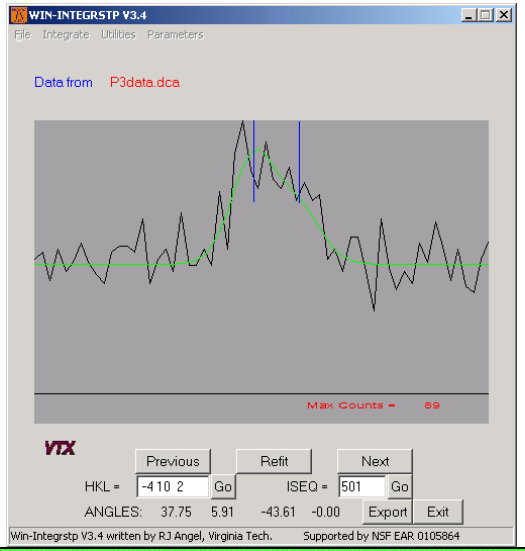
Reducing background

Use a point detector:

- *Additional collimation*

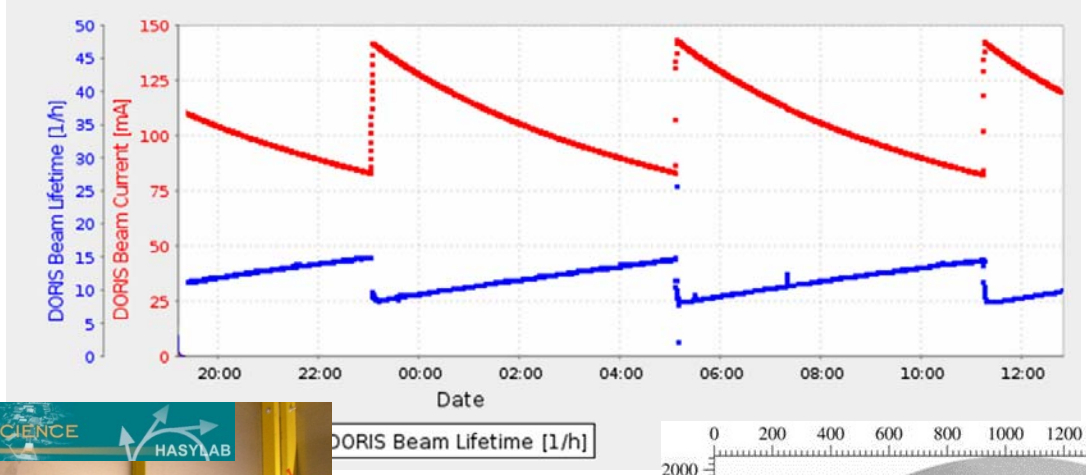


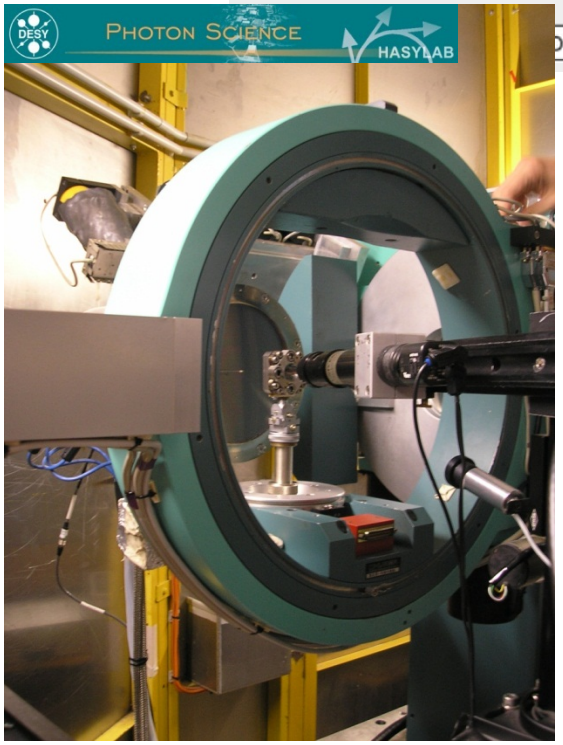
- *Optimised scan speed*
- *Step scans*
- *Profile fitting*
- *Recovery of weak data*

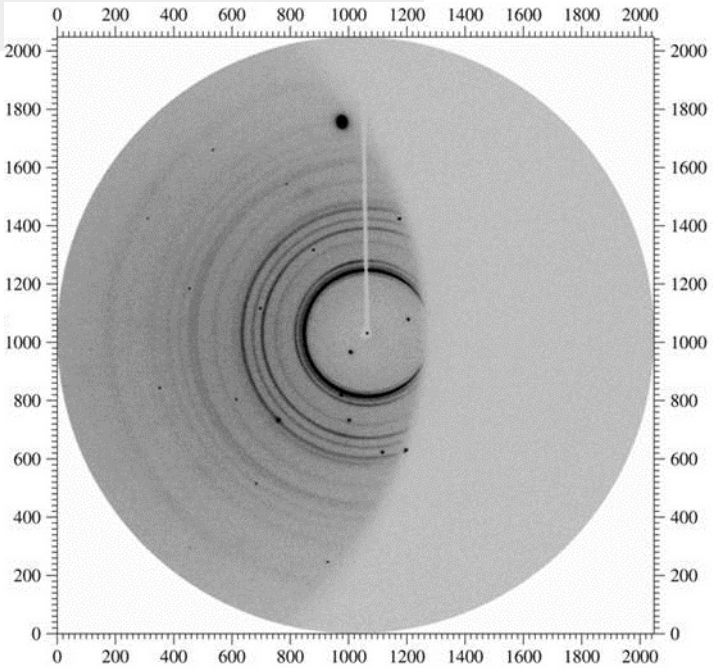


Ross: today, afternoon

Data collection at synchrotron sources



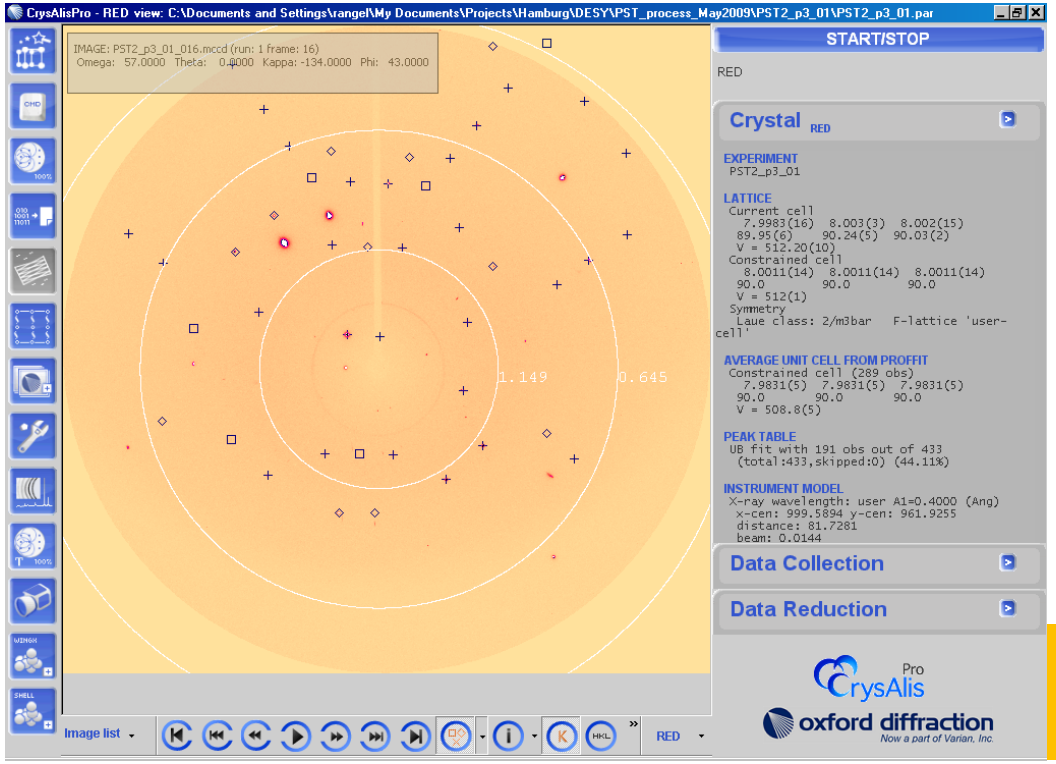




David and Michael: tomorrow

Indexing and integration

- **Similar to crystals in air**
  - **But tricks and software to overcome the challenges**



Intensity data collection

Integration

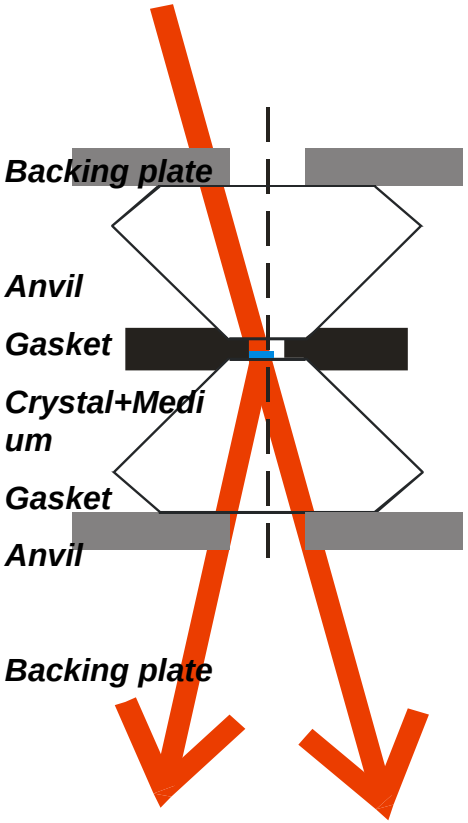
Absorption corrections

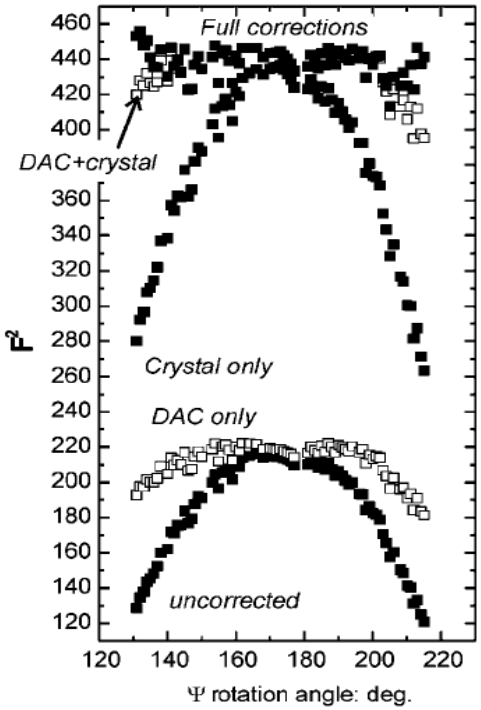
Refinement

Post-refinement analysis and publication

Absorption

- Much more to correct





Intensity data collection

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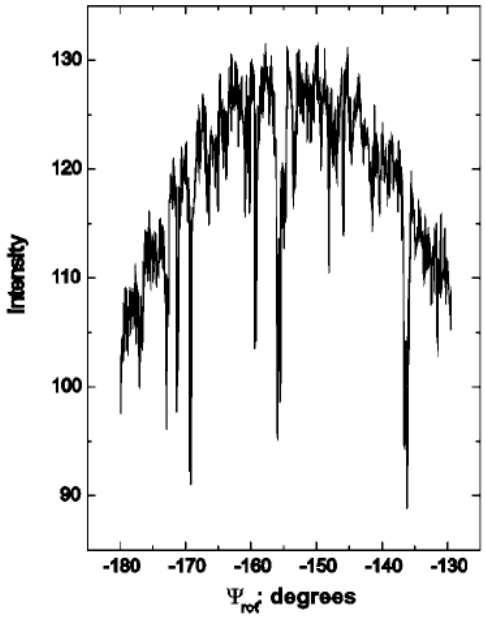
Ross: tomorrow

Refinement

- Much more sensitive to outlier data



- Lower resolution data
- Approaches:
  - Robust-resistant weighting
  - Restraints
  - Careful evaluation of outliers

Intensity data collection

Integration

Absorption corrections

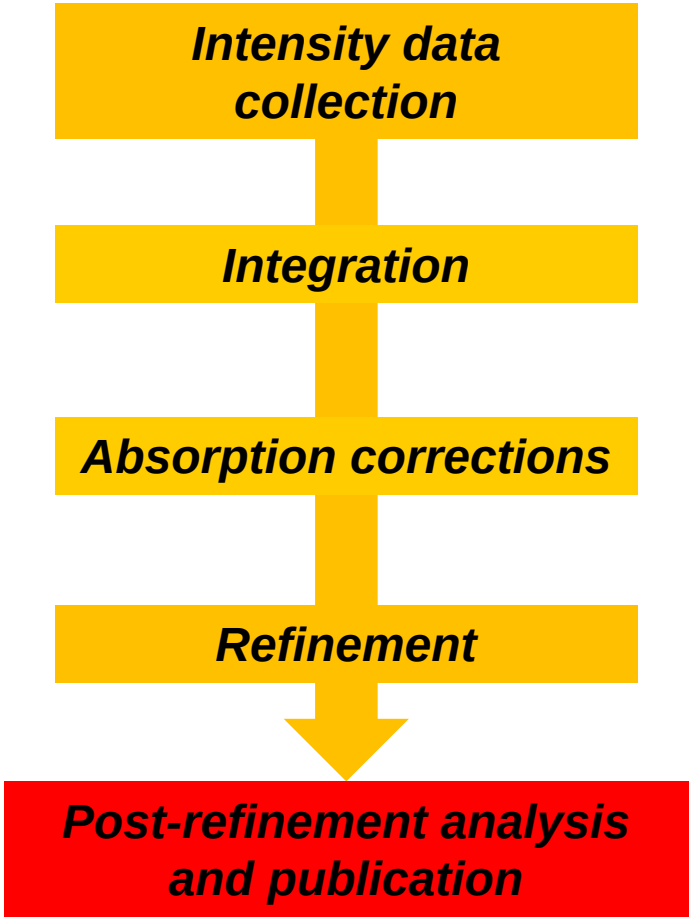
Refinement

Post-refinement analysis and publication

Karen + Andrzej: tomorrow

Post-refinement analysis

- **Structure validation**
  - **Getting past the cif-checker**
- **Parametric data:**
  - **Challenges**
  - **Opportunities to exploit self-consistency**



Karen, Ross and others: tomorrow

Workshop overview

- **Today**
  - **Cells and cell loading**
  - **Data Collection**
  - **Equations of state**
  - **Data integration**

- **Tomorrow**
  - **Synchrotron data collection**
  - **Absorption corrections**
  - **Refinement**
  - **Structure validation**
  - **Eos fitting**
  - **Problem solving**

Intensity data collection

Integration

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