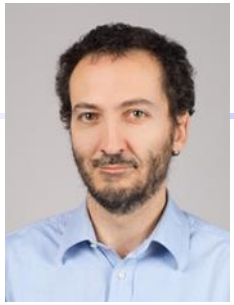
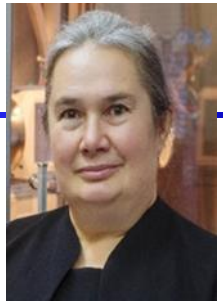
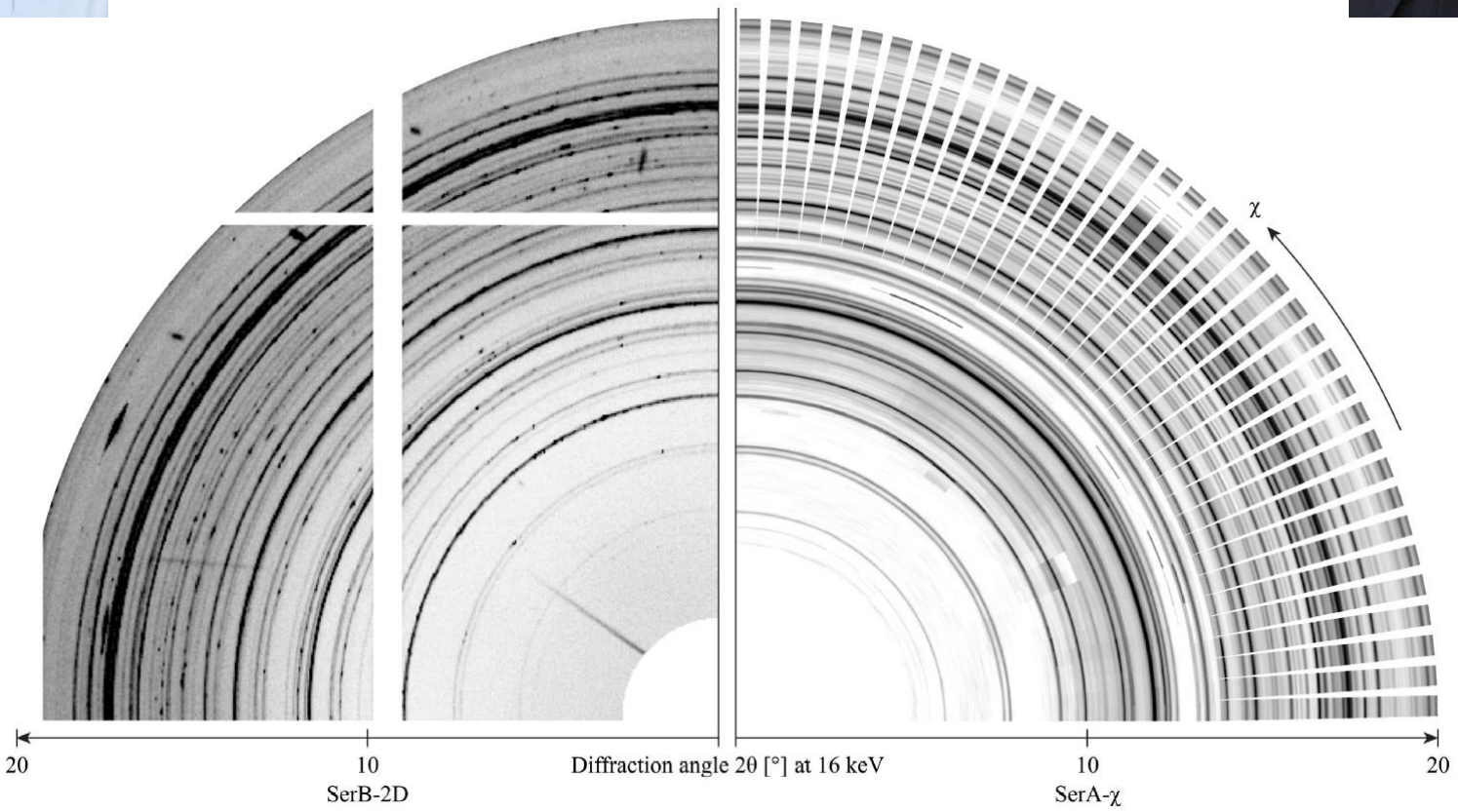


Dr. Nicola Casati

Prof. Elena Boldyreva

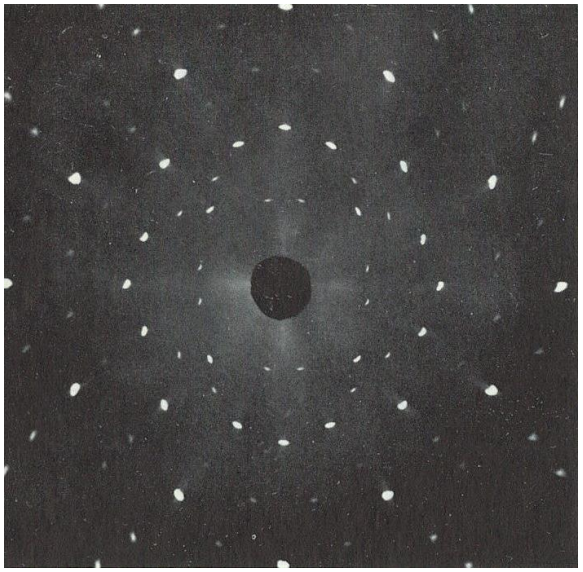


nicola.casati@psi.ch, eboldyreva@catalysis.ru



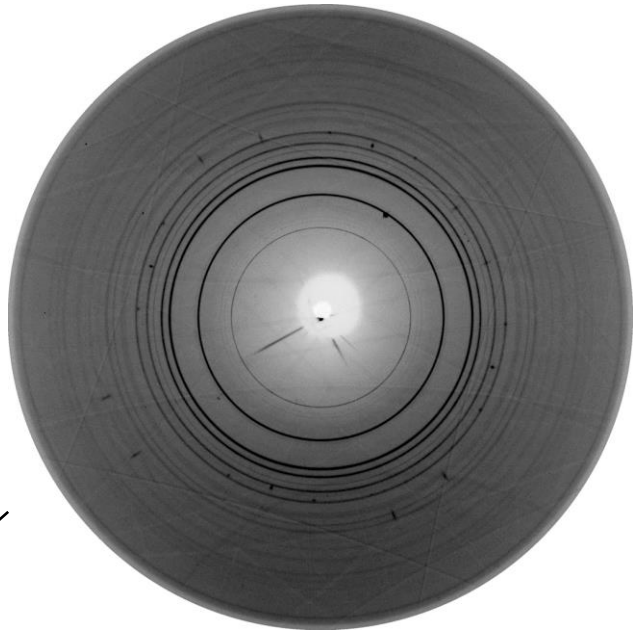
Powder Diffraction raw data

Diffraction data

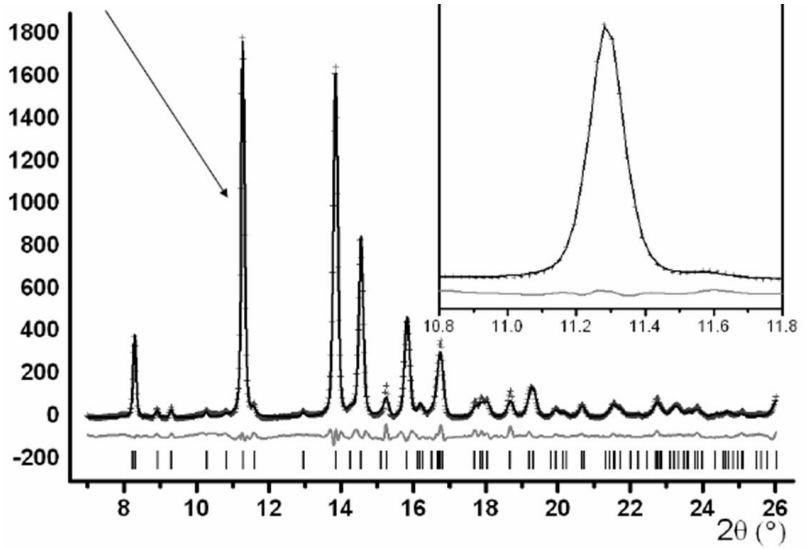


Less and less information easily available:

Single-crystal diffraction
multiple images collected



2D Powder diffraction
single image collected

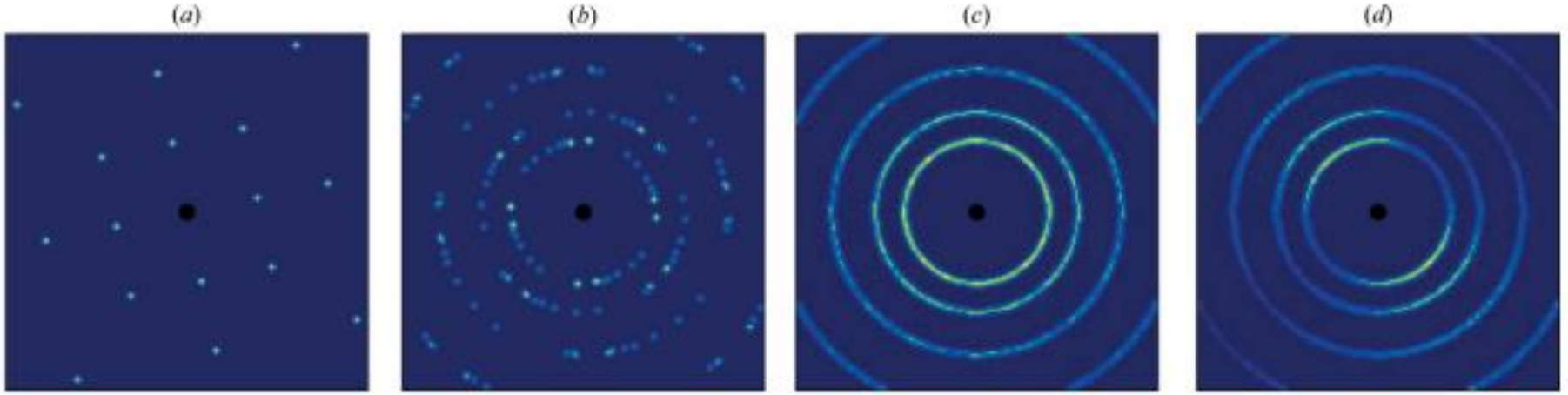


Powder diffraction after integration
Information loss! (position, overlap etc.)

Powder Diffraction – if so much information is lost, why still used? When is it preferable / unavoidable?

- To represent all the sample,
- To identify the phases in the sample, in particular, to analyse phase composition of multi-component samples (qualitatively and quantitatively),
- to measure the unit cell parameters and volume and their variations with temperature, pressure, as functions of the composition of solid solutions, concentration of defects, strain and stress,
- to estimate the size of crystallites, domains,
- to find the preferred orientation of particles,
- to estimate the content of the amorphous phase(s) in relation to the crystalline phase(s),
- to solve an unknown crystal structure, if a single crystal cannot be obtained,
- to refine a crystal structure that has been preliminary roughly solved based on poor-quality or low-completeness single-crystal diffraction data.

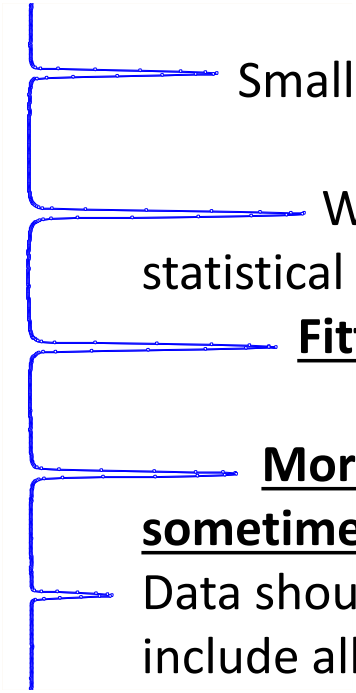
Powder Diffraction: not only peak positions and integral intensities



(a) a perfect single crystal;
(b) a small number (Nc = 10) of domains with uniform pole distribution;
(c) a large number (Nc = 1000) of domains, again with uniform pole distribution;
(d) Nc = 1000 with anisotropic pole distribution.

Binns, J., Darmanin, C., Kewish, C. M., Pathirannahalge, S. K., Berntsen, P., Adams, P. L., ... & Martin, A. V. (2022). Preferred orientation and its effects on intensity-correlation measurements. IUCrJ, 9(2), 231-242.

Powder Diffraction



Smaller sized datasets, less information

Working well for measurements/experiments requiring statistical analysis; e.g. Quantification

Fitting and refinement are prone to end in false minima

More often one has to go back and look again at raw data, sometimes after years

Data should then not simply be a sequence of angles and intensities, but include all aspects necessary to interpretation (metadata).

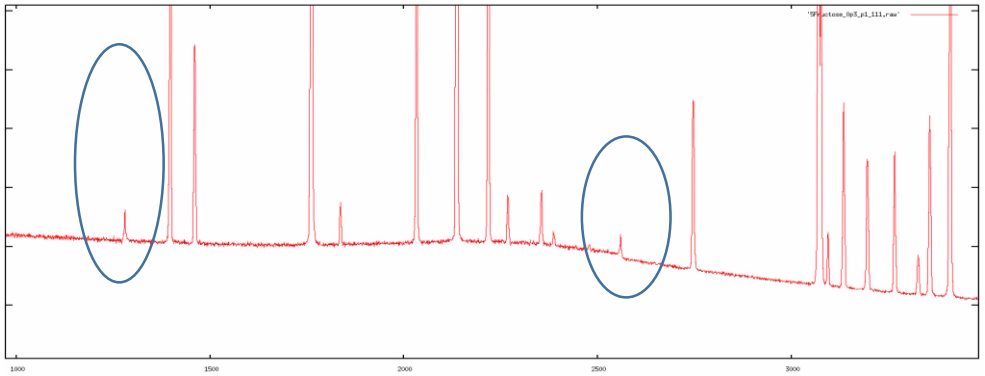
Not only the **angular positions** of the diffraction maxima and their **integral intensities**, but also the **shapes** of the reflections, the **background**, the presence of some **non-indexed reflections**, the **2Θ range** measured are important

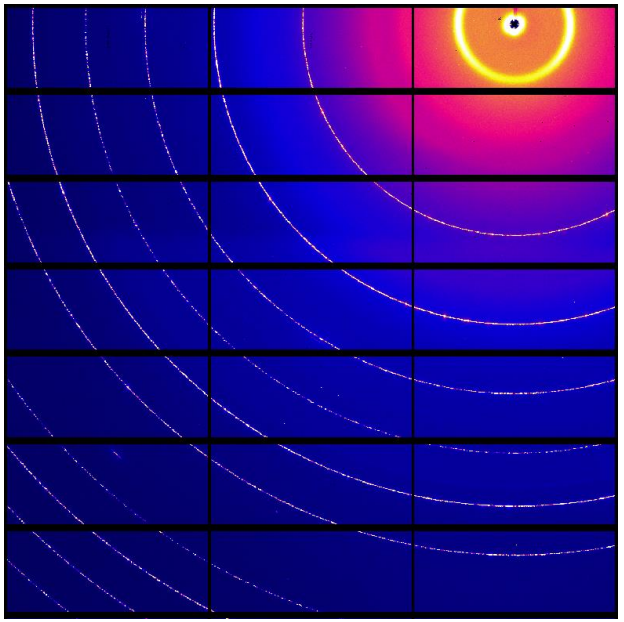
Raw data are incomplete without metadata

Raw diffraction data, processing

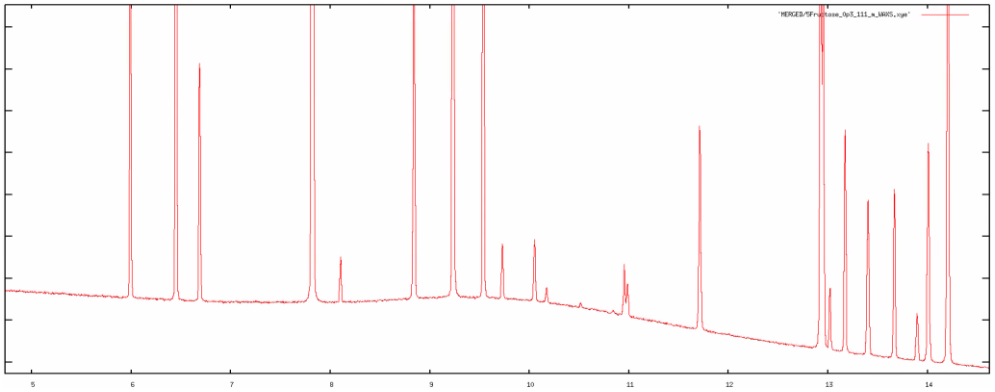
Data processed by most used programs are in 2θ-I or better 2θ-I-σ(I) format

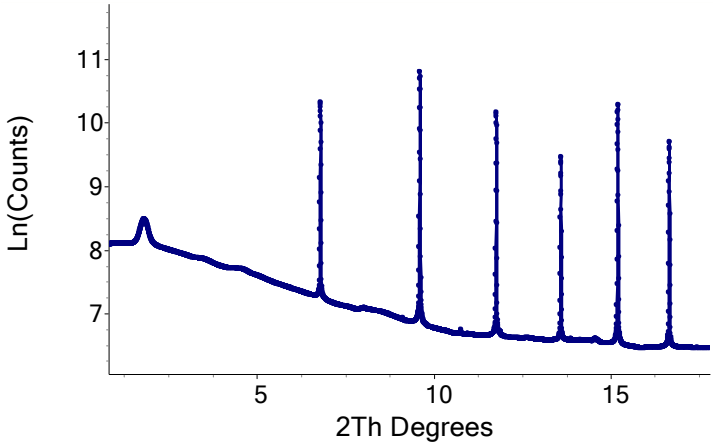
Often though this is not the lowest level of data:





Angular calibration and flatfield



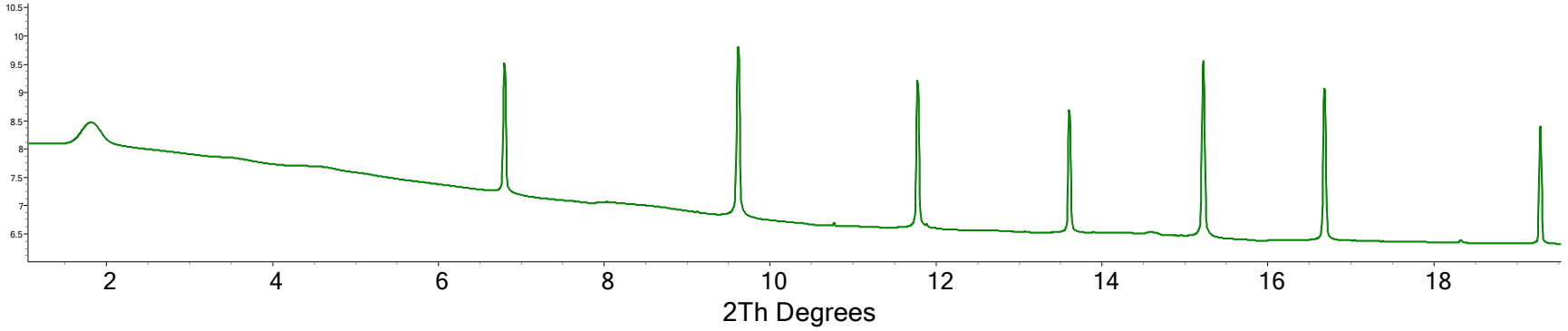


Data processing and metadata

A bare minimum metadata is the wavelength, or wavelength spread

In many cases, though, data could be of limited value unless the full **Instrumental Resolution Function (IRF)** is known. This is needed to extract higher level information, beyond the simple fingerprinting. Should normally be kept as metadata

2D -> 1D, effect of correct angular calibration (angular bias) and area masking

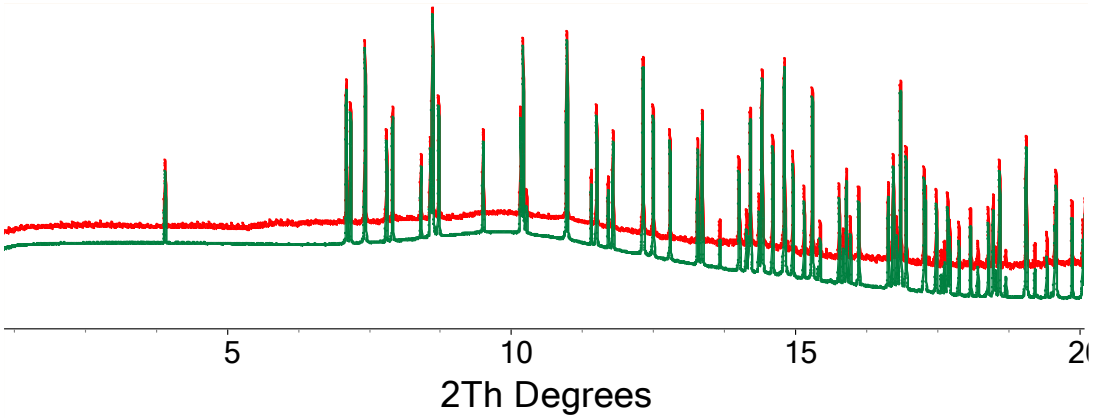


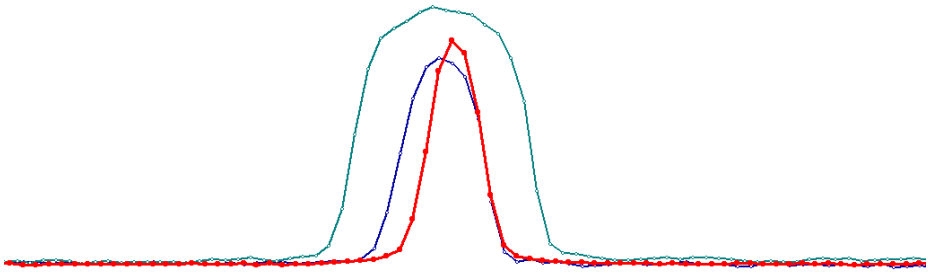
Wrong detector flatfield may also lead to non-statistical noise

Information on processing is essential to re-evaluate old data. It is also often a major source of error and after re-processing correctly better information can be extracted

Things that enter data …

Fluorescence: pattern with no fluorescence in green, in red the pattern with fluorescence, including a higher background and non-statistical noise.

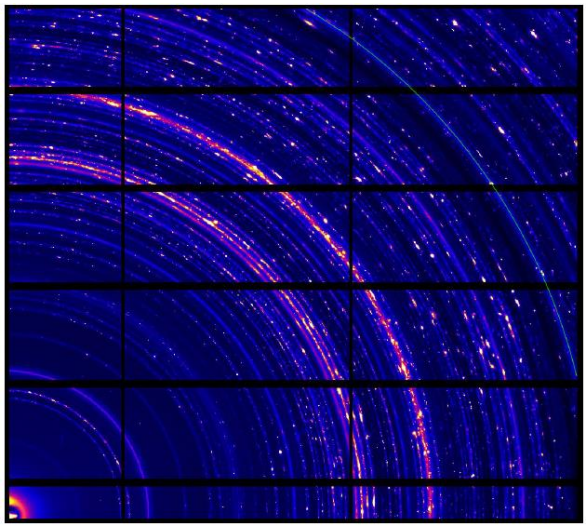
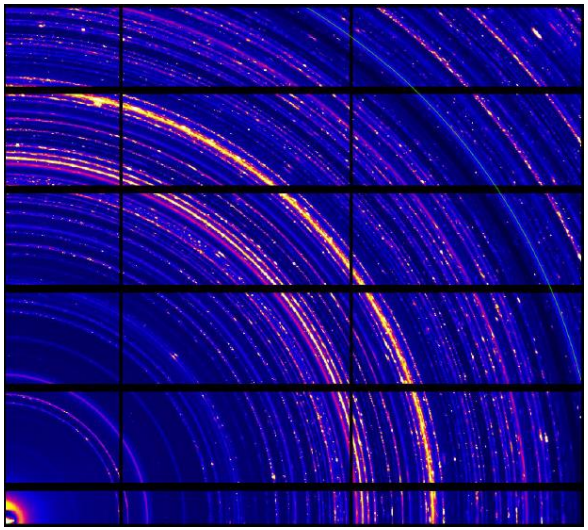
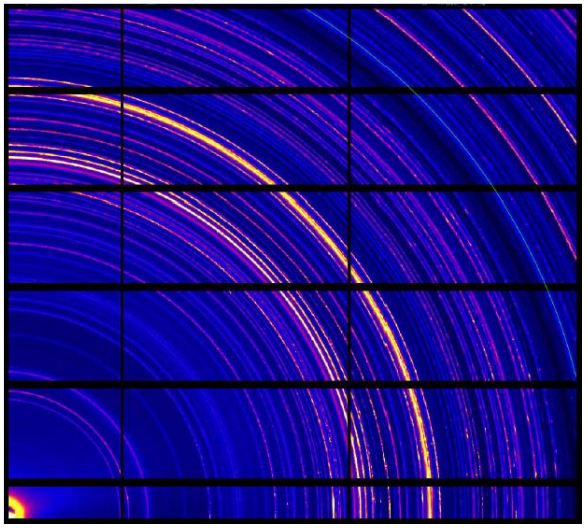




Sample holder size: Fructose [1 1 0], blue 0.3 mm capillary, green 0.7 mm capillary, red 0.7 mm capillary with 0.3 mm slits (slits have a wrong offset, resulting in a different angular position)

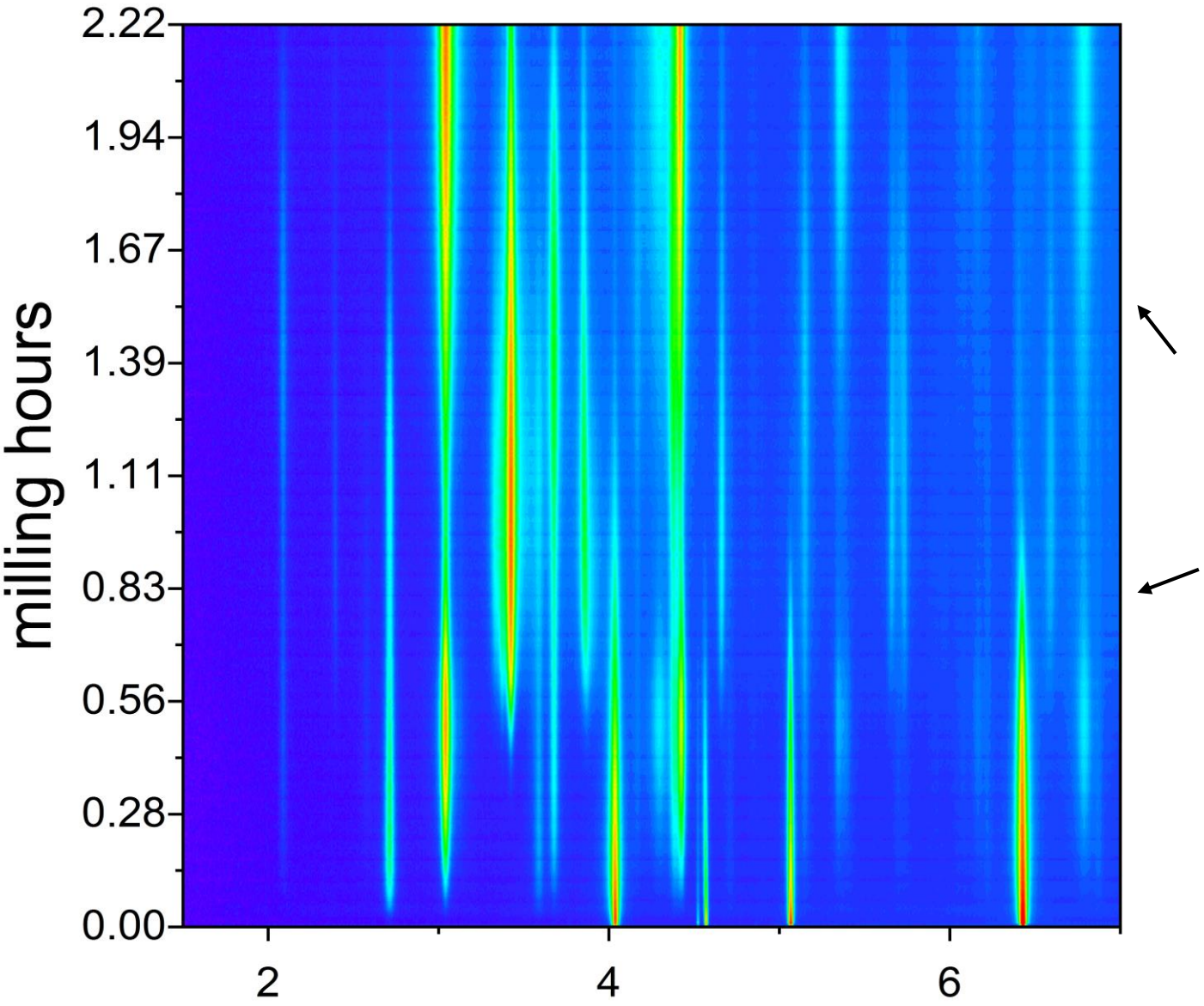
Temperature, sample origin, sample holder, these are simple parameter to record and keep. **Many things may influence the final pattern** which instead we cannot fully control, composition may lead to fluorescence and may not be known at the beginning, radiation sensitivity may not be known either and could affect the pattern in long measurements (or in synchrotron ones)

Particle Statistics…

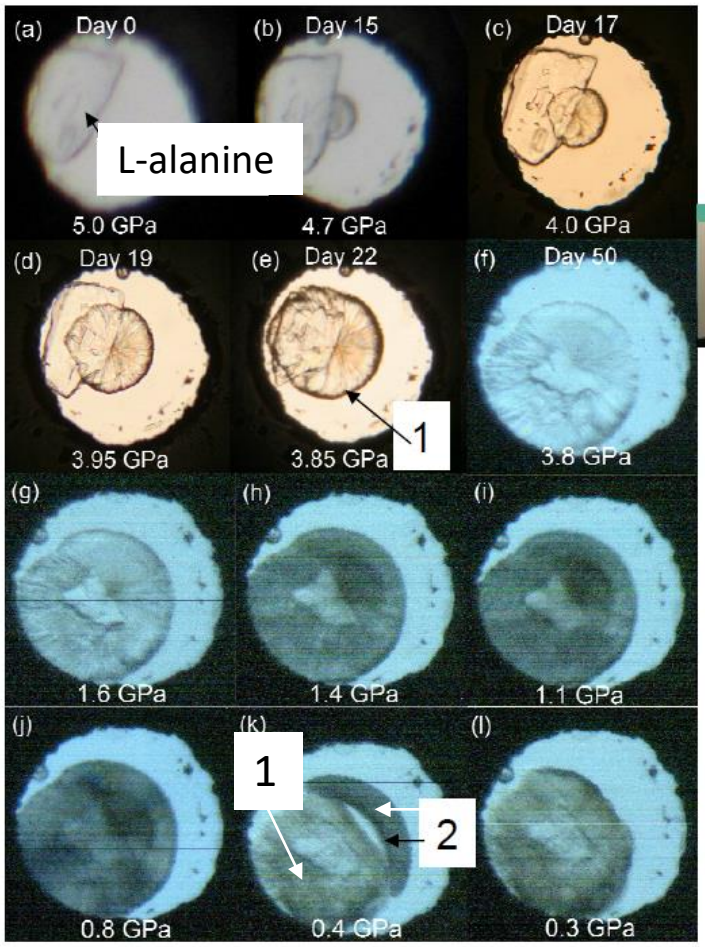
The level of spinning, rocking the sample should be recorded, not always a 2D image is available to re-evaluate the quality of the statistics.

No alternative to keeping all images

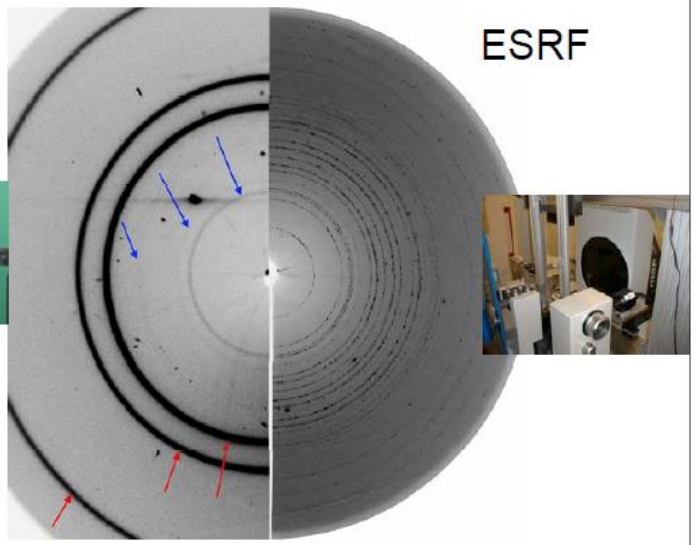


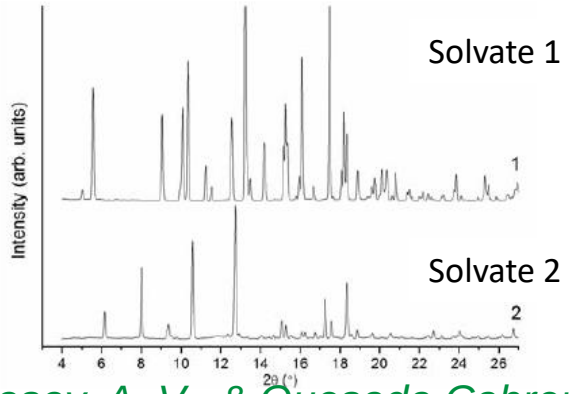
synchrotron top up, as perturbation (less intensity) every 3 minutes

Keeping sample photographs for non-homogeneous / varying samples

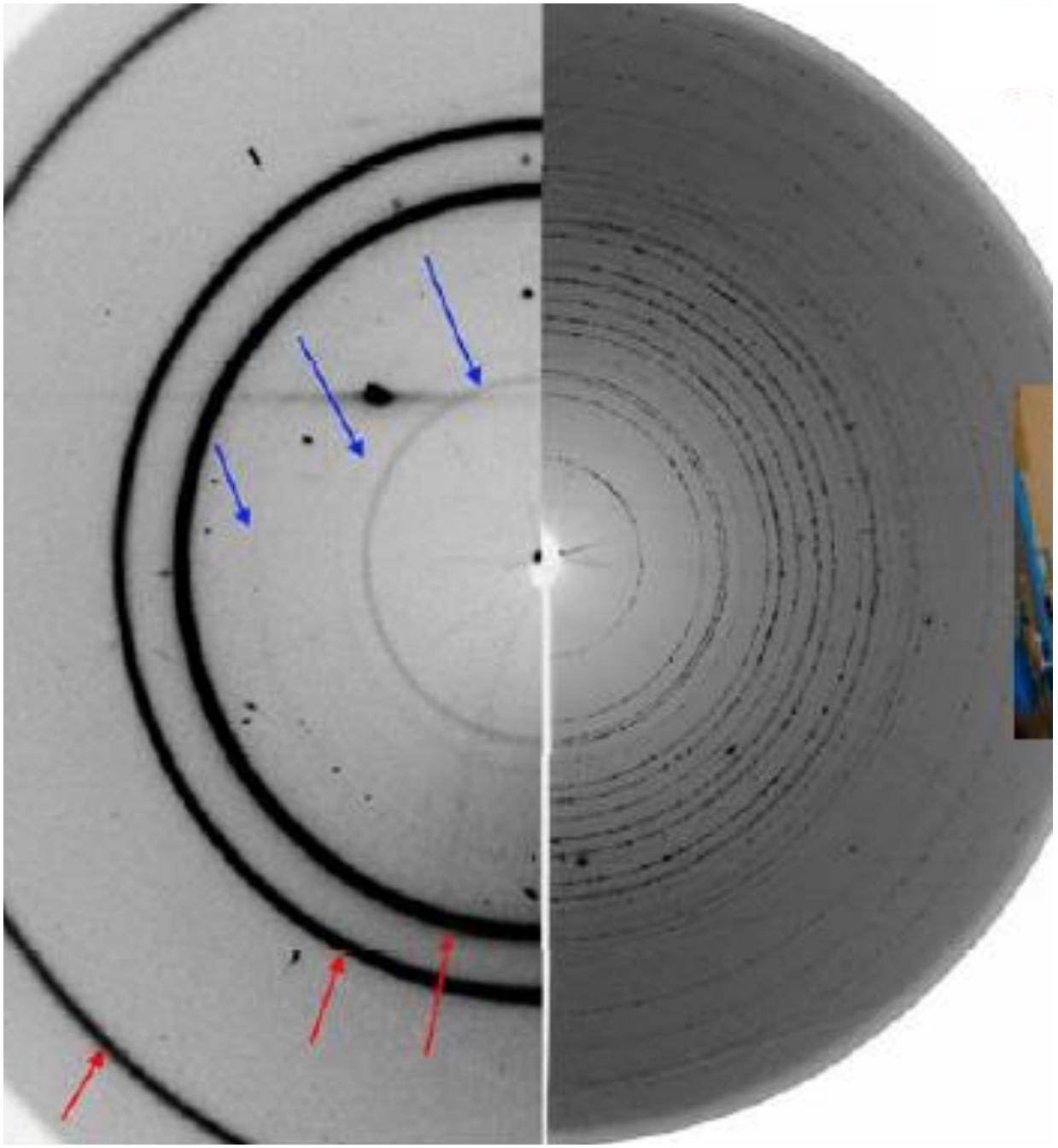


NSU, Huber

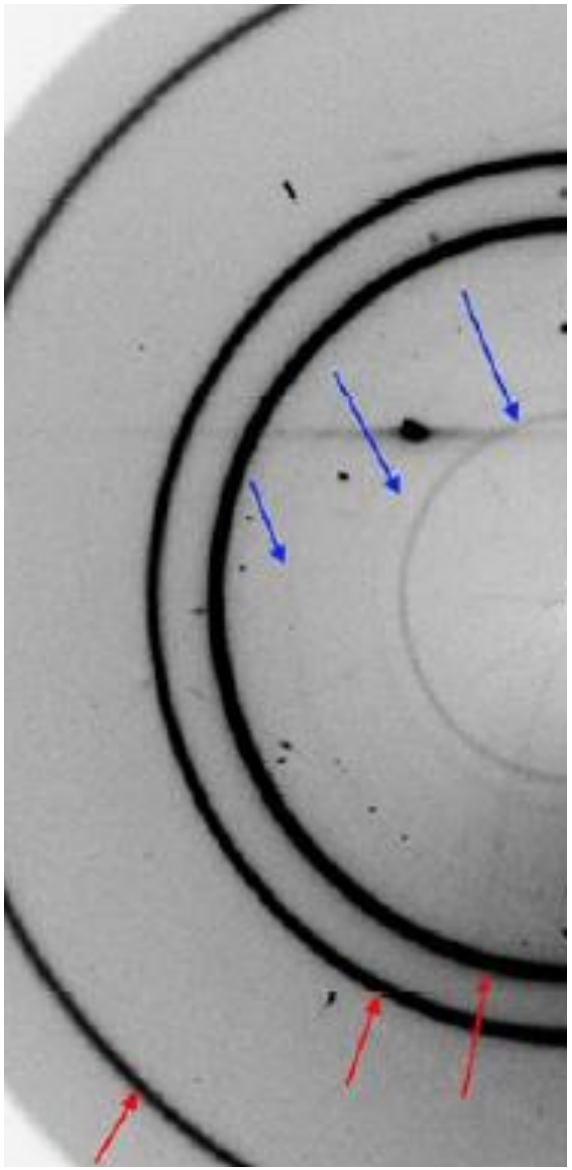


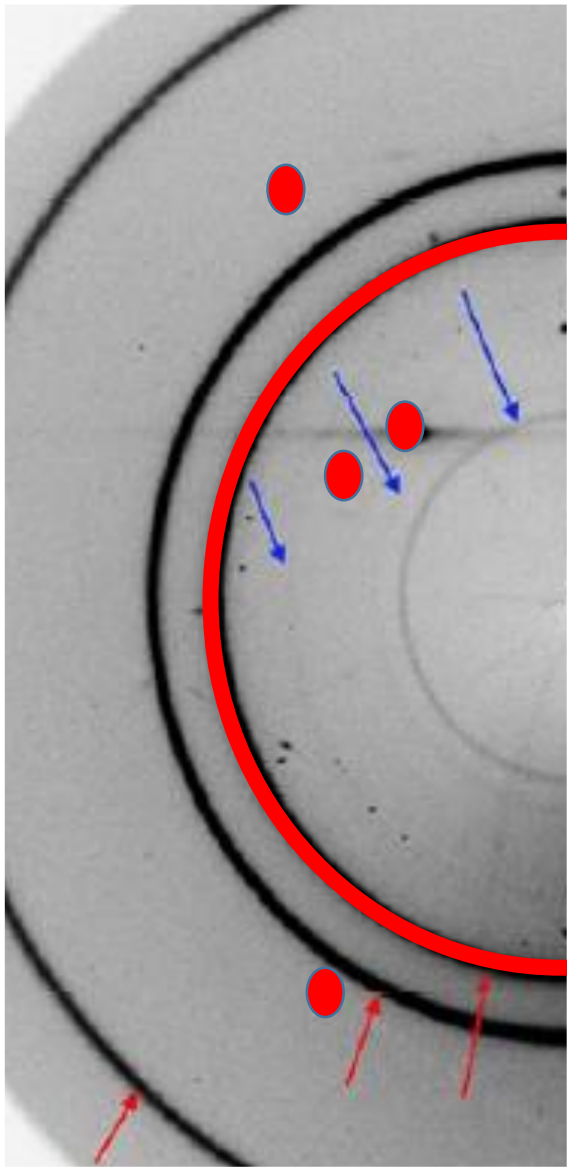


Tumanov, N. A., Boldyreva, E. V., Kolesov, B. A., Kurnosov, A. V., & Quesada Cabrera, R. (2010). Pressure-induced phase transitions in L-alanine, revisited. Acta Crystallographica Section B: Structural Science, 66(4), 458-471.

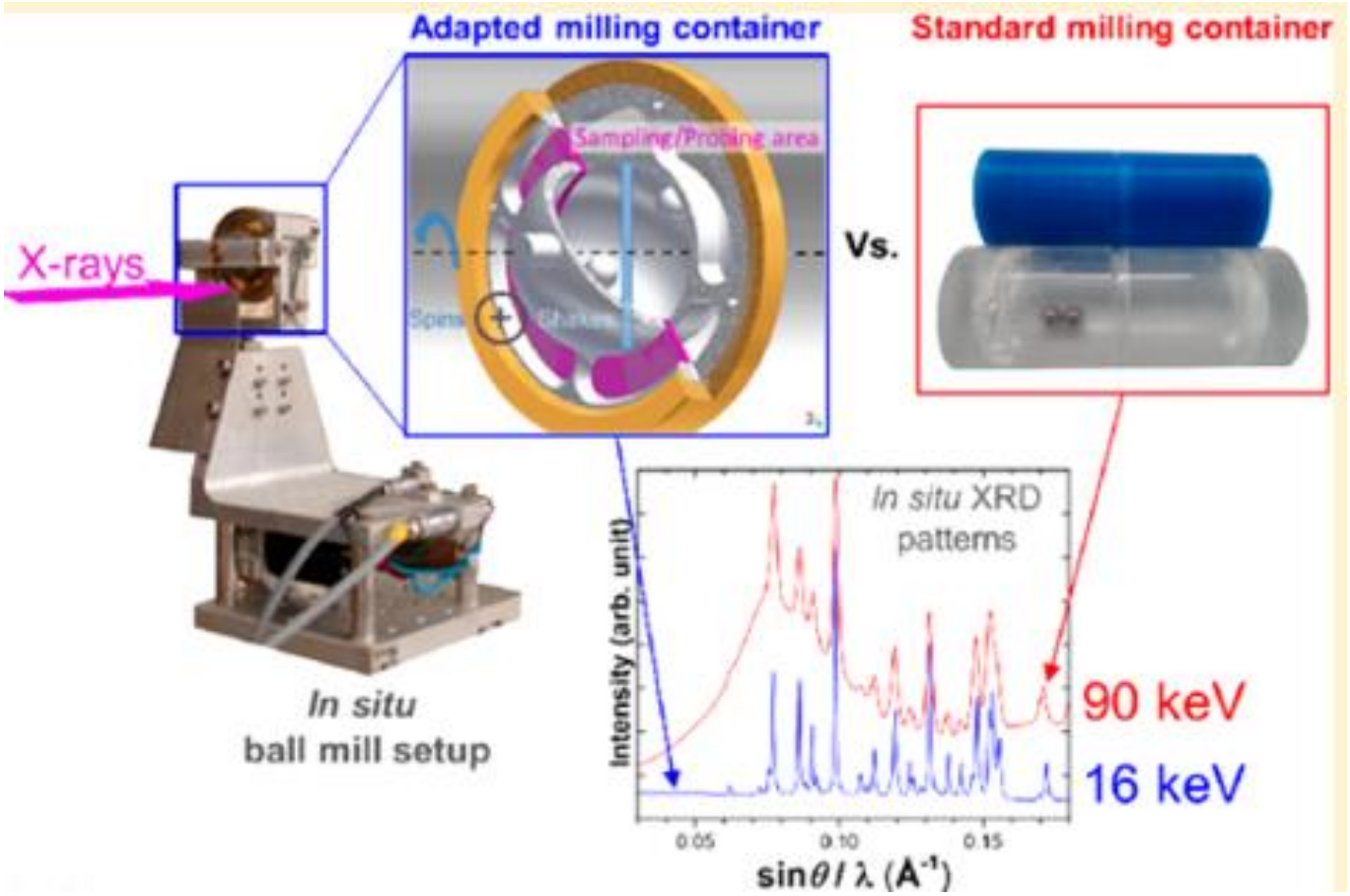


Masking is essential for processing high-pressure data





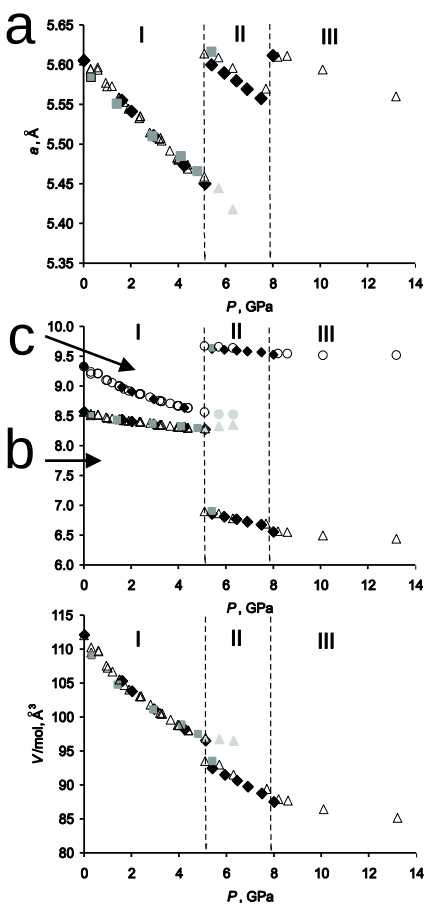
Innovation

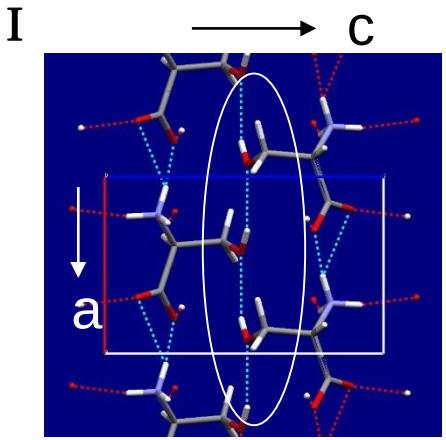


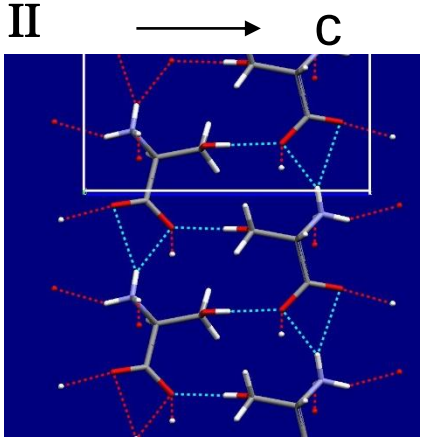
Ban, V., Sadikin, Y., Lange, M., Tumanov, N., Filinchuk, Y., Černý, R., & Casati, N. (2017). Innovative in situ ball mill for X-ray diffraction. Analytical chemistry, 89(24), 13176-13181

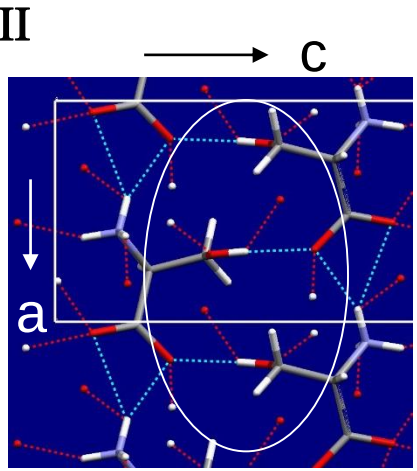
Why re-visit old data? A case study

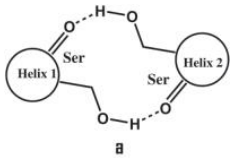
Rotation of H-bonded fragments
(phase transitions in L-serine, OH…O bonds)

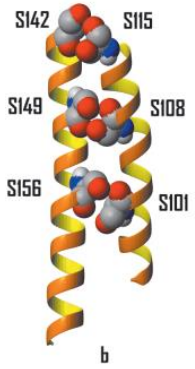






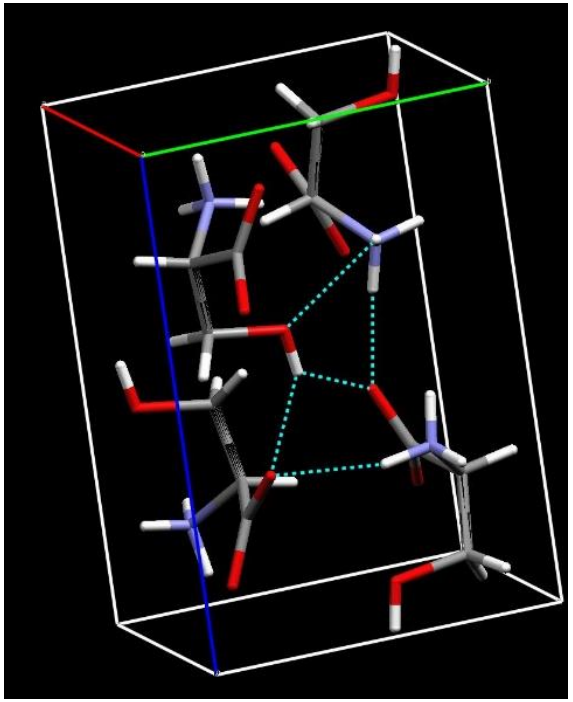




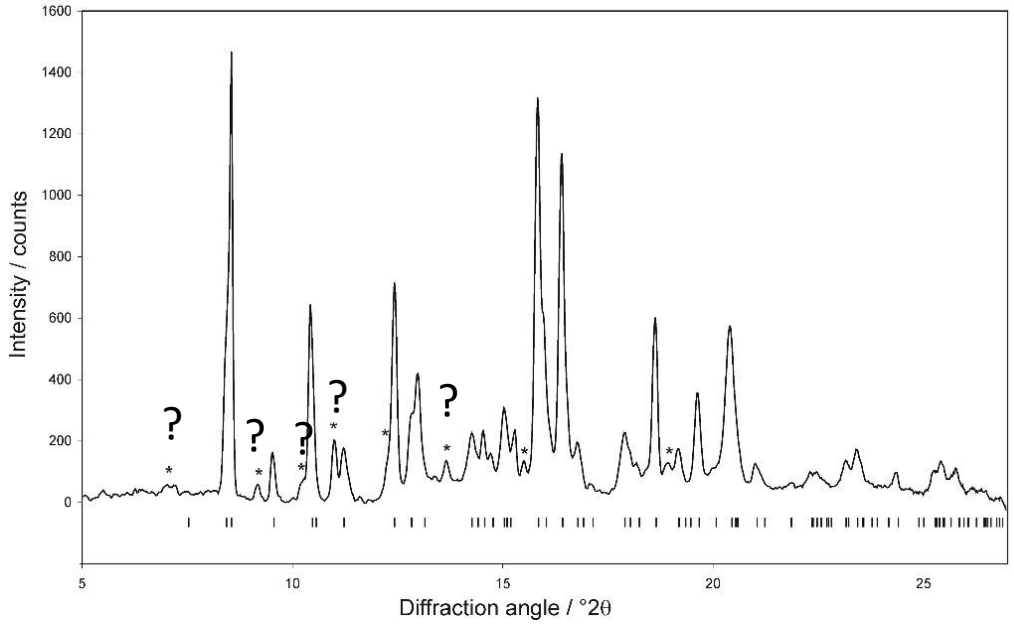


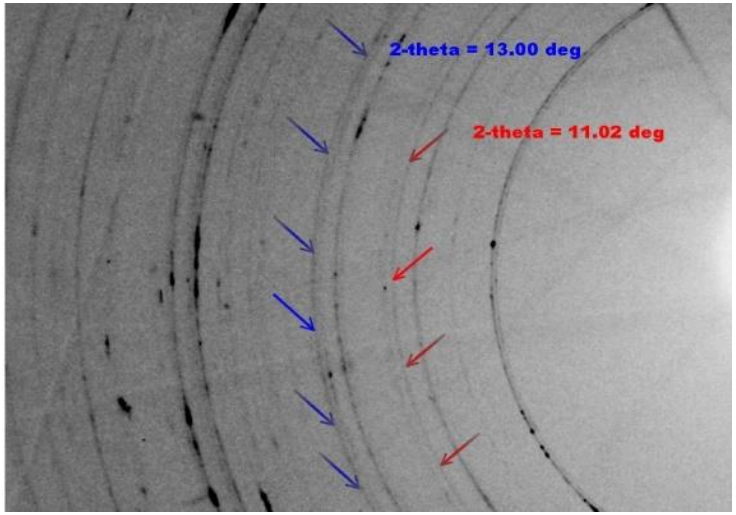
E. Boldyreva, H. Sowa et al., 2005, 2006;
S. Moggach, S. Parsons et al., 2005, 2006

L-serine III, 8 GPa



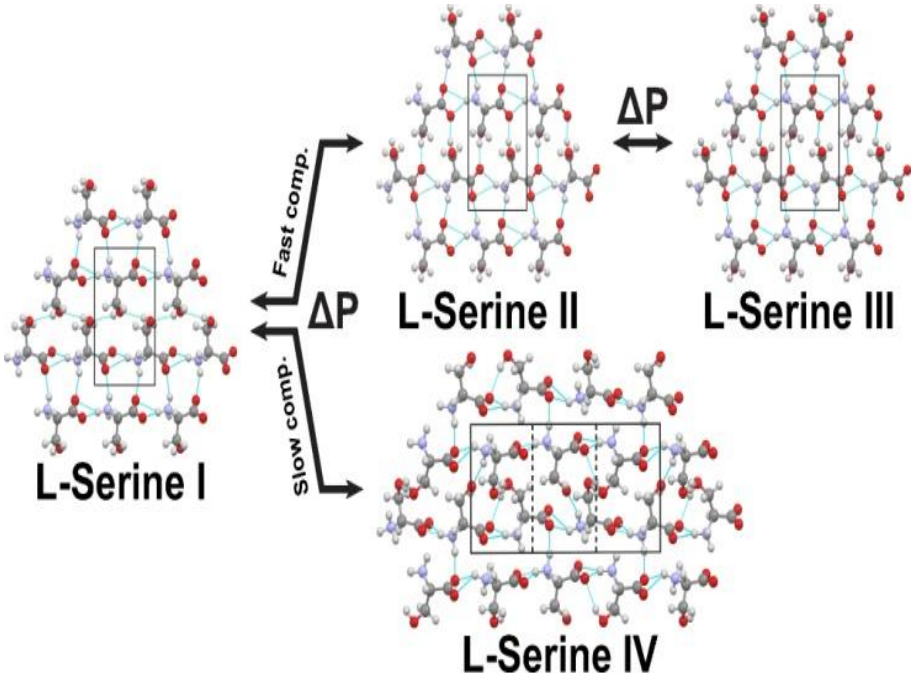
Single crystal data /
Powder data

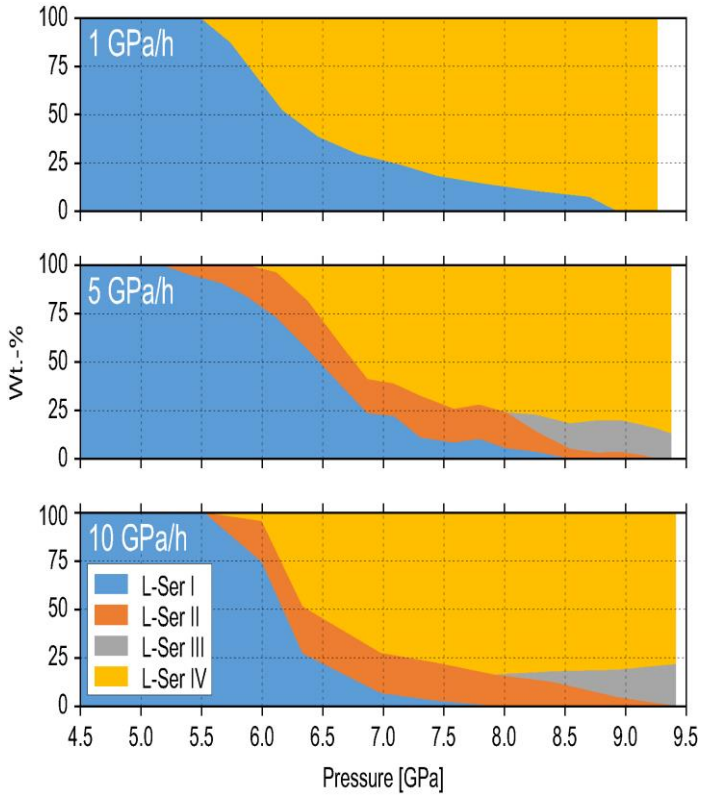




Boldyreva, E. V., Sowa, H., Seryotkin, Y. V., Drebushchak, T. N., Ahsbahs, H., Chernyshev, V., & Dmitriev, V. (2006). Pressure-induced phase transitions in crystalline L-serine studied by single-crystal and high-resolution powder X-ray diffraction. Chemical Physics Letters, 429(4-6), 474-478

Influence of compression rate on phase transitions





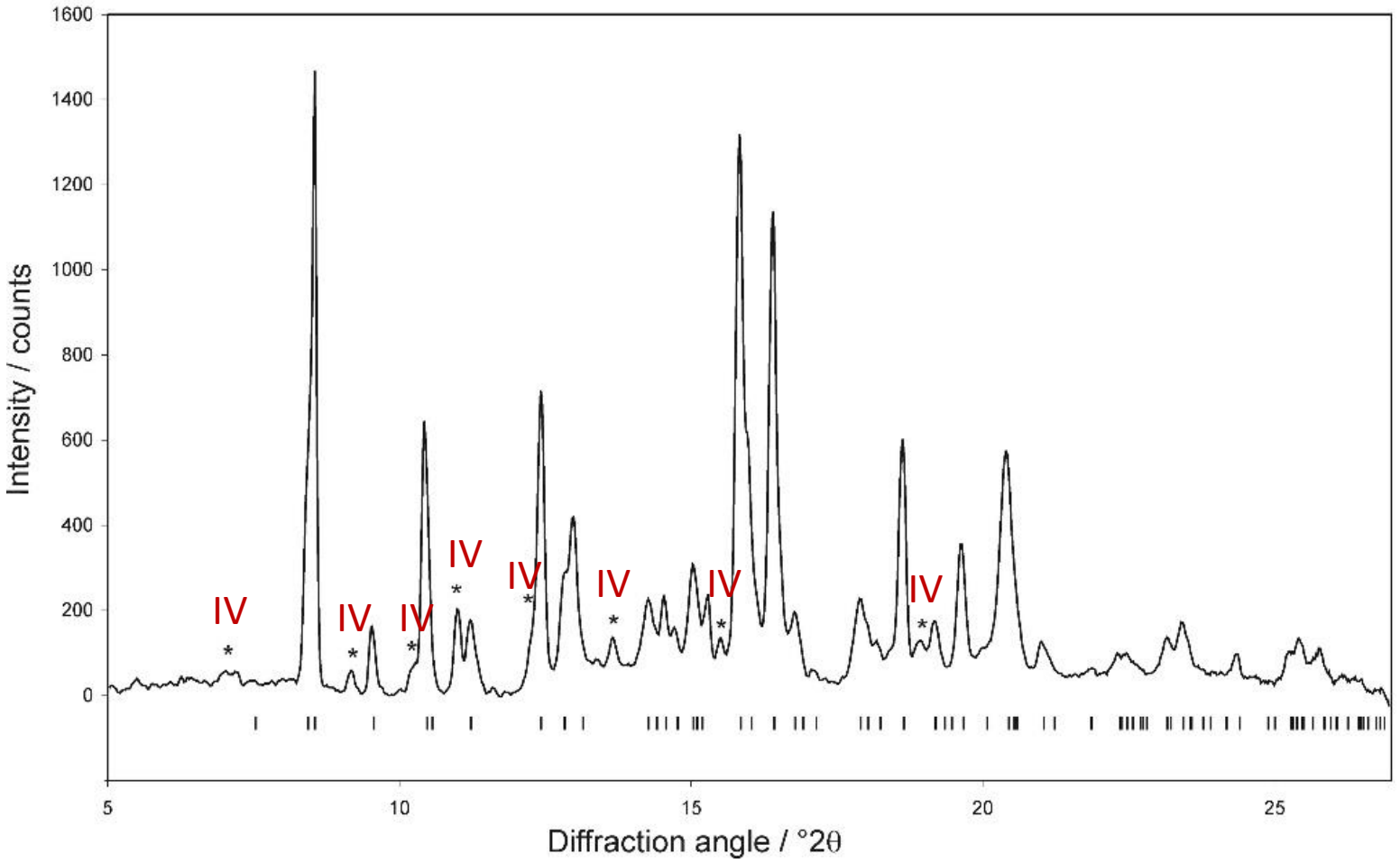
L-serine I -> L-serine II: slow nucleation, fast nuclei growth;

L-serine I -> L-serine IV: faster nucleation, very slow nuclei growth

Fisch, M., Lanza, A., Boldyreva, E., Macchi, P., & Casati, N. (2015). The Journal of Physical Chemistry C, 119(32), 18611-18617

L-serine III-IV, 8 GPa

Powder data from 2005 re-processed in 2015



Instead of conclusions

Data is not information,
Information is not knowledge,
Knowledge is not understanding,
understanding is not wisdom.
C. Stoll