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

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

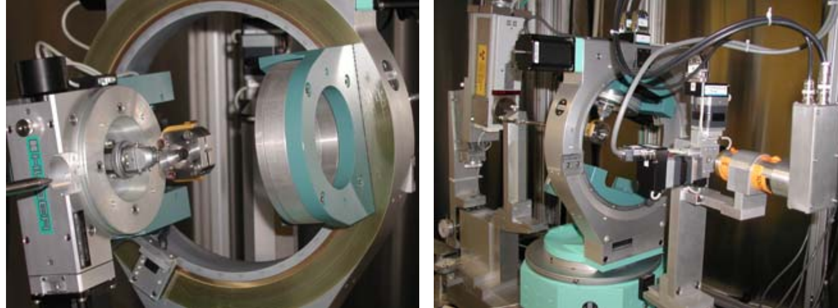


## Single crystal and powder

- **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)**

## Cell parameters at high pressure

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



*In-house single-crystal X-ray diffraction.*

*Eulerian cradle diffractometers (Huber, P4, Stadi4), Single software*

*Cell parameters to a precision of 1 part in 30,000*

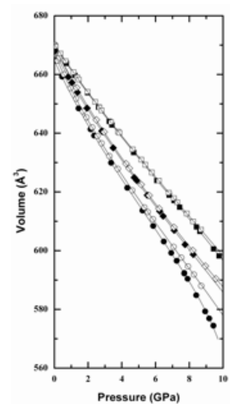


**Tiziana: tomorrow** VTX

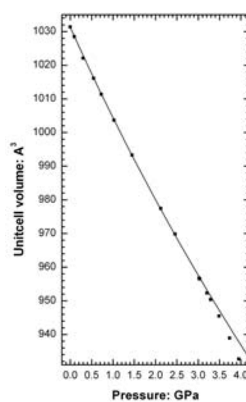
## Equations of State and Phase Transitions

- ***Precise cell parameter data allows studies of small changes in EoS and of phase transitions:***

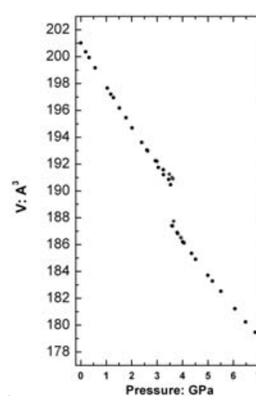
*Order/disorder in plagioclase Sochalski-Kolbus et al. (2011)*




*Softening in $CuCO_3$ Spencer et al. (2011)*




*Isosymmetric phase transition in kalsilite. Gatta et al. (2011)*



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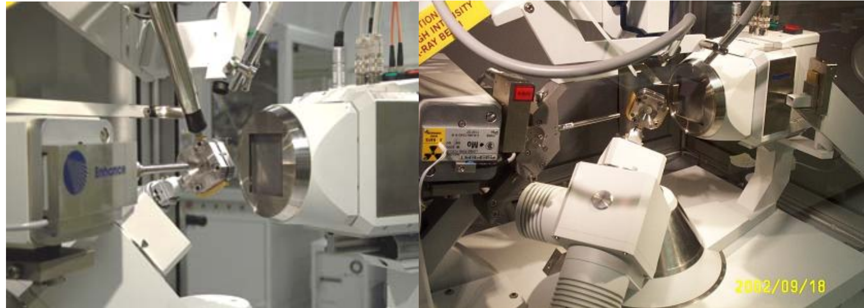
## Determining structures at high pressure

***Precise intensity data to measure small changes in structures at high pressures:***




*Single-crystal X-ray diffraction.*

*Point and CCD detectors.*

*Beamlines and in-house*

*Ronald & Benedetta: today*



## Determining structures at high pressure

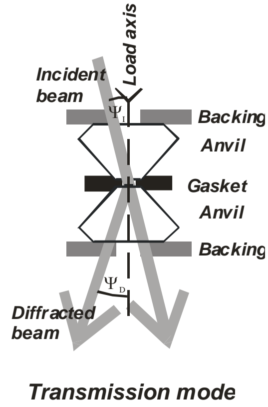
*Very precise data to measure very small changes in structures at high pressures.*

*Single crystal diffraction is only worth the extra effort if it produces data significantly superior to powder diffraction.*

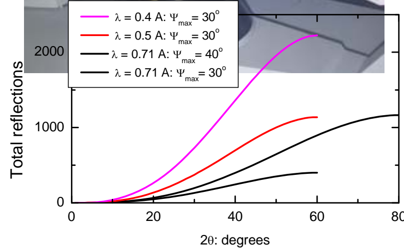
*Challenges:*

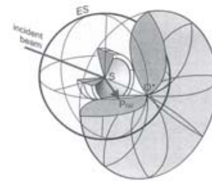
- *Limited access*
- *Low signal (but higher than powder)*
- *Background scattering*
- *Absorption by cell components*
- *Maintaining hydrostatic conditions*

## Diamond-anvil geometry



## Limited access



Miletich, RiM volume

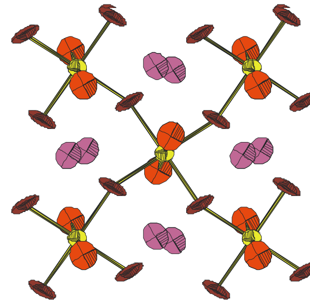
*Fewer reflections means:*

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

## Limited access

*Lab: partially overcome by simulations to:*

- *predict the effects of restricted access*
- *choose best orientation*



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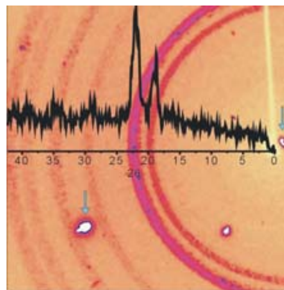
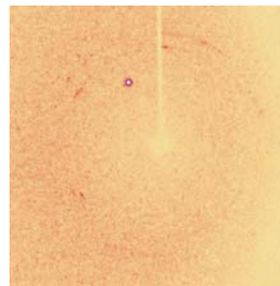
## Reducing background

*Everything you see is background!*




*Conventional DAC with Be seats, steel gasket*



*DAC with steel seats and rhenium gasket*

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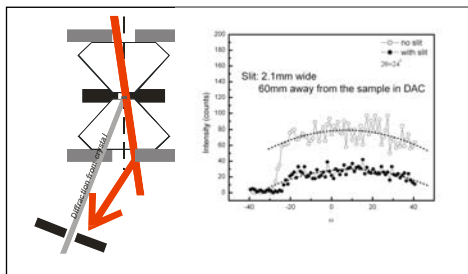
## Reducing background

### Use a point detector:

- Additional collimation




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

Ross: today

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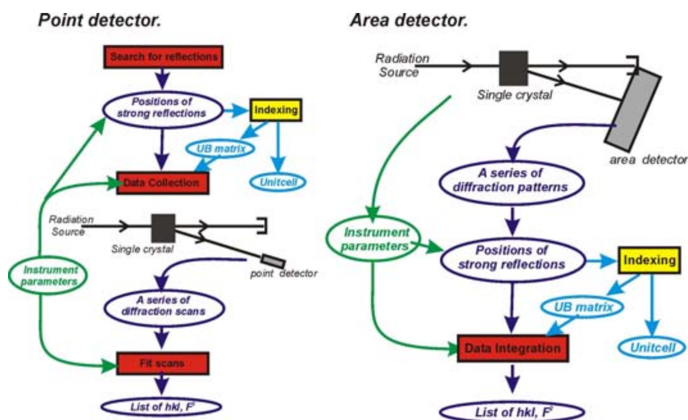
## Intensity data collection




**Area detector is "shoot first and ask questions later"**

**Point detector needs more work at the diffractometer**



Ronald & Benedetta: today

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## Intensity data integration with area detectors

- Indexing
  - Identification of sample spots for indexing
  - Indexing algorithms to handle 2-d data
  - Masking of blank areas of detector
- Integration
  - Background subtraction: global + local
- Commercial and non-commercial software solutions available
- These processes can be automated

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**Software Fayre: today**

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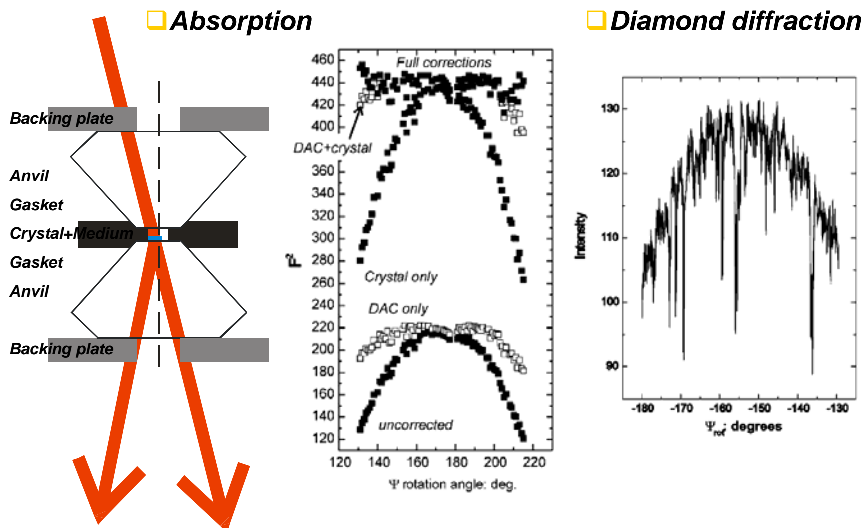
## Post-integration data corrections

- *Absorption*
- *Diamond diffraction*

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**Karen & Ross: tomorrow**

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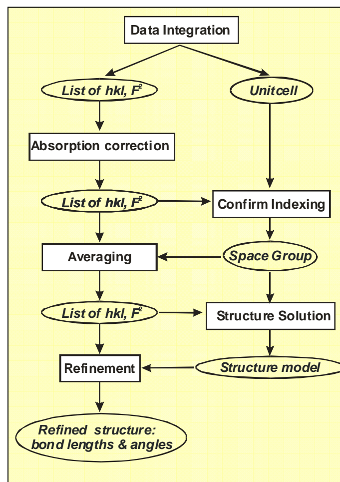
## Post-integration steps

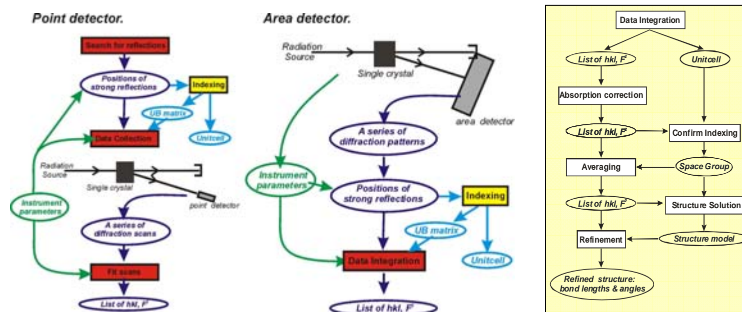
- Data reduction
  - Critical for HP data
  - Absorption corrections
  - Averaging
- Structure solution
  - Limited data coverage
  - Often not ab-initio
- Refinement
  - Robust-resistant weighting
  - Restraints
  - Careful evaluation of outliers
- Structure validation




Karen, Ross & Tonci: tomorrow



## Workshop Overview




- Today
  - Experiment design
  - Data Collection
  - Data integration

- Tomorrow
  - Equations of State
  - Data reduction
  - Refinement
  - Structure validation
  - Problem solving