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Sincrotrone

"Gilberto Vlaic" XVIII School on Synchrotron Radiation: Fundamentals, Methods and Applications



Elettra Sincrotrone Trieste



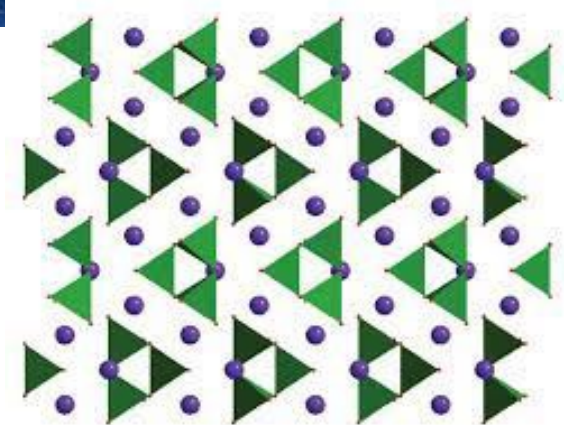
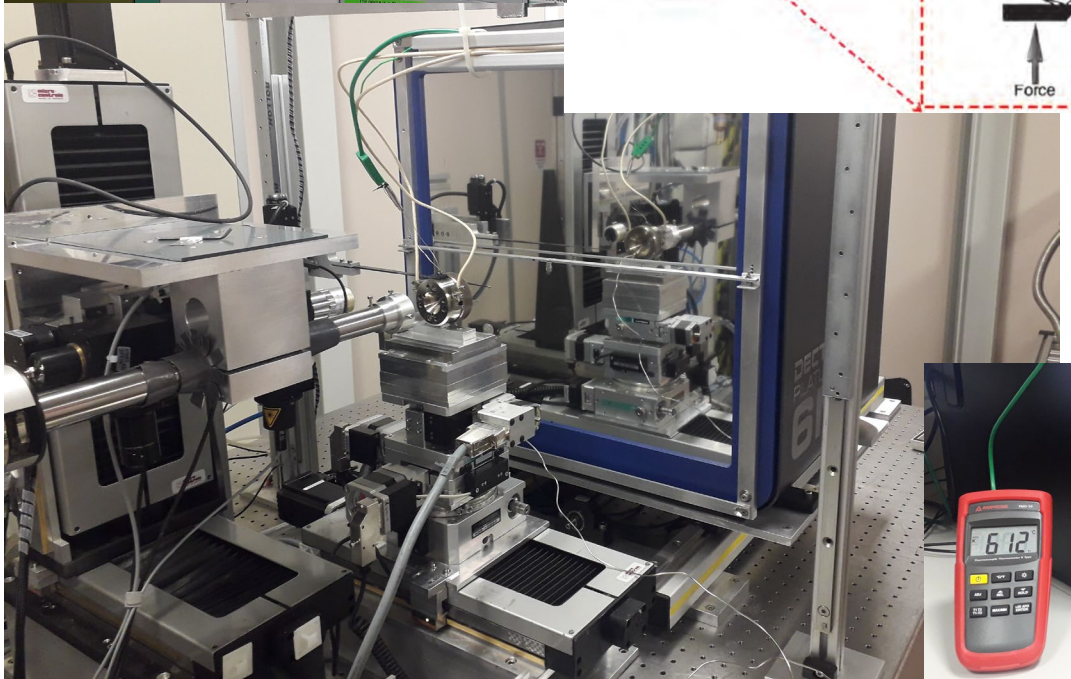
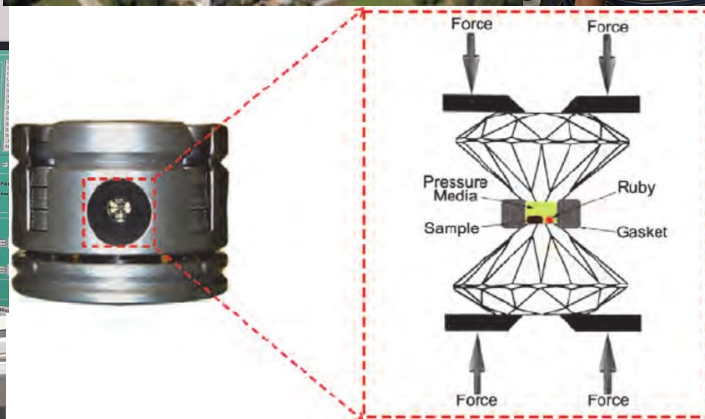
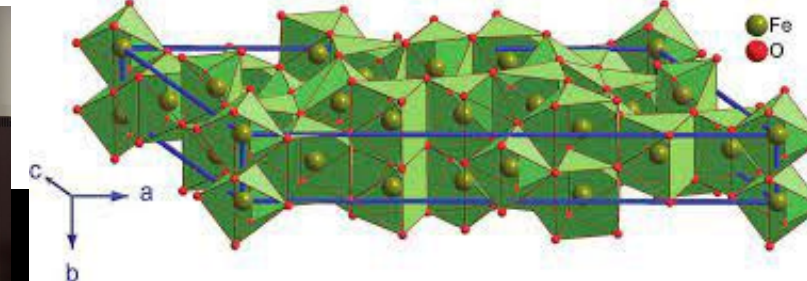
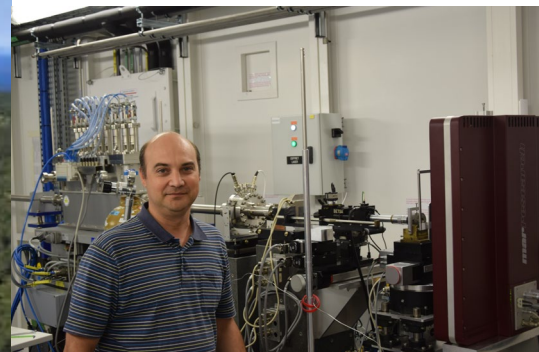
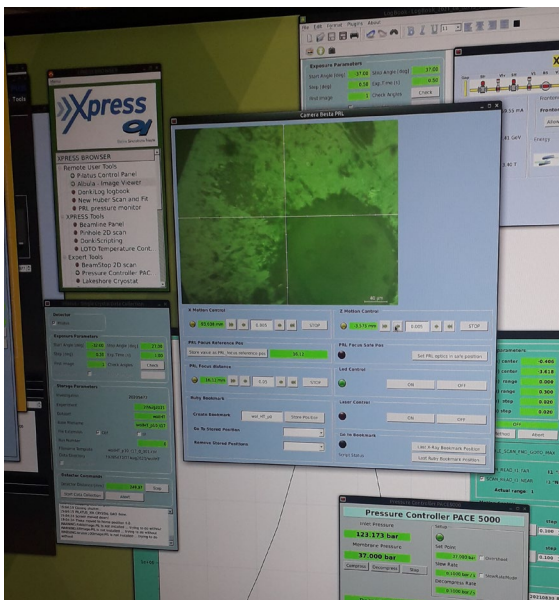
Analysis of diffraction data

Marco Merlini

Earth Science Department
Università degli Studi di
Milano (Italy)
marco.merlini@unimi.it



UNIVERSITÀ DEGLI STUDI DI MILANO





Museo delle collezioni mineralogiche, gemmologiche, petrografiche e giacimentologiche presso il Dipartimento di Scienze della Terra
Università degli Studi di Milano

1) GEOMETRY of diffraction (powder diffraction experiments)

1.1) Monochromators

1.2) Calibration of beamline parameters

1.3) Use of unit cell volume for determination of bulk properties (i.e. thermal expansion, etc.)

1.4) Microstructure (i.e. crystallite size)

2) INTENSITY of diffraction

2.1) Quantitative analysis

2.2) Structure determination (powder and single crystals)

3) EXAMPLES

3.1) Diffraction tomography

3.2) Single crystal at extreme conditions

3.3) Single crystal data processing

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Bragg's law

Laue equations

Rietveld fit

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Structure factor

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Software:

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Fit2D

Dioplas

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GSAS

GSAS-II

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- 3.1) Diffraction tomography
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*Crystal structure database
(American Mineralogist database)*

*Single crystal data reduction
(multipurpose – inorganic)*



https://unimi2013-my.sharepoint.com/:f:/g/personal/marco_merlini_unimi_it/IgBIU_djZpY9RliK8yWpamc-AfOLTVCYGXyDZZ_HBo-uf1s?e=F3jlrf



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- Installing GSAS-II: Overview
- GSAS-II Documentation
- Mailing List
- Reporting GSAS-II Bugs
- Customizing GSAS-II
- Help: GSAS-II will not start
- Notes for GSAS-II Developers
- Miscellaneous GSAS-II Links
- GSAS-II Statistics: Usage & Size

Related Topics

Documentation index

- Next: 1. Installing GSAS-II:

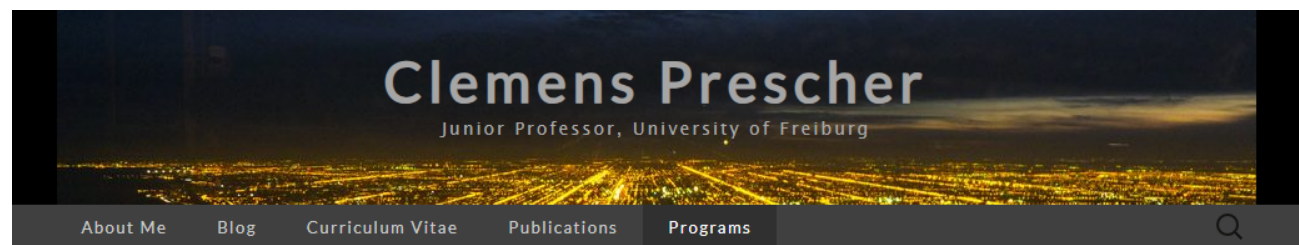
GSAS-II Home Page



Tip: A new section in the GSAS-II web documentation, **Announcements in “GitHub Discussions”** is now in use as a source of information on new capabilities added to GSAS-II.

Welcome to the home page for GSAS-II, a unique and comprehensive open source Python project for determination of crystal structures and diffraction-based materials characterization for crystalline solids on all scales, from perovskites through proteins, using both powder and single-crystal diffraction and with both x-ray and neutron probes. Refinements can combine measurements from laboratory and synchrotron x-rays, as well as constant wavelength or time-of-flight neutron sources. It provides structure solution and refinement, as well as extensive visualization capabilities.

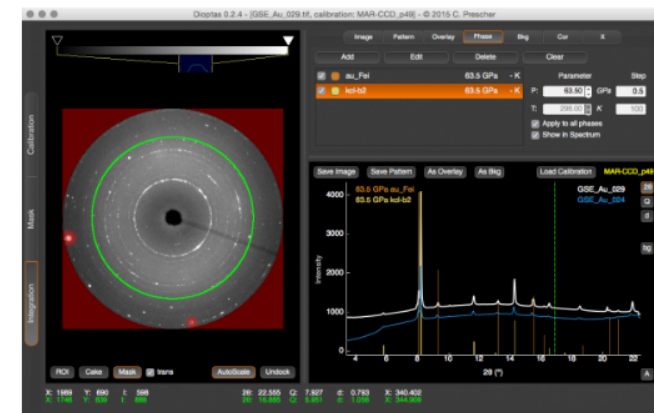
[1. Installing GSAS-II: Overview — GSAS-II v5.6.0 documentation](#)



Dioptas

Dioptas is a Python-based program for on-the-fly data processing and exploration of two-dimensional X-ray diffraction area detector data. It is specifically designed for the large amount of data collected at XRD beamlines at synchrotrons. Its fast data reduction algorithm and graphical data exploration capabilities make it ideal for online data processing during XRD experiments and batch post-processing of large numbers of images.

Dioptas is written with interactivity and speed in mind while still being as versatile as possible. It employs an algorithm for calibration of any possible detector geometry, features easy-to-use masking tools, and offers very fast data exploration and phase analysis capabilities. The tunable calibration procedure enables the calibration of even the most complex geometries, including very large detector tilts, the primary beam being outside of the image and very spotty diffraction pattern of the calibrant. The main part of the software is the opportunity to interactively explore the 2d image and integrated pattern at the same time. The very fast integration algorithm (around 0.1s for an 2048px X 2048px image), a reliable tunable automatic background subtraction algorithm and the possibility to display phase lines make it a viable tool for realtime processing online at the beamline. Thus, enabling very fast decision making during the course of the experiment.





American Mineralogist Crystal Structure Database

This site is an interface to a crystal structure database focused on minerals and solids of interest to mineralogists.

For questions about AMCSD, please [Contact Us](#).

Mineral

Author

Chemistry

Includes:

Excludes:

Cell Parameters and Symmetry

Diffraction Search

General Search

Display ☐ amc long form ☒ amc short form ☐ cif

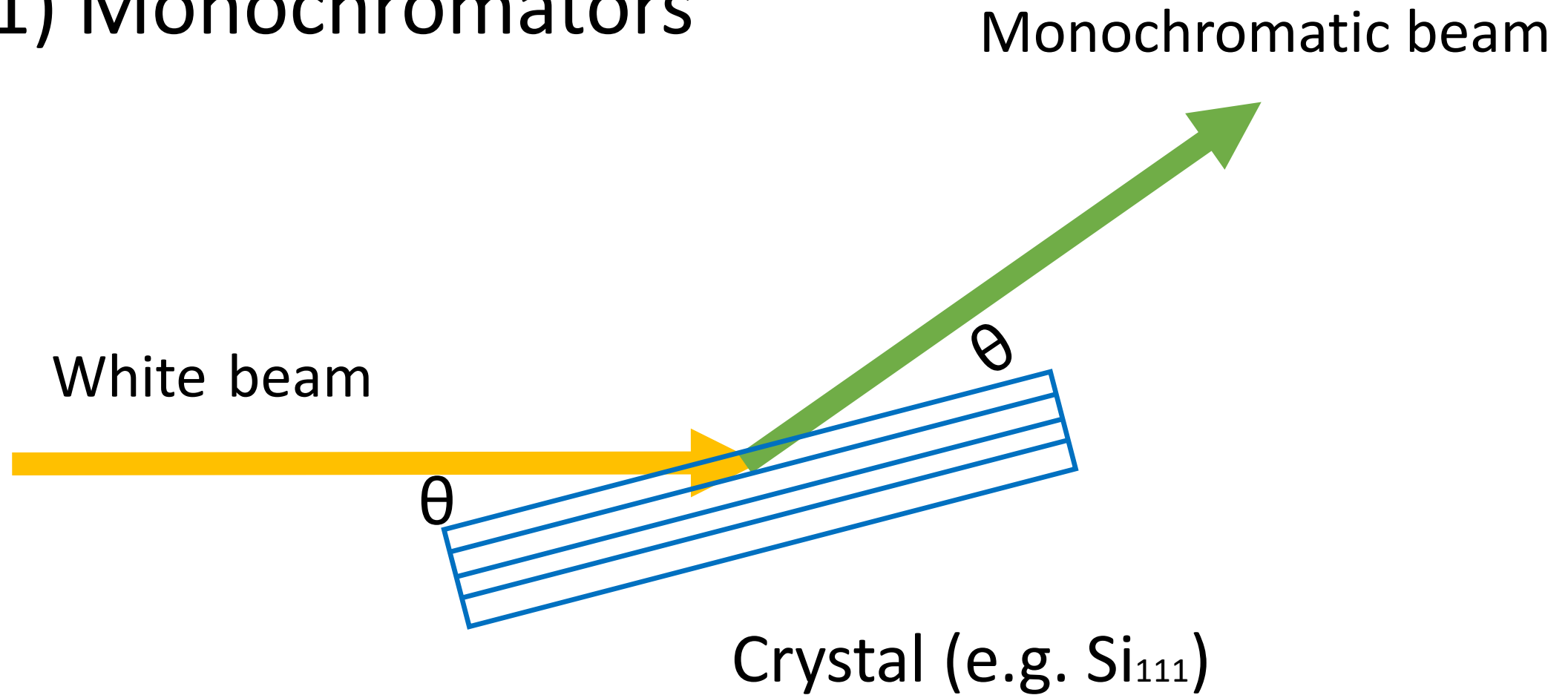
SEARCH

RESET

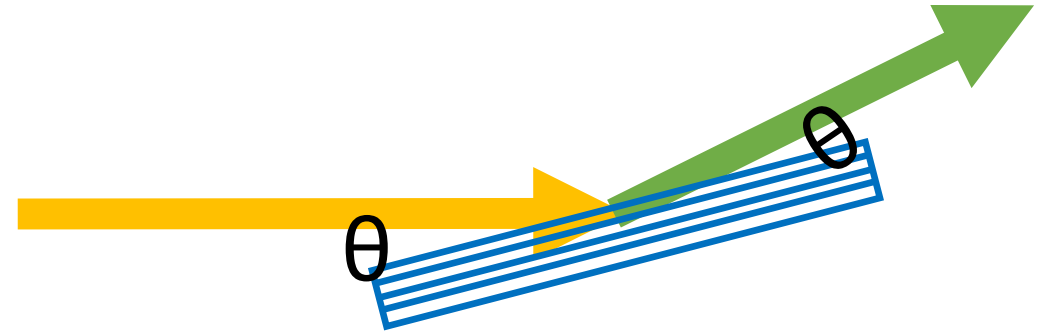
?

[AMCSD – RRUFF – Comprehensive Database of Mineral Data](#)

1.1) Monochromators

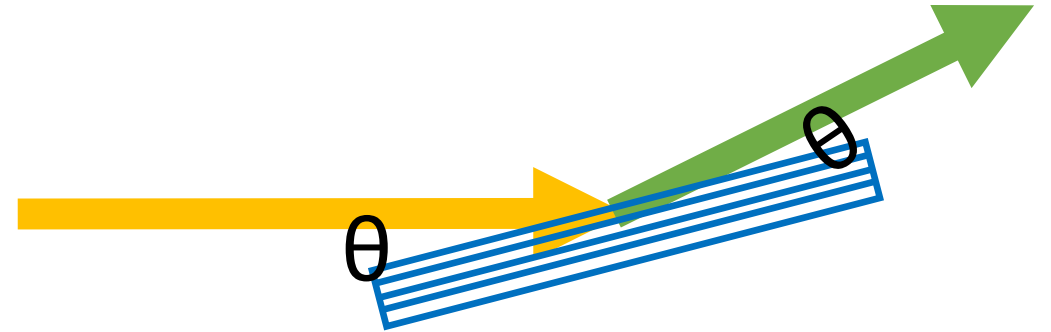


1.1) Monochromators



At which theta angle should be set a Si_{111} monochromator to get 30keV ?

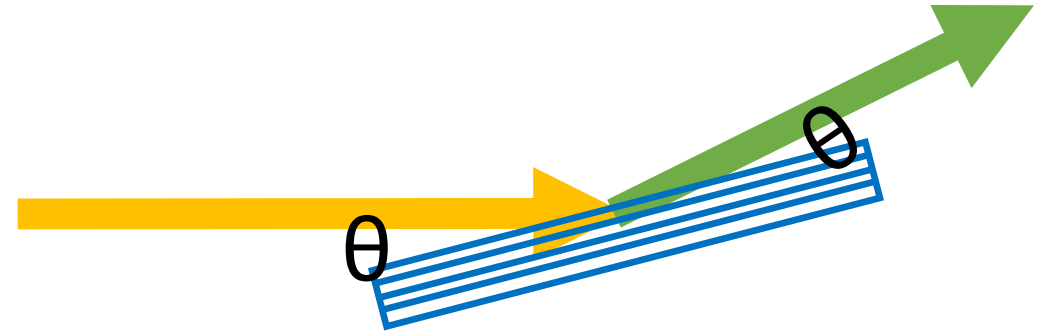
1.1) Monochromators



At which theta angle should be set a Si_{111} monochromator to get 30keV ?

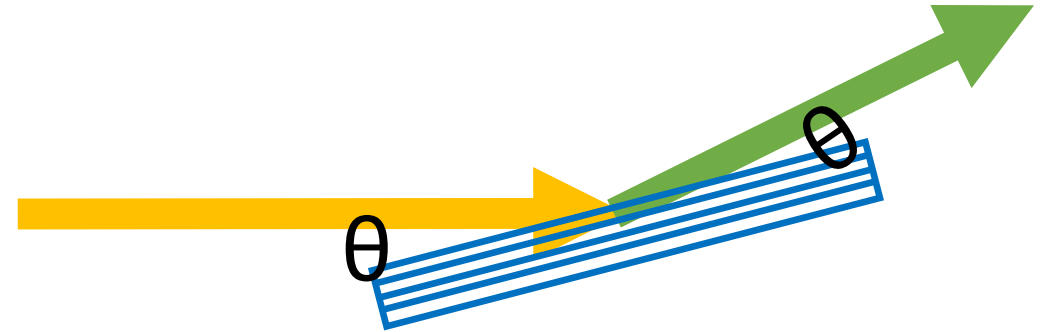
- Need Bragg's law and crystallographic (unit cell) parameters of crystalline silicon

1.1) Monochromators



Bragg's law: $2d_{hkl} \sin\theta = (n)\lambda$

1.1) Monochromators



Bragg's law: $2d_{hkl} \sin\theta = (n)\lambda$

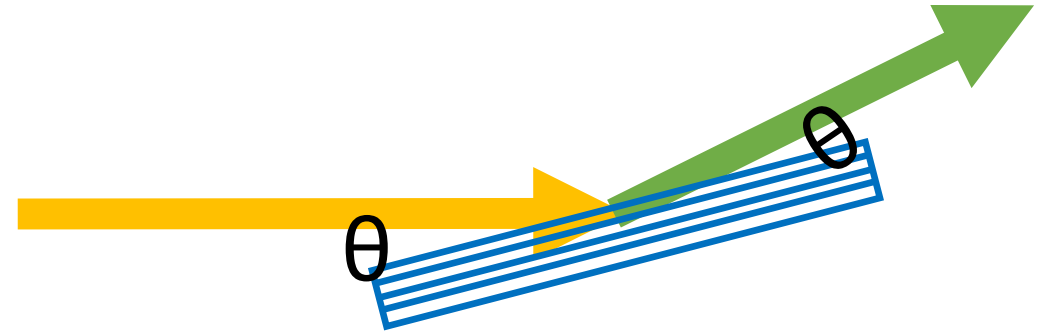
$$E = h\nu = hc/\lambda$$

$$E(\text{keV}) = 12.4 / \lambda(\text{\AA})$$

12.398...

12.39841930...

1.1) Monochromators



Bragg's law: $2d_{hkl} \sin\theta = (n)\lambda$

$$E = h\nu = hc/\lambda$$

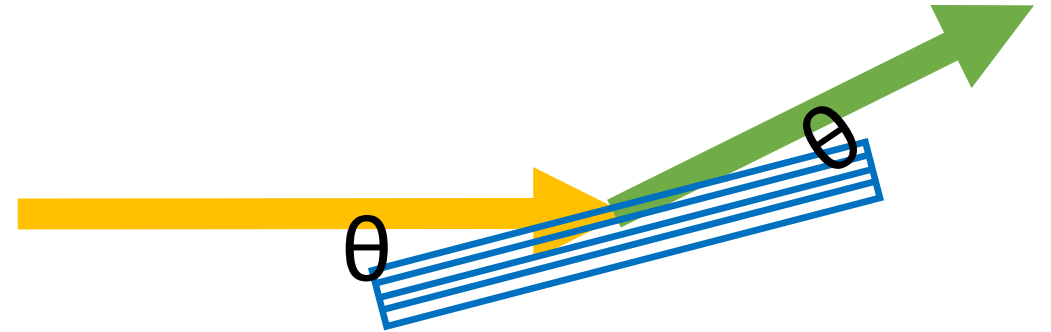
$$E(\text{keV}) = 12.4 / \lambda(\text{\AA})$$

12.398...

12.39841930...

$30 \text{ keV} : \lambda = 0.41328 \text{ \AA}$

1.1) Monochromators



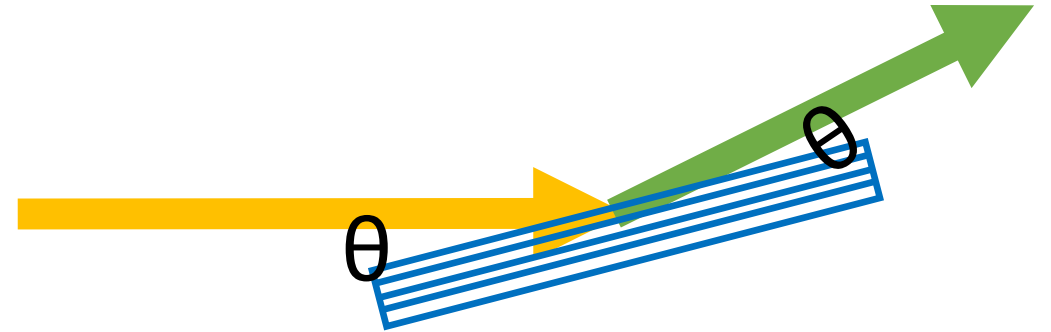
Bragg's law: $2d_{hkl} \sin\theta = (n)\lambda$

Silicon: cubic, $a = 5.43102 \text{ \AA}$

$$1/d^2 = (h^2 + k^2 + l^2)/a^2$$

$$d_{111} = 3.13560 \text{ \AA}$$

1.1) Monochromators



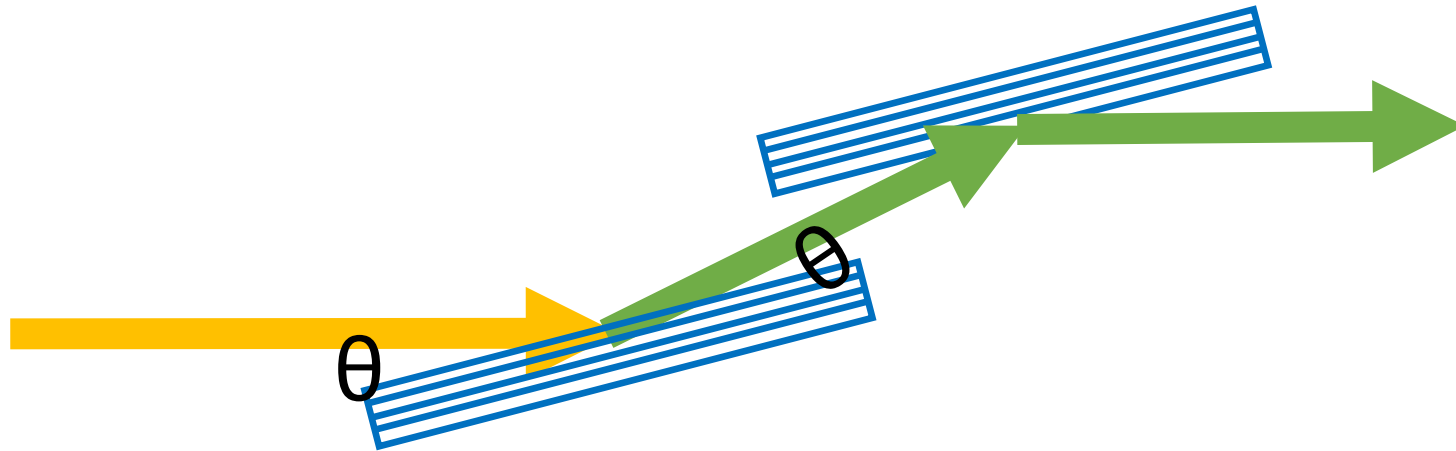
Bragg's law: $2d_{hkl} \sin\theta = (n)\lambda$

$$\lambda = 0.41328 \text{ \AA}$$

$$d_{111} = 3.13560 \text{ \AA}$$

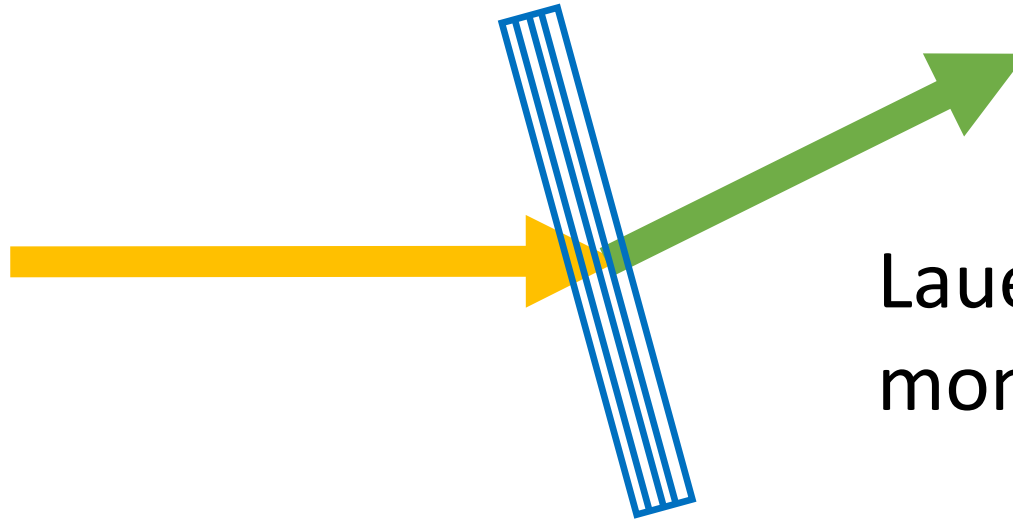
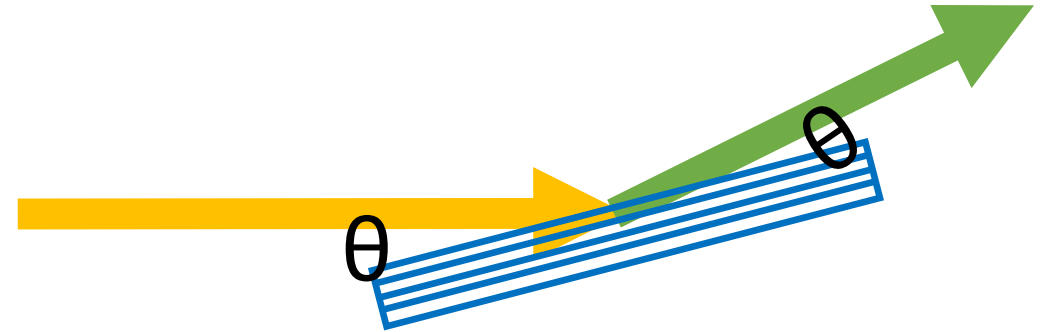
$$\Theta = 3.7786^\circ$$

1.1) Monochromators



Double parallel monochromators

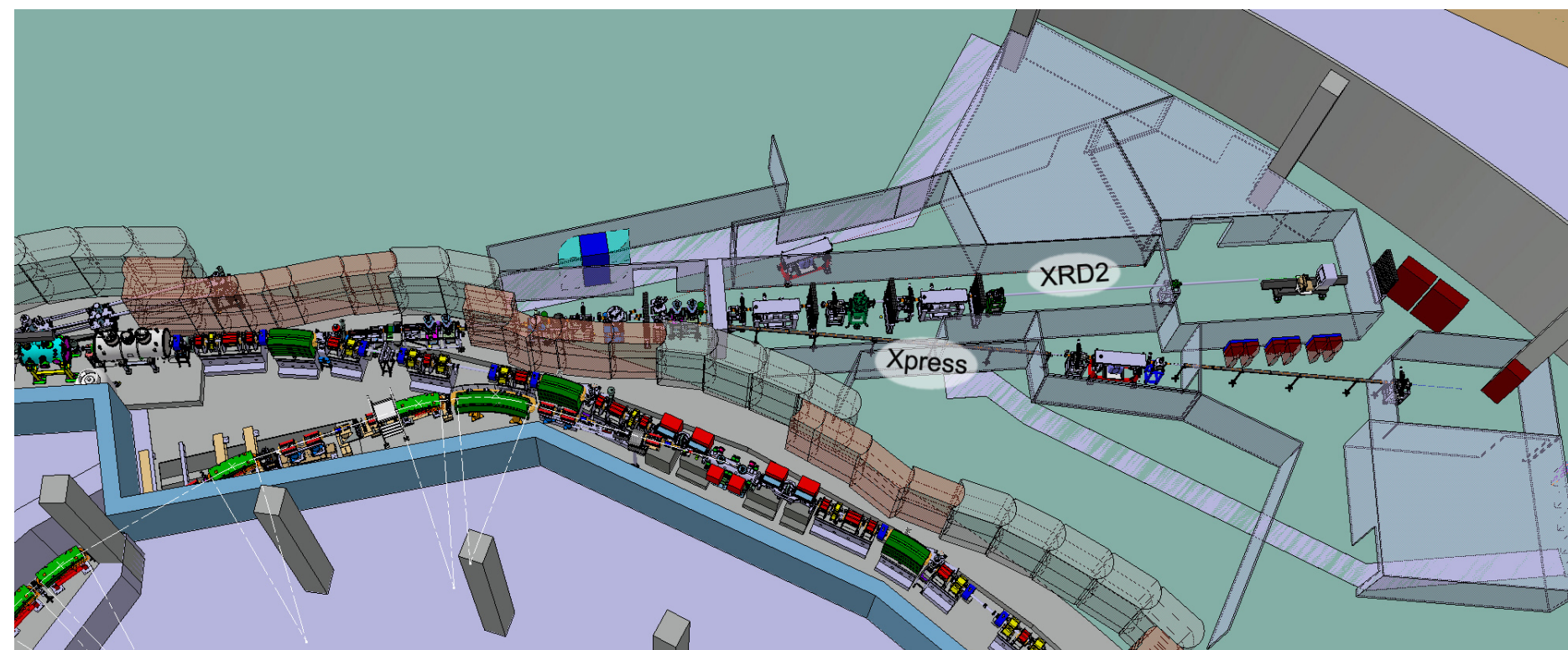
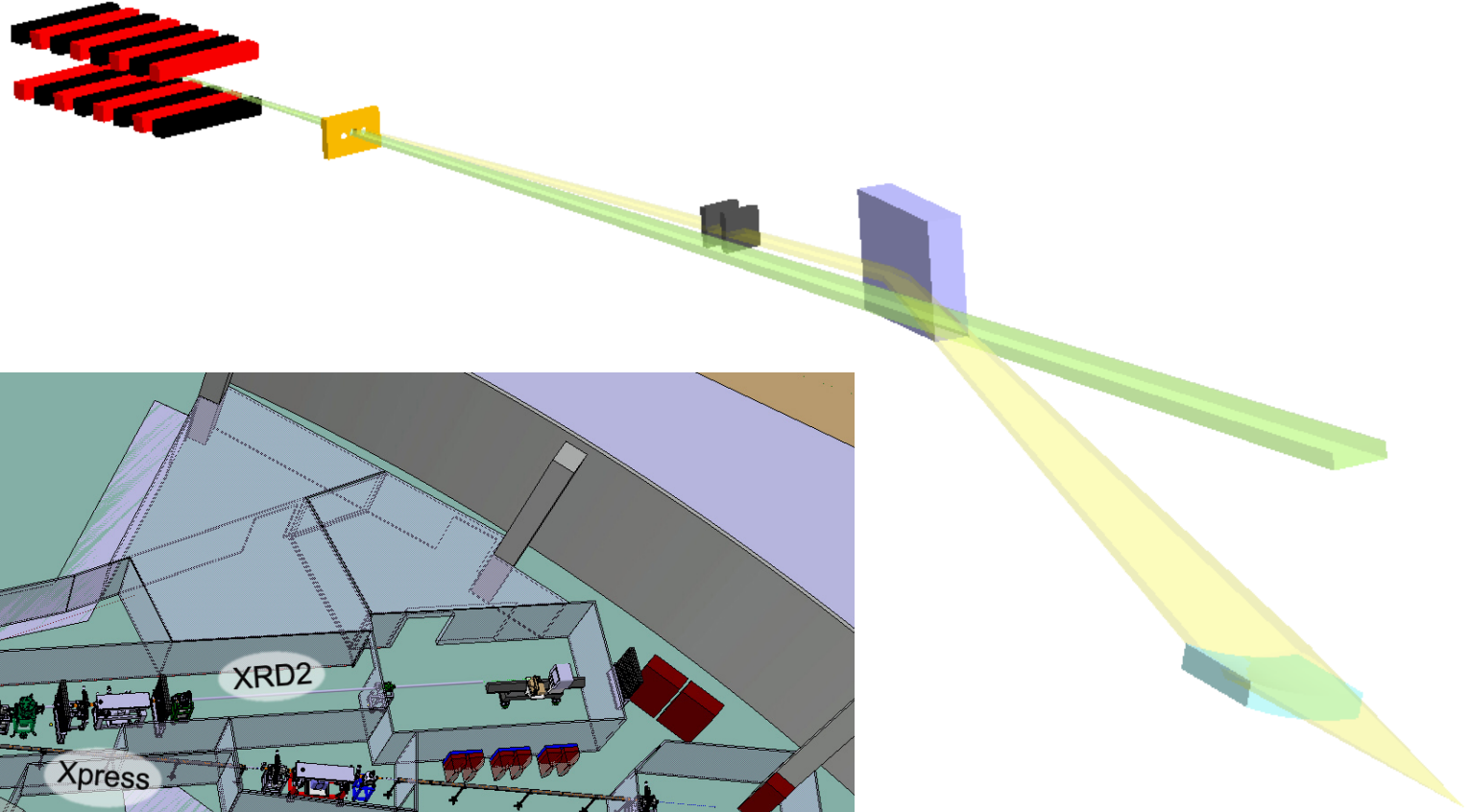
1.1) Monochromators



Laue geometry
monochromator

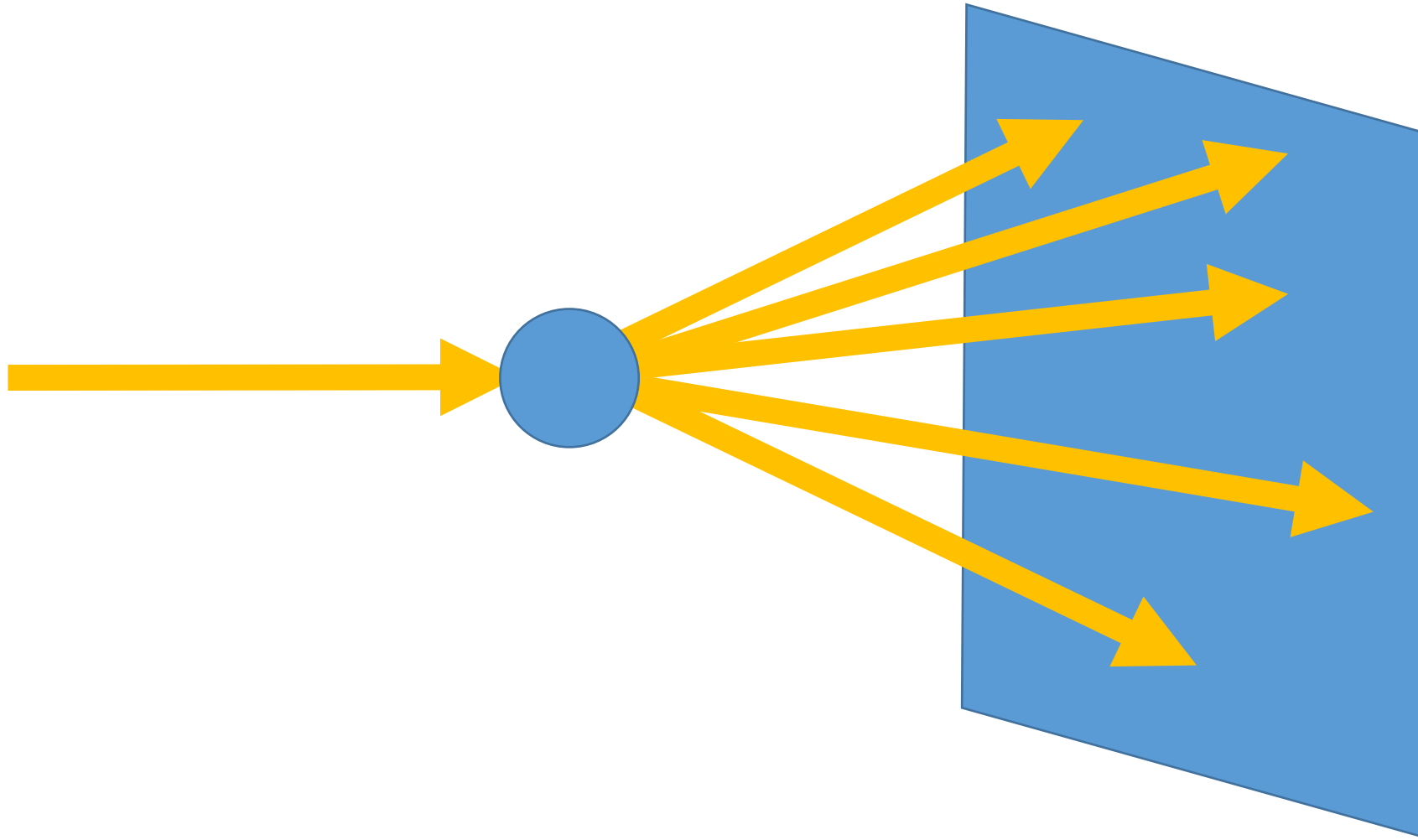
Or single monochromator for
specific purposes (i.e. two
beamlines on single source)

1.1) Monochromators

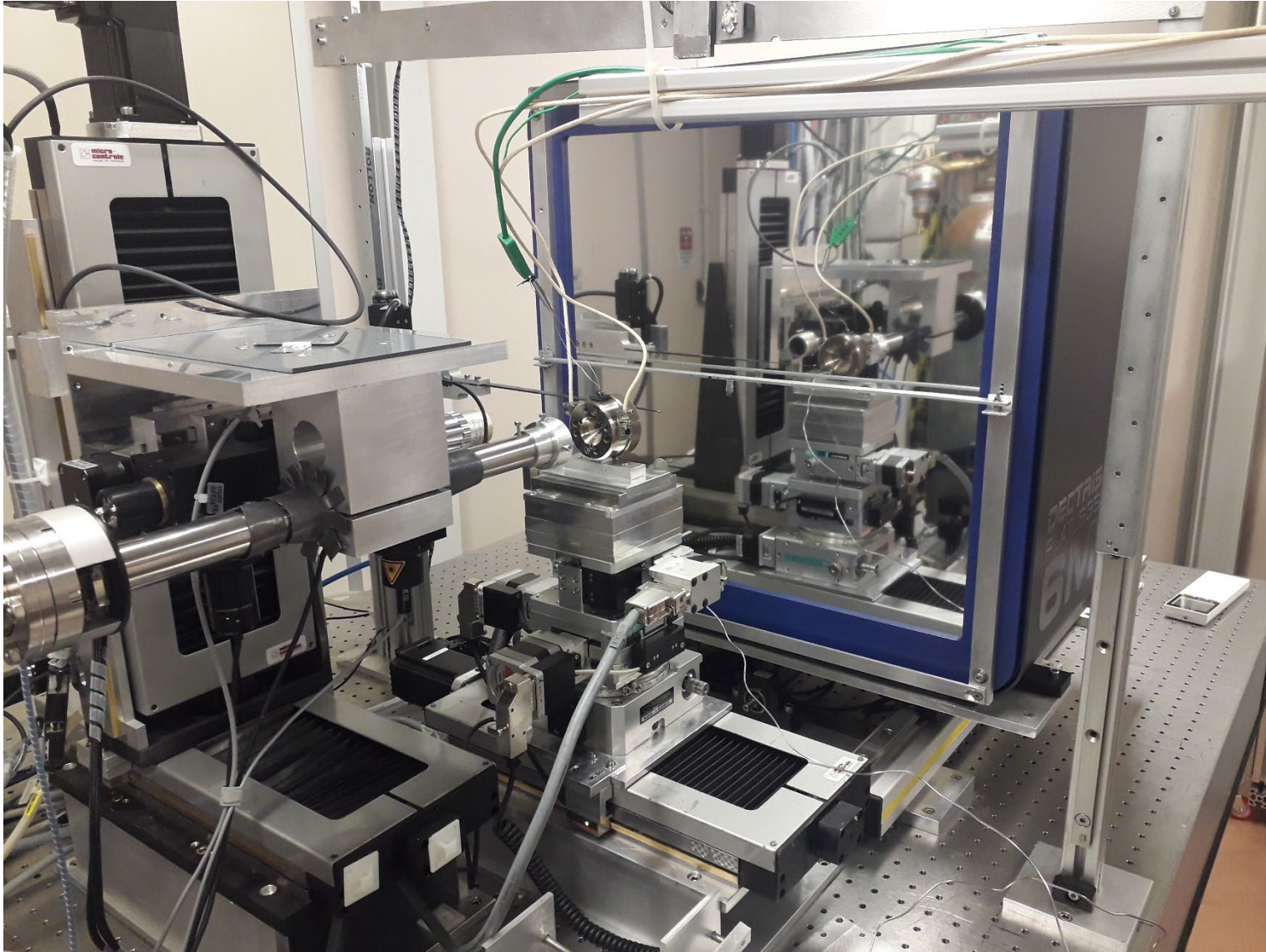


Courtesy of A. Lausi & P. Lotti

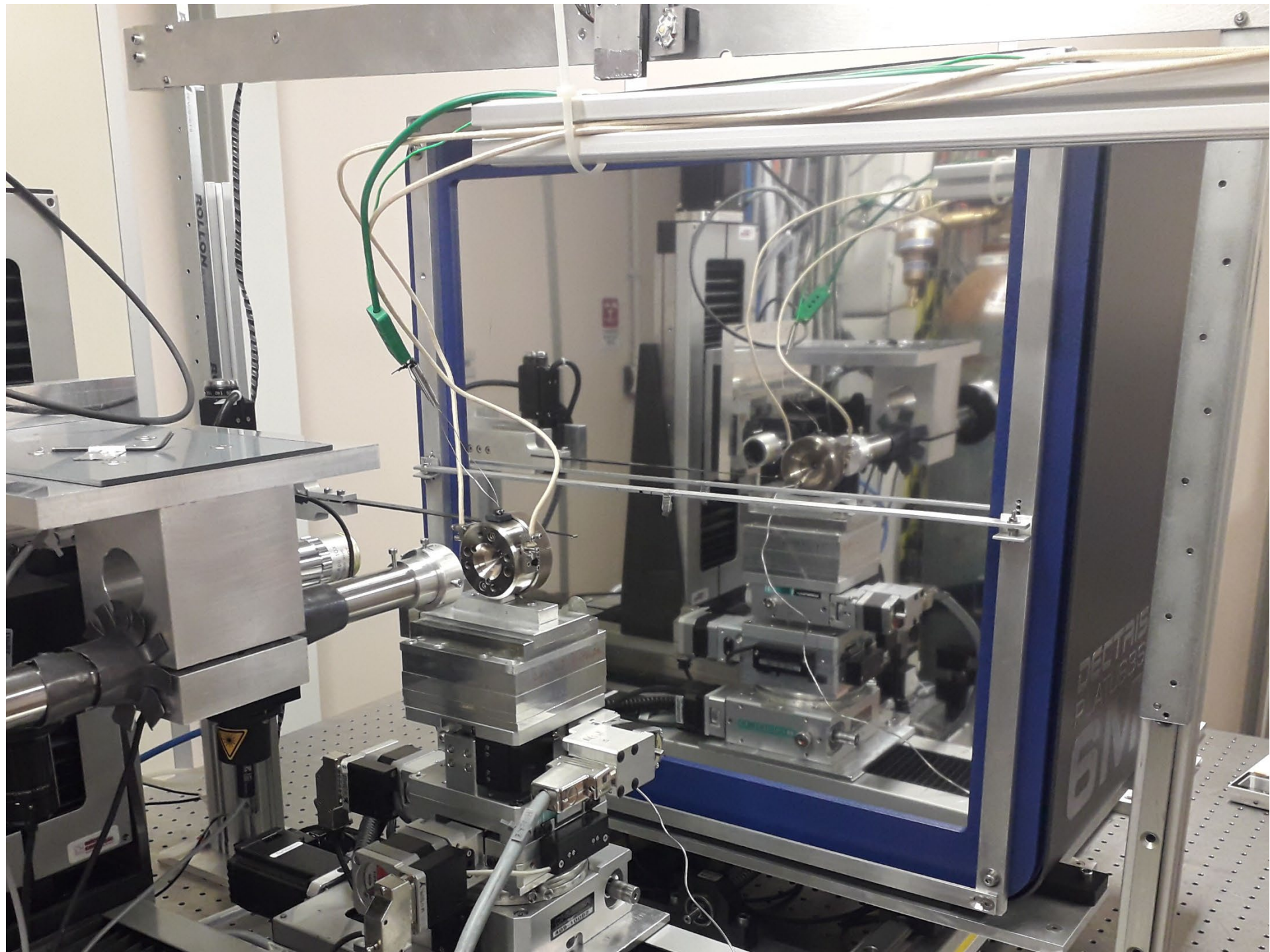
1.2) Calibration of beamline parameters

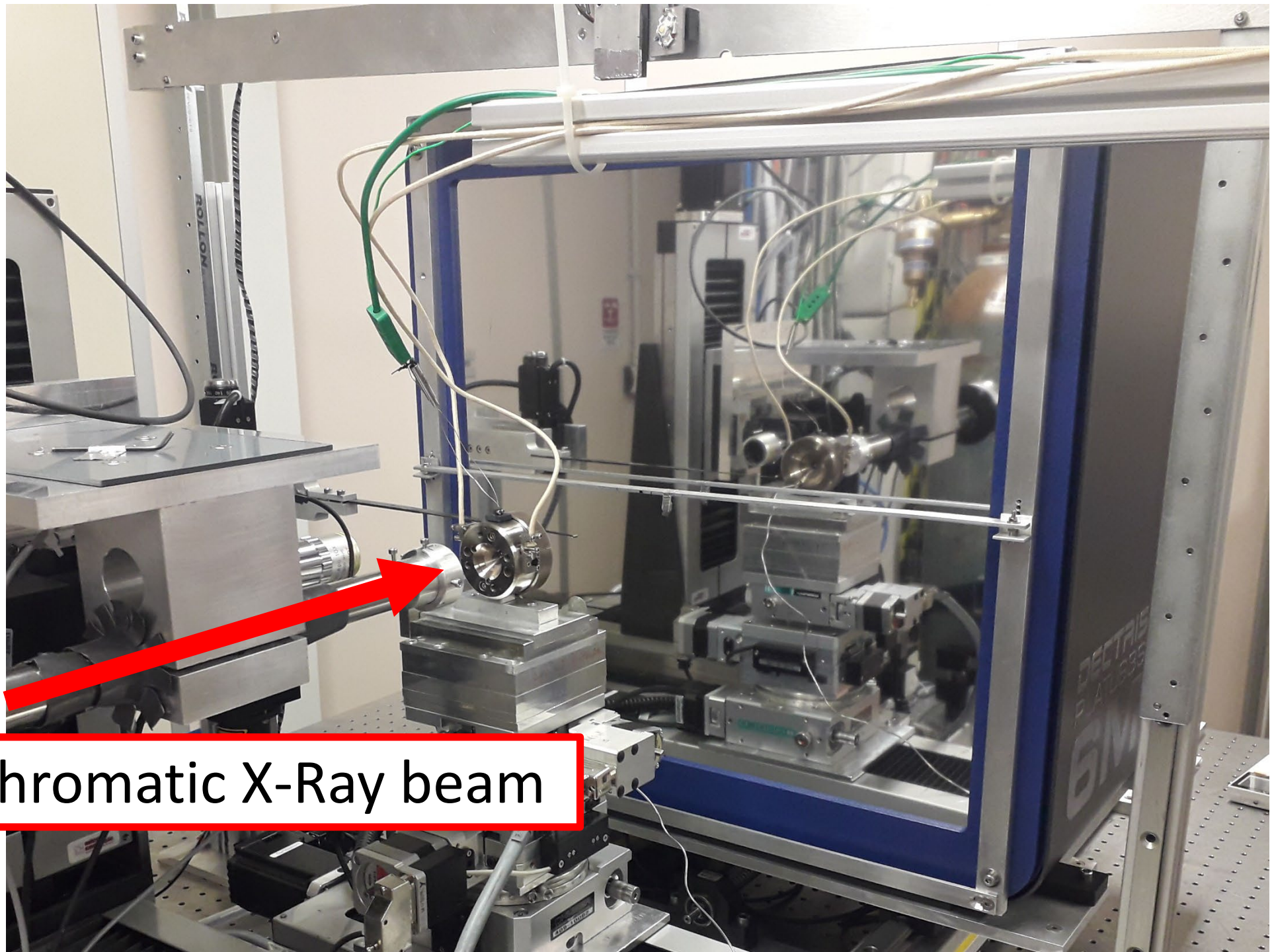


1.2) Calibration of beamline parameters

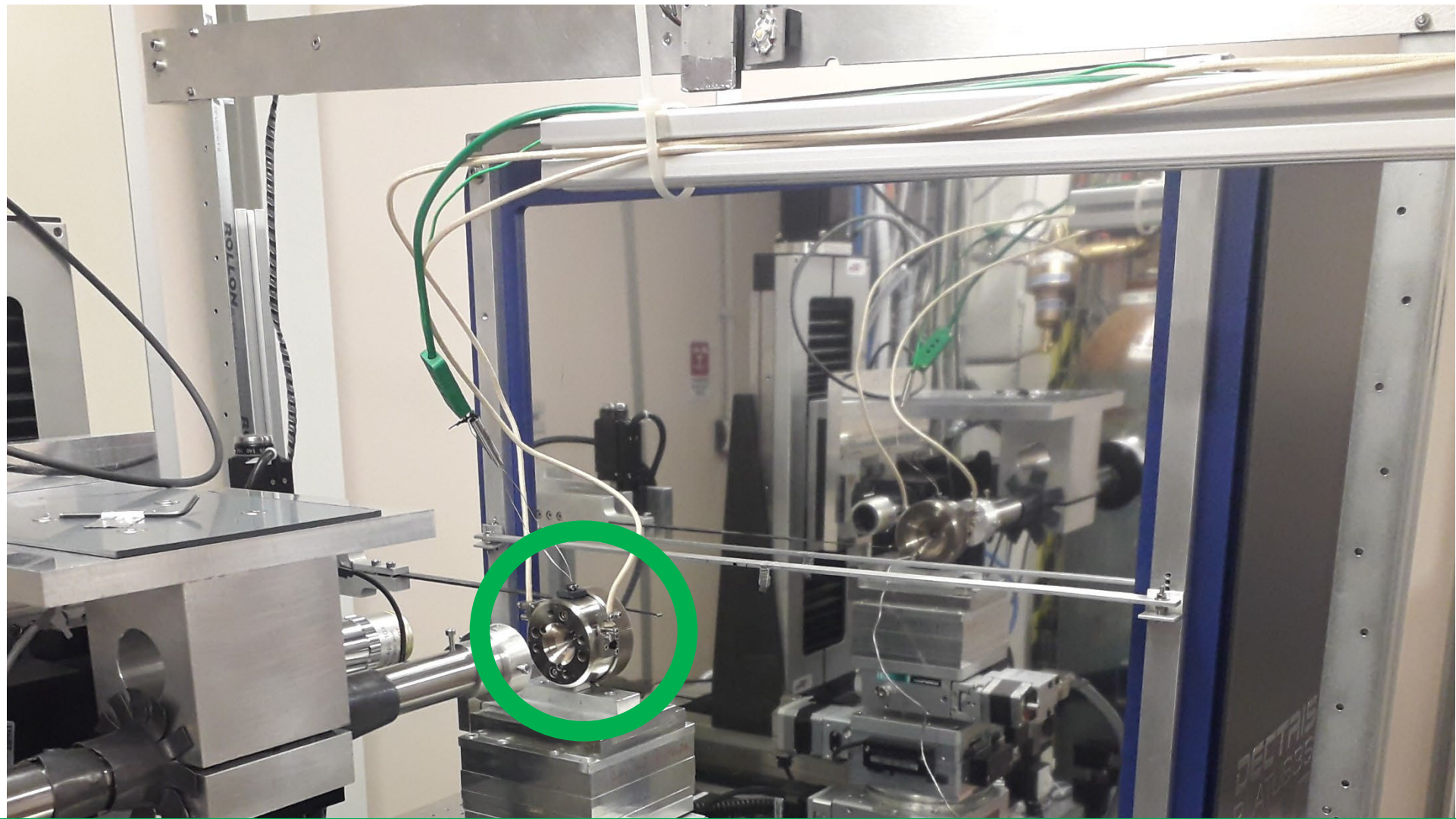


XPRESS @ Elettra



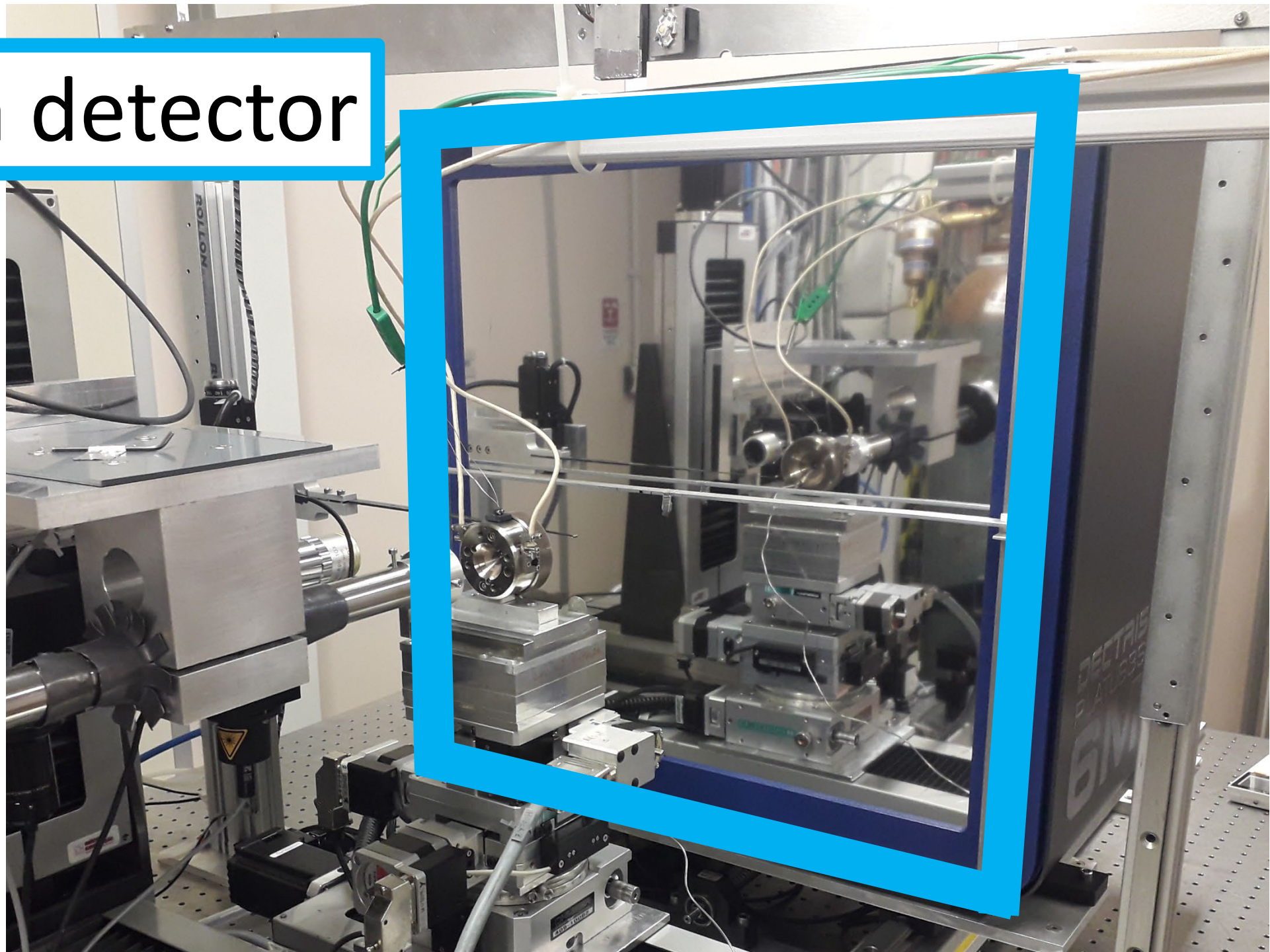


Monochromatic X-Ray beam

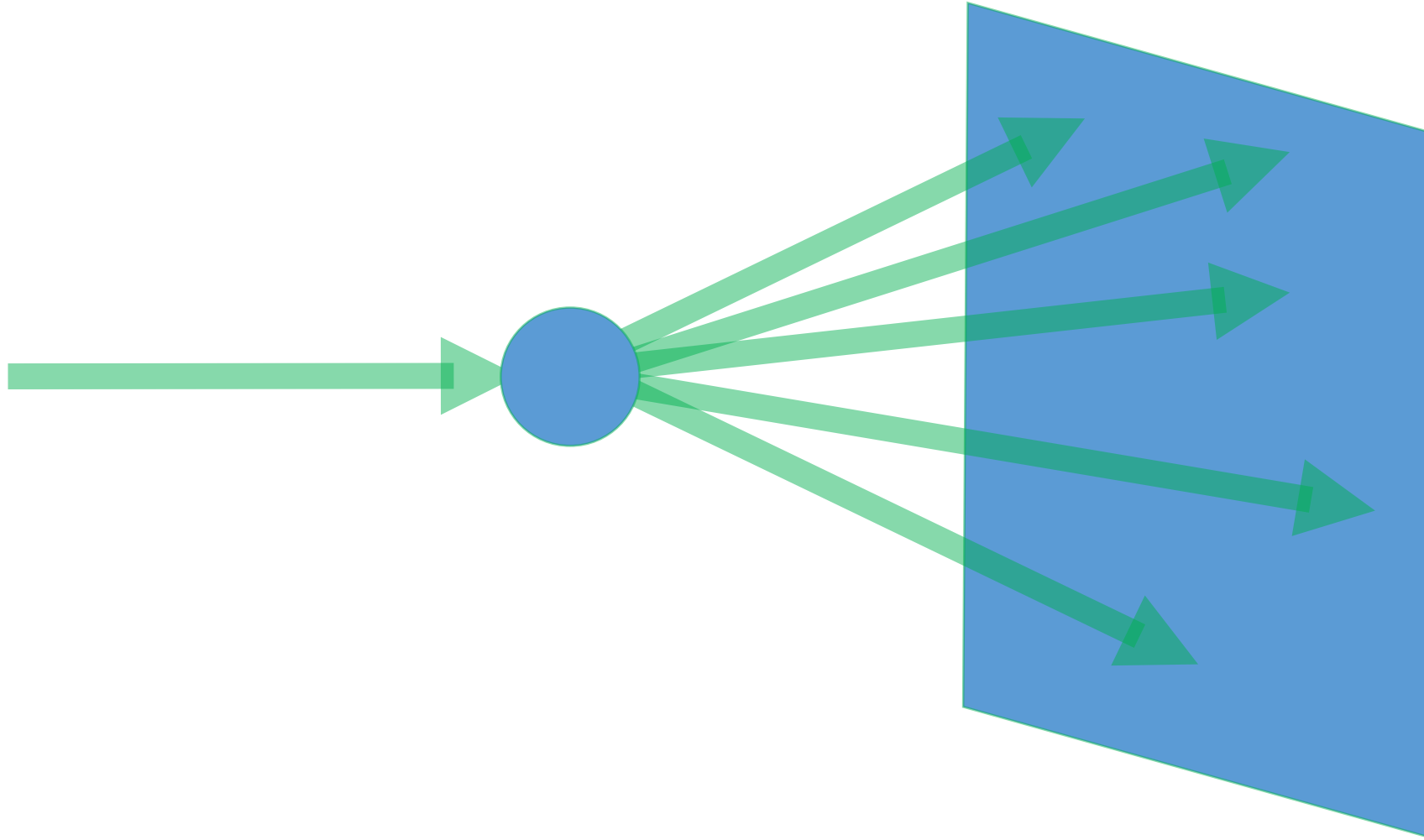


Sample
(High pressure / High temperature Diamond Anvil Cell)

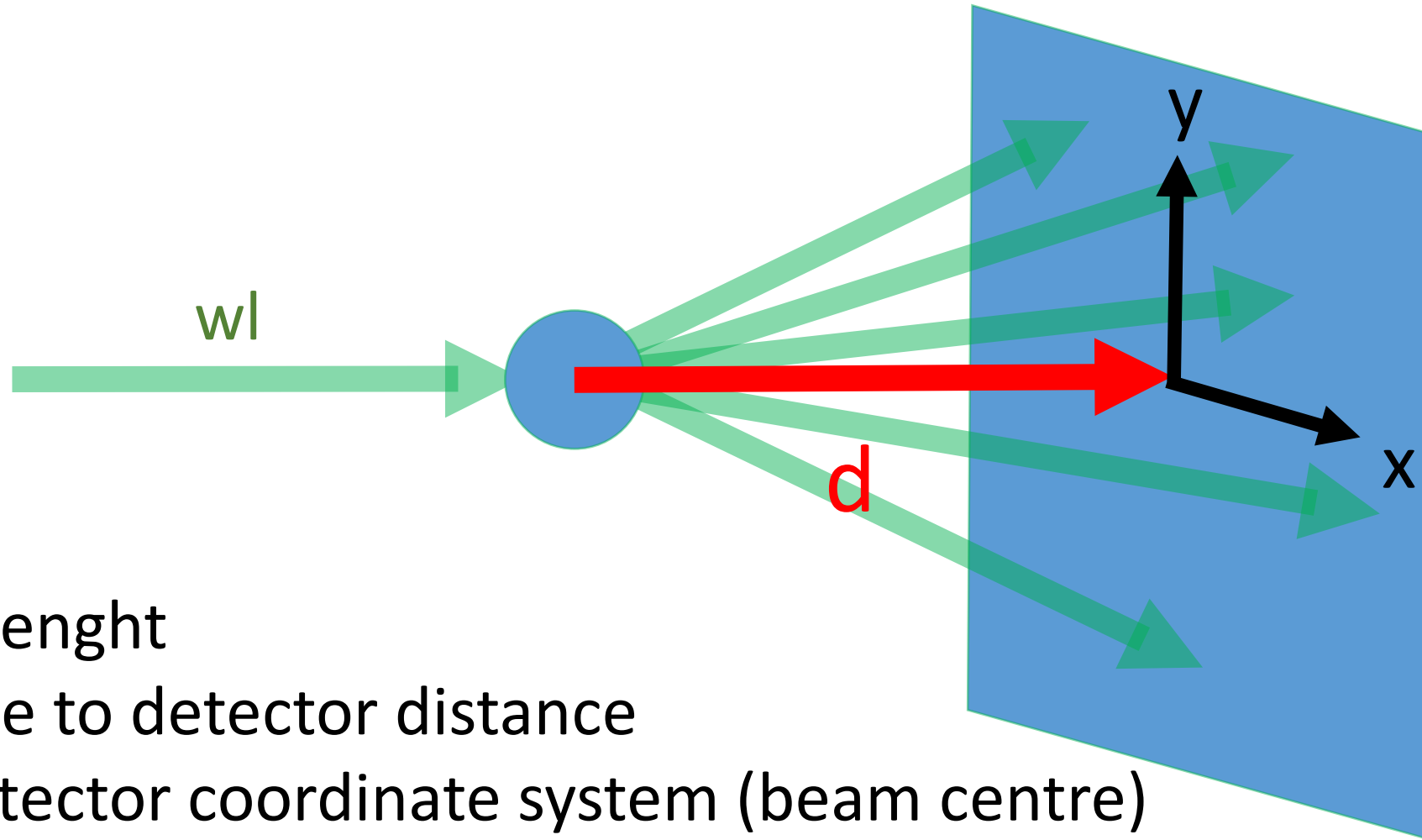
Area detector



1.2) Calibration of beamline parameters



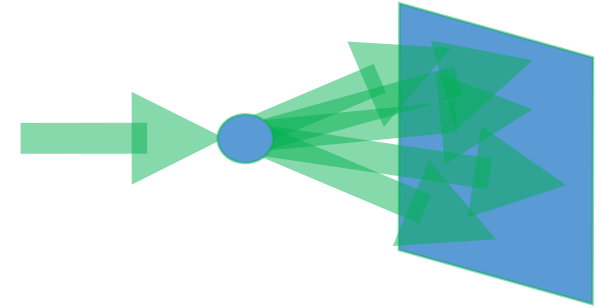
1.2) Calibration of beamline parameters



- Wavelength
- Sample to detector distance
- X,Y detector coordinate system (beam centre)
- Detector tilt

1.2) Calibration of beamline parameters

- Calibration against a powder (single crystal) reference sample with well known lattice parameter
- Operation normally done by beamline staff, but users should know how to do
- Standards: Silicon, LaB₆, CeO₂.....
- Software: FIT2D, Dioptas



1.2) Calibration of beamline parameters

1 of 1

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[View at Publisher](#)

High Pressure Research

Volume 14, Issue 4-5, 1996, Pages 235-248

Two-dimensional detector software: From real detector to idealised image or two-theta scan (Article)

Hammersley, A.P., Svensson, S.O., Hanfland, M., Fitch, A.N., Häusermann, D. 

Europ. Synchrotr. Radiation Facility, BP 220, 38043 Grenoble Cedex, France

Abstract

Detector systems introduce distortions into acquired data. To obtain accurate angle and intensity information, it is necessary to calibrate, and apply corrections. Intensity non-linearity, spatial distortion, and non-uniformity of intensity response, are the primary considerations. It is better to account for the distortions within scientific analysis software, but often it is more practical to correct the distortions to produce 'idealised' data. Calibration methods and software have been developed for single crystal diffraction experiments, using both approaches. For powder diffraction experiments the additional task of converting a two-dimensional image to a one-dimensional spectrum is used to allow Rietveld analysis. This task may be combined with distortion correction to produce intensity information and error estimates. High-pressure experiments can introduce additional complications and place new demands on software. Flexibility is needed to be able to integrate different angular regions separately, and to produce profiles as a function of angle of azimuth. Methods to cope with awkward data are described, and examples of the techniques applied to data from high pressure experiments are presented.

[View references \(32\)](#)

Fit2D

Metrics 

[View all metrics >](#)

3054  Citations in Scopus
99th Percentile

5.46  Field-Weighted Citation
Impact



PlumX Metrics

Usage, Captures, Mentions,
Social Media and Citations
beyond Scopus.

Cited by 3054 documents

[Investigation of the precipitation of Na₂SO₄ in supercritical water](#)

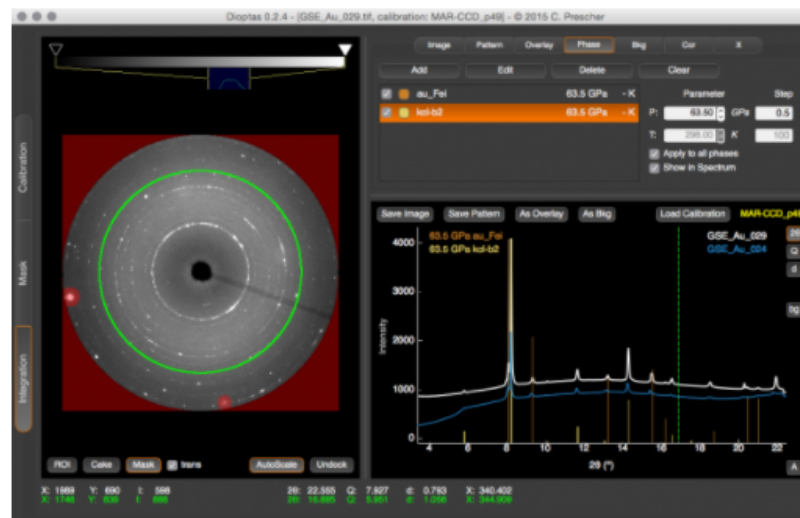
Voisin, T. , Erriguible, A. , Philippot, G.
(2017) *Chemical Engineering Science*

[The critical role of Si doping in enhancing the stability of M₆C carbides](#)

Dioptas

Dioptas is a Python-based program for on-the-fly data processing and exploration of two-dimensional X-ray diffraction area detector data. It is specifically designed for the large amount of data collected at XRD beamlines at synchrotrons. Its fast data reduction algorithm and graphical data exploration capabilities make it ideal for online data processing during XRD experiments and batch post-processing of large numbers of images.

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Distribution

Dioptas is mainly distributed via an open-source repository at <http://github.com/Dioptas/Dioptas>. However, since some of the required packages can be hard to install on some operating systems by non-expert end-users, we also provide executable packages which can be downloaded by using the link below. Dioptas is cross-platform compatible and has been tested on Windows 7, Windows 8, 10, Mac OS X and Linux Debian systems. Dioptas has a very fast-growing user base and is currently employed for online data processing and post experiment data analysis at CARS(Sectors 13–15, APS), HPCAT (Sector 16, APS), ID27 (ESRF), ID9 (ESRF), ID31 (ESRF) and ECB P02.2 (Petra III). Furthermore, non-high pressure beamlines and in-house laboratories are starting to adapt it.

Publications

A paper about Dioptas has been published in High Pressure Research:

- Prescher, C., Prakapenka, V.B., 2015. DIOPTAS : a program for reduction of two-dimensional X-ray diffraction data and data exploration. *High Press. Res.* 35:3, 223–230. [link](#)

- Silicon NIST collected at XPRESS beamline (Elettra)
 - Pilatus 6M area detector
 - Approximate sample to detector distance: 250 mm (from uncalibrated motor position)
 - Beam energy: ~ 25 keV (i.e. ~ 0.495)
 - Pixel size: 0.172x0.172 mm
-
- Using Fit2D and Dioptas to calibrate experimental geometry and integrate powder diffraction from samples



Copyright 1987-2016 Andy Hammersley / ESRF

Use of FIT2D implies acceptance of

the " Conditions of Use "

(Click on "CONDITIONS")

Note: The text window can

contain important

information !

V18.002

CONDITIONS

I ACCEPT

HELP

DON'T ACCEPT



Image Cake Pattern

Load File

Calibration Parameters

Start values

Distance: 200.000 nm ☒
 Wavelength: 0.334400 Å ☐
 Polarization: 0.990
 Pixel width: 79 µm
 Pixel height: 79 µm
 Calbrant: LaB6

Rotate +90

Rotate -90

Flip horizontal

Flip vertical

Reset transformations

Peak Selection

Current Ring Number: 1

☒ automatic increase

☐ automatic peak search

☒ single peak search

Search size: 10

Undo

Clear All Peaks

Refinement Options

☒ automatic refinement

☐ use mask

☐ transparent

Peak Search Algorithm: Massif

Delta 2Th: 0.1

Intensity Mean Factor: 3.00

Intensity Limit: 55000

Number of rings: 15

Distortion Correction

Load Splinefile

None

pyFAI Parameters

Fit2d Parameters

Calibrate

Refine

x: 1976.2 y: 2105.2

Load Calibration

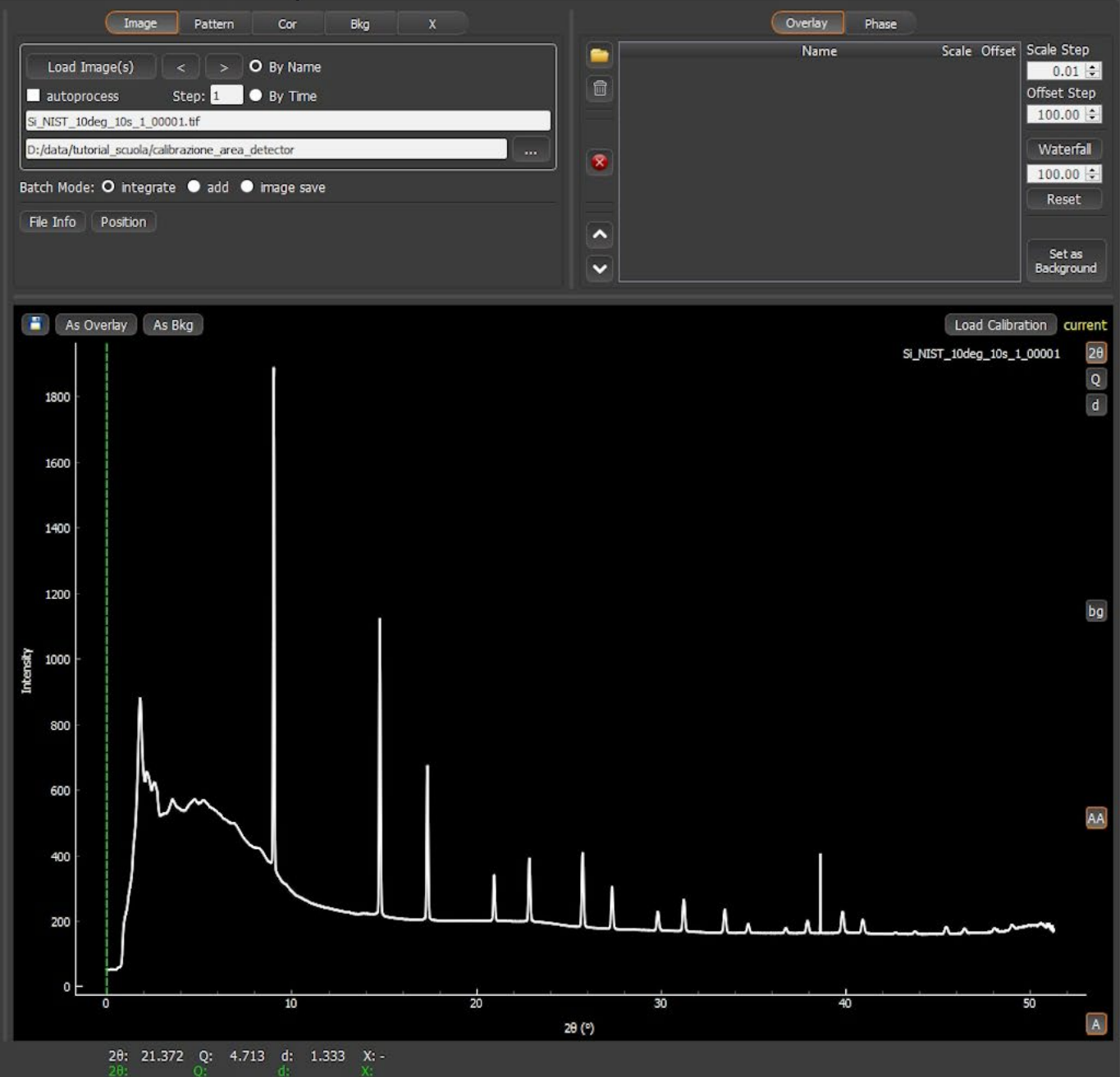
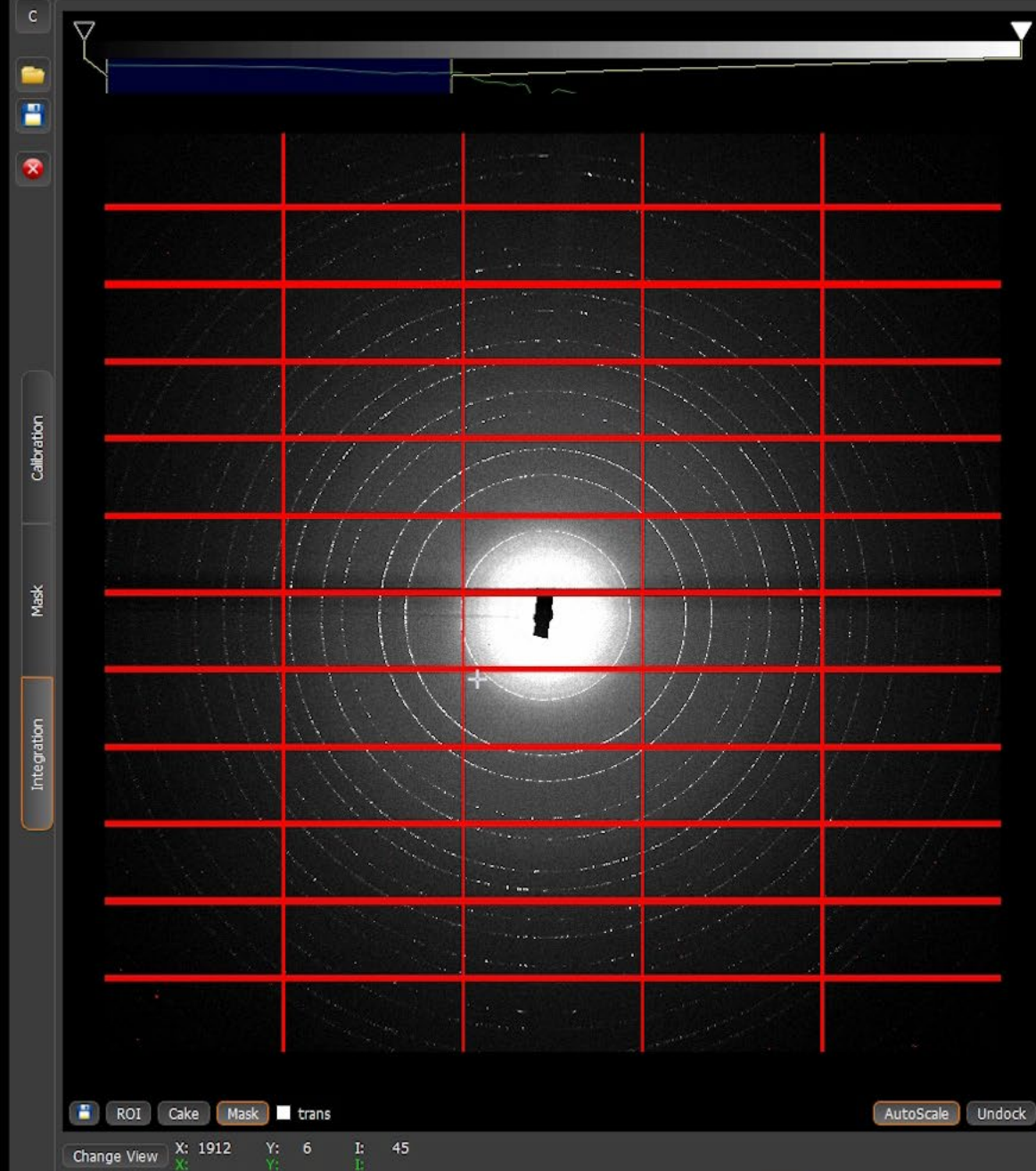
Save Calibration

Calibration

Mask

Integration

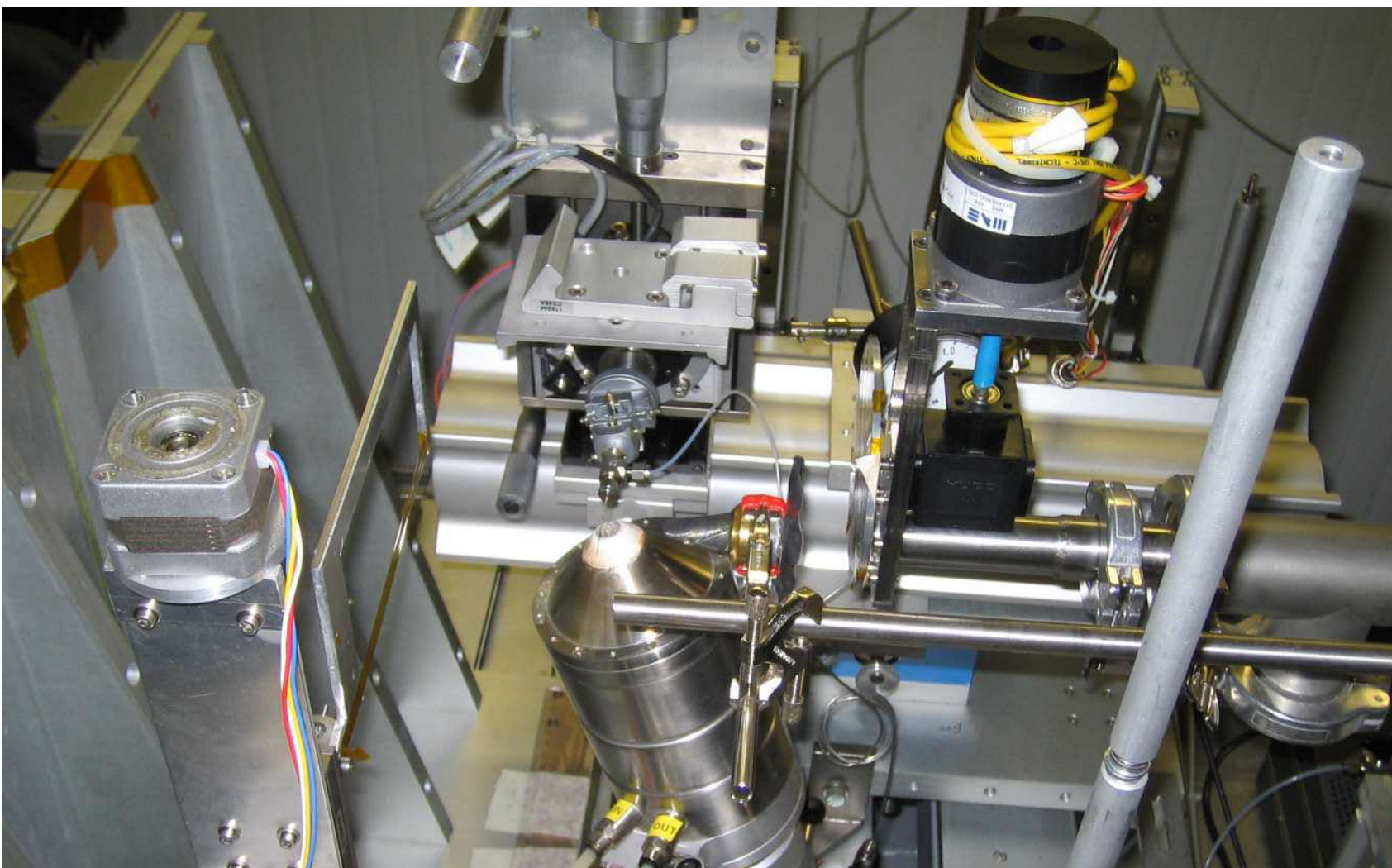
Integration of sample XRPD



1.3) Use of unit cell volume for determination of bulk properties: thermal expansion

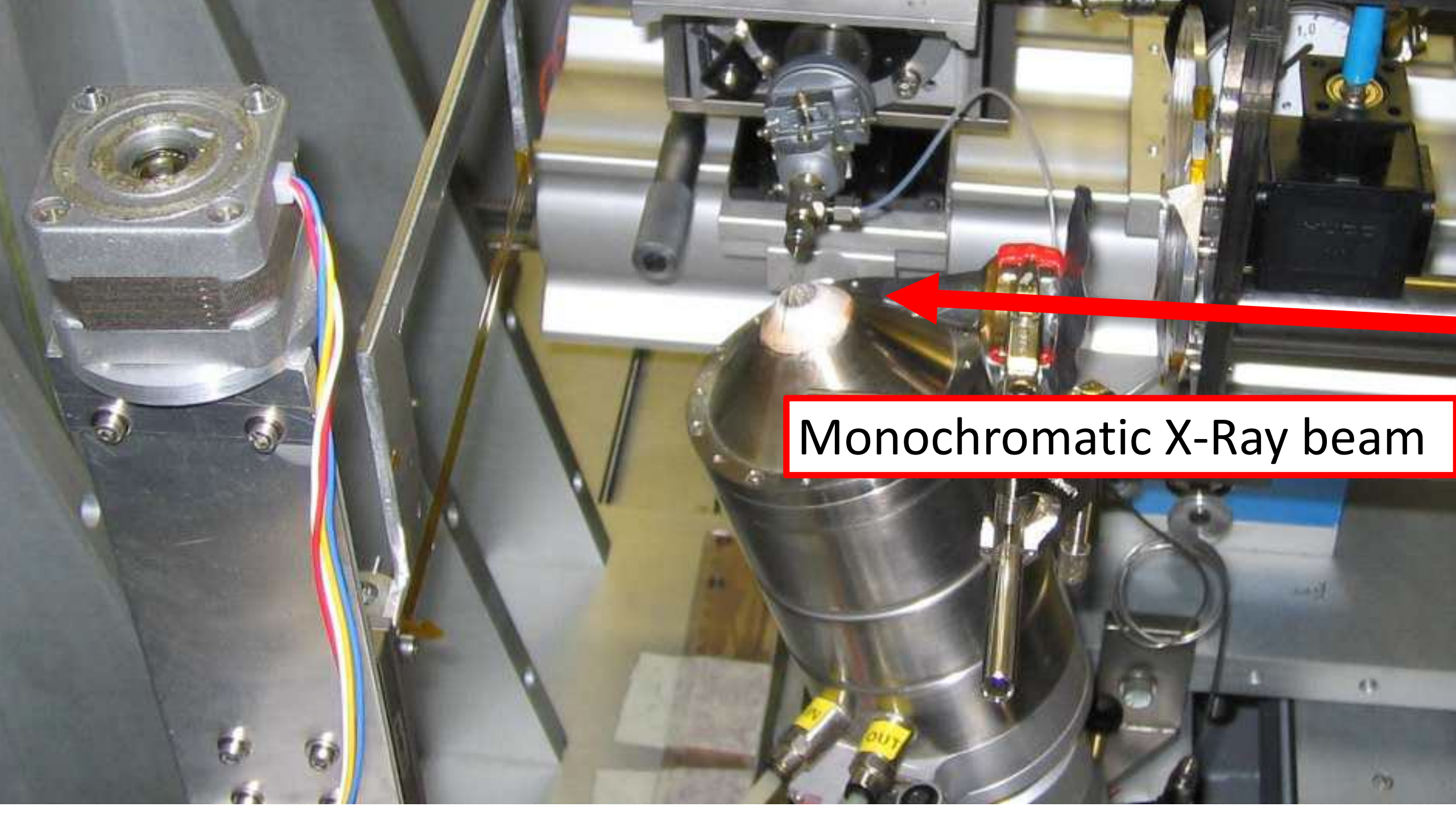
$$\begin{aligned}\text{Thermal expansion: } \alpha &= 1/V (\partial V / \partial T) \\ &= \partial \ln V / \partial T\end{aligned}$$

Determination of unit cell volume at different temperatures

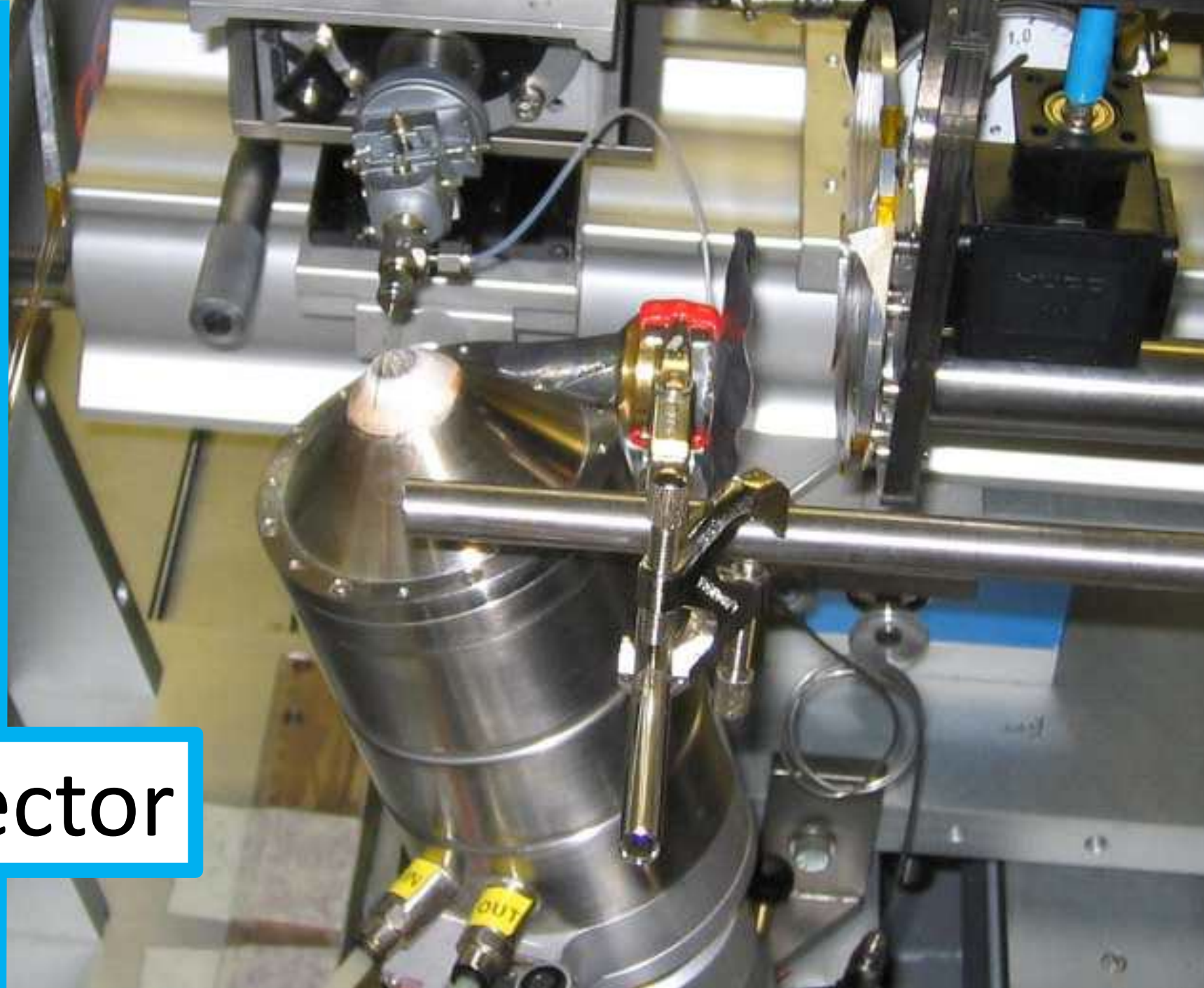


«Hystorical» (2005) beamline setup for HT X-ray powder diffraction @ GILDA beamline (CRG beamline – ESRF, now LISA beamline)

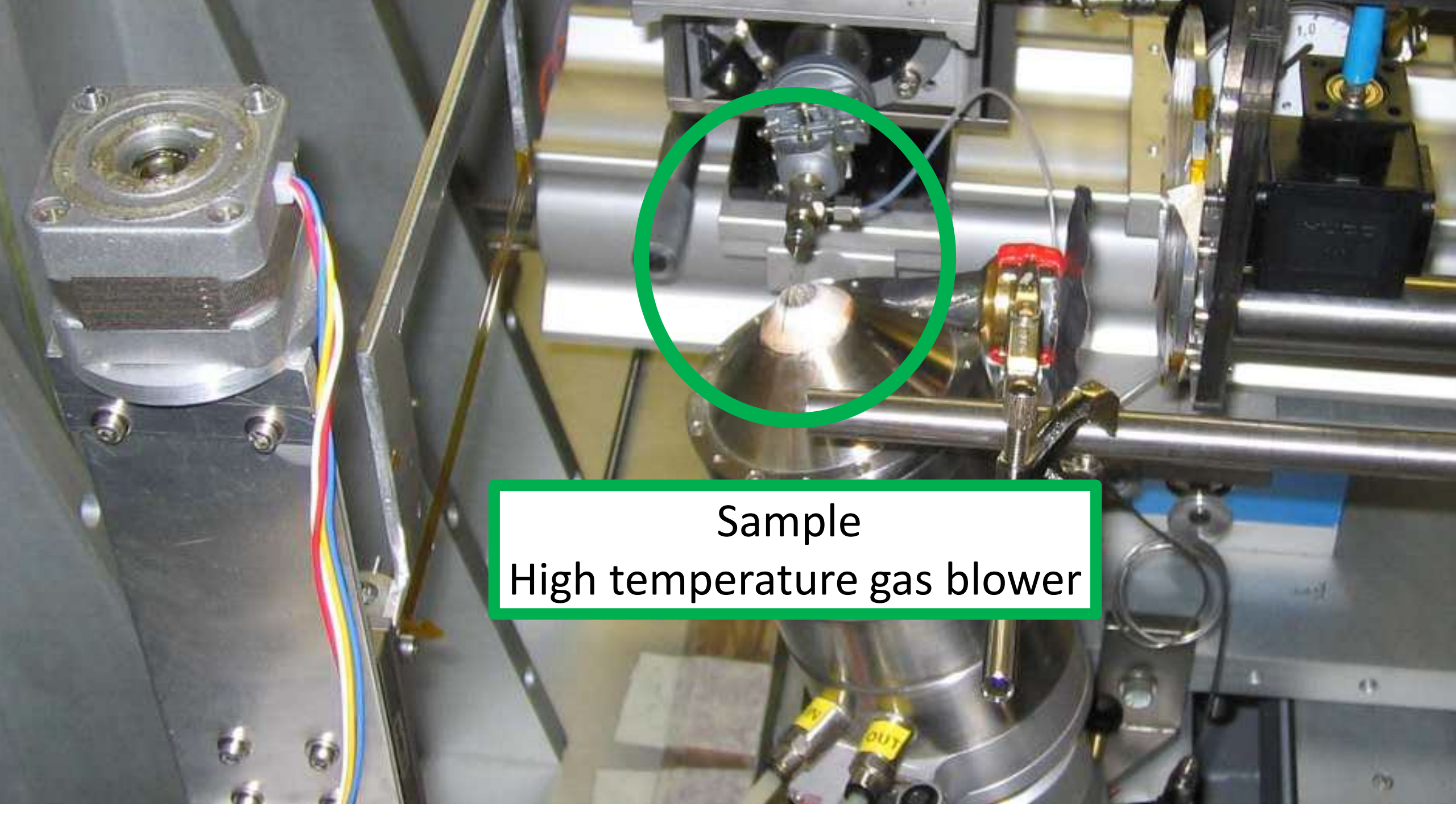




Monochromatic X-Ray beam



Area detector

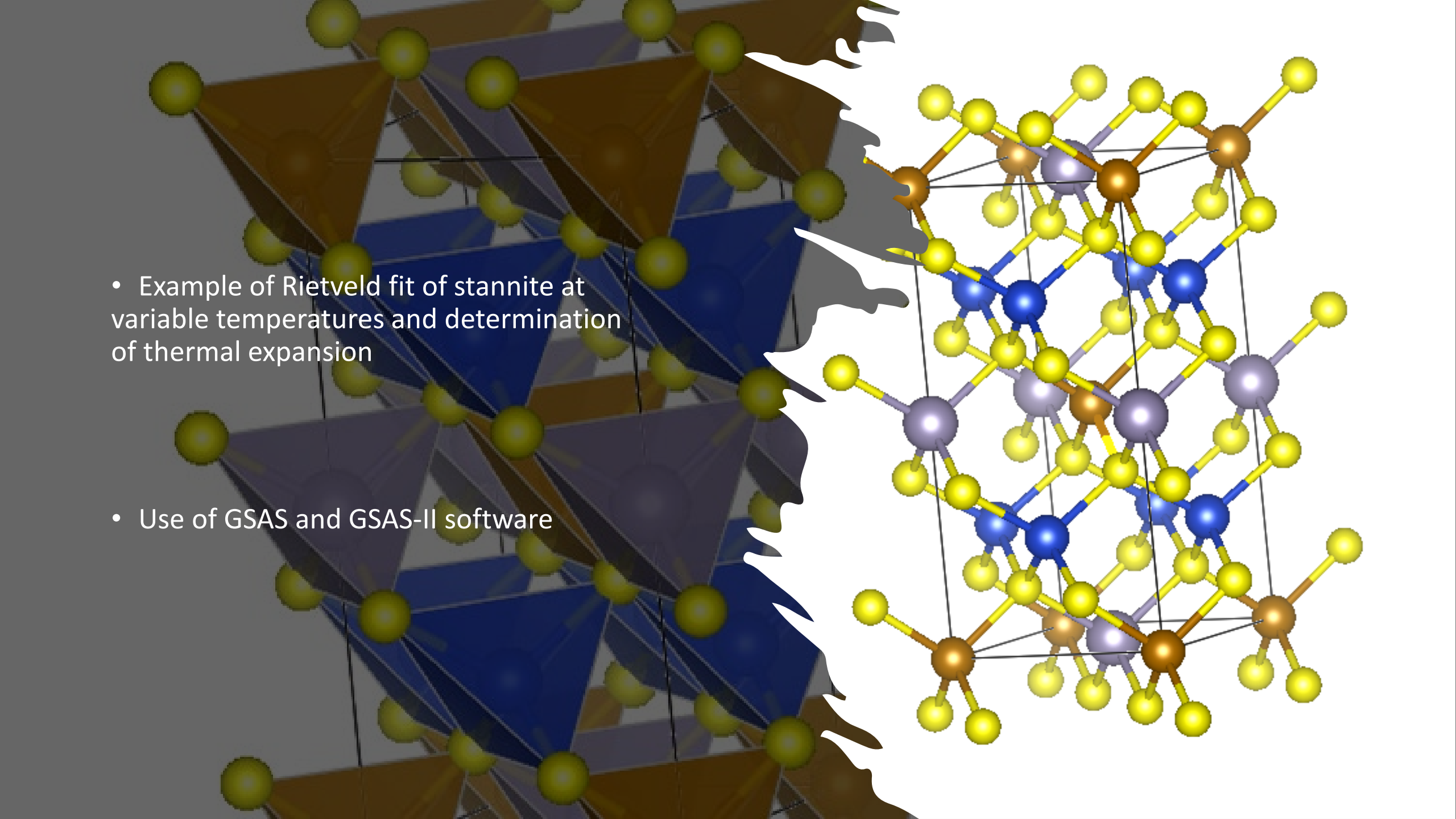


Sample
High temperature gas blower

Example: thermal expansion of stannite, $\text{Cu}_2\text{FeSnS}_4$



- Ore mineral for tin, together with cassiterite SnO_2
- Important structure in material science together with kesterite, $\text{Cu}_2\text{ZnSnS}_4$ (for photovoltaic application)
- In the last decade increase of publication on synthesis of these materials. The knowledge of structural behaviour as function of temperature, chemistry, etc... is relevant for stabilization of phases with specific properties



- Example of Rietveld fit of stannite at variable temperatures and determination of thermal expansion

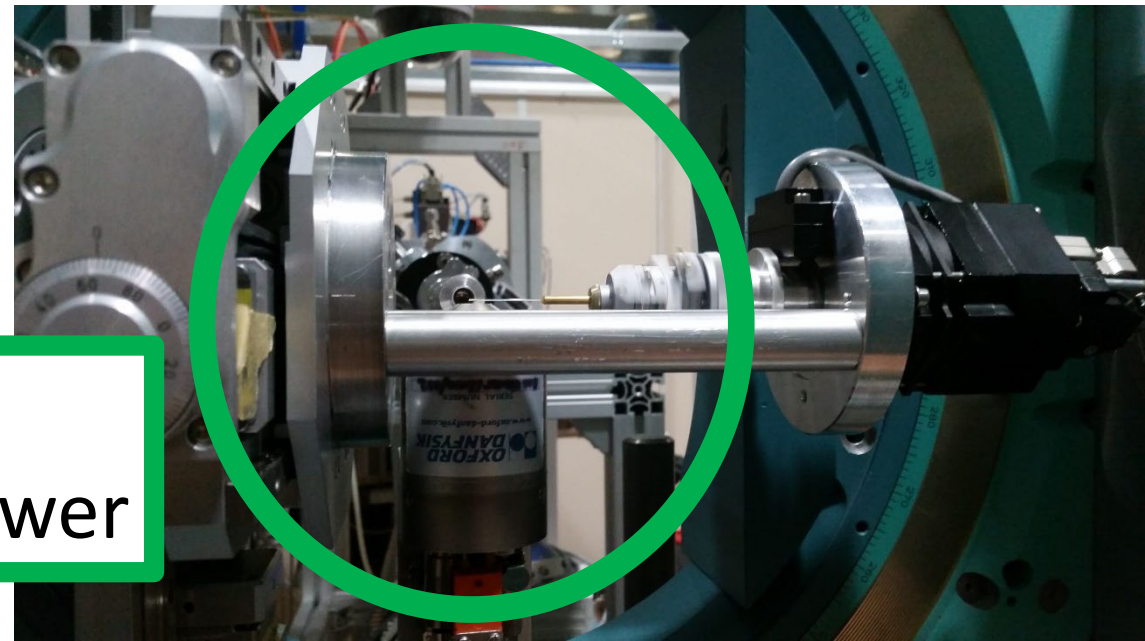
- Use of GSAS and GSAS-II software



Data collected @ MCX beamline (Elettra)

High resolution powder diffraction

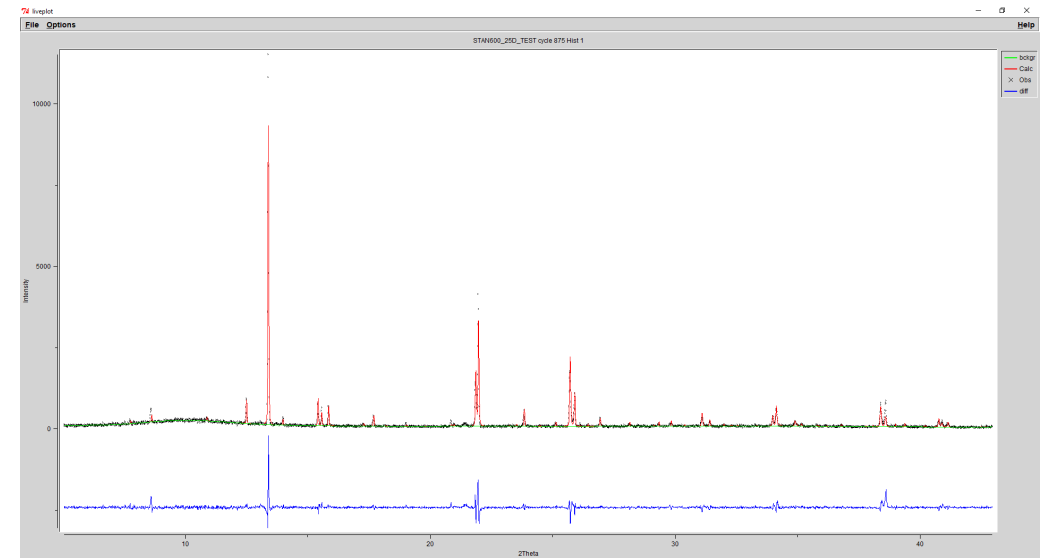
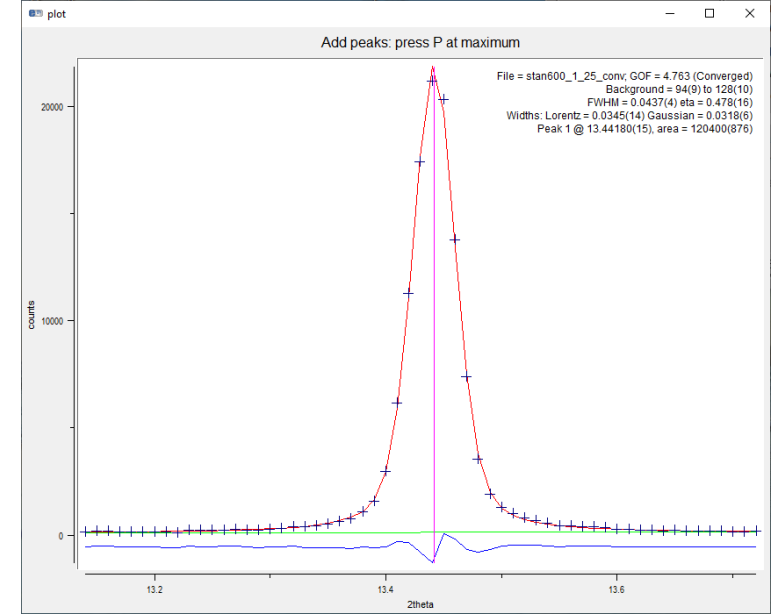
Sample
High temperature gas blower



Single peak fit: fast, useful for preliminary information on unit cell

Full profile fit: more accurate lattice parameter determination. It allows also structural and microstructural analysis, quantitative analysis...

Rietveld fit



Rietveld fit

Simulation of powder pattern

Least square minimization on experimental pattern

Refinable parameters:

Unit cell

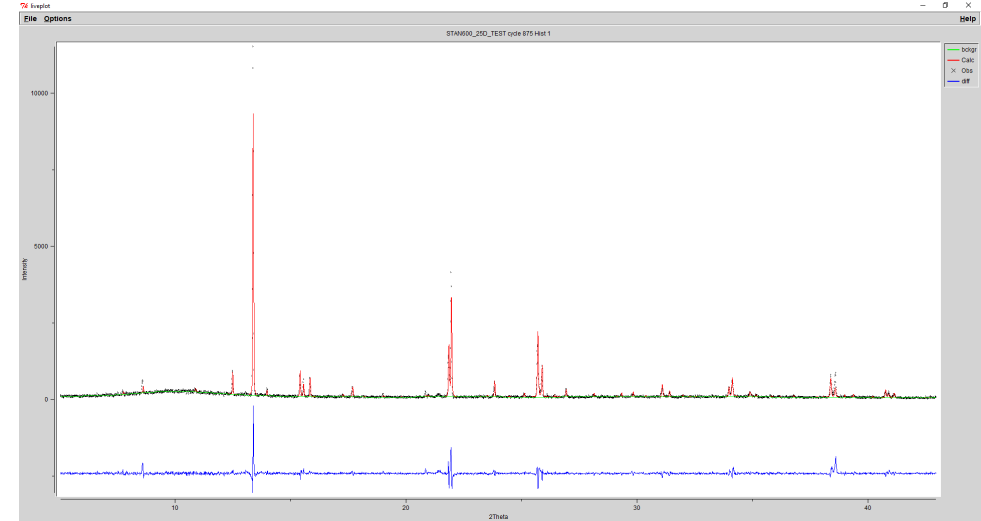
Scale factor

Crystal structure

Peak shape

Background

Other parameters (i.e. preferred orientation....)



Information needed:

1) Experimental pattern

2) Wavelength

3) Crystal structure (unit cell, symmetry and atomic coordinates)

(eventually other parameters, i.e. instrumental resolution...)

[Mineralogical Society of America](#), Founded December 30, 1919

The American Mineralogist Crystal Structure Database

The **Crystal Structure Database** has been compiled by Bob Downs and Paul Heese of the University of Arizona. It includes every structure published in both the American Mineralogist, The Canadian Mineralogist, the European Journal of Mineralogy and is beginning to include structures from Physics and Chemistry of Minerals.

The database is maintained under the care of the Mineralogical Society of America and the Mineralogical Association of Canada, and financed by the National Science Foundation.

The data is retrieved via a compound query using pop-up windows with the fields "Mineral Name", "Author", "Title", "Year", or "Volume".

A complete description of the American Mineralogist crystal structure database and use with interactive software is available ([pdf, 156 K](#))

Copyright © 1997 - 2021 [Mineralogical Society of America](#). All rights reserved. Email any comments, suggestions or problems with site to webmaster@minsocam.org or write Mineralogical Society of America, 3635 Concorde Pkwy Ste 500, Chantilly, VA 20151-1110 United States Tel +1 (703) 652-9950 Fax +1 (703) 652-9951

American Mineralogist Crystal Structure Database

This site is an interface to a crystal structure database that includes every structure published in the American Mineralogist, The Canadian Mineralogist, European Journal of Mineralogy and Physics and Chemistry of Minerals, as well as selected datasets from other journals. The database is maintained under the care of the Mineralogical Society of America and the Mineralogical Association of Canada, and financed by the National Science Foundation.

stannite	Mineral
	Author
	Chemistry Search
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Should the use of the database require a citation, then please use: Downs, R.T. and Hall-Wallace, M. (2003) The American Mineralogist Crystal Structure Database. American Mineralogist 88, 247-250. ([pdf file](#))

Contact [Robert T Downs](#) for suggestions and corrections.

☐ Stannite



Bonazzi P, Bindi L, Bernardini G P, Menchetti S



The Canadian Mineralogist 41 (2003) 639-647

A model for the mechanism of incorporation of Cu, Fe and Zn in the stannite - kesterite series, $\text{Cu}_2\text{FeSnS}_4$ - $\text{Cu}_2\text{ZnSnS}_4$

Sample: Fe100

_database_code_amcsd 0005838

5.4495 5.4495 10.726 90 90 90 I-42m

atom	x	y	z	Uiso
Cu(4d)	0	1/2	1/4	.01924
Fe(2a)	0	0	0	.01219
Sn(2b)	0	0	1/2	.01025
S(8i)	.75581	.75581	.87012	.01134

Unit cell and spacegroup

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Atomic coordinates

Atomic displacement
parameters

☐ Stannite



Bonazzi P, Bindi L, Bernardini G P, Menchetti S



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S(8i)	.75581	.75581	.87012	.01134
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CIF:

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Information File

Calculation of powder pattern

$$2d_{hkl} \sin\theta = (n)\lambda$$

Bragg's law + structure factor

$$F_{hkl} = \sum_{j=1}^n f_j \exp\left(\frac{2\pi i}{\lambda} \vec{r}_j \cdot \vec{S}\right)$$

Calculation of diffraction angle as function of hkl (Miller index) + calculation of intensity of each diffraction

Structure factor

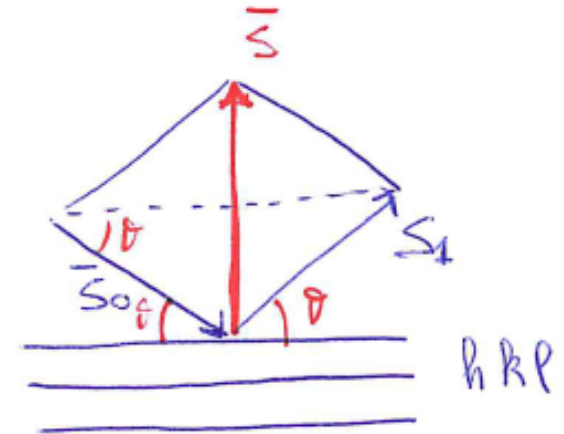
Intensity of diffraction: function of atomic species and structure

$$F_{hkl} = \sum_{j=1}^n f_j \exp \left(\frac{2\pi i}{\lambda} \vec{r}_j \cdot \vec{S} \right)$$

f_j = atomic scattering factor

$\vec{r}_j$ = atomic position vector (i.e. atomic coordinates)

$\vec{S}$ = scattering vector $(s_1 - s_0)$ s_1 : direction of diffracted beam
 s_0 : direction of primary beam



Peak list

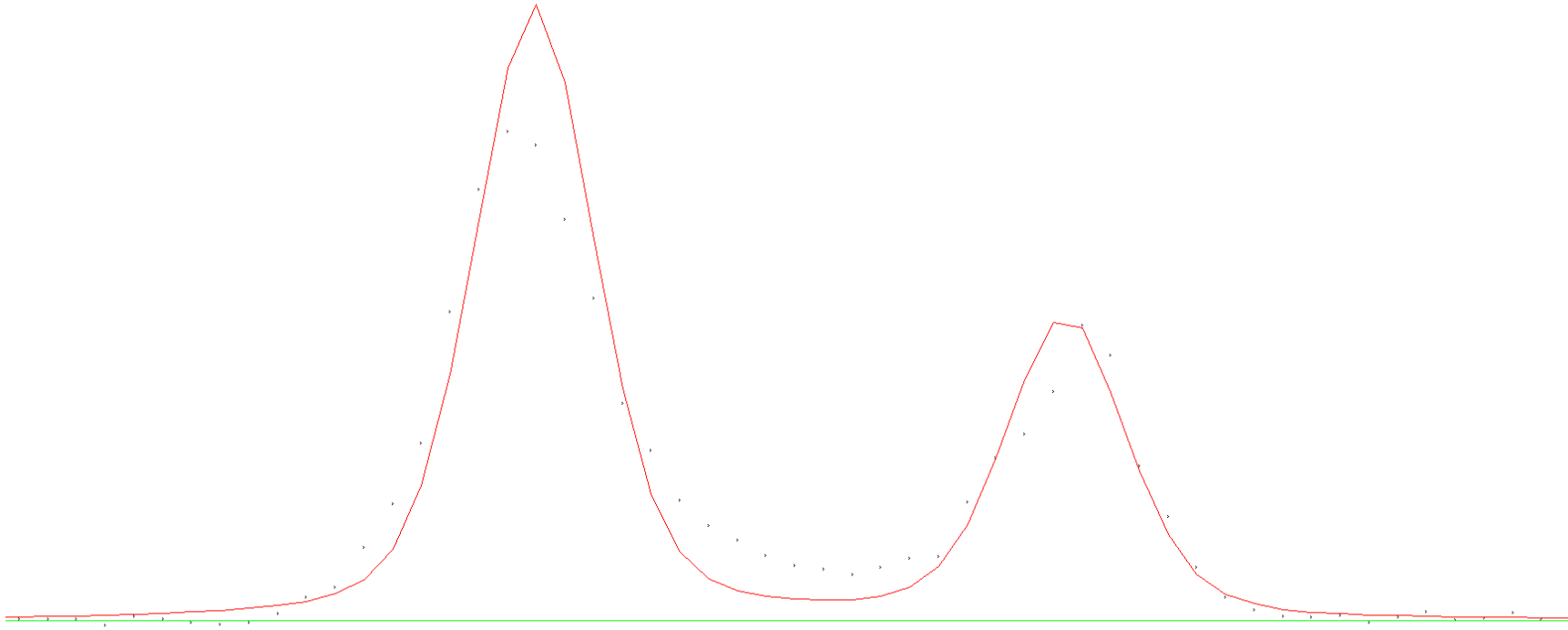
No.	h	k	l	d [Å]	2Theta[deg]	I [%]
1	0	0	2			
2	1	0	1			
3	1	1	0			
4	1	1	2			
5	1	0	3			
6	2	0	0			
7	0	0	4			
8	2	0	2			
9	2	1	1			
10	1	1	4			
11	2	1	3			
12	1	0	5			
13	2	2	0			
14	2	0	4			
15	2	2	2			
16	3	0	1			
17	3	1	2			
18	1	1	6			
19	2	2	4			
20	3	2	1			
21	3	1	4			
22	4	0	0			
23	0	0	8			
24	2	2	6			
25	3	3	2			
26	3	1	6			
27	4	0	4			
28	2	0	8			
29	4	2	4			
30	2	2	8			

Peak list

No.	h	k	l	d [Å]	2Theta[deg]	I [%]
1	0	0	2	5.36700	7.788	
2	1	0	1	4.85700	8.608	
3	1	1	0	3.85200	10.860	
4	1	1	2	3.12900	13.379	
5	1	0	3	2.99000	14.004	
6	2	0	0	2.72400	15.380	
7	0	0	4	2.68300	15.616	
8	2	0	2	2.42900	17.261	
9	2	1	1	2.37640	17.646	
10	1	1	4	2.20220	19.054	
11	2	1	3	2.01380	20.856	
12	1	0	5	1.99800	21.023	
13	2	2	0	1.92580	21.821	
14	2	0	4	1.91240	21.975	
15	2	2	2	1.81360	23.189	
16	3	0	1	1.79130	23.481	
17	3	1	2	1.64090	25.669	
18	1	1	6	1.62320	25.954	
19	2	2	4	1.56520	26.933	
20	3	2	1	1.49620	28.200	
21	3	1	4	1.45030	29.112	
22	4	0	0	1.36250	31.034	
23	0	0	8	1.34220	31.515	
24	2	2	6	1.31140	32.275	
25	3	3	2	1.24930	33.927	
26	3	1	6	1.24150	34.147	
27	4	0	4	1.21500	34.915	
28	2	0	8	1.20440	35.233	
29	4	2	4	1.10990	38.344	
30	2	2	8	1.10170	38.641	

Peak list

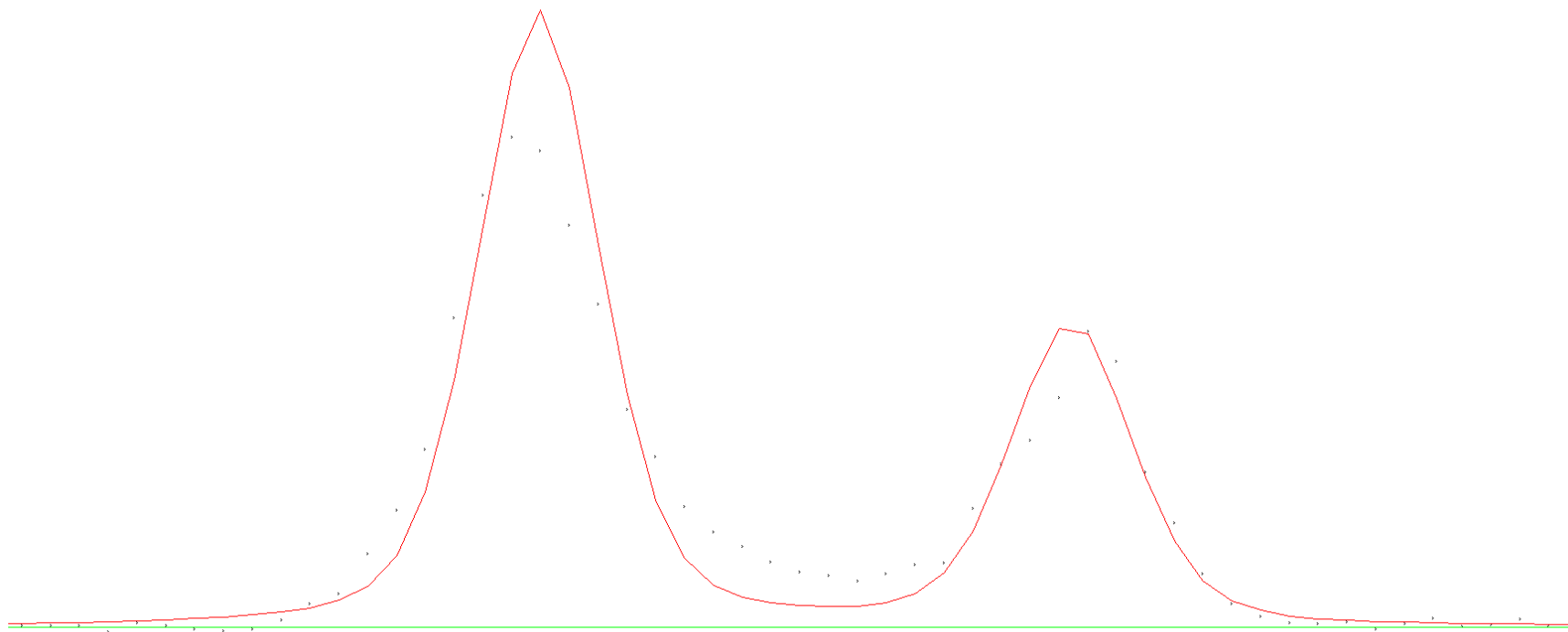
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2	1	0	1	4.85700	8.608	3.0
3	1	1	0	3.85200	10.860	2.0
4	1	1	2	3.12900	13.379	100.0
5	1	0	3	2.99000	14.004	1.0
6	2	0	0	2.72400	15.380	6.0
7	0	0	4	2.68300	15.616	4.0
8	2	0	2	2.42900	17.261	2.0
9	2	1	1	2.37640	17.646	2.0
10	1	1	4	2.20220	19.054	1.0
11	2	1	3	2.01380	20.856	1.0
12	1	0	5	1.99800	21.023	1.0
13	2	2	0	1.92580	21.821	15.0
14	2	0	4	1.91240	21.975	27.0
15	2	2	2	1.81360	23.189	1.0
16	3	0	1	1.79130	23.481	1.0
17	3	1	2	1.64090	25.669	13.0
18	1	1	6	1.62320	25.954	7.0
19	2	2	4	1.56520	26.933	2.0
20	3	2	1	1.49620	28.200	1.0
21	3	1	4	1.45030	29.112	1.0
22	4	0	0	1.36250	31.034	2.0
23	0	0	8	1.34220	31.515	1.0
24	2	2	6	1.31140	32.275	1.0
25	3	3	2	1.24930	33.927	2.0
26	3	1	6	1.24150	34.147	3.0
27	4	0	4	1.21500	34.915	1.0
28	2	0	8	1.20440	35.233	1.0
29	4	2	4	1.10990	38.344	3.0
30	2	2	8	1.10170	38.641	2.0



Simulation of diffraction:

Sum of simulated peaks

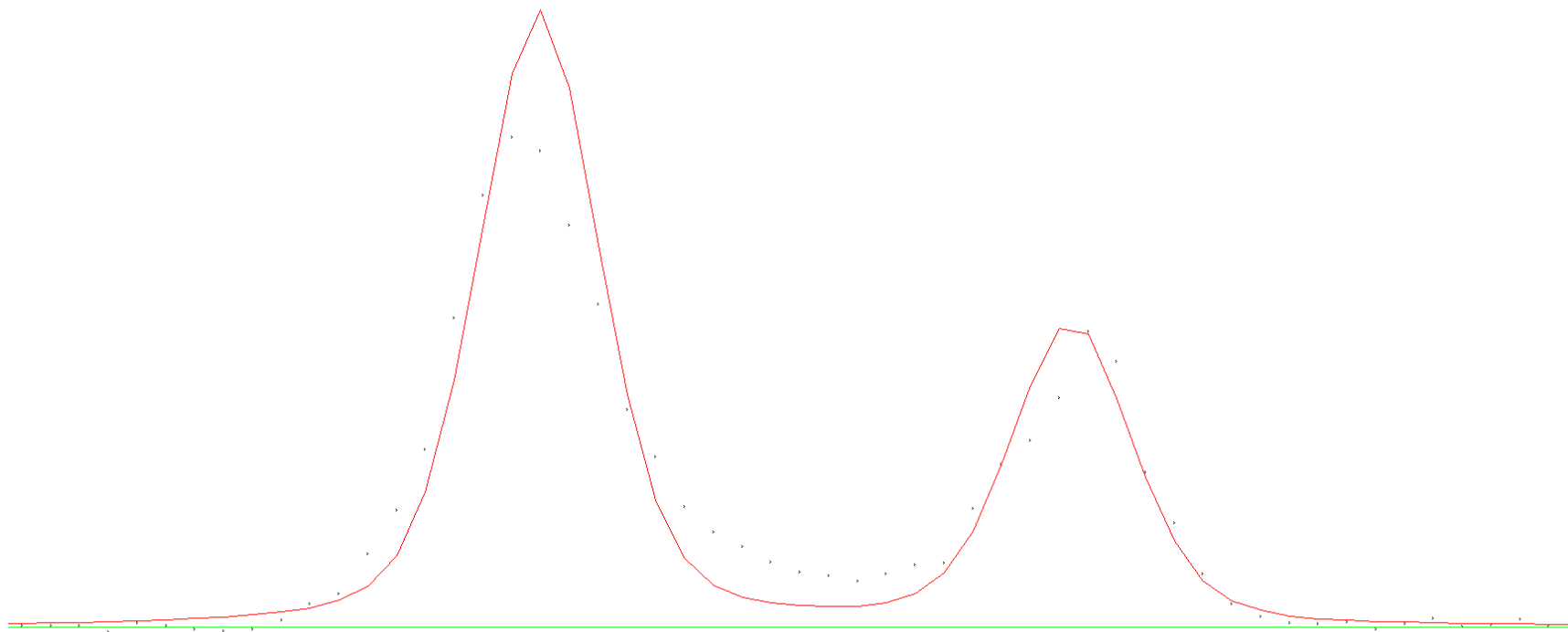
Peak position (bragg's law) + peak scale factor (Structure factor) + peak shape



$h_1 \ k_1 \ l_1$

$h_2 \ k_2 \ l_2$

Peak position: bragg's law

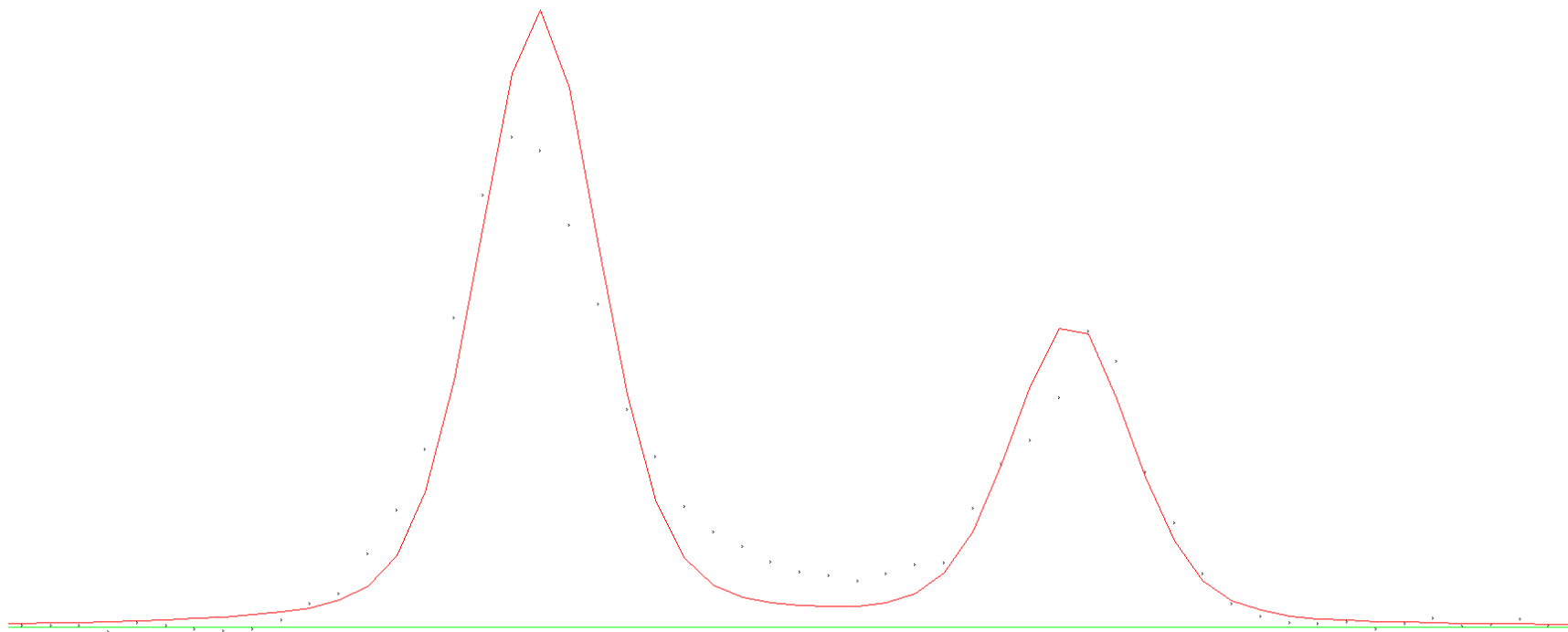


Scale factor (proportional to squared structure factor)

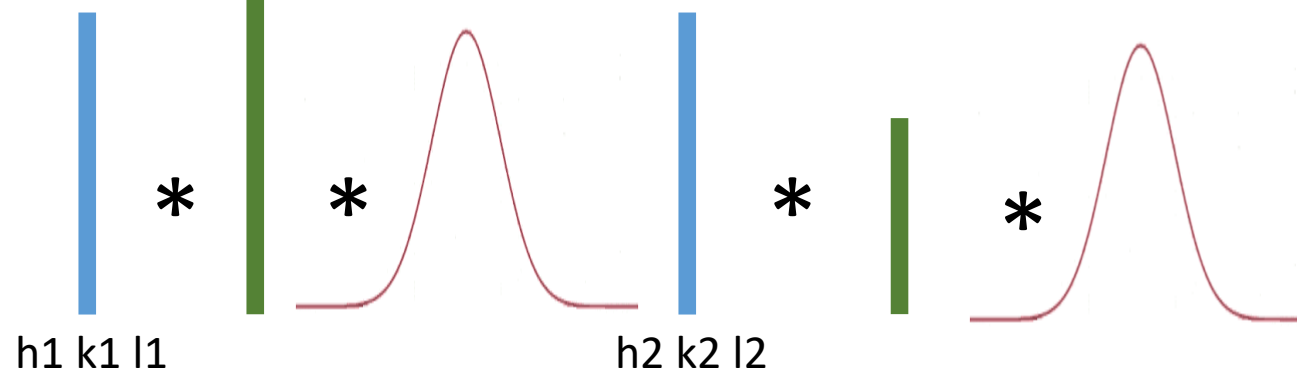
Peak position: bragg's law

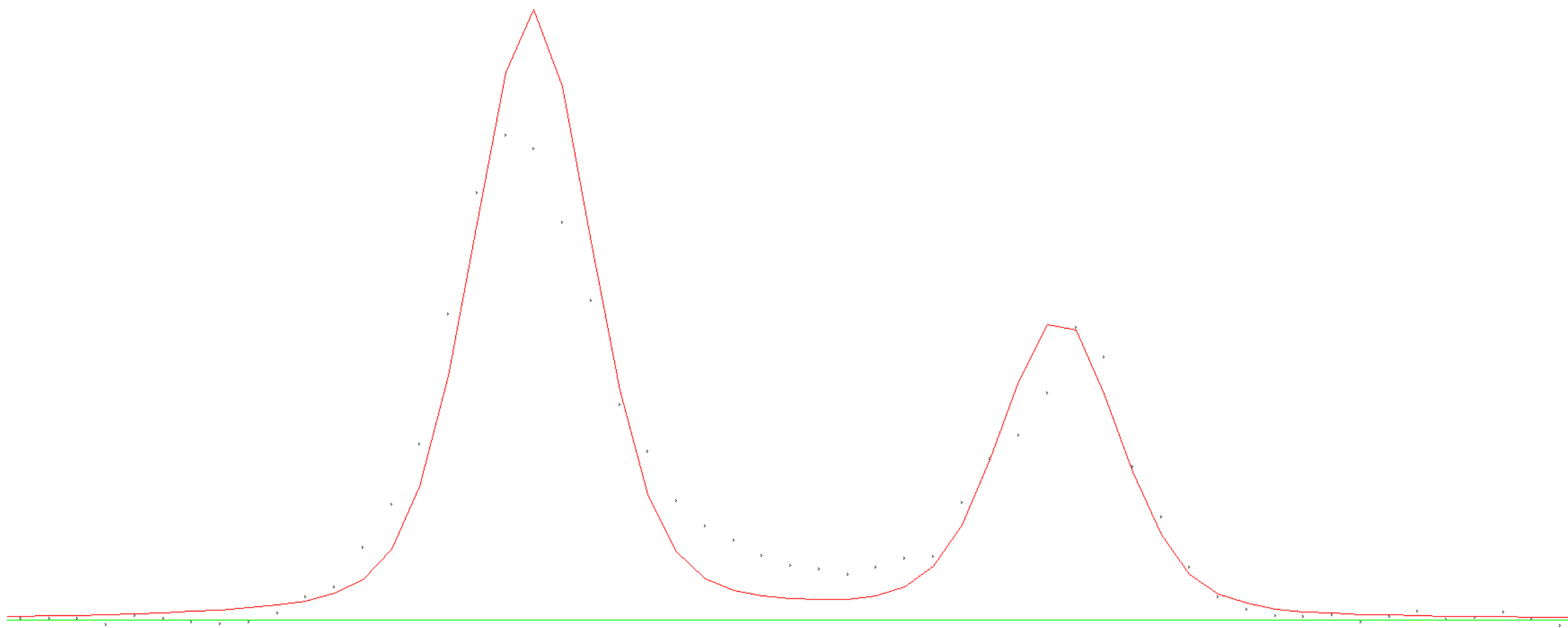
$h_1 k_1 l_1$ *

$h_2 k_2 l_2$ *



Peak shape (i.e. gaussian, lorentian, pseudo-Voigt, etc...)





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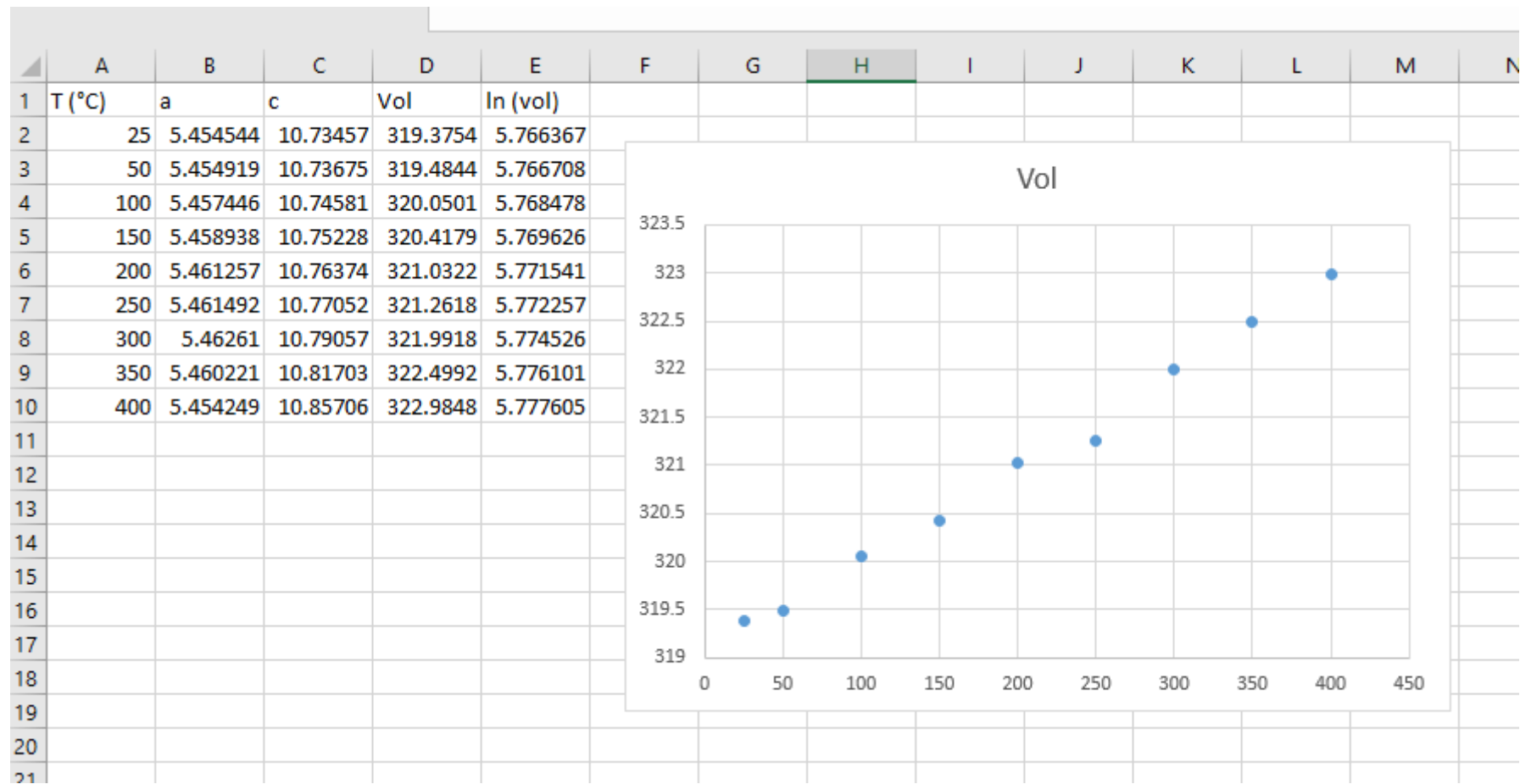
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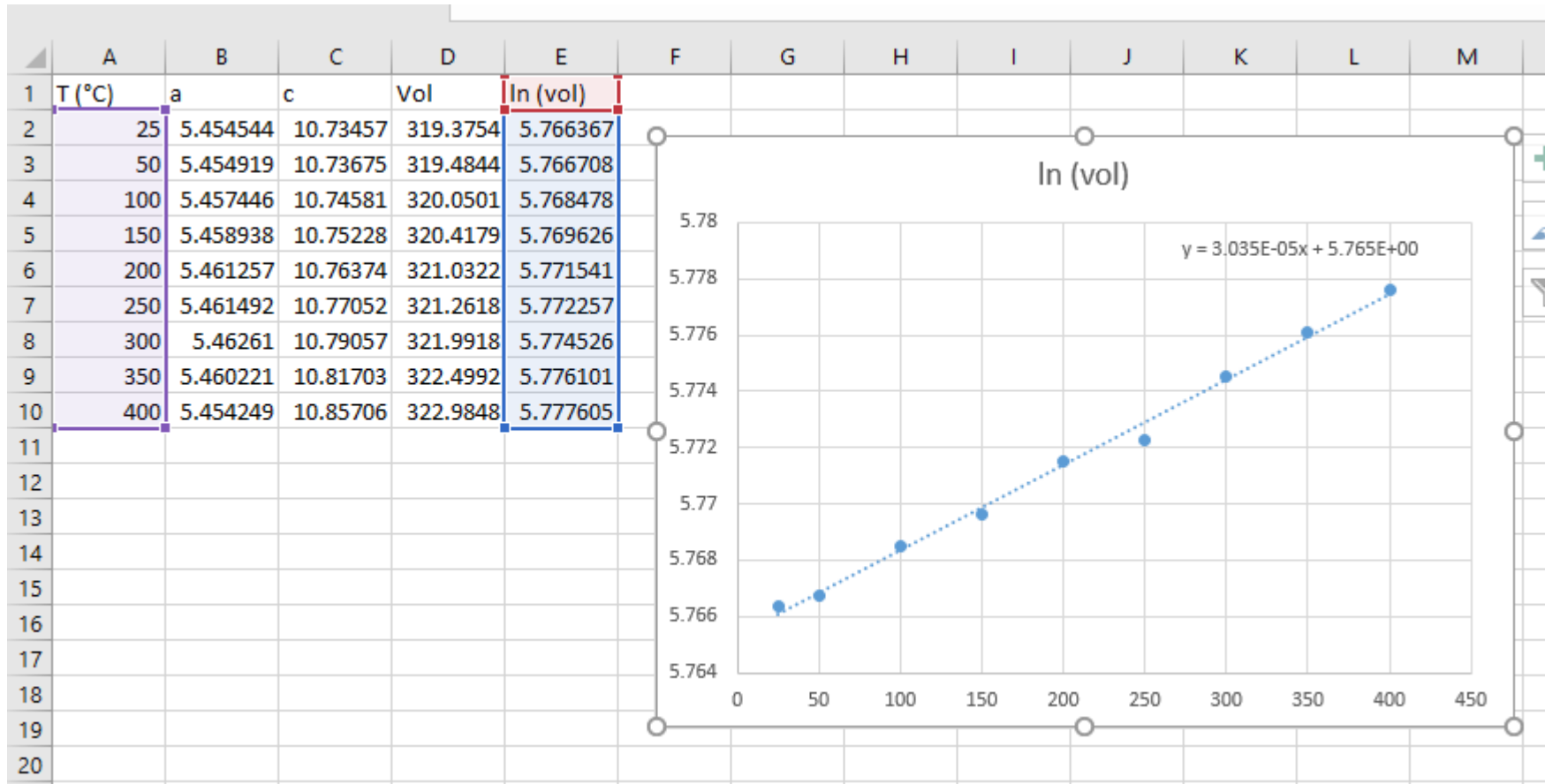
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$$\alpha = 1/V (\partial V/\partial T) = \partial \ln V / \partial T$$

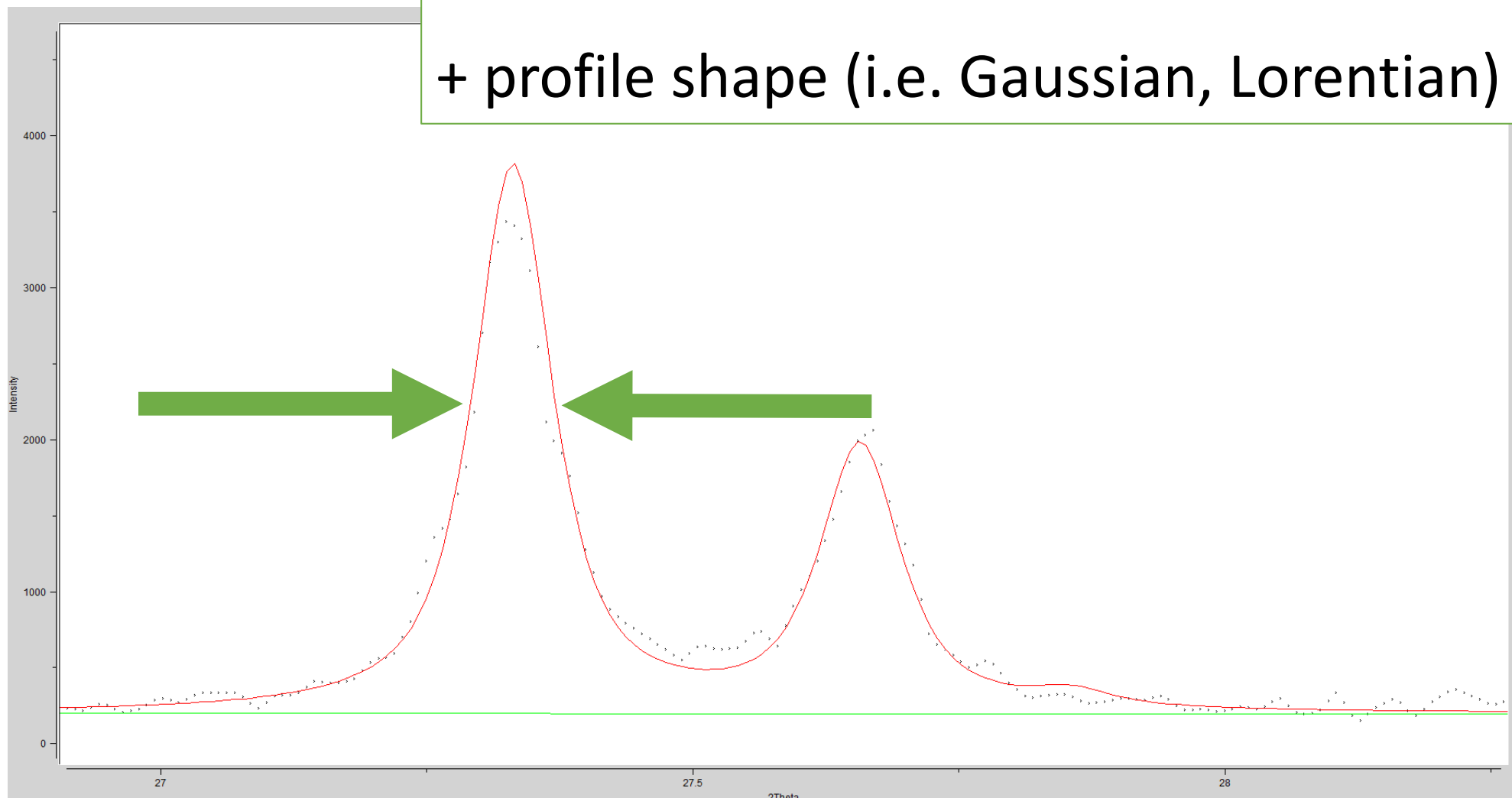
Linear thermal expansion: $\alpha = 30.4 \cdot 10^{-6} \text{ (K}^{-1}\text{)}$



Peak profile

FWHM (Full width at Half Maximum)

+ profile shape (i.e. Gaussian, Lorentian)

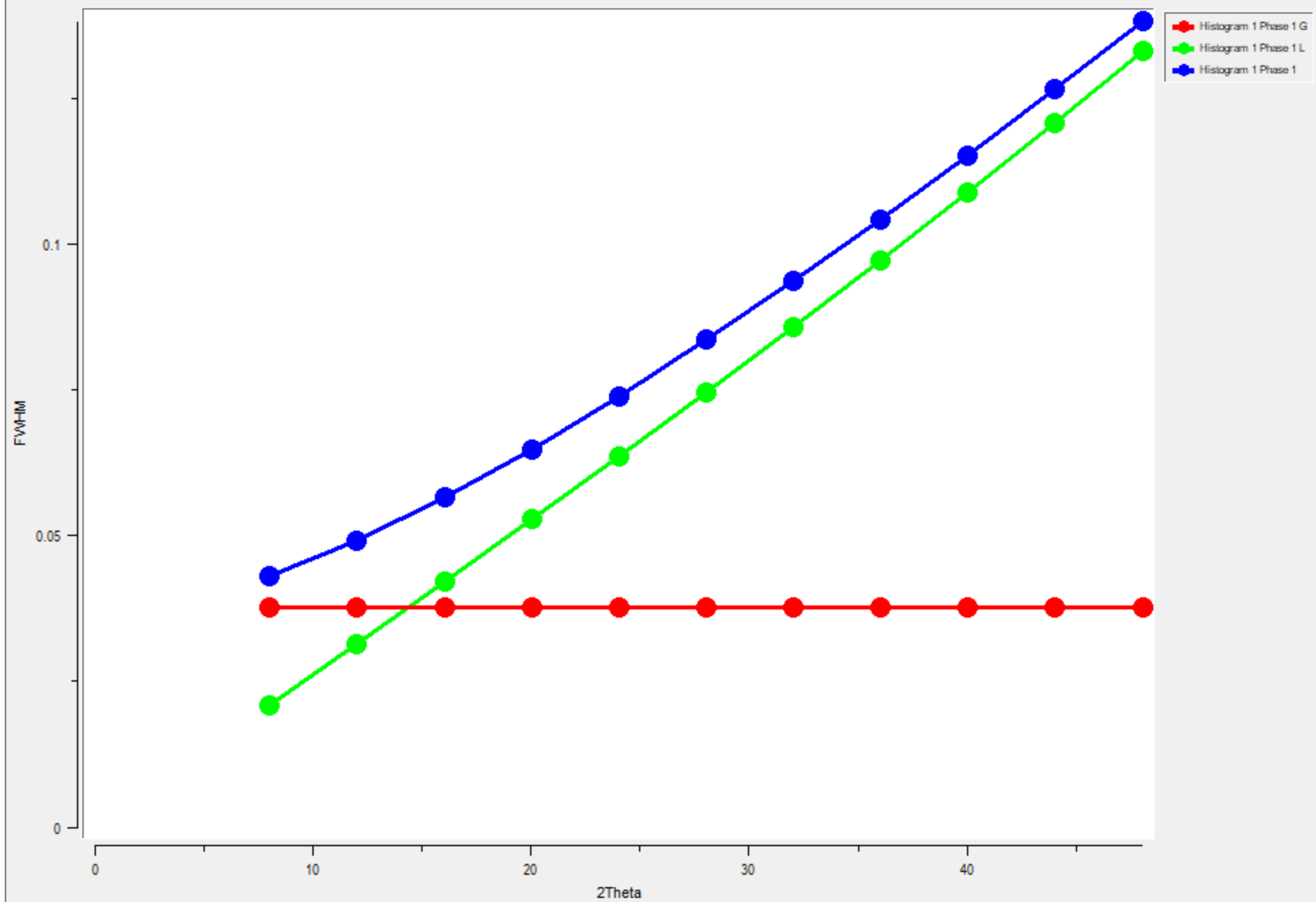


Pseudo-Voigt: Gaussian (G) +Lorentian (L)

Hist 1 -- Phase 1 (type 2)

Damping		6	Peak cutoff		0.00100	Change Type		
GU	☒	0.000000E+00	GV	☒	0.000000E+00	GW	☒	0.370000E+02
LX	☒	0.844205E+02	LY	☒	0.100000E+02	trns	☐	0.000000E+00
	☐	0.000000E+00		☐	0.000000E+00		☐	0.000000E+00

GU, GV, GW and LX, LY describe the variation of FWHM of a Gaussian and a Lorentian as function of 2theta angle



Hist 1 -- Phase 1 (type 2)

Damping

Peak cutoff

GU ☒

GV ☒

GW ☒

LX ☒

LY ☒

trns ☐

☒

☒

☒

From GSAS manual

The variance of the peak, σ_2 , varies with 2Θ as

$$\sigma^2 = U \tan^2 \Theta + V \tan \Theta + W + \frac{P}{\cos^2 \Theta}$$

where U, V and W are the coefficients described by Cagliotti, Pauletti and Ricci in 1958 (Nucl. Instrum., **3**, 223) and P is the Scherrer coefficient for Gaussian broadening. The Lorentzian coefficient, γ , varies as

$$\gamma = \frac{X + X_e \cos \phi}{\cos \Theta} + \left(Y + Y_e \cos \phi + \gamma_L d^2 \right) \tan \Theta$$

The first term is the Lorentzian Scherrer broadening and includes an anisotropy coefficient, X_e . The second term describes strain broadening and also includes an anisotropy coefficient. If a sublattice is defined by use of “stacking fault vectors”, then

Example: estimation of crystallite size in cubic ZrO₂
(nominally 5 nm by TEM)

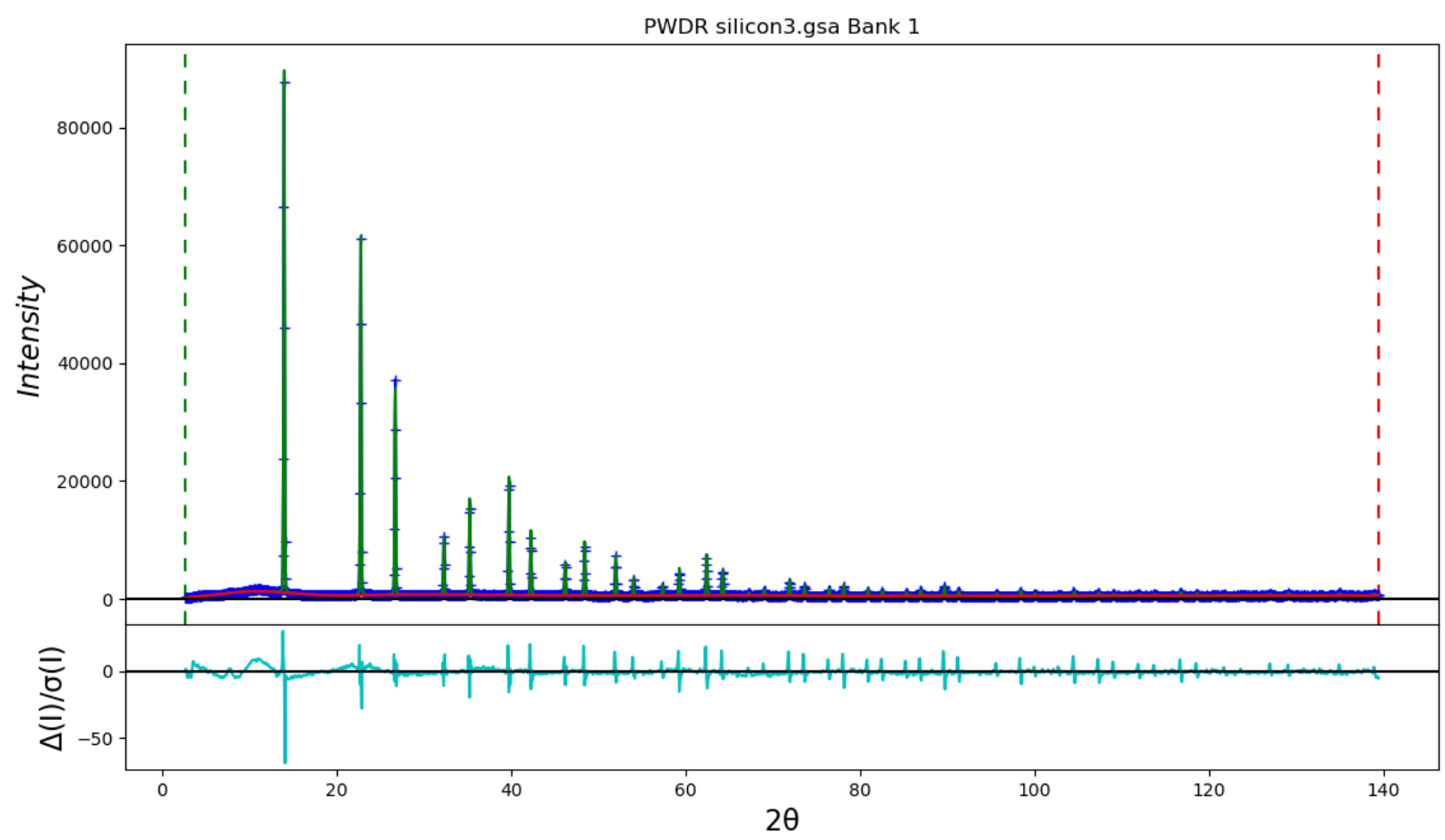
- Determination of experimental broadening using a standard (i.e. LaB₆, Silicon)
- Profile fitting of ZrO₂ (using GSAS-II software, which has implemented the deconvolution of sample broadening from instrumental broadening)

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 - Restraints
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 - Phases
 - Silicon
 - PWDR silicon3.gsa Bank 1
 - Comments
 - Limits
 - Background
 - Instrument Parameters
 - Sample Parameters
 - Peak List
 - Index Peak List
 - Unit Cells List
 - Reflection Lists

Histogram Type: PXC Bank: 1

Name (default)	Value	Refine?
Azimuth:	0.00	
Lam (Å): (0.729320)	0.747631	☒
Zero (0.0000):	0.259	☒
Polariz. (0.9600):	0.96	☐
U (0.000):	0.0	☐
V (0.000):	0.0	☐
W (5.402):	33.843	☒
X (0.000):	0.0	☐
Y (0.000):	0.0	☐
Z (0.000):	0.0	☐
SH/L (0.00200):	0.002	☐

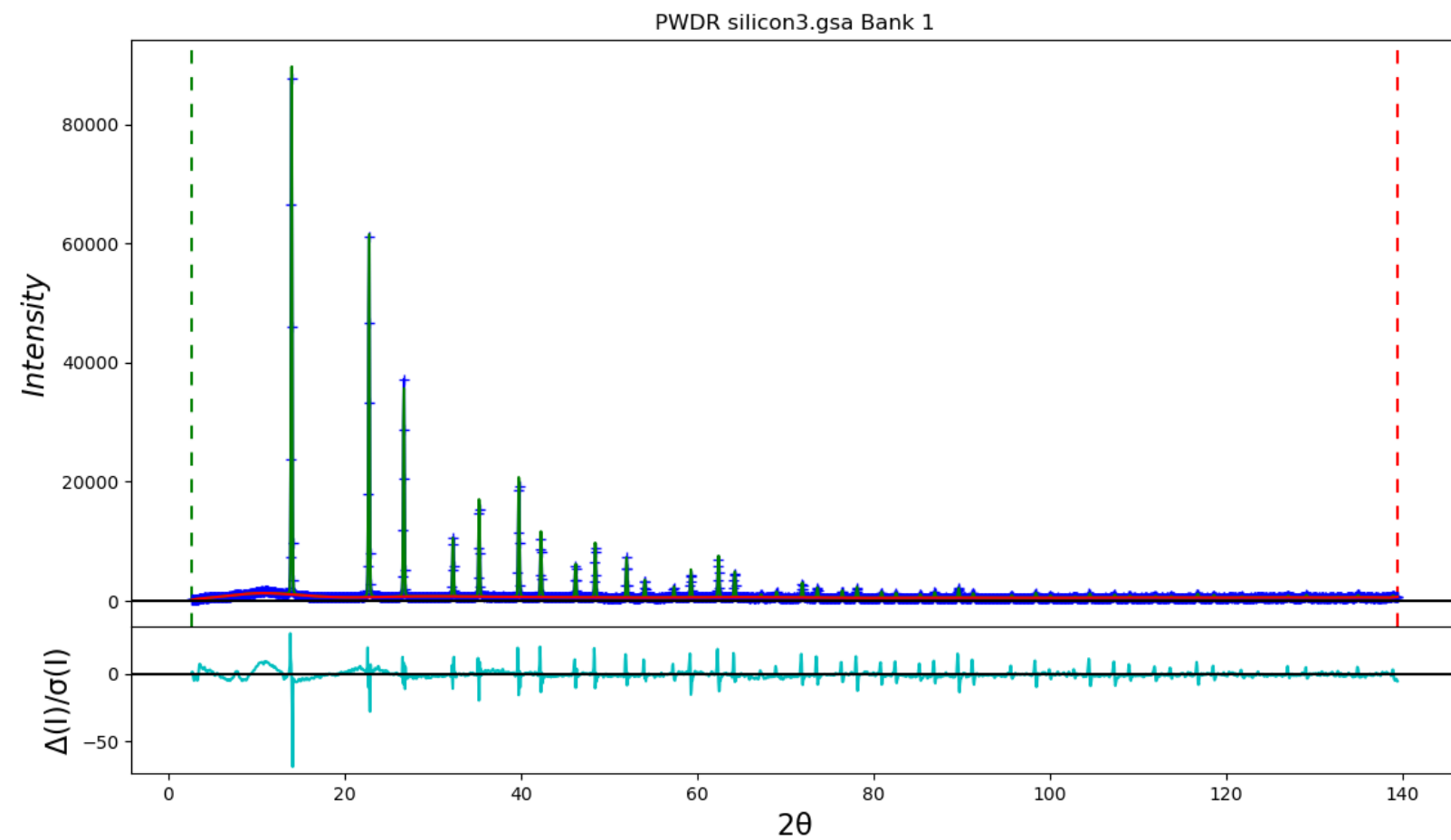
Peak Widths Powder Patterns



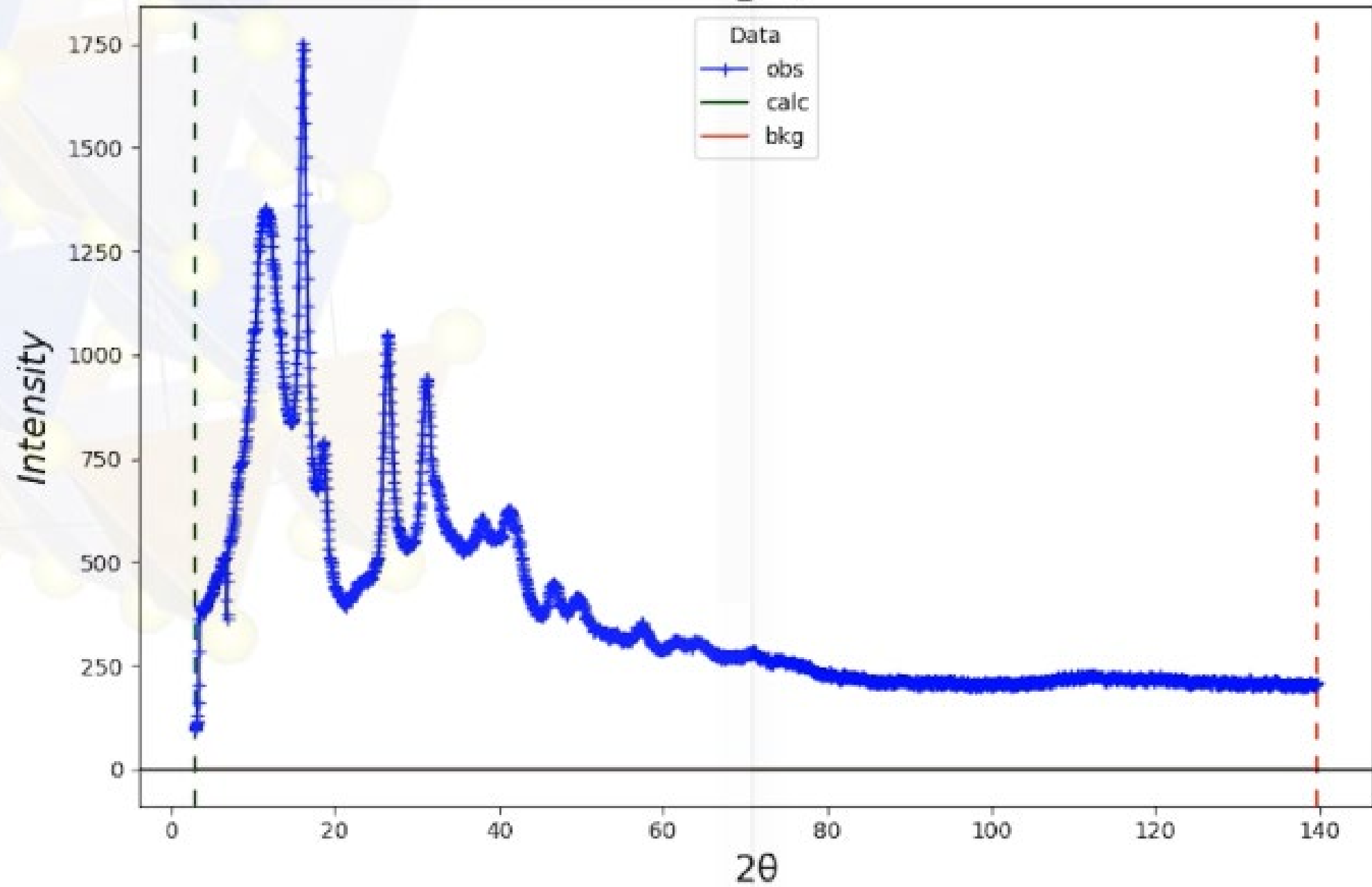
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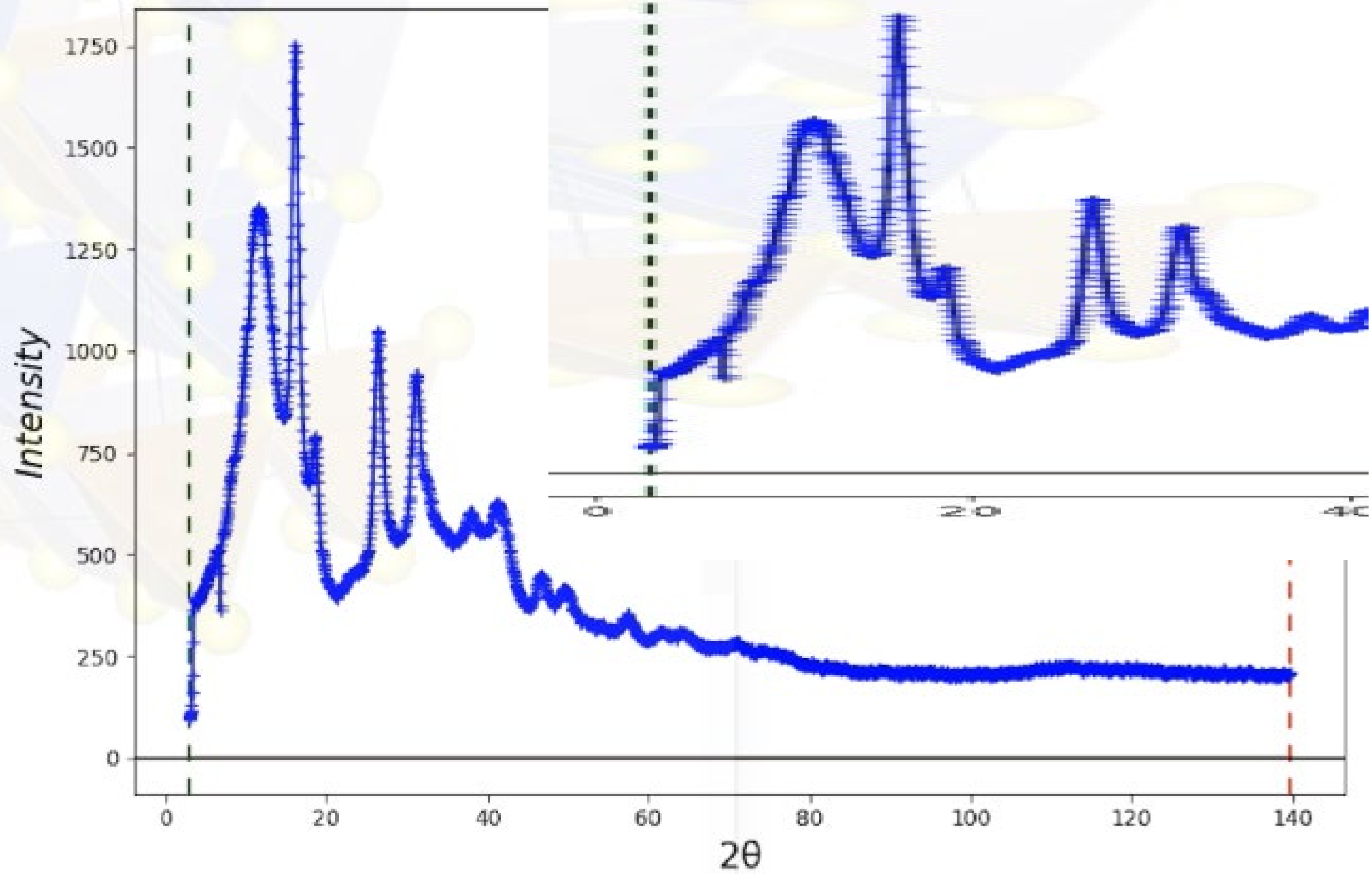
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 - Restraints
 - Rigid bodies
 - Phases
 - Silicon
 - PWDR silicon3.gsa Bank 1
 - Comments
 - Limits
 - Background
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 - Reflection Lists

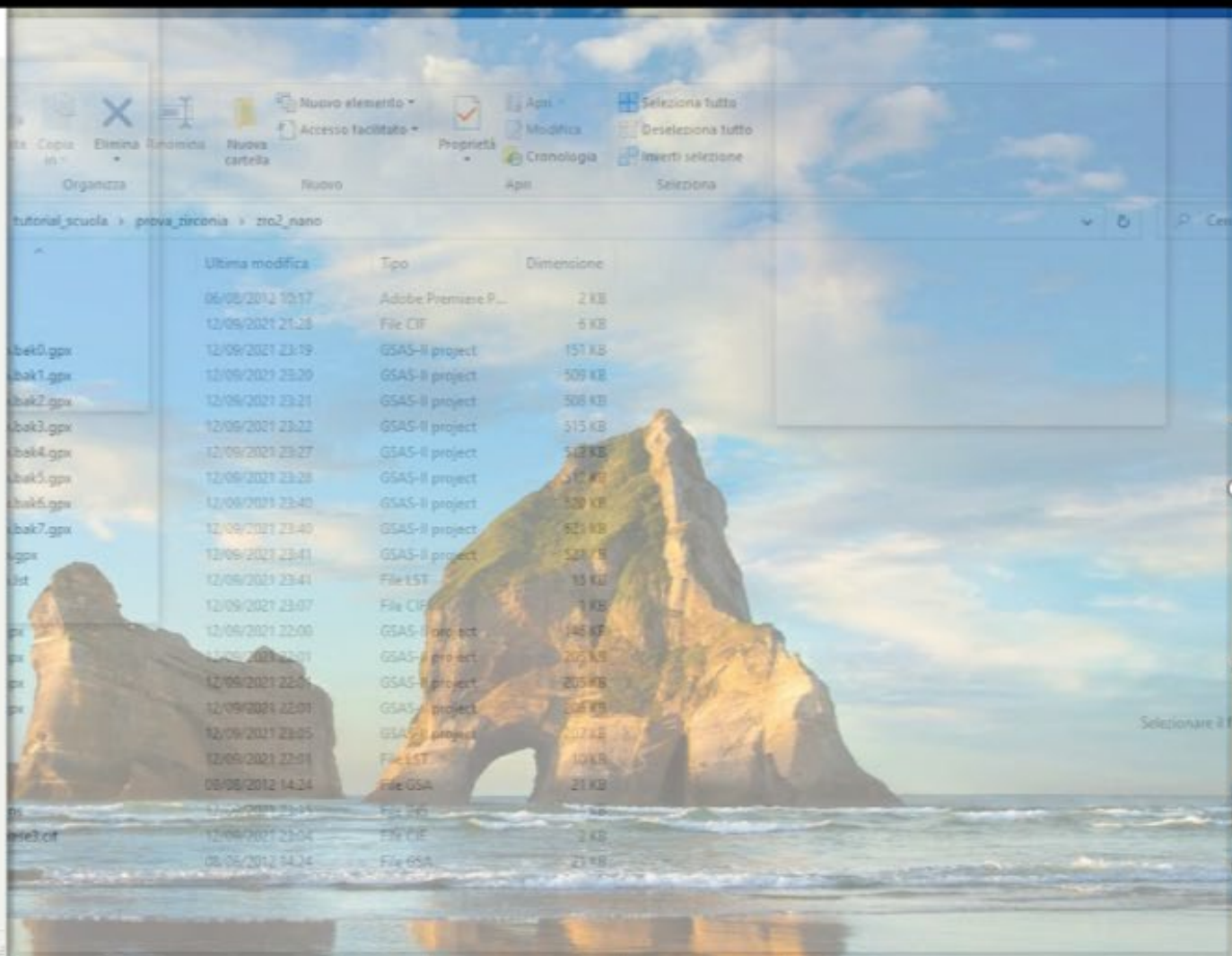
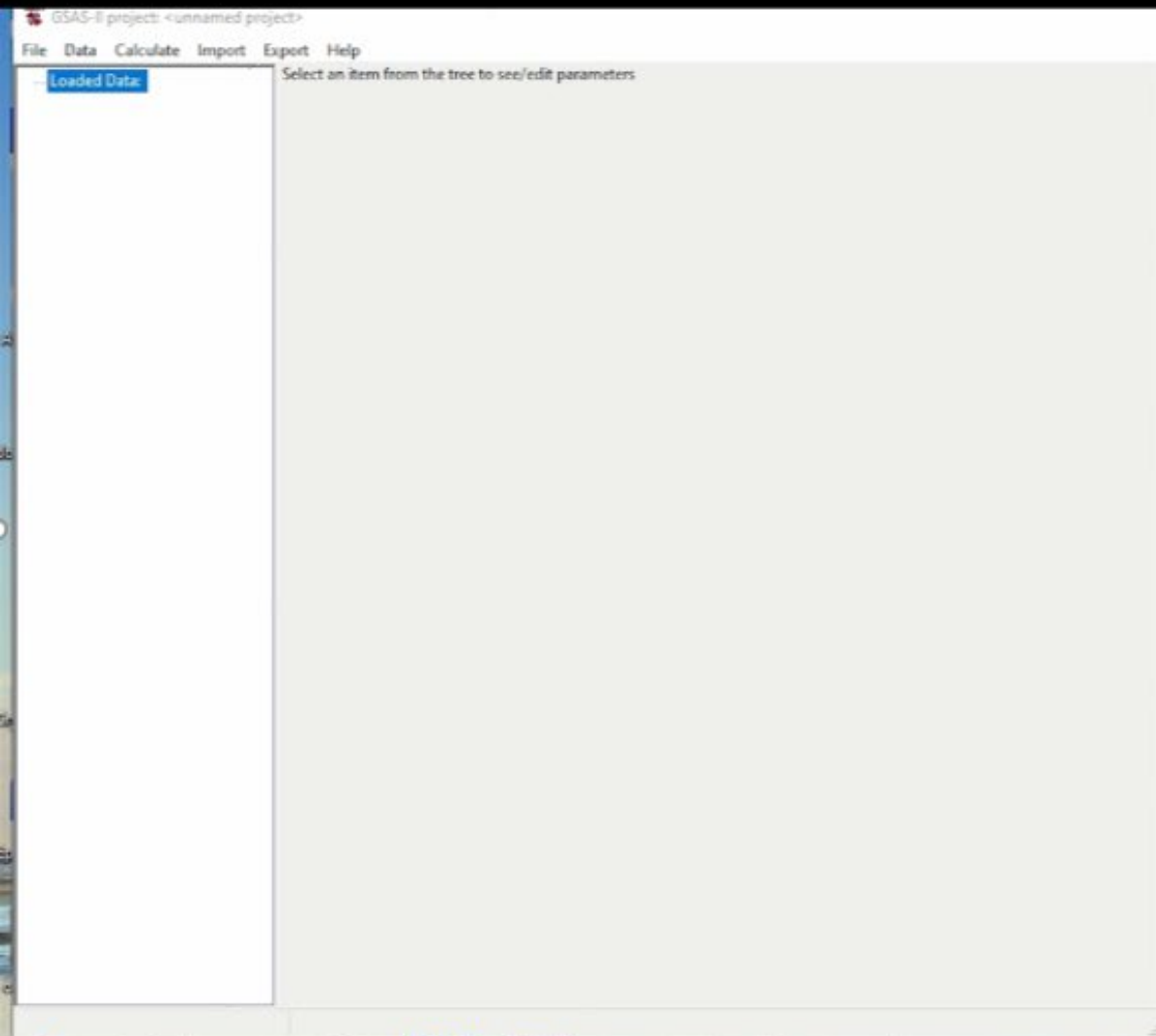
Histogram Type: PXC Bank: 1		
Name (default)	Value	Refine?
Azimuth:	0.00	
Lam (Å): (0.729320)	0.747631	☒
Zero (0.0000):	0.259	☒
Polariz. (0.9600):	0.96	☐
U (0.000):	0.0	☐
V (0.000):	0.0	☐
W (5.402):	33.843	☒
X (0.000):	0.0	☐
Y (0.000):	0.0	☐
Z (0.000):	0.0	☐
SH/L (0.00200):	0.002	☐



PWDR zrrm1_01.gsa Bank 1





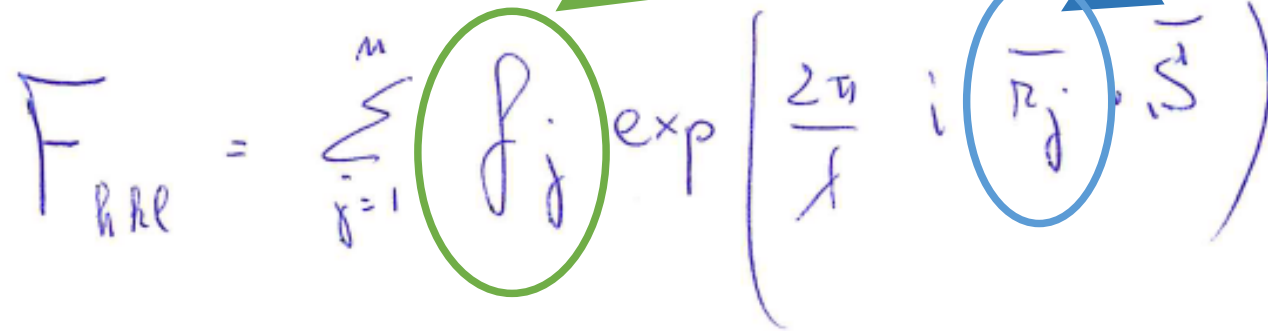


2) Intensity of diffraction: function of atomic species and structure

$$F_{hkl} = \sum_{j=1}^n f_j \exp \left(\frac{2\pi i}{\lambda} \vec{r}_j \cdot \vec{S} \right)$$

Structure factor

Intensity of diffraction: function of atomic species and structure



The diagram shows the structure factor equation $F_{hkl} = \sum_{j=1}^m f_j \exp \left(\frac{2\pi}{\lambda} i \vec{r}_j \cdot \vec{S} \right)$. A green arrow points from the text 'atomic species' to the term f_j , which is circled in green. A blue arrow points from the text 'structure' to the term $\vec{r}_j \cdot \vec{S}$, which is circled in blue.

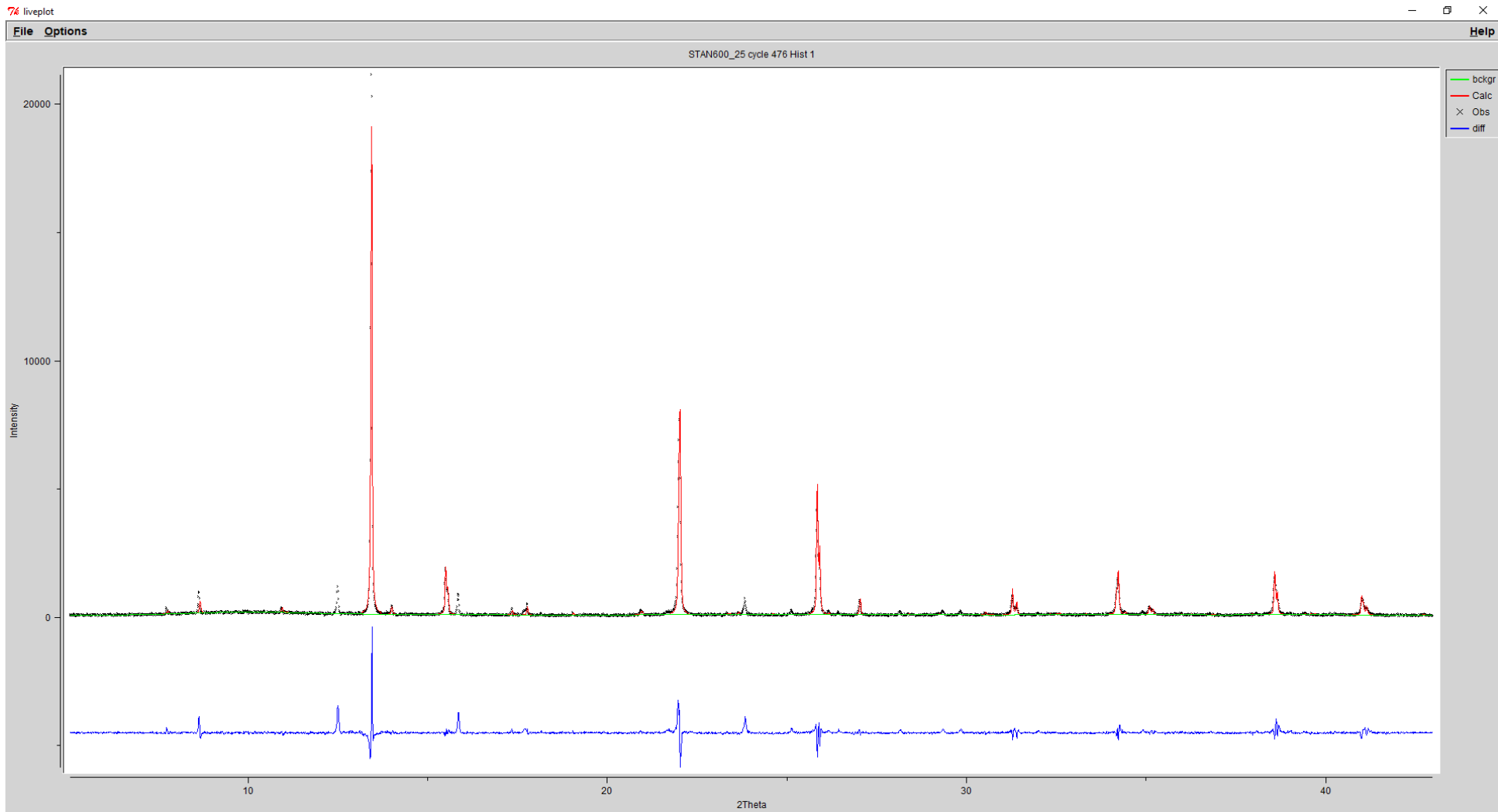
$$F_{hkl} = \sum_{j=1}^m f_j \exp \left(\frac{2\pi}{\lambda} i \vec{r}_j \cdot \vec{S} \right)$$

Structure factor

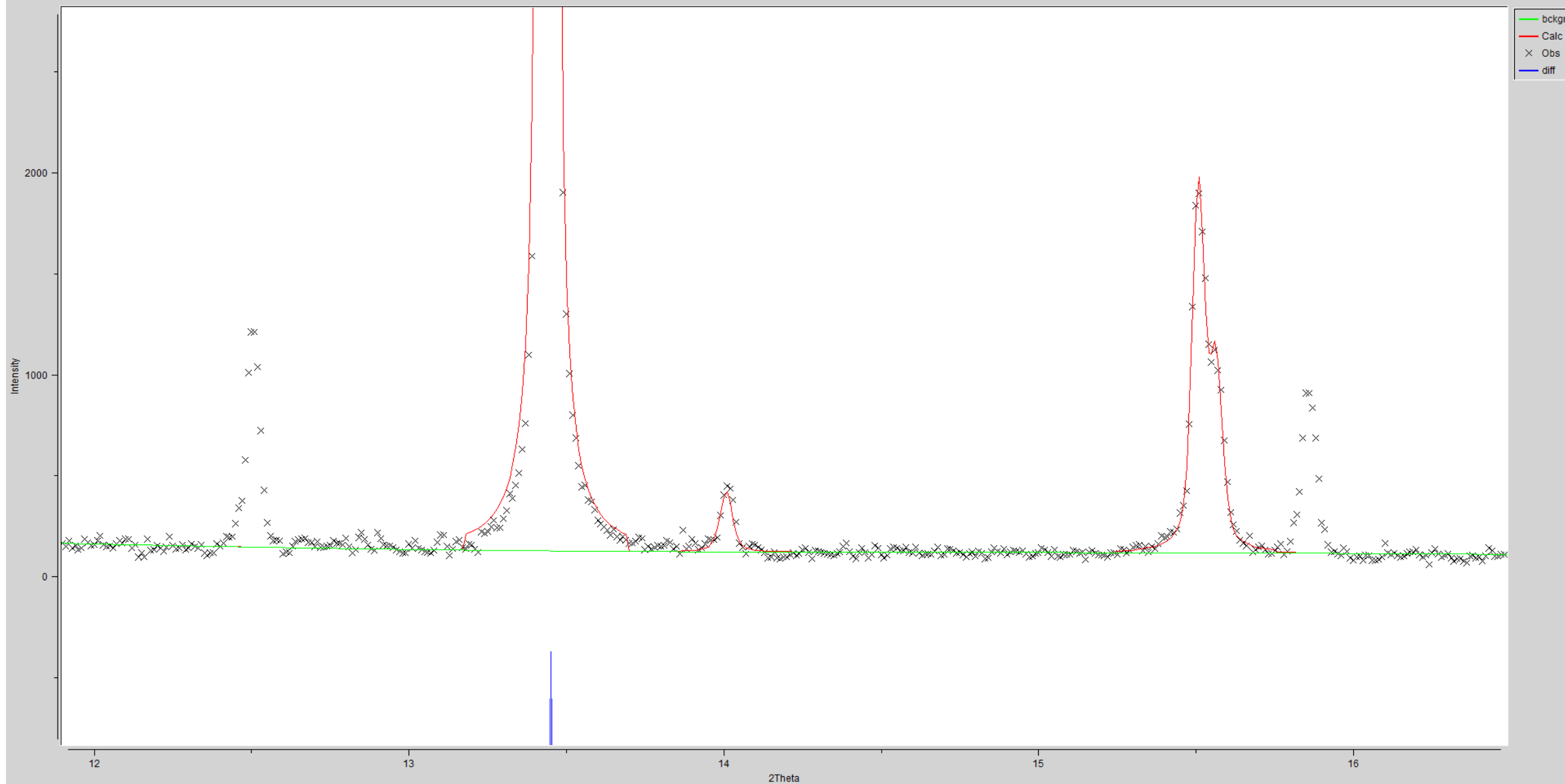
- Use of intensity for quantitative analysis and for structure determination

Quantitative analysis:

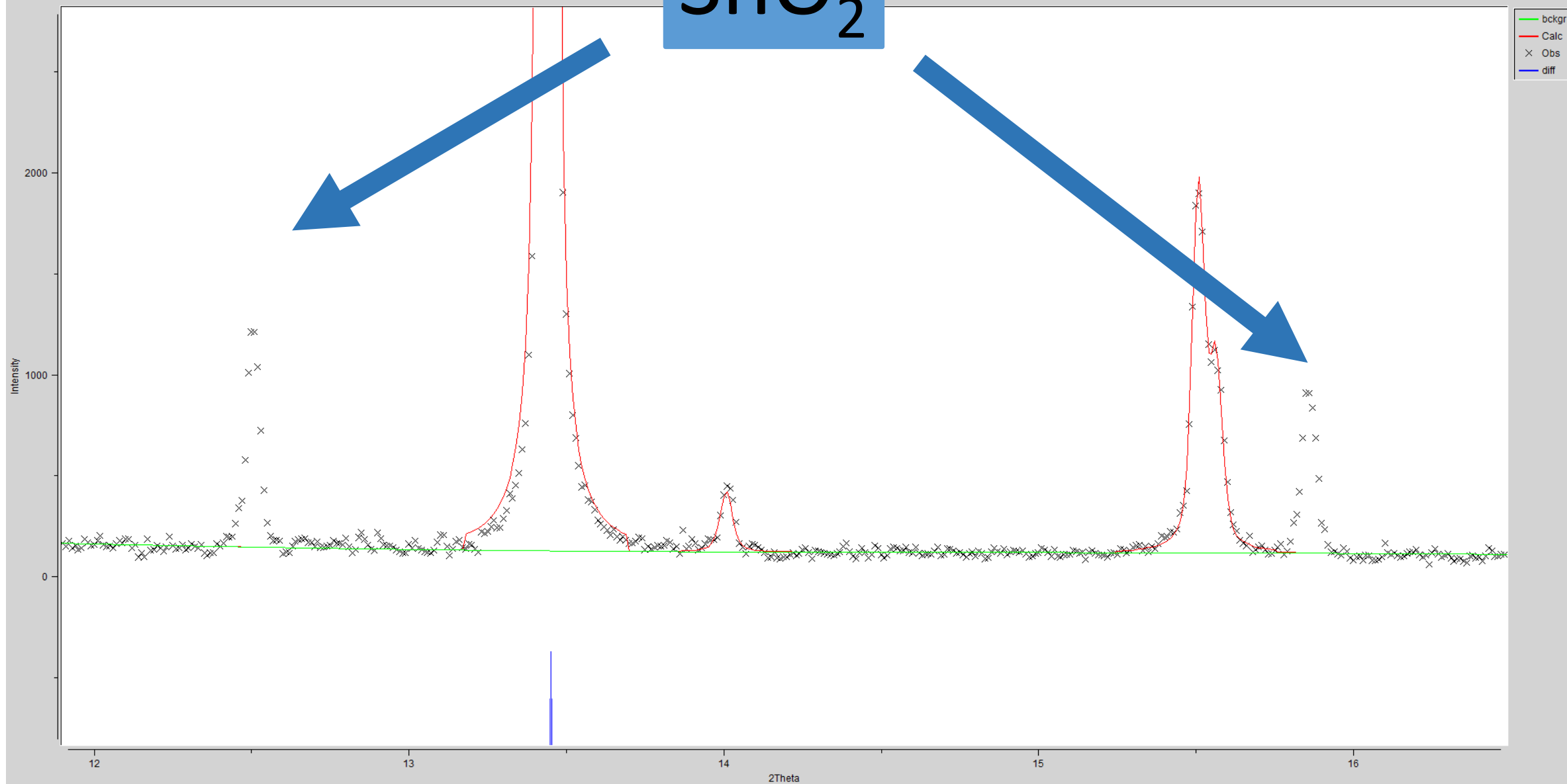
Stannite $\text{Cu}_2\text{FeSnS}_4$ – Rietveld fit – few peaks not fitted



STAN600_25 cycle 476 Hist 1



SnO₂



File Options Powder Xtal Graphs Results Calc Macro Import/Export Help

expnam expedt genes powpref powplot lstview liveplot

LS Controls Phase Histogram Scaling Profile Constraints MD Pref Orient SH Pref Orient

Phase: 1 2 Replace

title: sno2

Add
Phase

a 4.741430

b 4.741430

c 3.188082

Edit
Cell

Refine Cell


 α 90.0000

 β 90.0000

 γ 90.0000

Cell damping

5

* name	type	ref/damp	fractional coordinates			Mult	Occupancy	Uiso
1 SN1	SN	0 0 0	0.000000	0.000000	0.000000	2	1.0000	0.01000
2 O2	O	0 0 0	0.307000	0.307000	0.000000	4	1.0000	0.01000

Add New Atoms

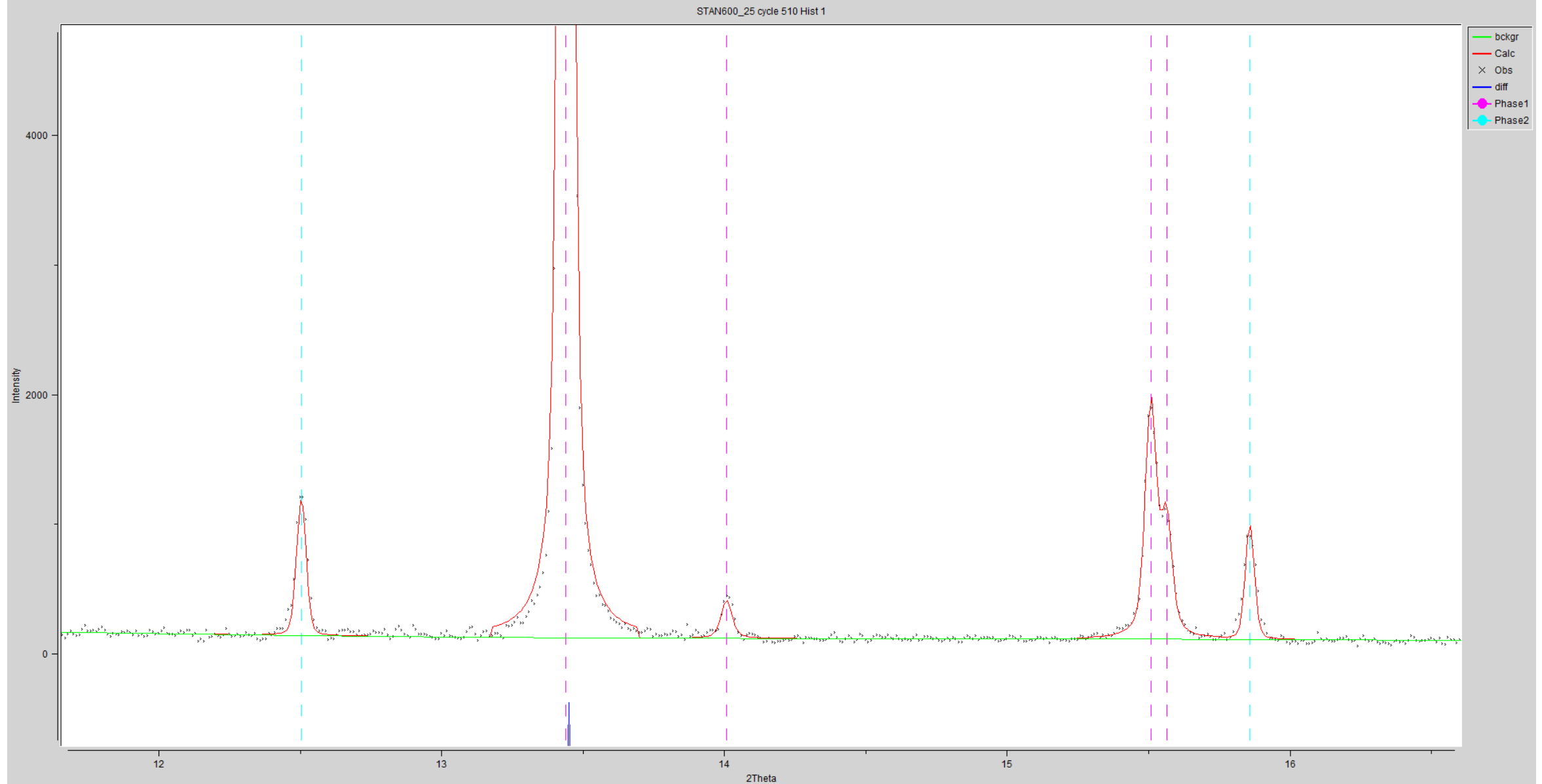
☐ X ☐ U ☐ F

0

0

0

Xform Atoms



Calculated unit cell formula weight: 301.376, density: 6.982gm/cm**3

Phase/element fractions for phase no. 1

Hist Elem: 1 1 PXC
Fraction : 2.26796
Sigmas : 0.775638E-01
Shift/esd: 0.00
Wt. Frac.: 0.96004
Sigmas : 0.131197E-02

96 % Stannite

Phase/element fractions for phase no. 2

Hist Elem: 1 1 PXC
Fraction : 0.267887
Sigmas : 0.666184E-02
Shift/esd: 0.00
Wt. Frac.: 0.39959E-01
Sigmas : 0.953988E-03

4 % SnO₂

Phase/element fraction sum(shift/error)**2 : 0.00

Lattice parameters for powder data:
Phase 1

Structure determination / refinement

EXPGUI interface to GSAS: d:/data/elettra_analysis/MCX/stannite/stannite_2021/gsas/STAN600_25.EXP

File Options Powder Xtal Graphs Results Calc Macro Import/Export Help

expnam expedt genes powpref powplot lstview liveplot

LS Controls Phase Histogram Scaling Profile Constraints MD Pref Orient SH Pref Orient

Phase: 1 2 Replace title: from D:/data/elettra_analysis/MCX/stannite/agosto_2016/

Add Phase

a 5.410244 b 5.410244 c 10.781814 Edit Cell Refine Cell ☒

α 90.0000 β 90.0000 γ 90.0000 Cell damping 5

*	name	type	ref/damp	fractional coordinates			Mult Occupancy		Uiso
1	CU1	CU	0 U9 F9	0.000000	0.500000	0.250000	4	1.0005	0.02234
2	FE2	FE	0 U9 F9	0.000000	0.000000	0.000000	2	1.1676	0.02852
3	SN3	SN	0 U9 F9	0.000000	0.000000	0.500000	2	0.9018	0.02130
4	S4	S	X9 U9 0	0.759331	0.759331	0.869389	8	1.0000	0.01838

File Options Powder Xtal Graphs Results Calc Macro Import/Export Hel									
expnam	expedt	genes	powpref	powplot	lstview	liveplot			
LS Controls		Phase	Histogram	Scaling	Profile	Constraints	MD Pref Orient	SH Pref Orient	
Phase:		1	2	Replace	title: from D:/data/elettra_analysis/MCX/stannite/agosto_2016				
Add Phase	a	5.410243	b	5.410243	c	10.781816	Edit Cell	Refine Cell	☒
	α	90.0000	β	90.0000	γ	90.0000		Cell damping	5
* name	type	ref/damp	fractional coordinates			Mult Occupancy		Uiso	
1 CU1	CU	0 U9 F9	0.000000	0.500000	0.250000	4	1.0000	0.02229	
2 FE2	FE	0 U9 F9	0.000000	0.000000	0.000000	2	0.8224	0.03087	
3 SN3	SN	0 U9 F9	0.000000	0.000000	0.500000	2	0.7984	0.02048	
4 S4	S	X9 U9 0	0.759427	0.759427	0.869377	8	1.0000	0.01837	
5 Sn2	SN	0 U9 F9	0.000000	0.000000	0.000000	2	0.1776	0.03087	
6 Fe3	FE	0 U9 F9	0.000000	0.000000	0.500000	2	0.2016	0.02048	

Tools Style Objects

Structural models

☒ Show models
☐ Show dot surface

Style

☐ Ball-and-stick
☐ Space-filling
☒ Polyhedral
☐ Wireframe
☐ Stick

Volumetric data

☐ Show sections
☐ Show isosurfaces
☐ Surface coloring

Style

☒ Smooth shading
☐ Wireframe
☐ Dot surface

Crystal shapes

☐ Show shapes

Style

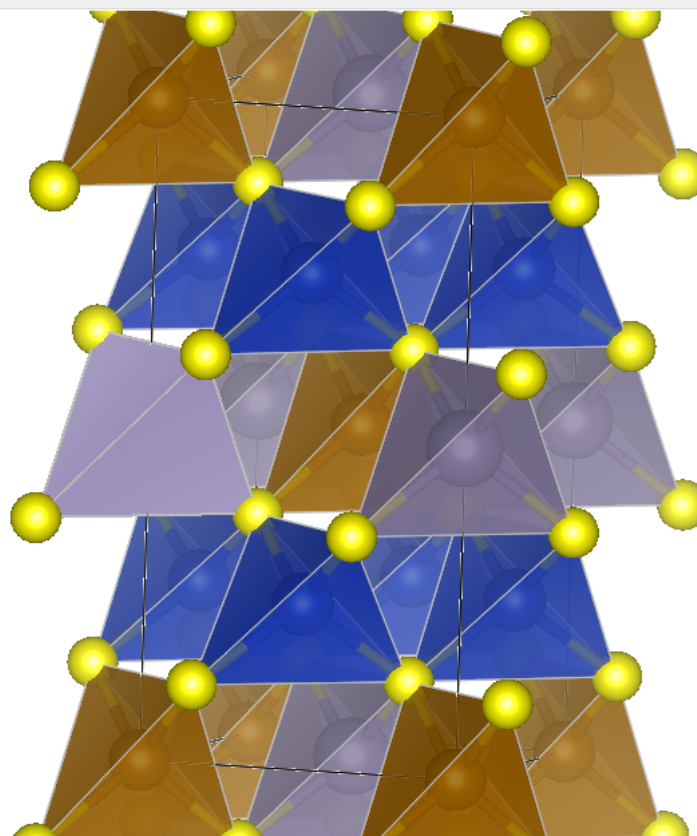
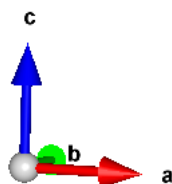
☒ Unicolor
☐ Custom color
☐ Wireframe

Properties...

Boundary...

Orientation...

STAN600_25_1.ins



```

4      S1  S  -0.26080 -0.26080  0.36936  ( 0, 0,-1)+ -x+1/2, -y+1/2, z+1/2
4      S1  S  -0.26080  0.26080  0.63064  ( 0,-1, 1)+ -y+1/2, x+1/2, -z+1/2
4      S1  S   0.26080 -0.26080  0.63064  (-1, 0, 1)+ y+1/2, -x+1/2, -z+1/2
4      S1  S   0.26080  0.26080  0.36936  (-1,-1,-1)+ x+1/2, y+1/2, z+1/2

```

```

l(SN1-S1) = 2.44289(0) Å
l(SN1-S1) = 2.44289(0) Å
l(SN1-S1) = 2.44289(0) Å
l(SN1-S1) = 2.44289(0) Å

```

```

-----
Average bond length = 2.4429 Å
Polyhedral volume = 7.4817 Å^3
Distortion index (bond length) = 0.00000
Quadratic elongation = 1.0000
Bond angle variance = 0.0047 deg.^2
Effective coordination number = 4.0000

```

Output Summary Comment

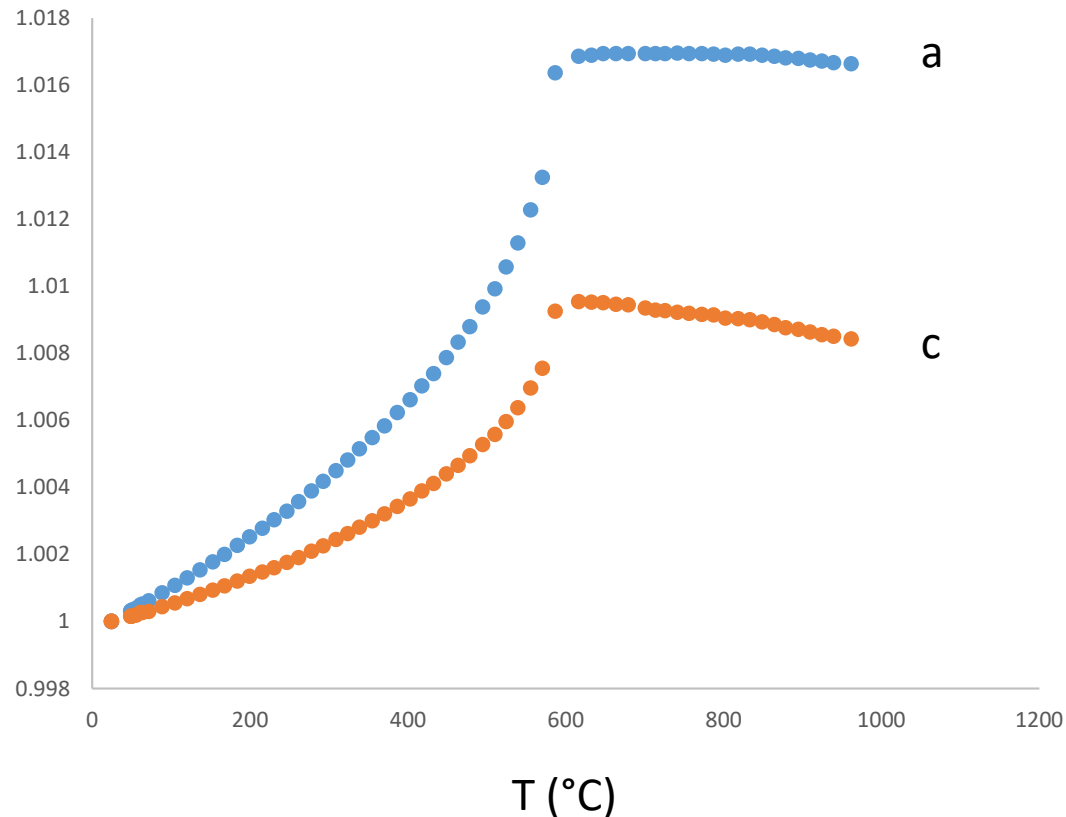


Summary

- Accuracy (and precision) in geometrical parameters (i.e. peak position, lattice parameter) is function of calibration
- Synchrotron experiments (especially in Bragg-Brentano – transmission -geometry) can result in improved accuracy compared to laboratory sources

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Thermal expansion of SiO₂ quartz

Normalized lattice parameters

Summary

- Synchrotron high resolution beamlines: improved angular resolution compared to laboratory sources
- Accurate determination of microstructural parameters (i.e. crystallite size, microstrain)

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American Mineralogist, Volume 90, pages 506–509, 2005

LETTER

Microscopic strain in synthetic pyrope-grossular solid solutions determined by synchrotron X-ray powder diffraction at 5 K: The relationship to enthalpy of mixing behavior

MONICA DAPIAGGI,^{1,*} CHARLES A. GEIGER,² AND GILBERTO ARTIOLI¹

¹Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano, I-20133 Milano, Italy
²Institut für Geowissenschaften, Christian-Albrechts-Universität, D-24098 Kiel, Germany

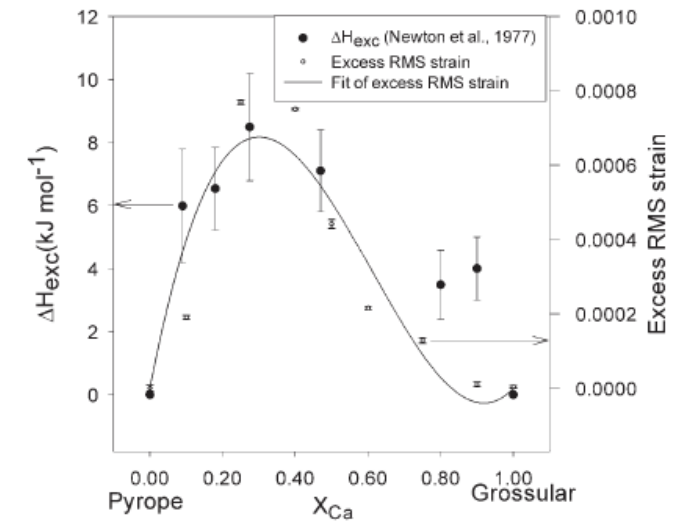
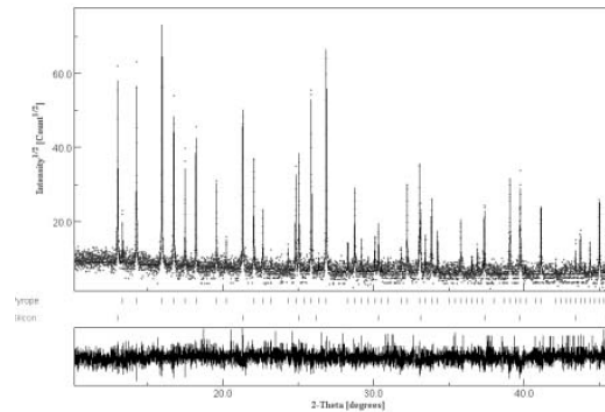
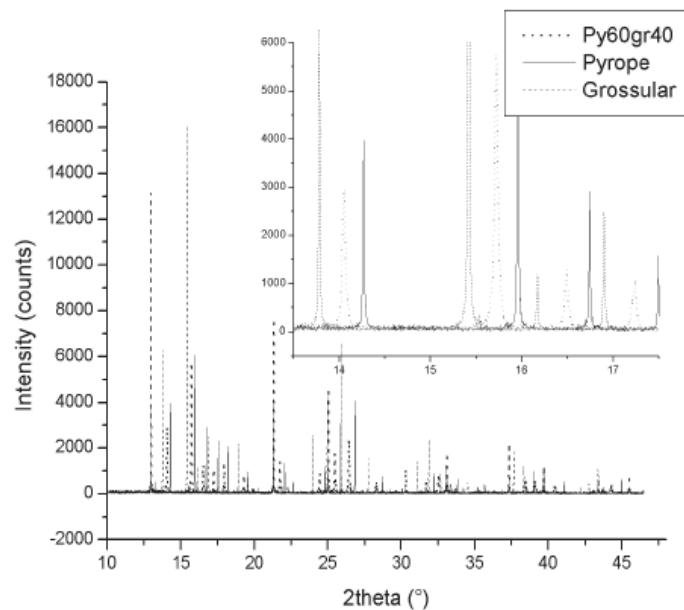


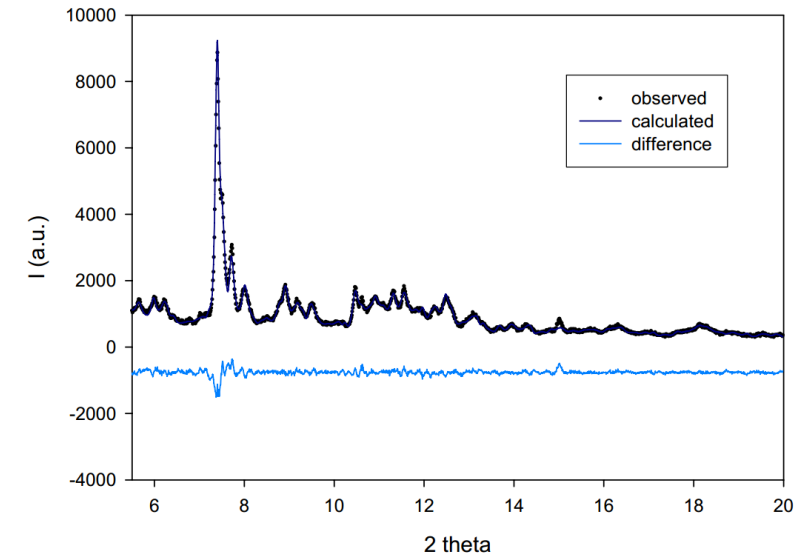
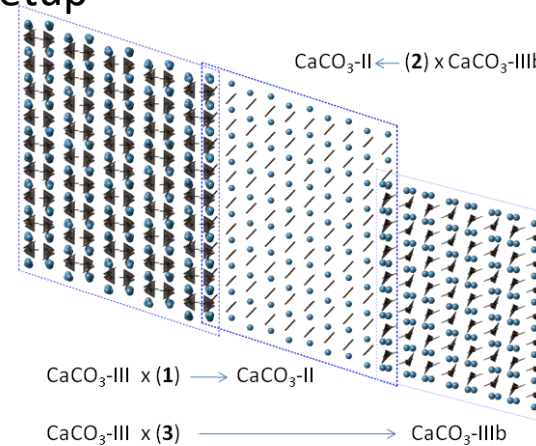
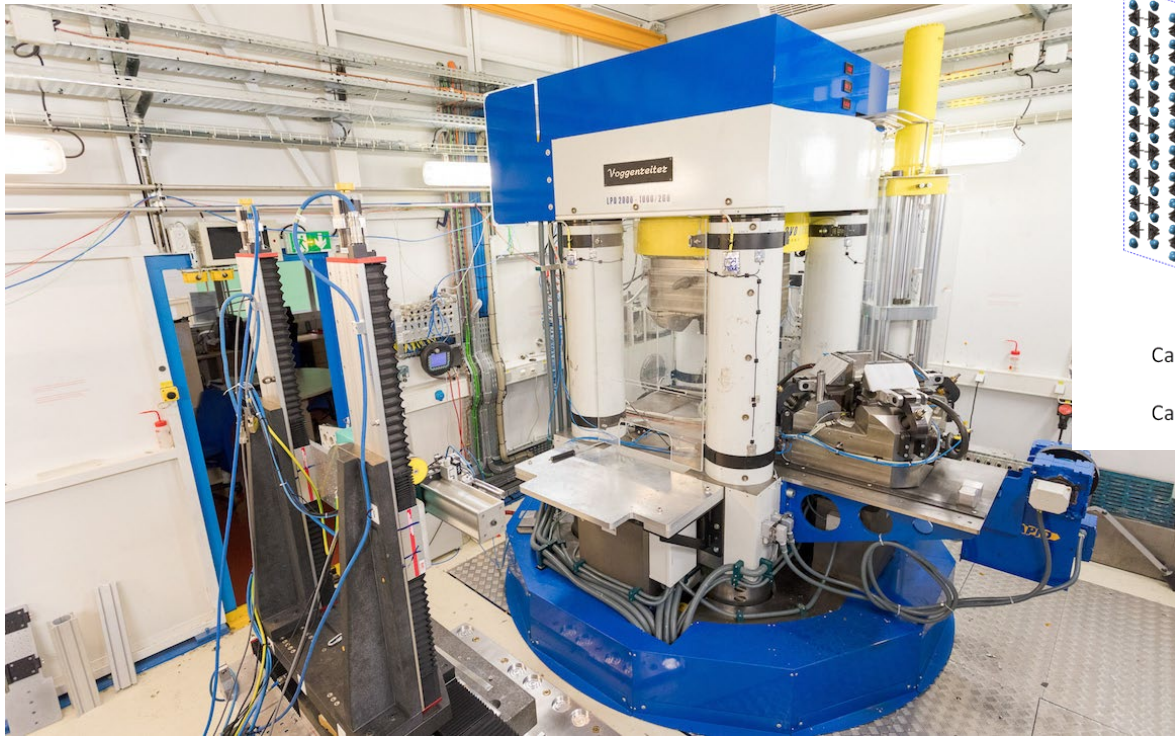
FIGURE 3. Experimental values of the excess enthalpies of mixing (open squares from Newton et al., 1977) and the excess RMS strain (black circles). The error bars represent 2σ variations in the determinations. The solid line is a two parameter asymmetric fit (Eq. 4) to the excess RMS strain data.

Summary

- Synchrotron diffraction with tunable energy – high energy can result in minimization of absorption effects.
Useful for structure determination of sample with atomic species with significant different atomic numbers
- Diffraction in complex environments
- Large experimental space for ad-hoc experimental setup

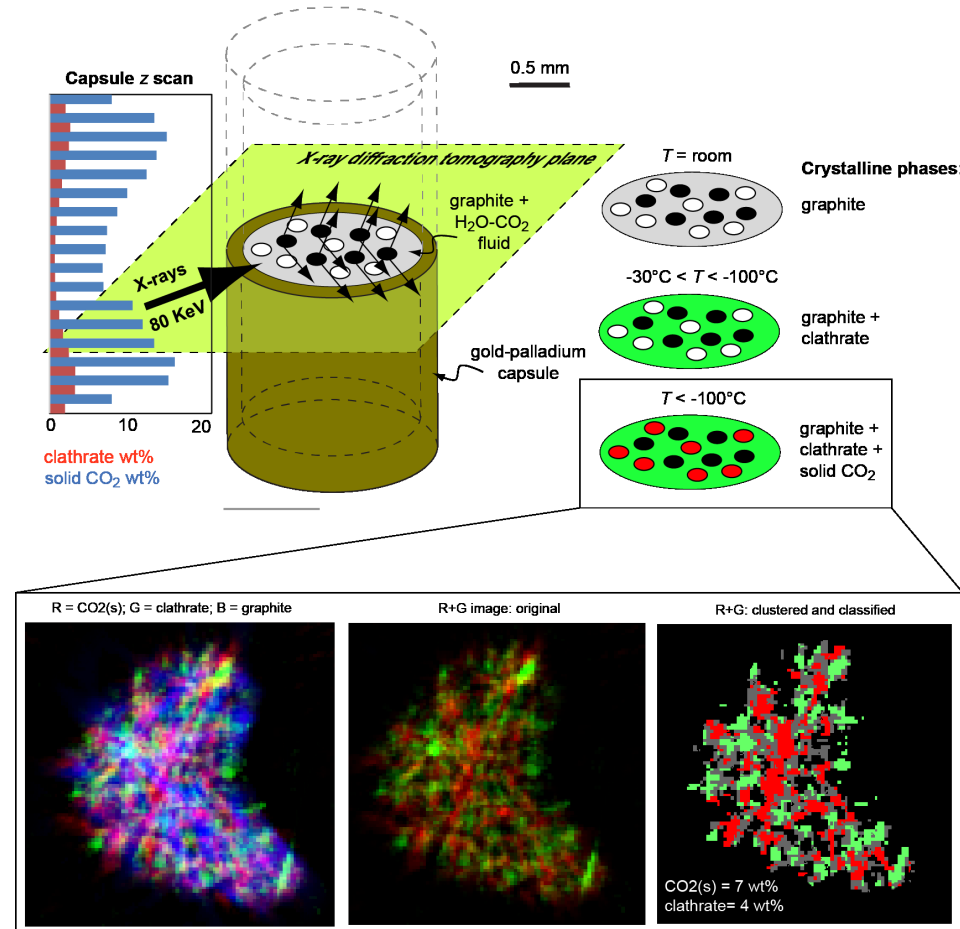
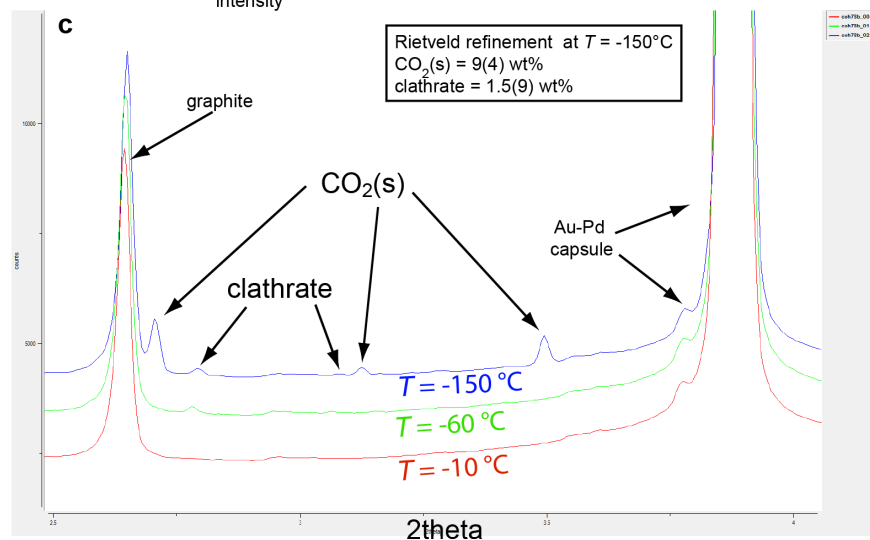
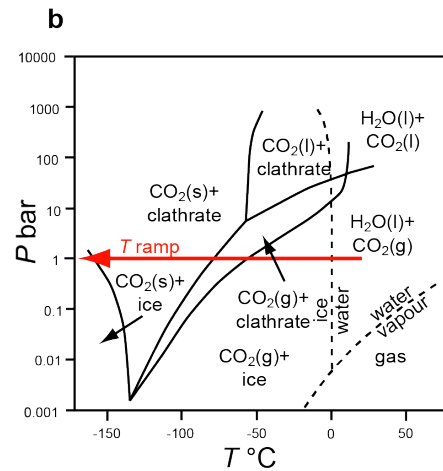
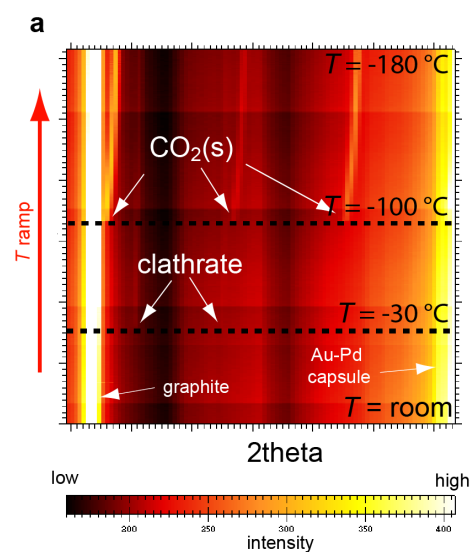
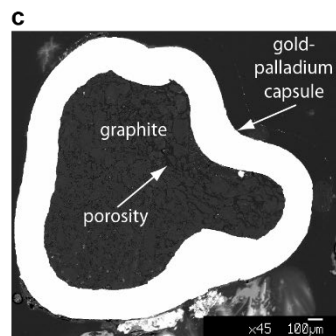
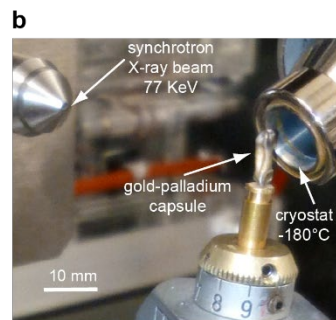
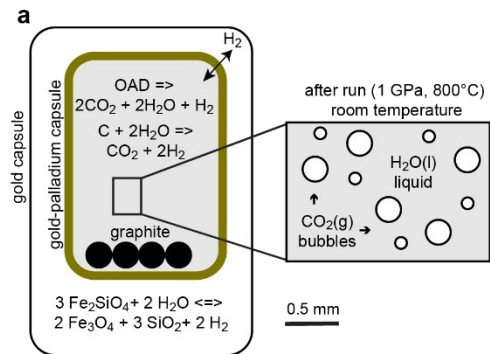
Summary

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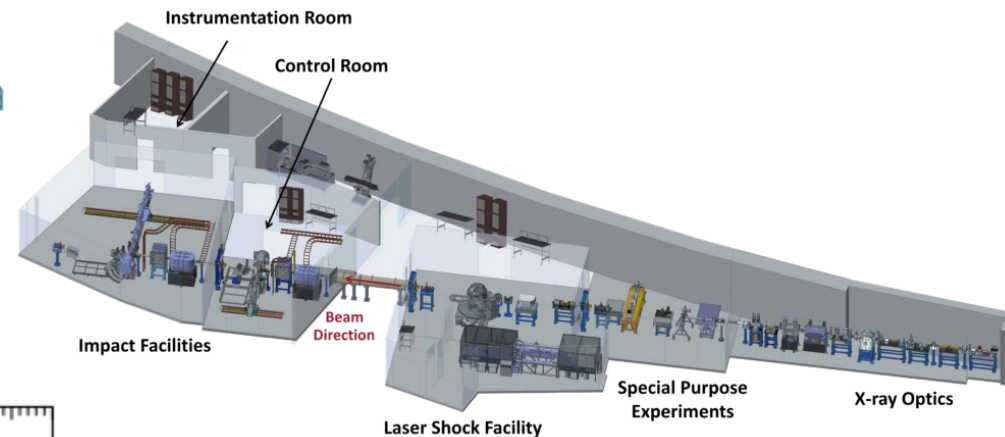
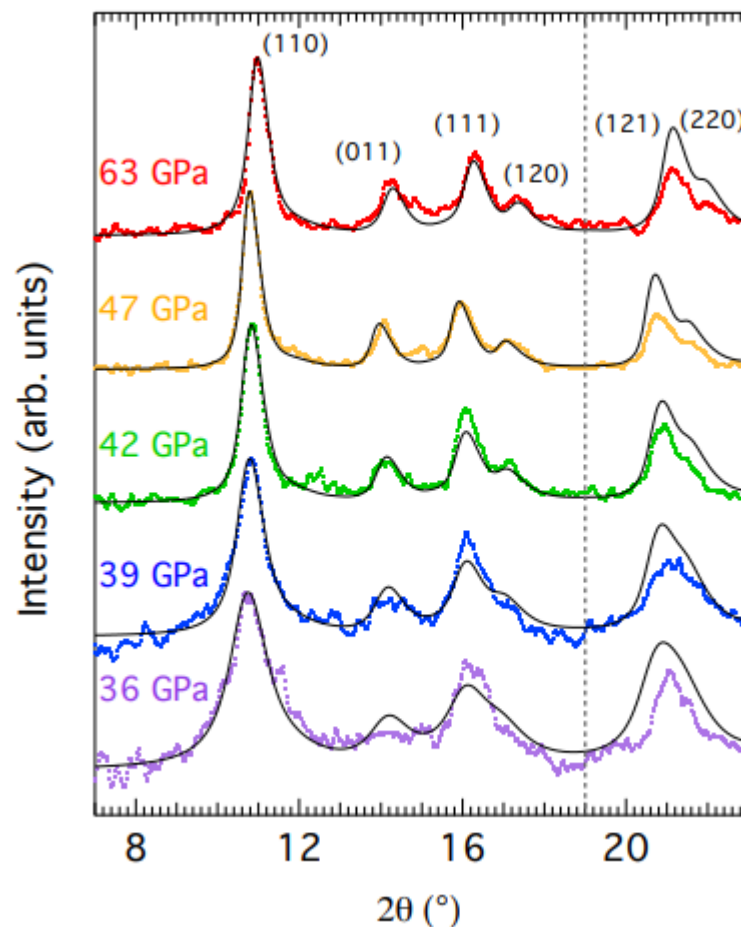
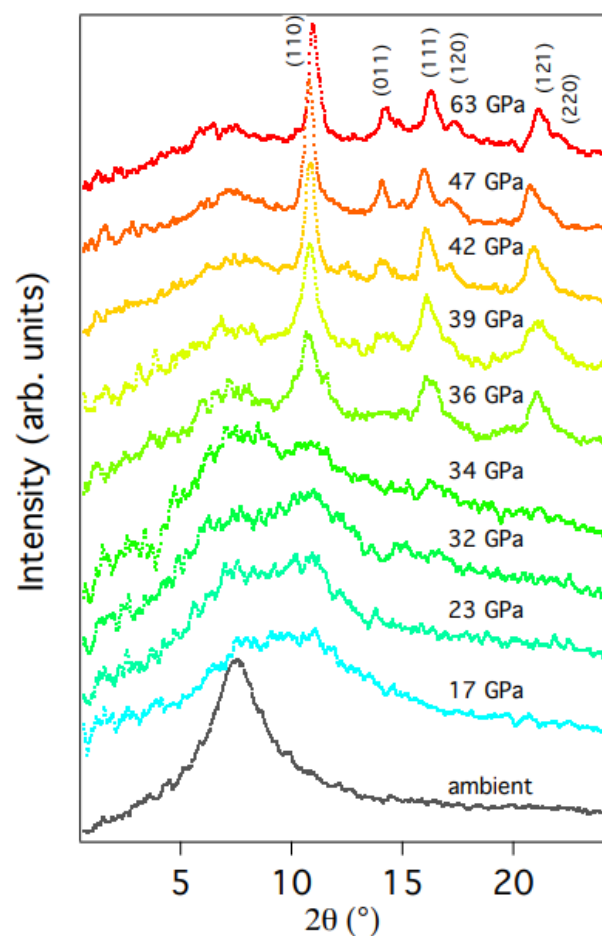
Rietveld fit of complex structural intergrow of different domain in high pressure phase

LVP – Large Volume Press @ ESRF ID06 beamline



In situ X-Ray Diffraction of Shock-Compressed Fused Silica

Sally June Tracy, Stefan J. Turneure, and Thomas S. Duffy
Phys. Rev. Lett. **120**, 135702 – Published 29 March 2018



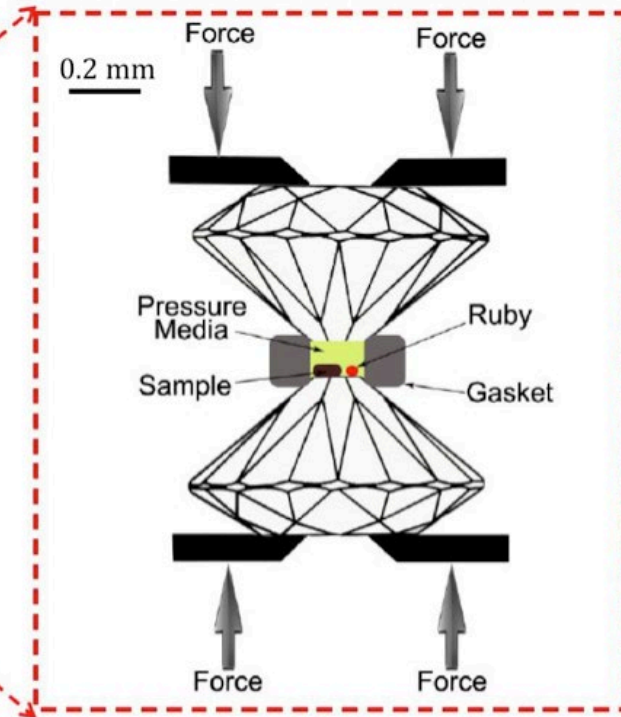
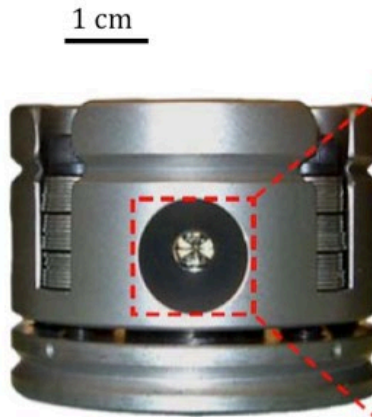
The diffraction data are combined with continuum-level measurements to reveal a complete picture of the material response from the atomic length scale to the continuum level, allowing for the unambiguous determination of the phase(s) formed at ~ 100 ns timescales from 12 to 63 GPa.

Plate impact experiments were carried out at the Dynamic Compression Sector of the Advanced Photon Source (APS). Planar shock waves in fused silica were generated using LiF impactors accelerated in a polycarbonate projectile to a velocity of 1.8–5.6 km/s using either a single-stage propellant gun or a two-stage light gas gun. A schematic of the impact

3) EXAMPLE of crystal structure determination from single crystals at «extreme conditions»

High-pressure and high-temperature

Diamond anvil cell



Diamond culet diameter

max pressure

1 mm
0.6 mm
0.3 mm
0.125 mm

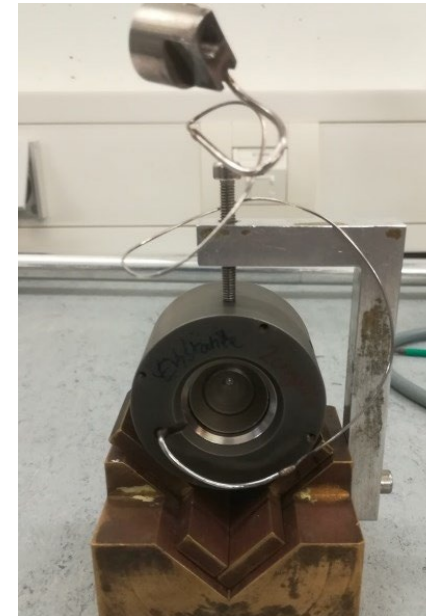
2 GPa
20 GPa
60 GPa
> 100 GPa

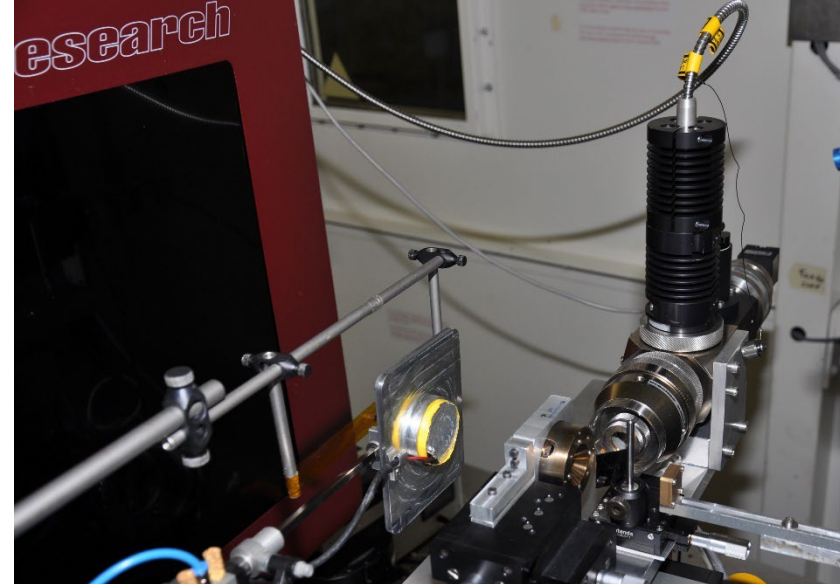
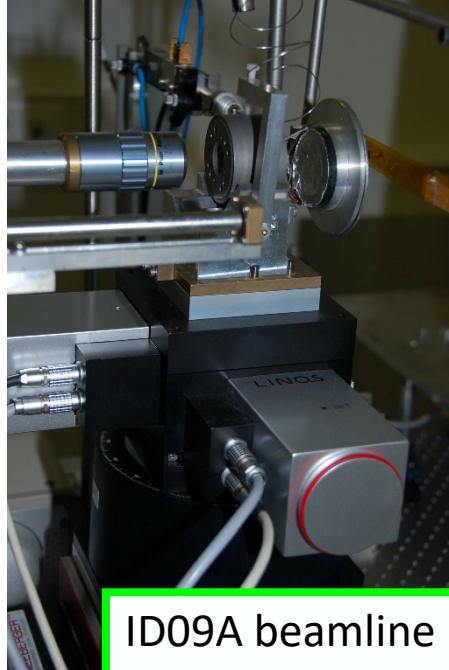
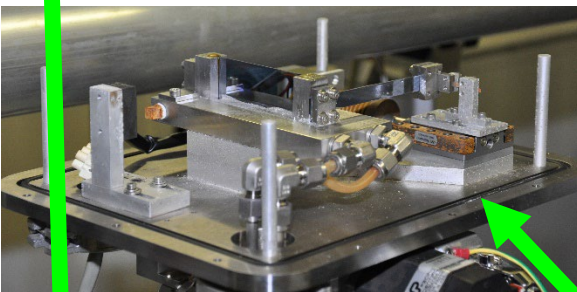
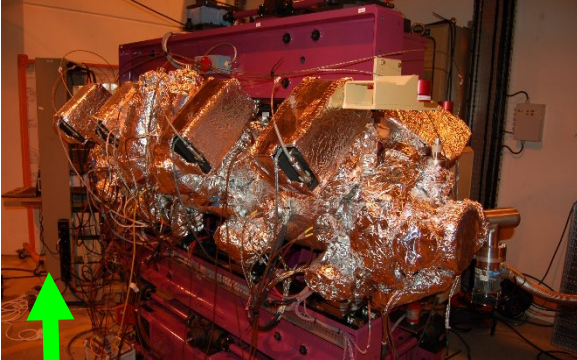
Force:

screws



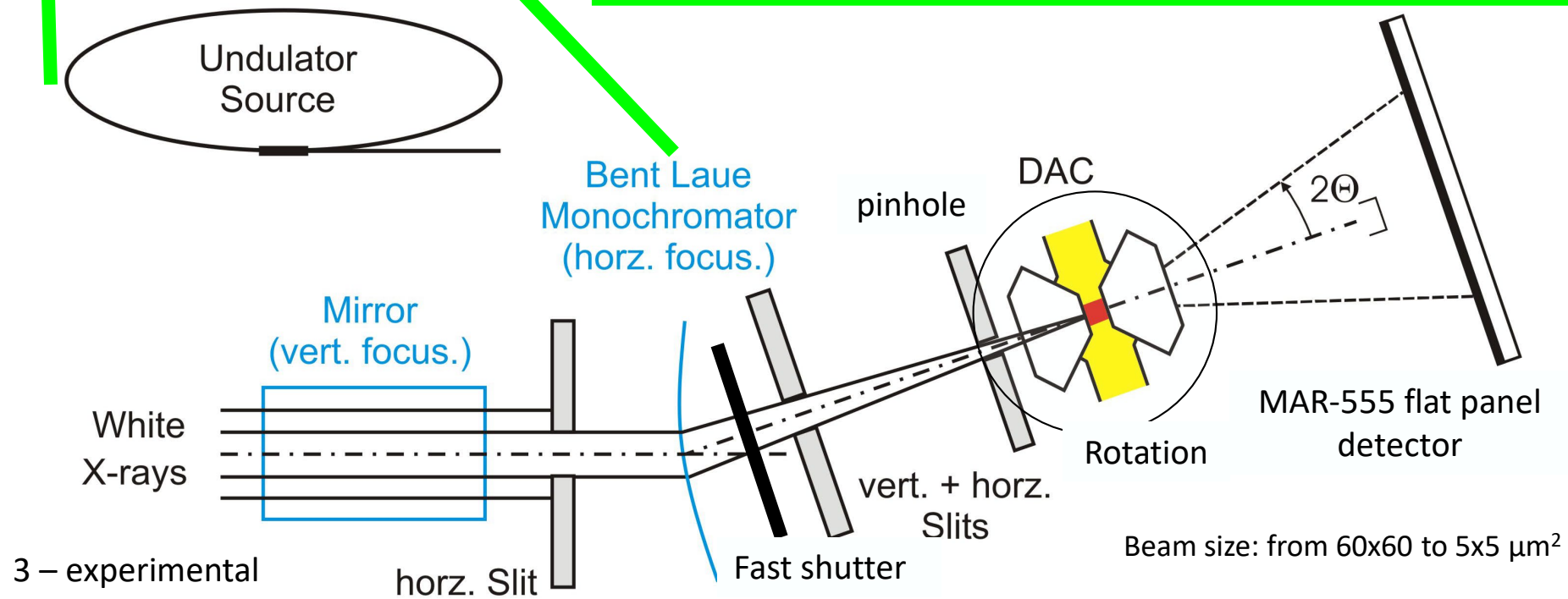
Gas under pressure
(0-200 bar)
and expanding
metallic membrane





ID09A beamline @ ESRF (Grenoble, France)

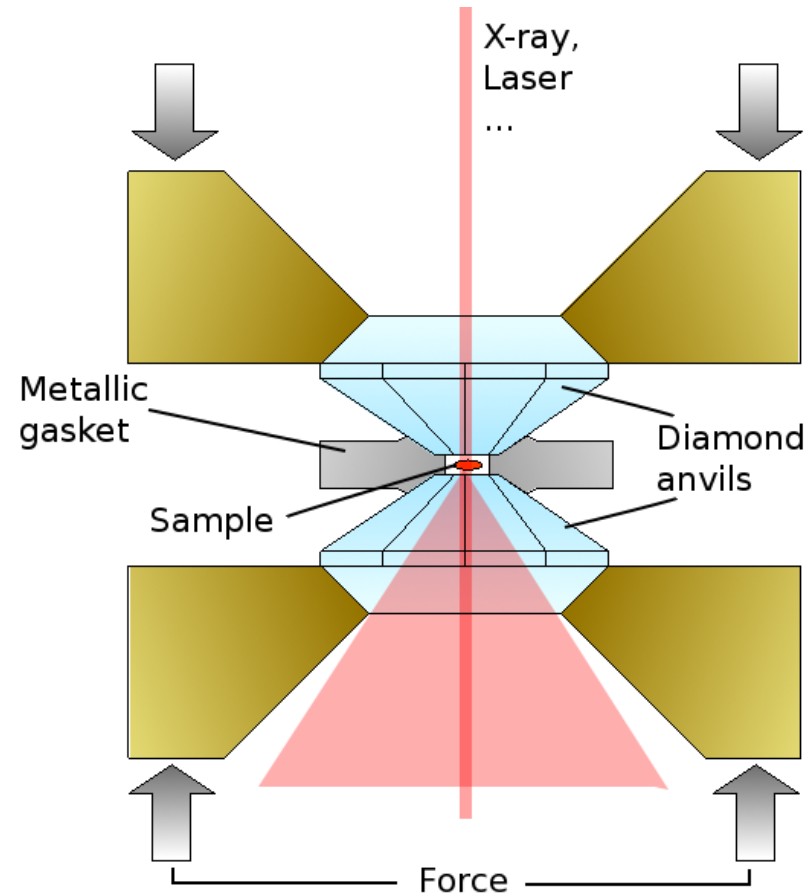
European Synchrotron Radiation Facility



Diamond Anvil Cell (DAC) +/- resistive heating +/- laser heating

P max: «routine» 1.5 Mbar – possible experiments up to 6 Mbar

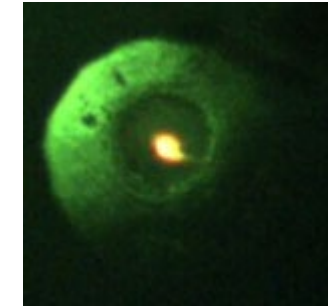
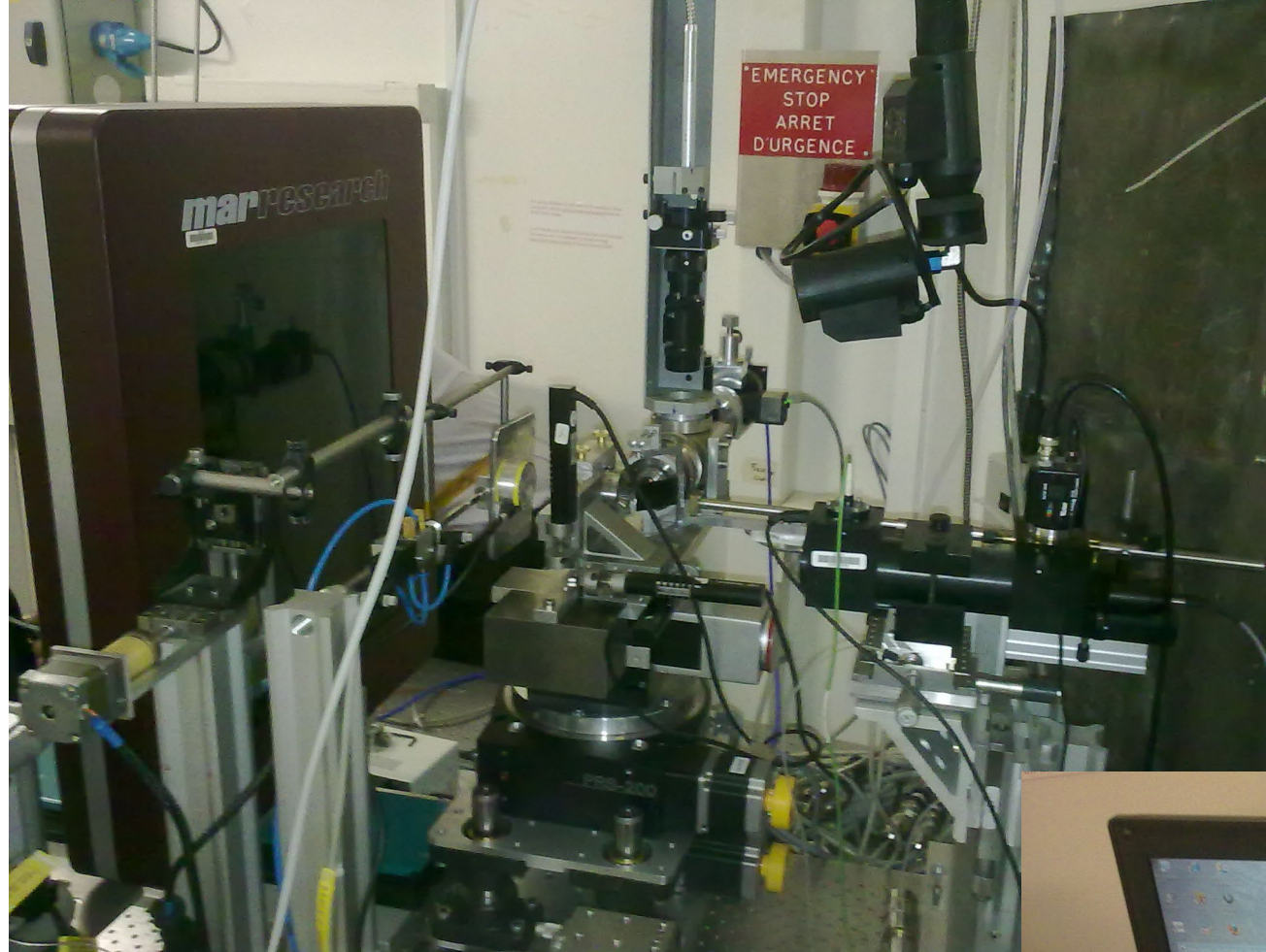
T max: cryostat + resistive: 5-1000 K; laser heating: up to 6000 K



X-ray diffraction
(powder, single crystal)

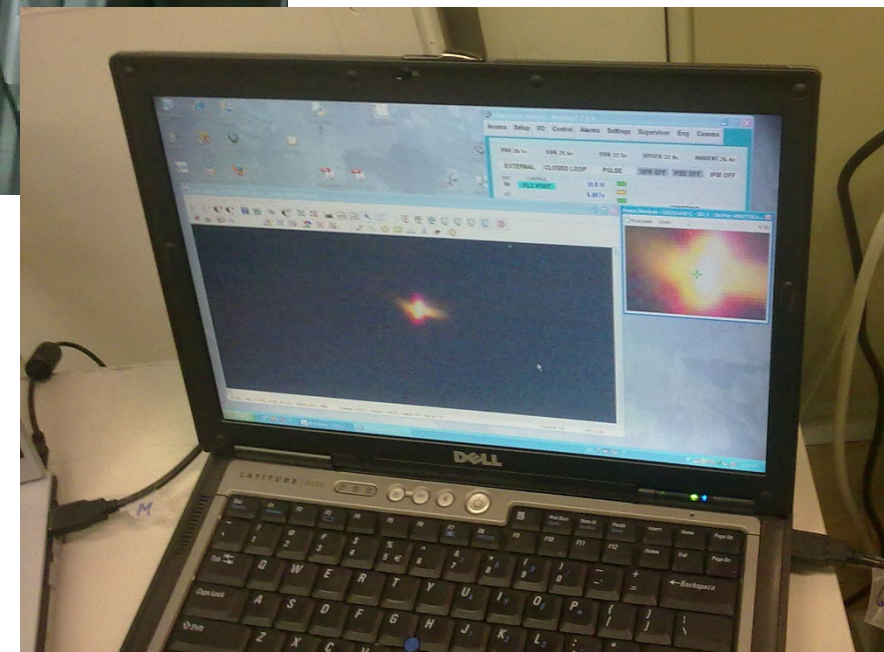
X-ray scattering

X-ray spectroscopy

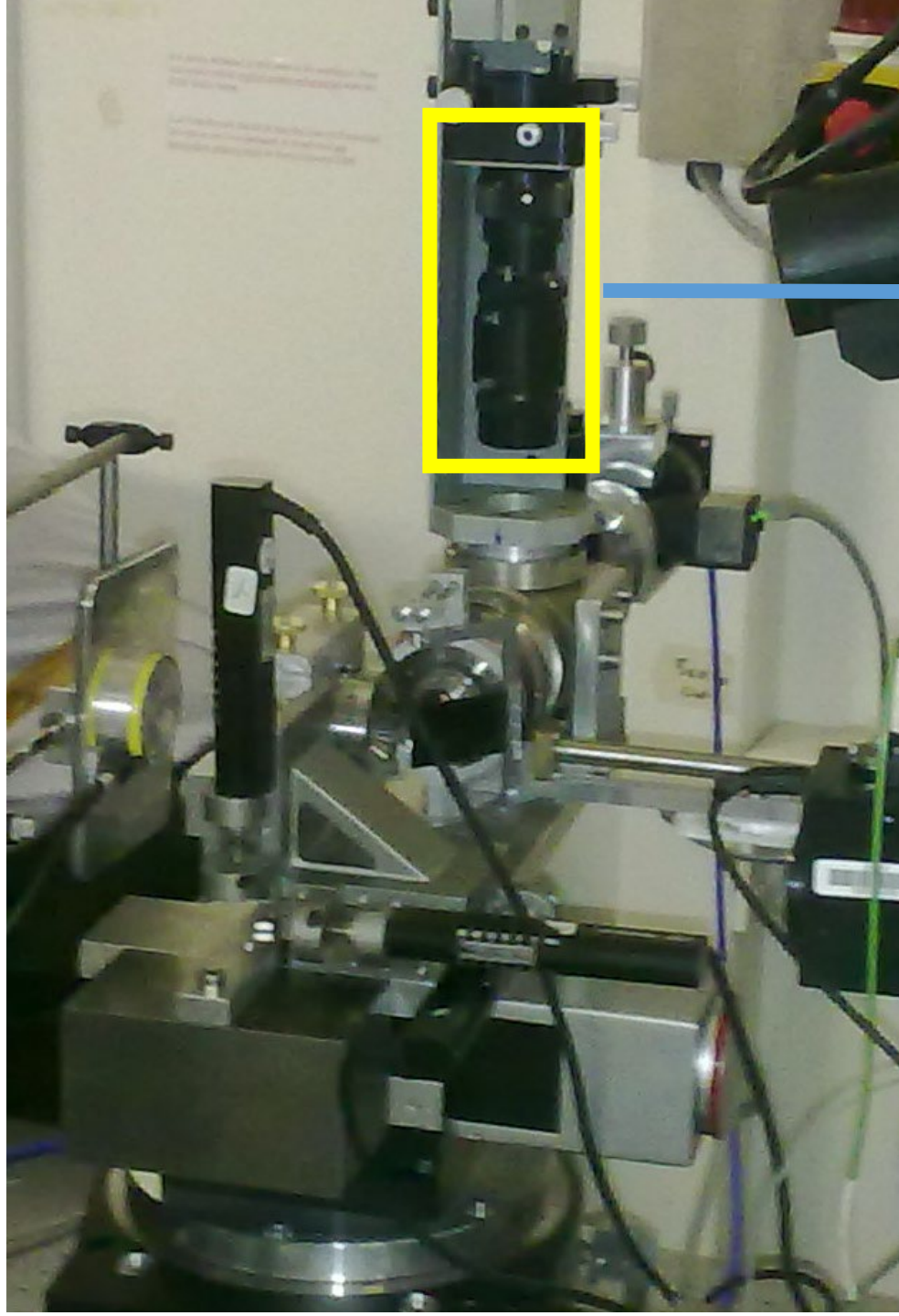


Portable laser heating system for single crystal diffraction

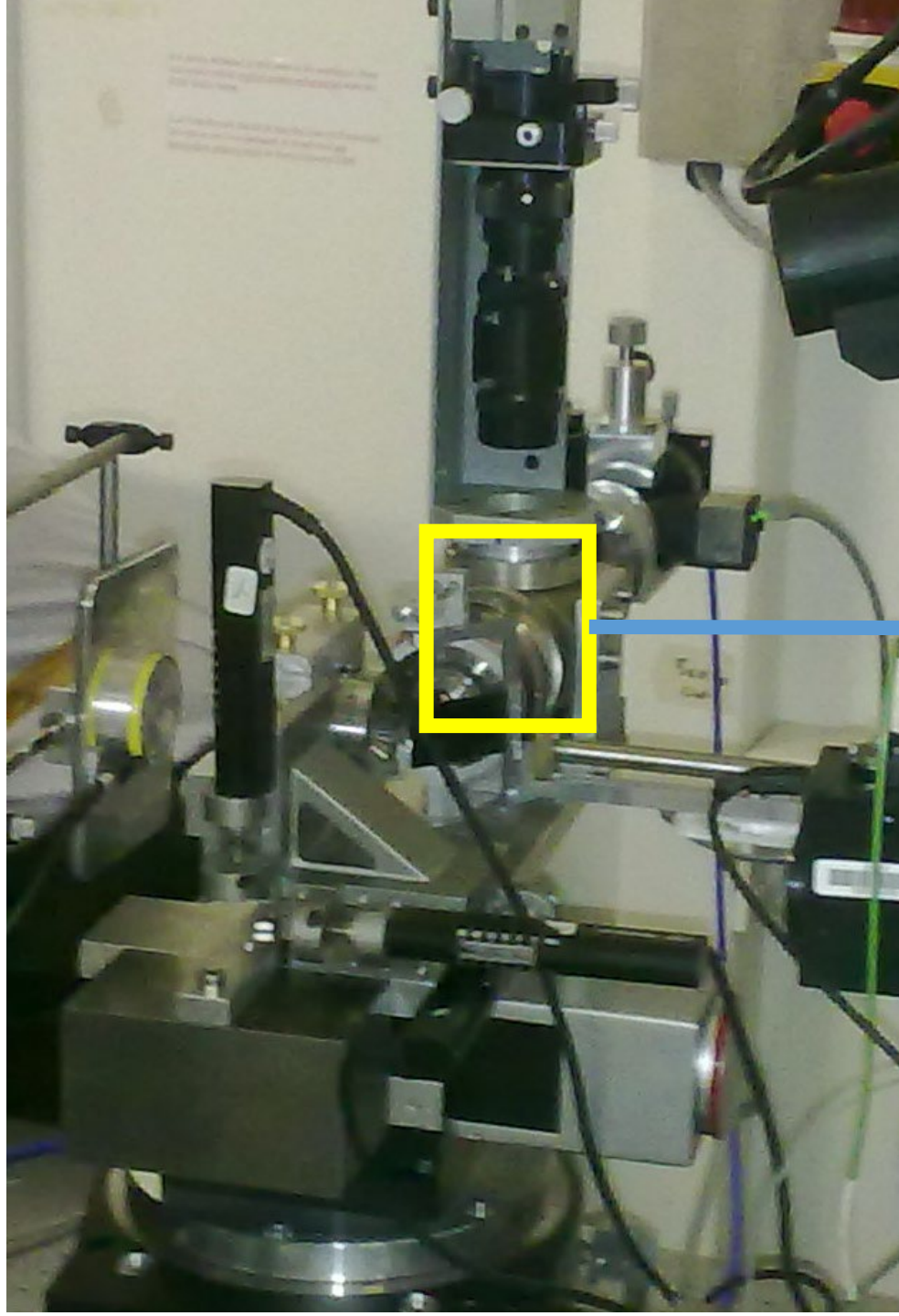
Dubrovinsky et al., HPR 2010



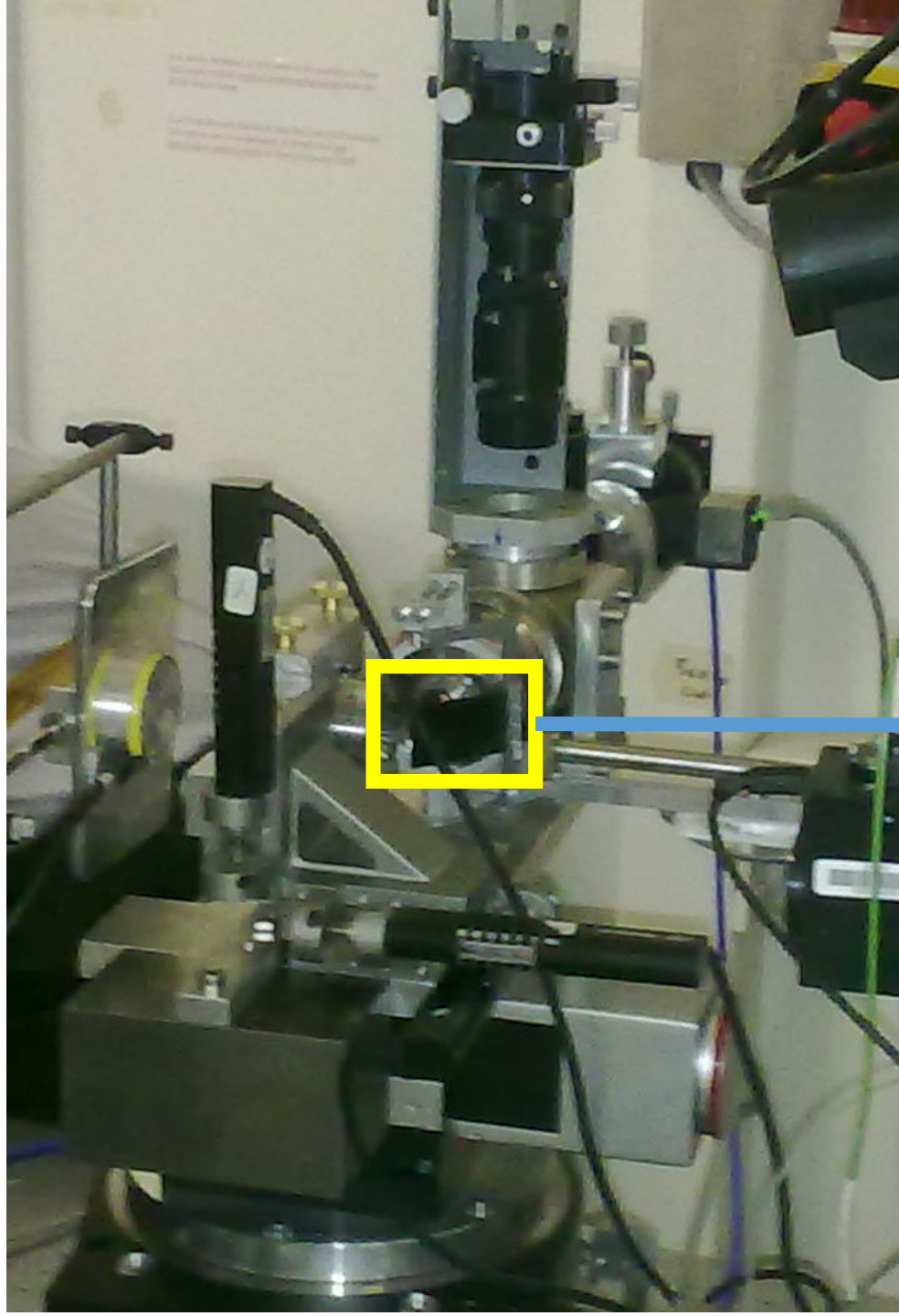




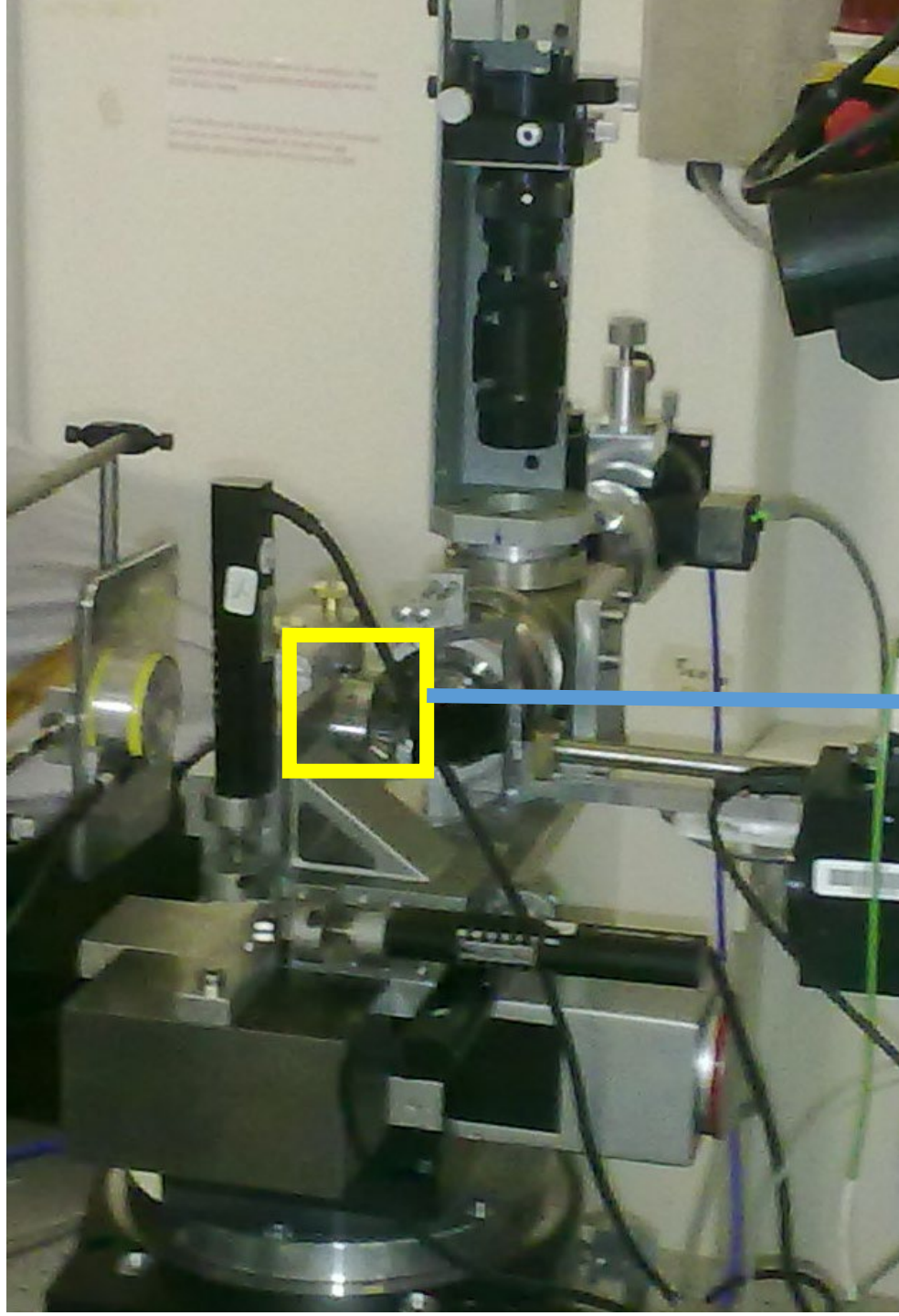
Incoming laser beam



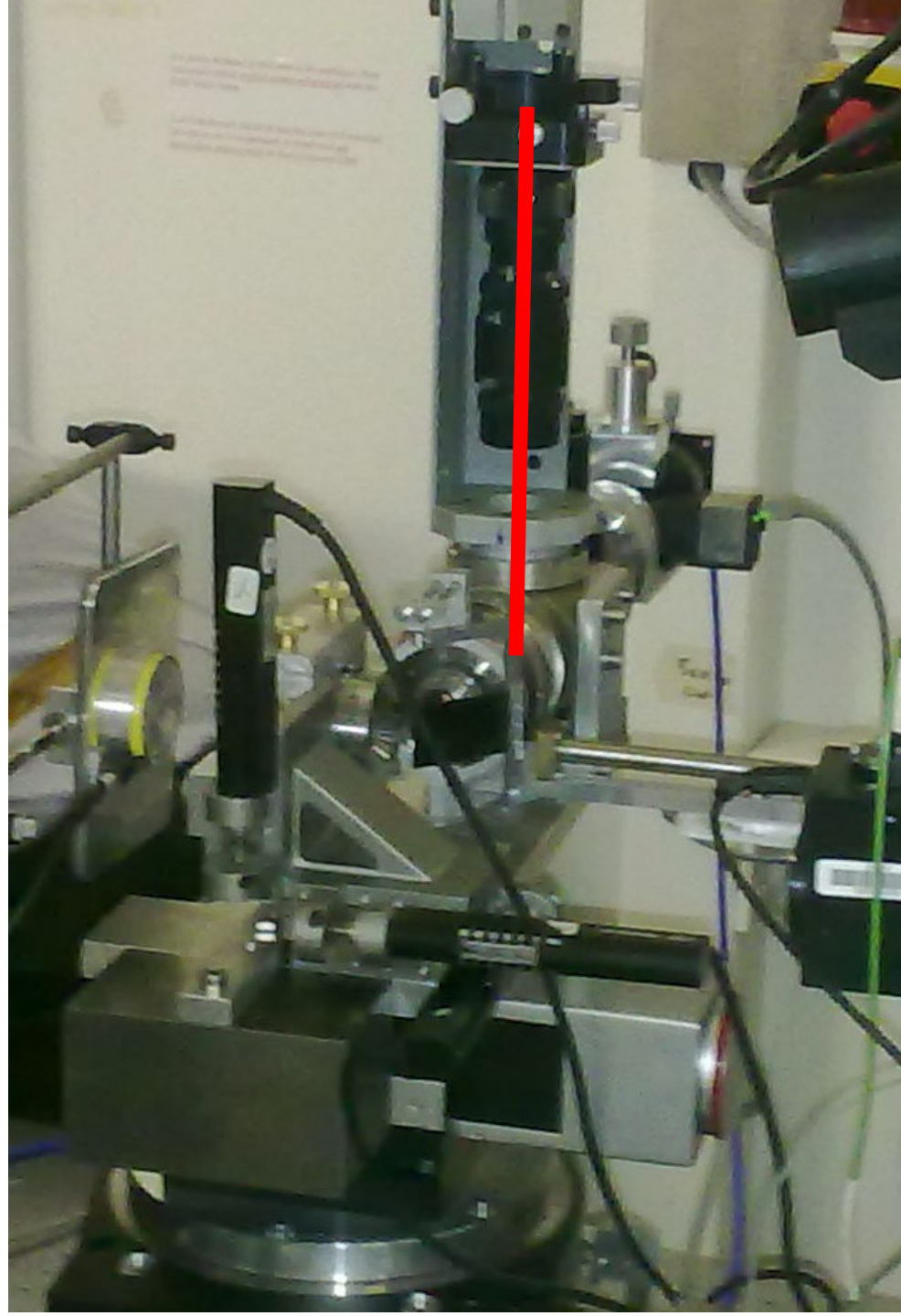
Mirror and lens

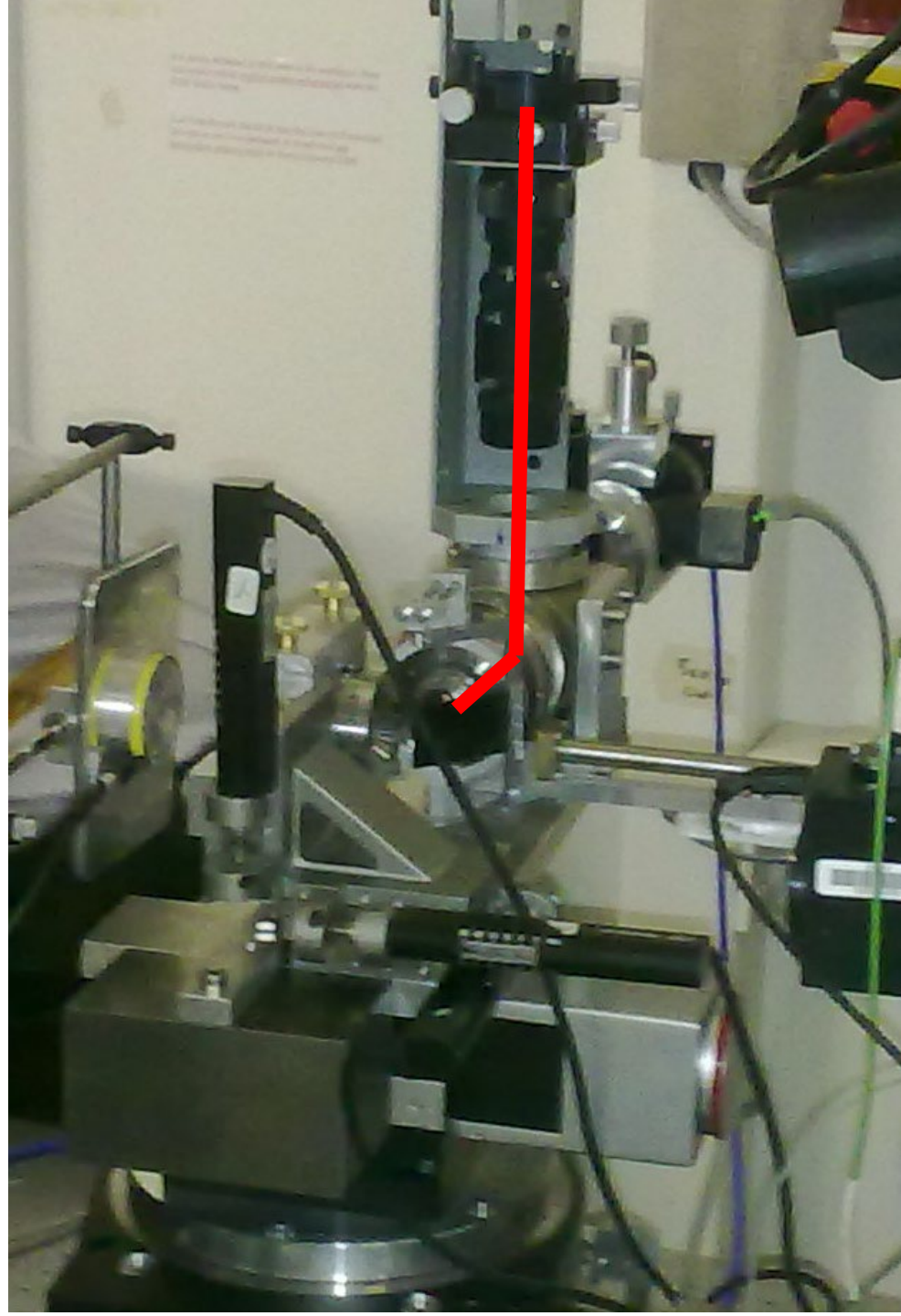


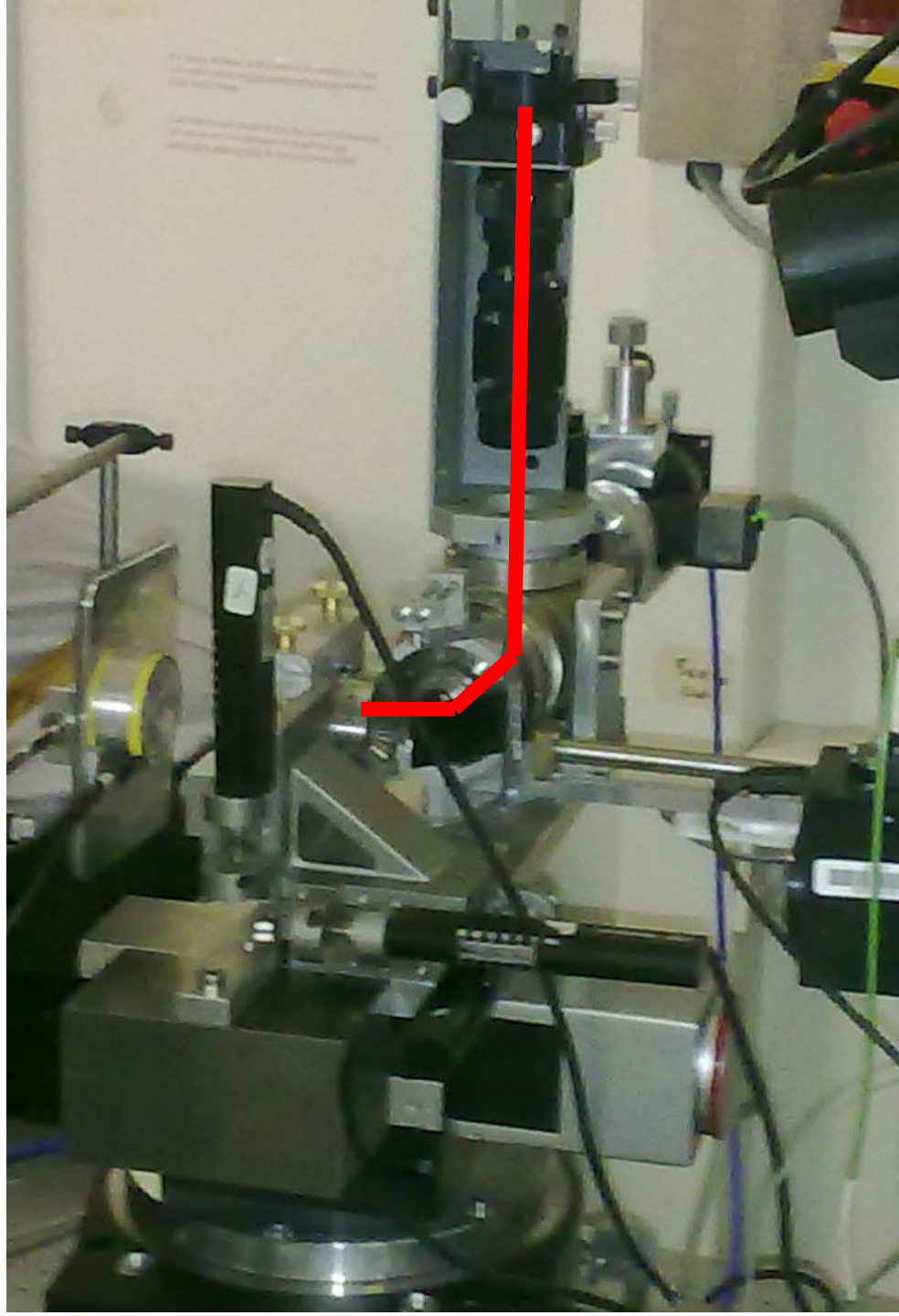
Mirror



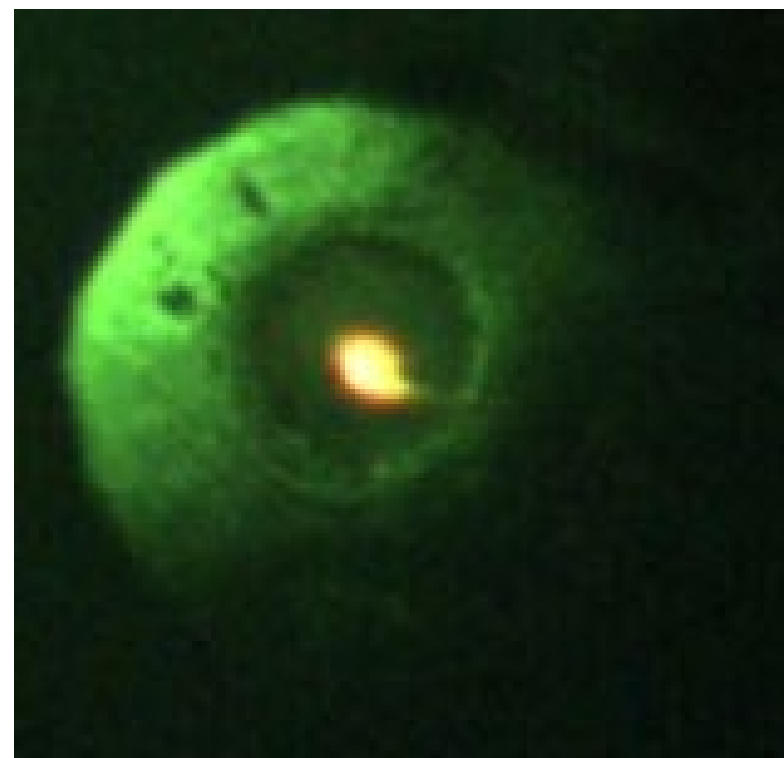
Diamond Anvil Cell

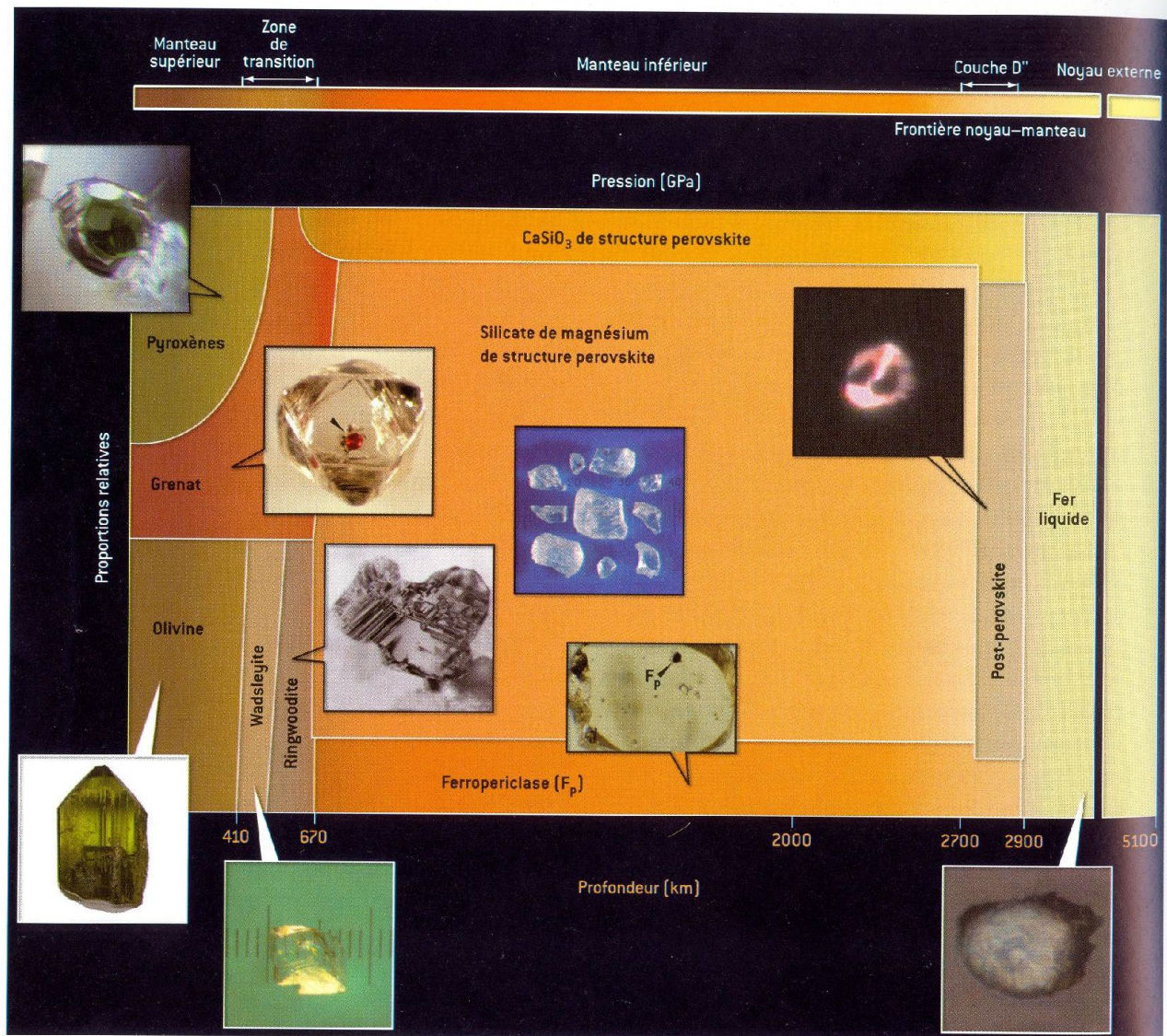






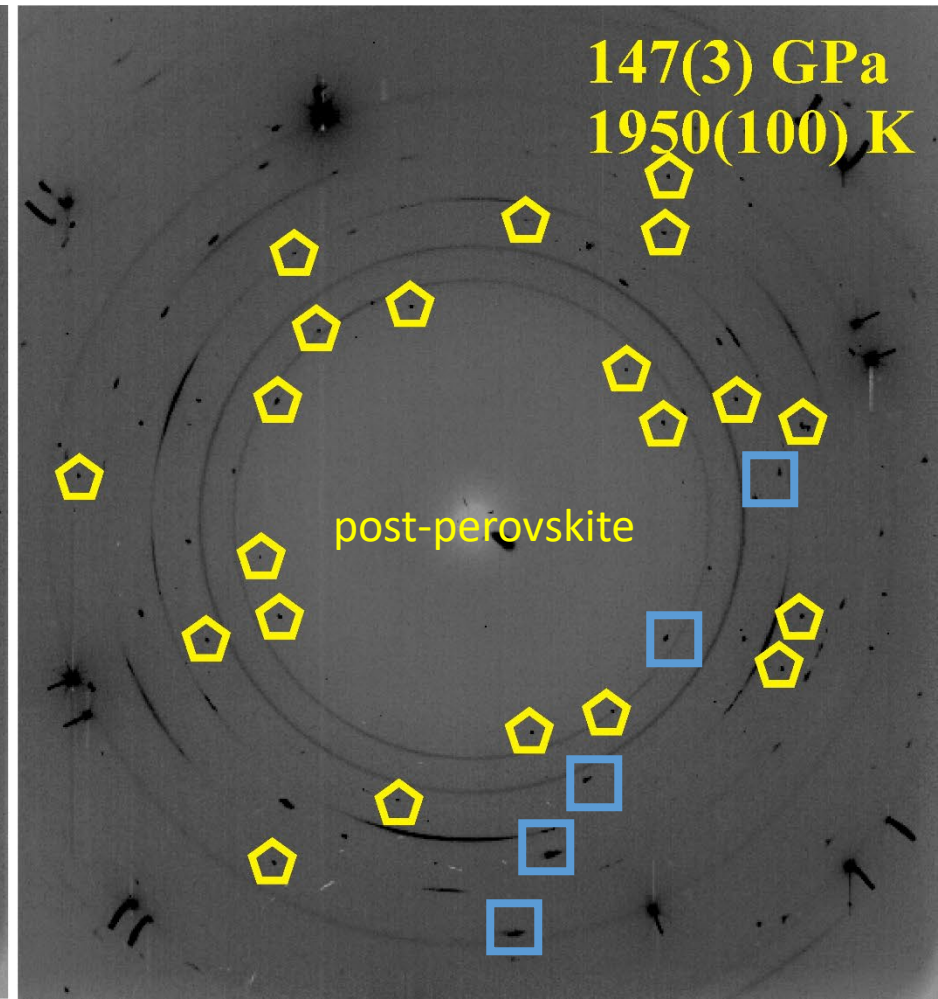
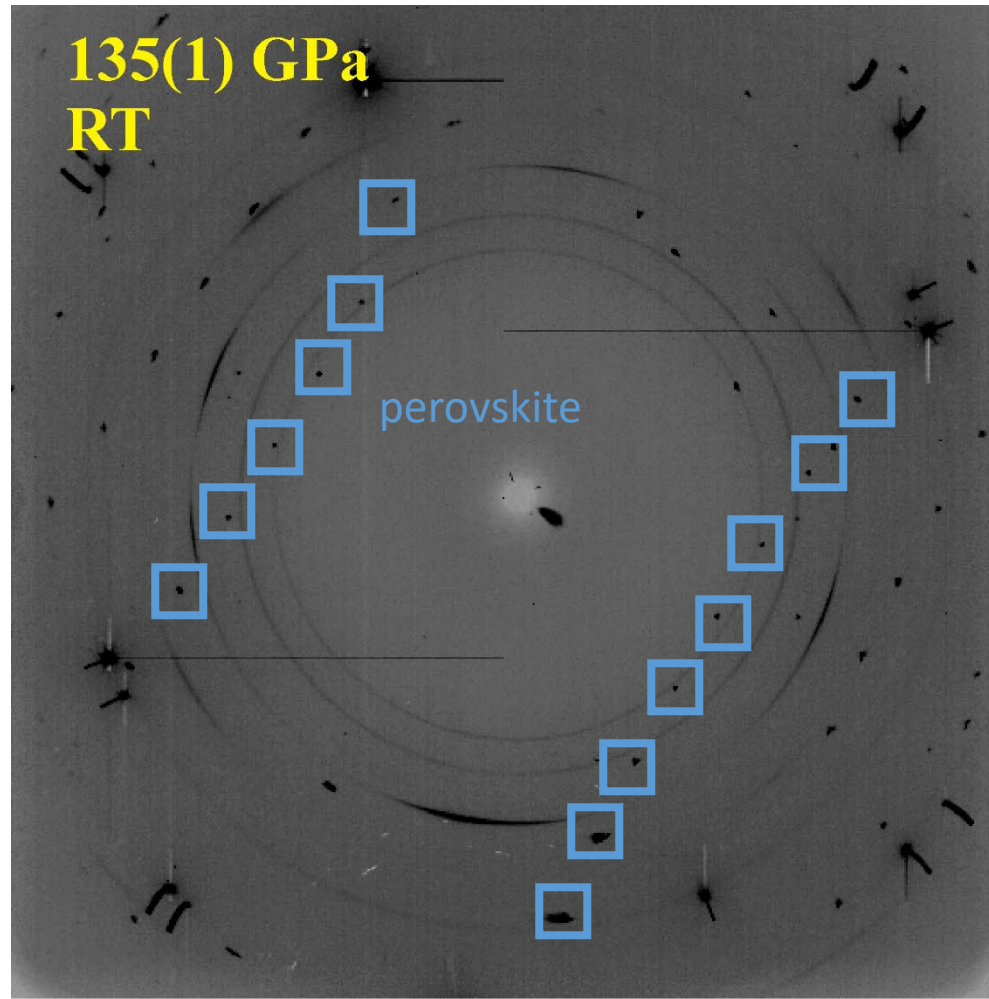
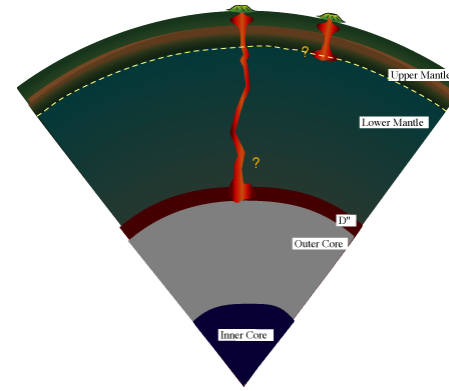
Single crystal laser heating
+ rotation of all the stage
for single crystal diffraction
data collection in situ @
HP/HT

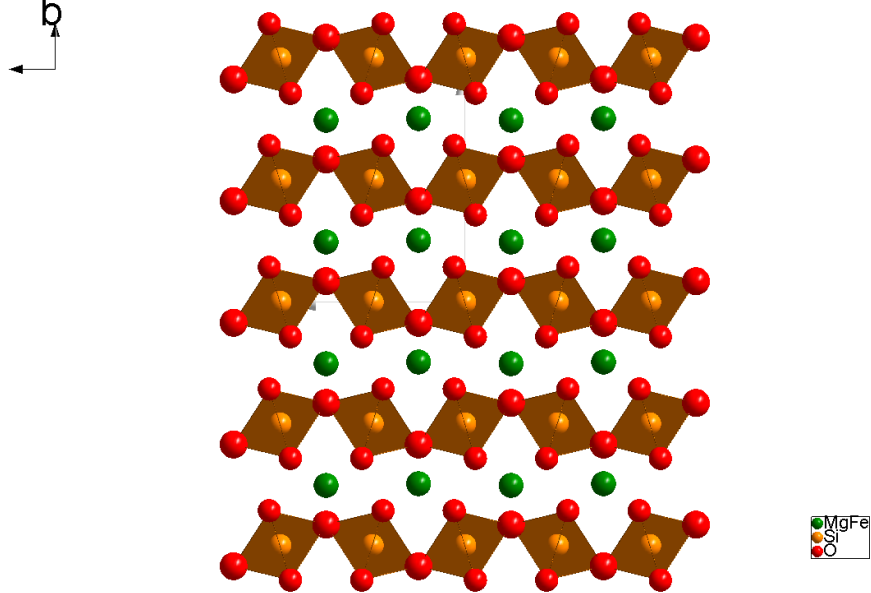




Single crystal diffraction

*In-situ growing of post-perovskite
@ 150 GPa & 2000 K*





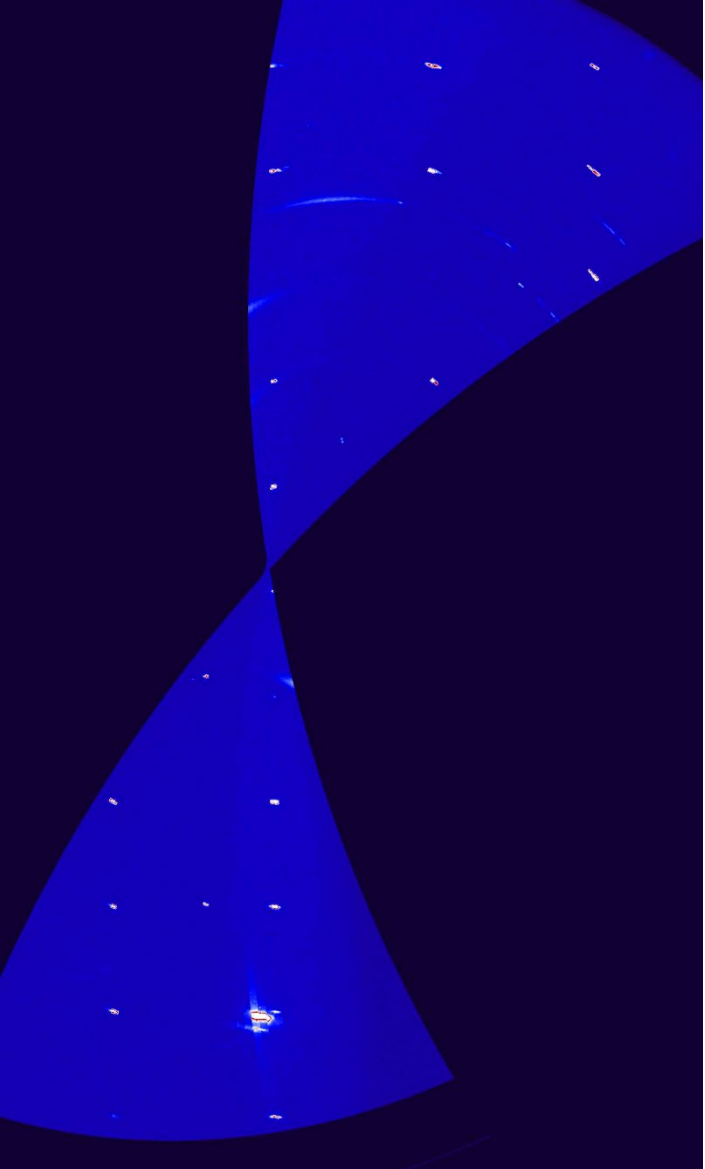
Crystal data

Formula sum	Fe ₁ Mg ₁ O ₁ Si ₁
Crystal system	orthorhombic
Space group	C m c m (no. 63)
Unit cell	$a = 2.477(7) \text{ \AA}$ $b = 8.03(2) \text{ \AA}$ $c = 6.109(13) \text{ \AA}$
Cell volume	121.51(50) $\text{\AA}^3$
Z	16
Pearson code	oC20

Post-perovskite,
struttura a
140 Gpa e 2000K

Atomic coordinates and isotropic displacement parameters (in $\text{\AA}^2$)

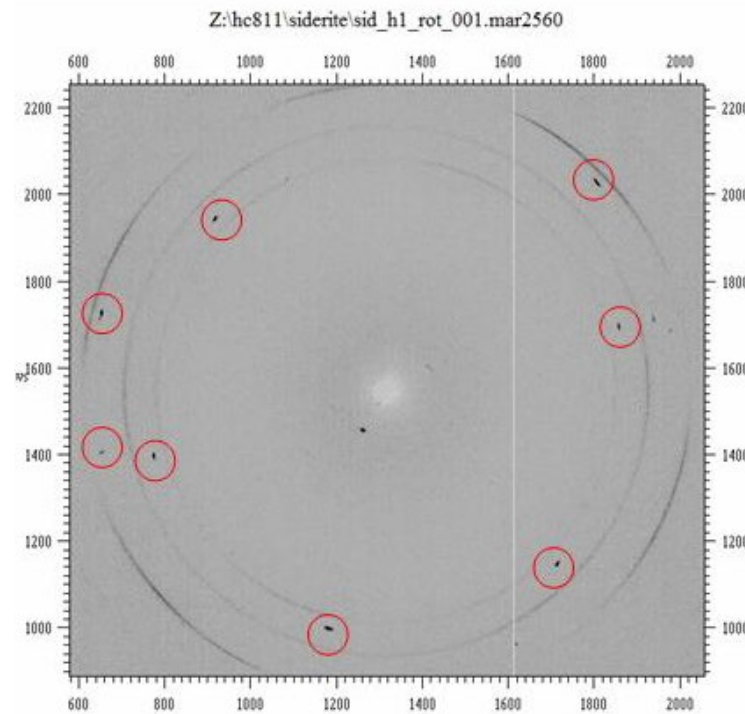
Atom	Wyck.	Occ.	x	y	z	U
Mg1	4c	0.703	0	0.25346	1/4	0.0149
Fe1	4c	0.297	0	0.25346	1/4	0.0149
Si	4a		0	0	0	0.0126
O1	4c		0	0.91453	1/4	0.0187
O2	8f		0	0.64244	0.44277	0.0130





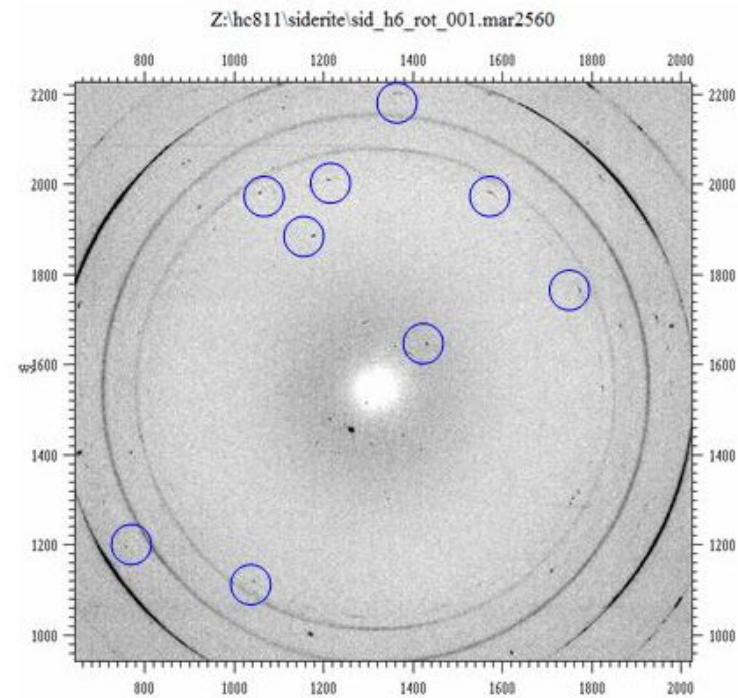
(Experiment with L. Dubrovinsky,
In-situ laser heating single crystal)

1Mbar, start heating



Low pressure FeCO_3

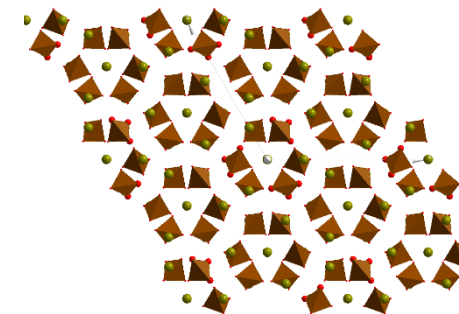
1 Mbar, 2500 K



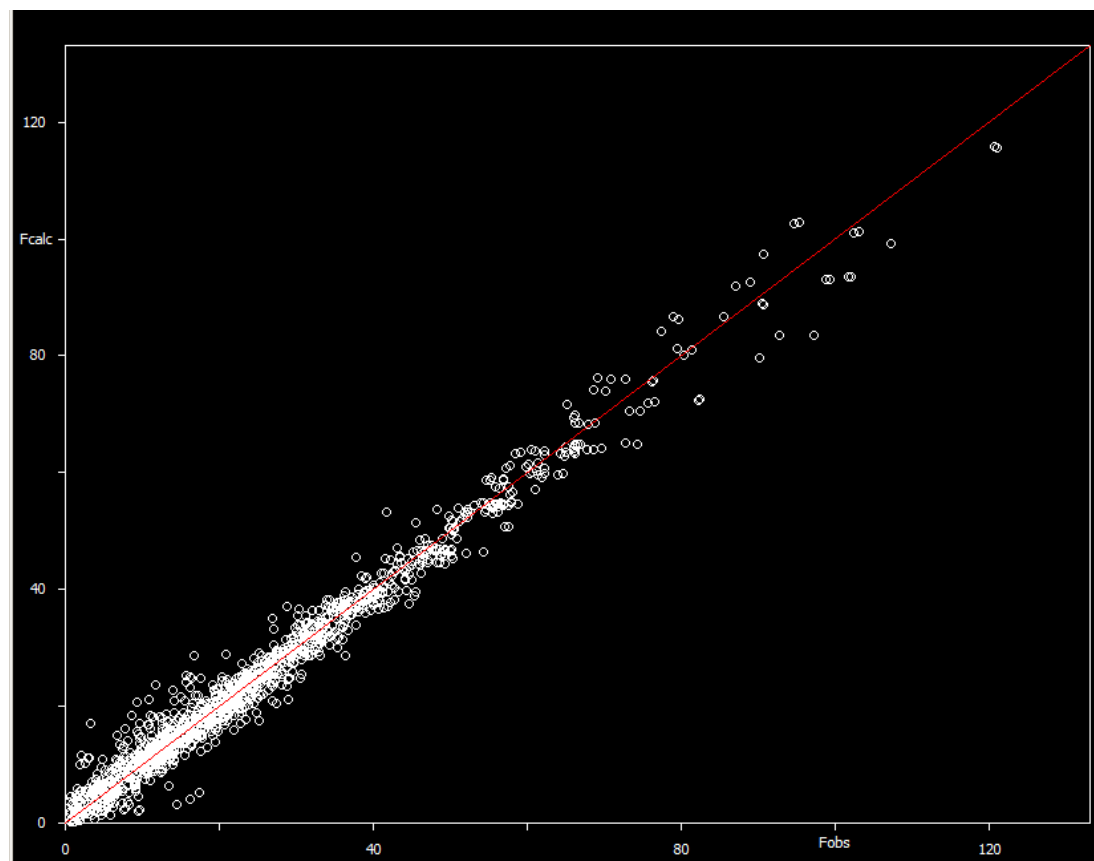
New single crystal diffraction of
high pressure Fe-carbonate
single crystal

Fe₄C₃O₁₂

Dataset collected at 1Mbar and ambient T



F_{calc}



F_{obs}

Solved and refined in P1,
pseudo symmetry
elements which suggests
possible HT R3c
symmetry

1116 obs

151 refined parameters

R(obs) 7 %

R(all) 8 %

```
|R factors : [1338=1116+222/151],      Damping factor:  0.9000 |
|GOF(obs)=  4.44      GOF(all)=  4.03    |
|Number of reflections excluded due to refinement options: 22+0 |
|R(obs)=  6.94      wR(obs)=  7.22      R(all)=  8.03      wR(all)=  7.27 |
|Last wR(all):  7.27 |
|Maximum change/s.u. :  0.0083 for z[C2] |
```

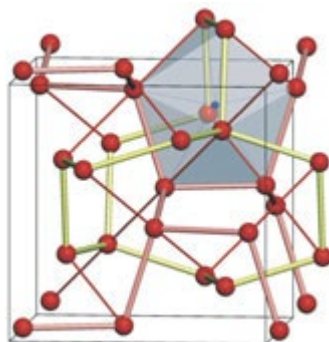
Complex structures of metals @ High Pressure

Letters to Nature

Nature **408**, 174-178 (9 November 2000) | doi:10.1038/35041515; Received 22 May 2000; Accepted 20 September 2000

New high-pressure phases of lithium

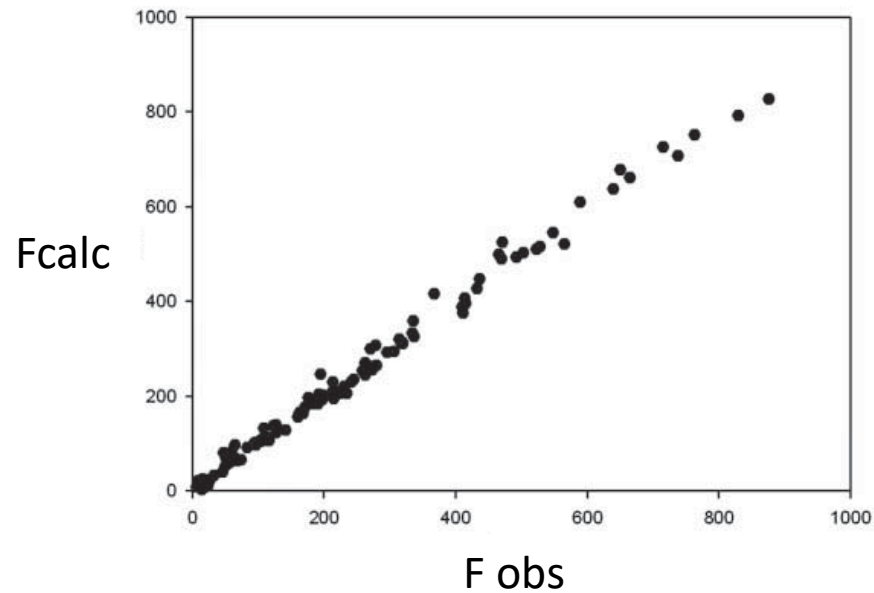
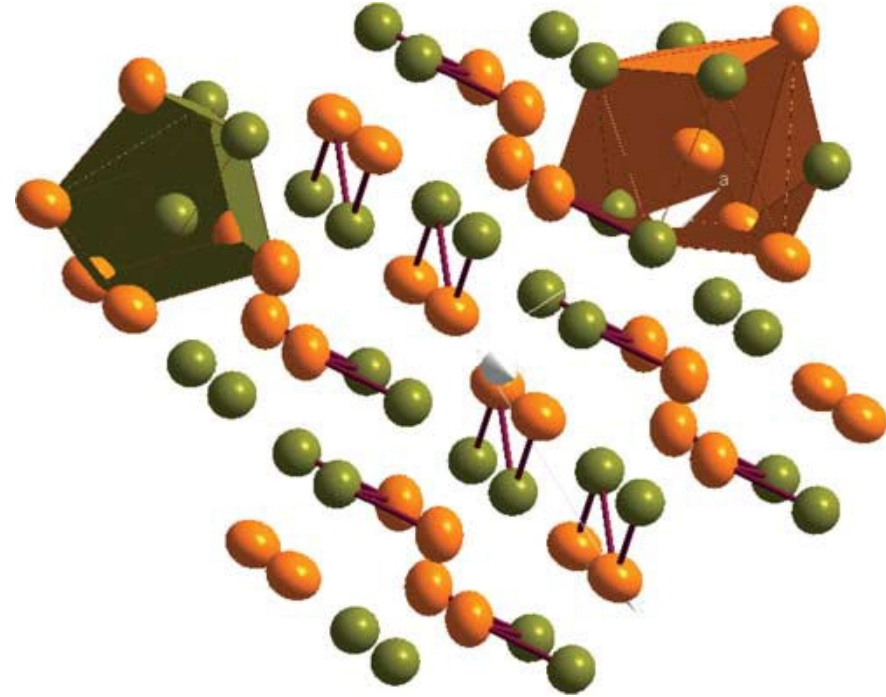
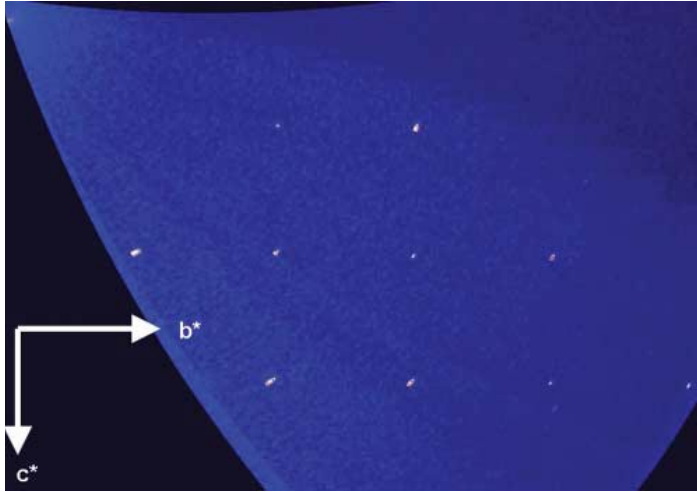
M. Hanfland¹, K. Syassen², N. E. Christensen³ & D. L. Novikov⁴



atomic cores. It was recently predicted¹ that at pressures below 100 GPa, dense Li may undergo several structural transitions, possibly leading to a 'paired-atom' phase with low symmetry and near-insulating properties. Here we report synchrotron X-ray diffraction measurements that confirm that Li undergoes pronounced structural changes under pressure. Near 39 GPa, the element transforms from a high-pressure face-centred-cubic phase, through an intermediate rhombohedral modification, to a cubic polymorph with 16 atoms per unit cell. This cubic phase has not been observed previously in any element; unusually, its

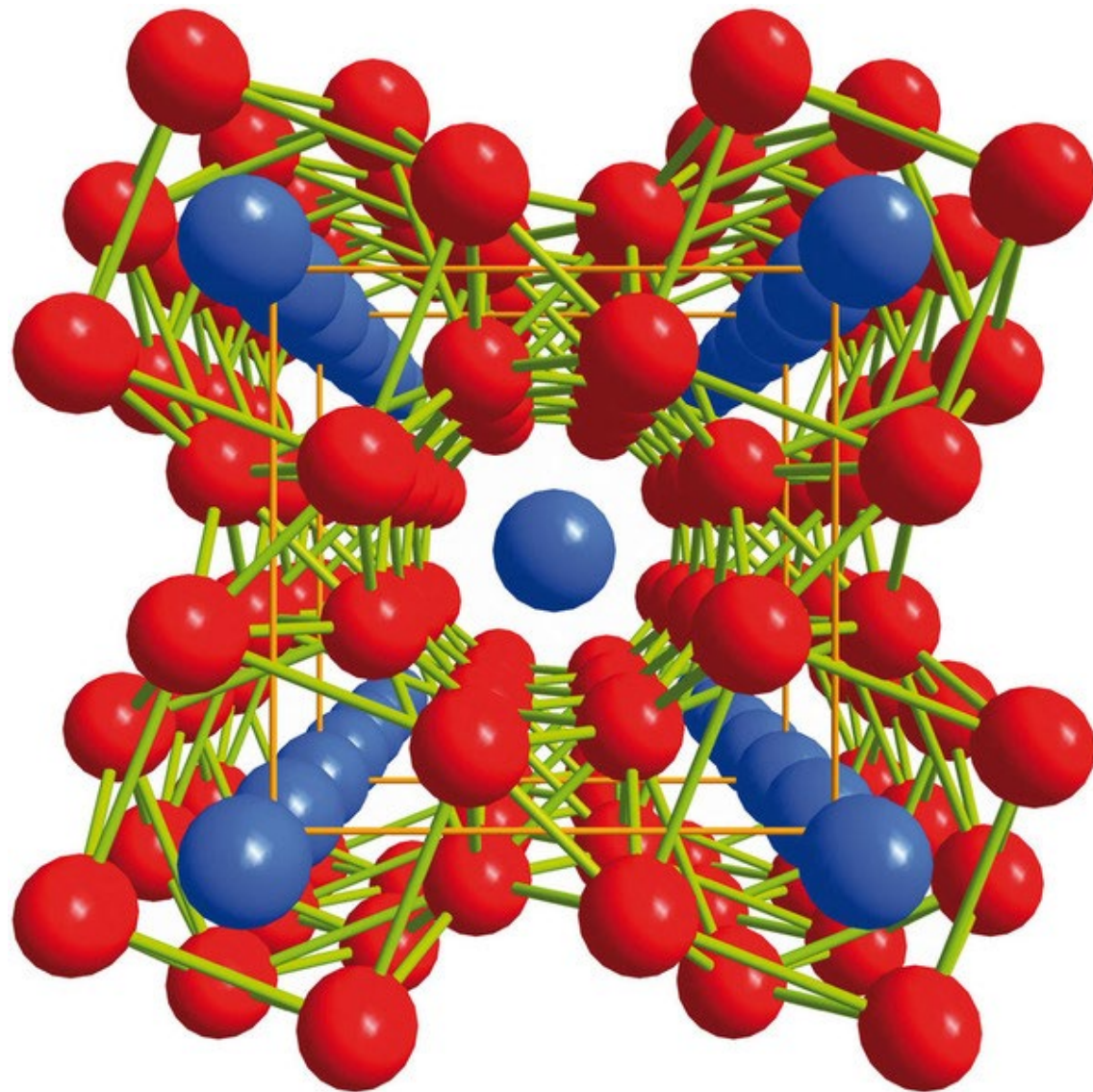
The predictions by Neaton and Ashcroft¹ are in sharp contrast to intuitive expectation that the application of hydrostatic pressure favours high-coordination crystal structures with metallic properties. In their theoretical simulations of dense Li, which are based on first principles band structure theory, they compare the relative stability of a number of crystal structures common among elemental solids. Their results clearly indicate a strong preference of dense Li to form low-symmetry structures. Therefore, experiments aimed at structure determinations of compressed Li are highly desirable. Furthermore, experimental high-pressure studies of Li are of fundamental interest, because they are expected to reveal new aspects relevant for the theoretical modelling of other light elements, including hydrogen², at high density.

Na oP8 structure determined at 118 GPa



MnP type structure

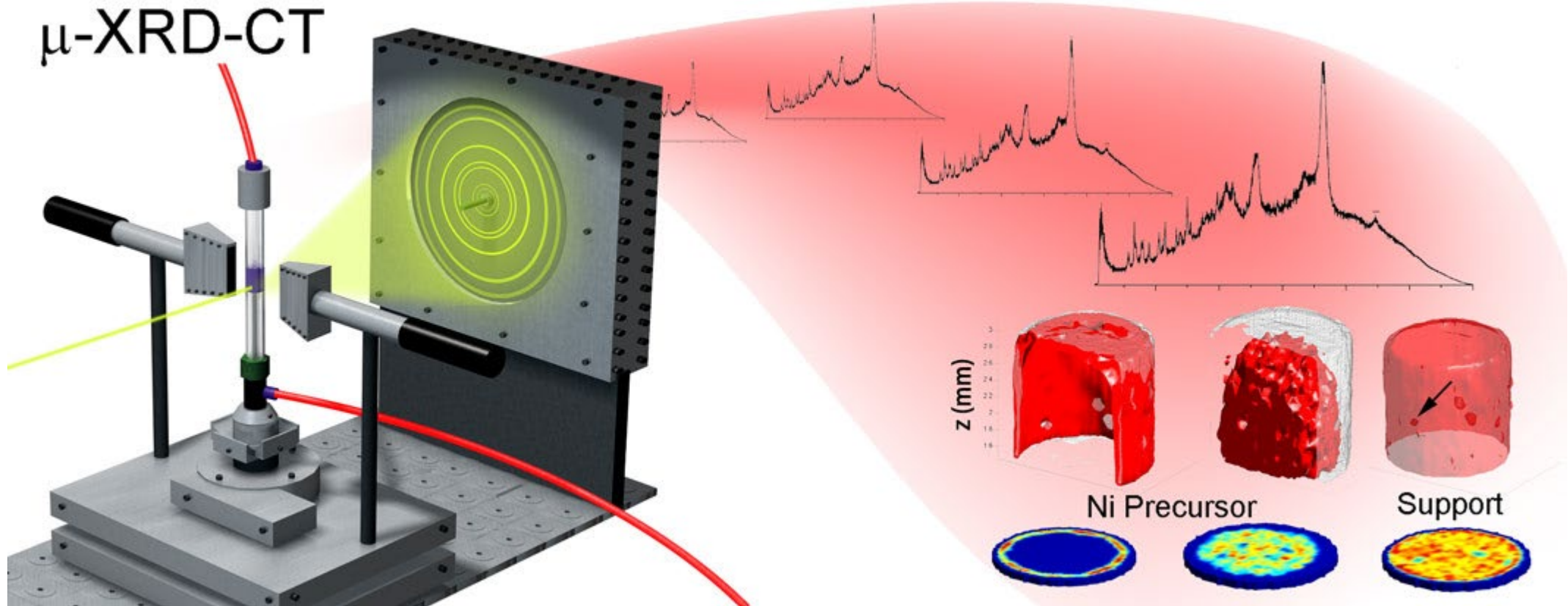
Single atomic species, but
binary compound type
structure



Na – host-guest structure $P > 125$ GPa

- Single crystal diffraction on crystals with size down to $0.005 \times 0.005 \times 0.005$ mm (almost routine) and even less
- Possibility to have structural information from single crystal data at non ambient conditions, not only with static measurements (i.e high pressure) but also during dynamic processes (i.e. variable magnetic field, temperature, etc) on second time scale

3) EXAMPLE: Diffraction tomography



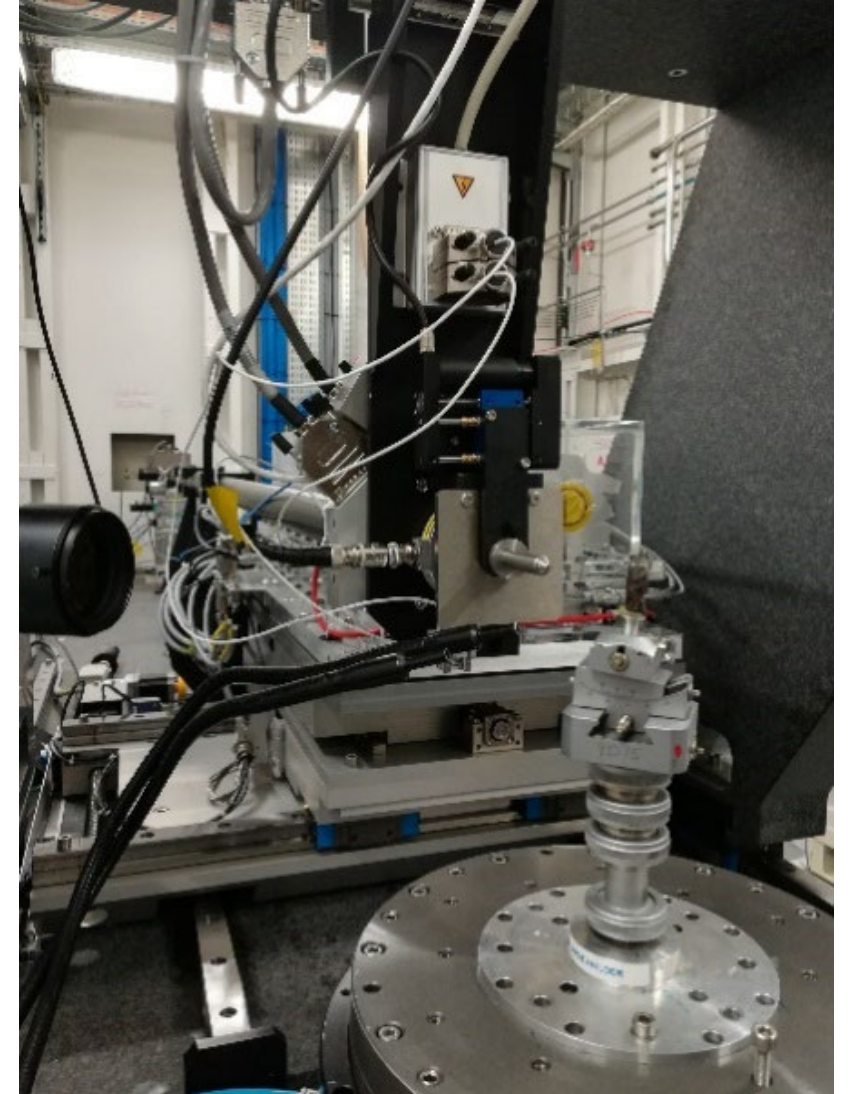
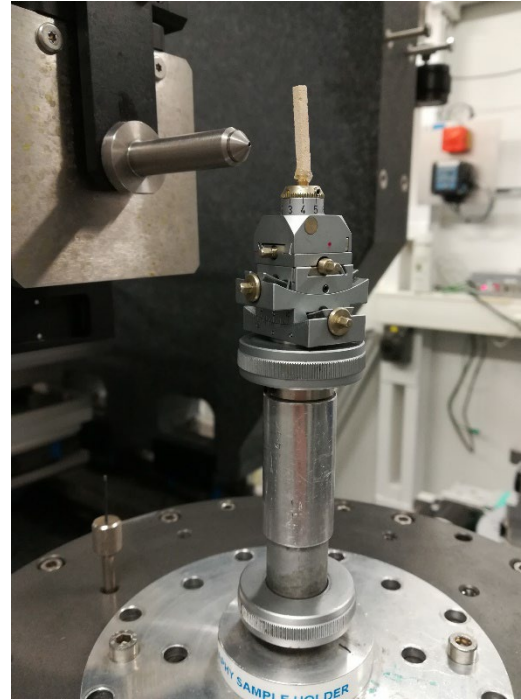
ESRF, ID15A

Courtesy of Marco Di Michiel

Experimental setup

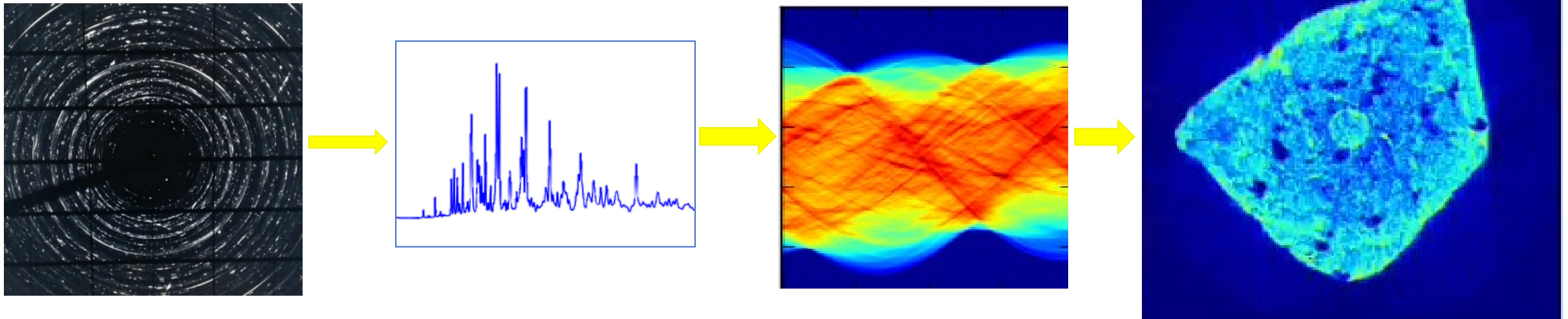
Energy	90 KeV
(λ)	0.137 Angstrom
Sample to detector distance	1.00/1.40 m
Data collection	Continuous rotation

- Monochromatic beam
- Continuous translation and rotation of the sample
- Diffraction data collection during translation and rotation



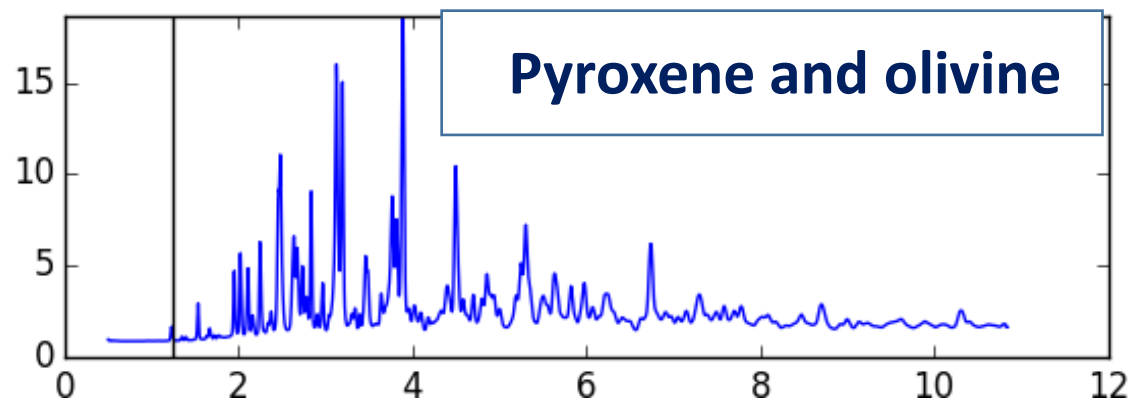
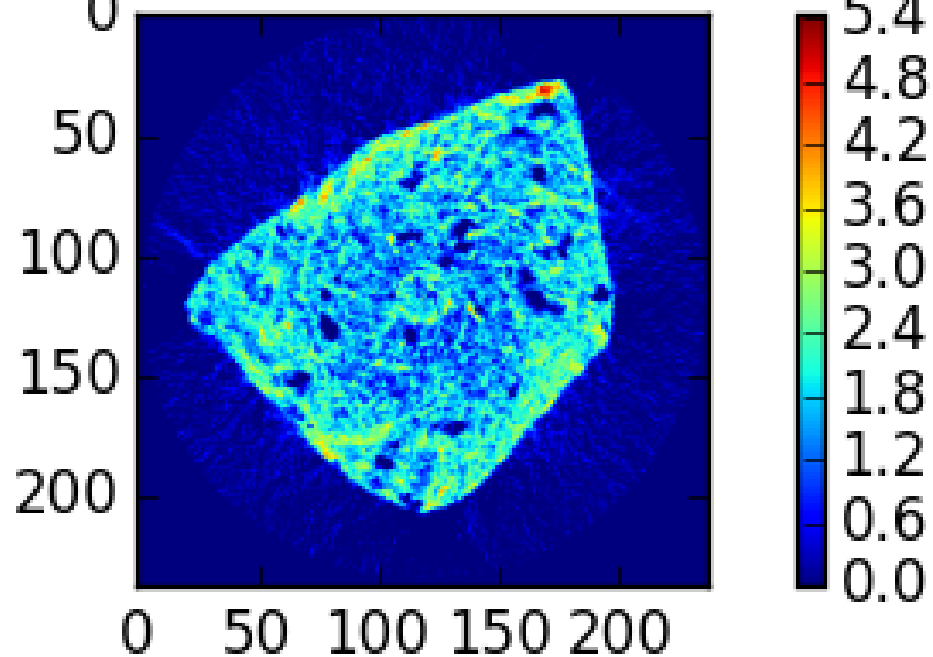
COSA SI OTTIENE?

- 2D diffraction
- Integration → from 2D to 1D powder pattern
- «Elaboration» of pattern (synogram)
- «Slices»

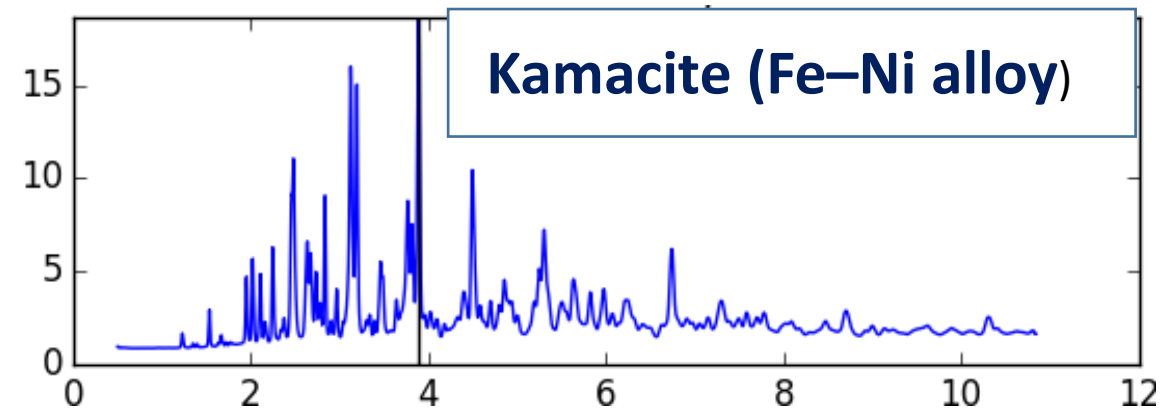
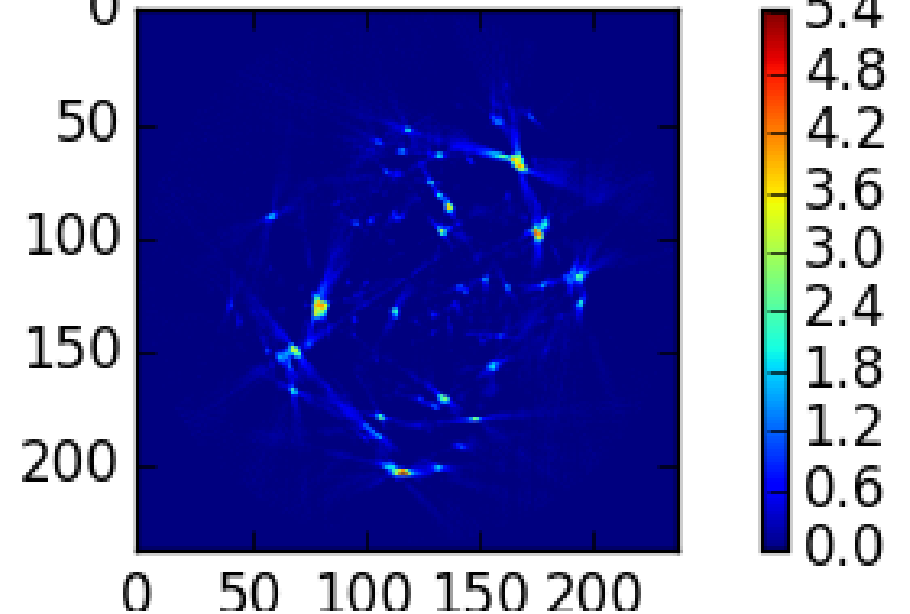


METEORITE from museum collection

Channel = 146; 2theta = 1.243

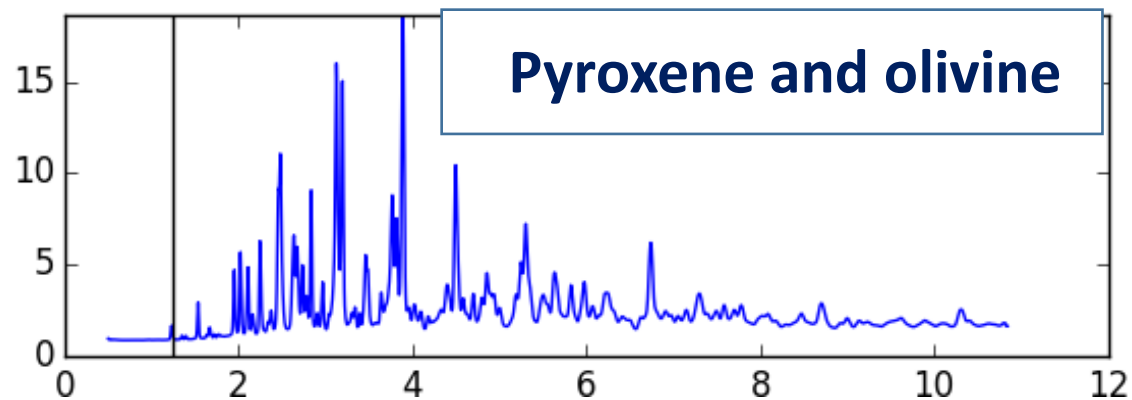
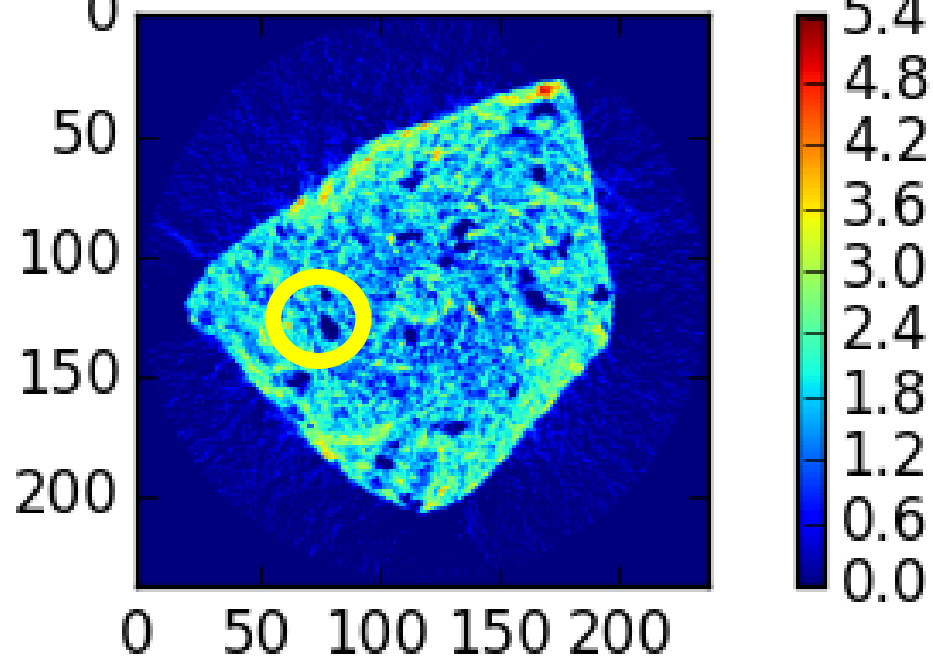


Channel = 667; 2theta = 3.888

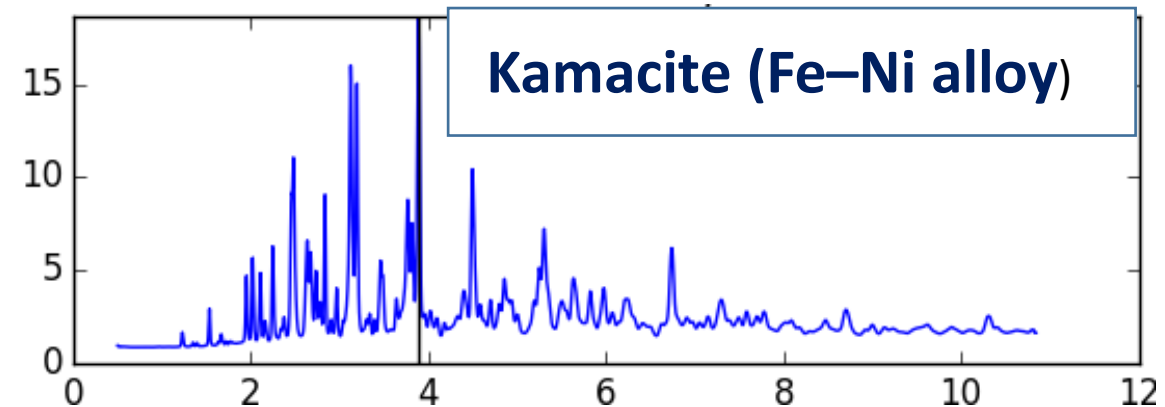
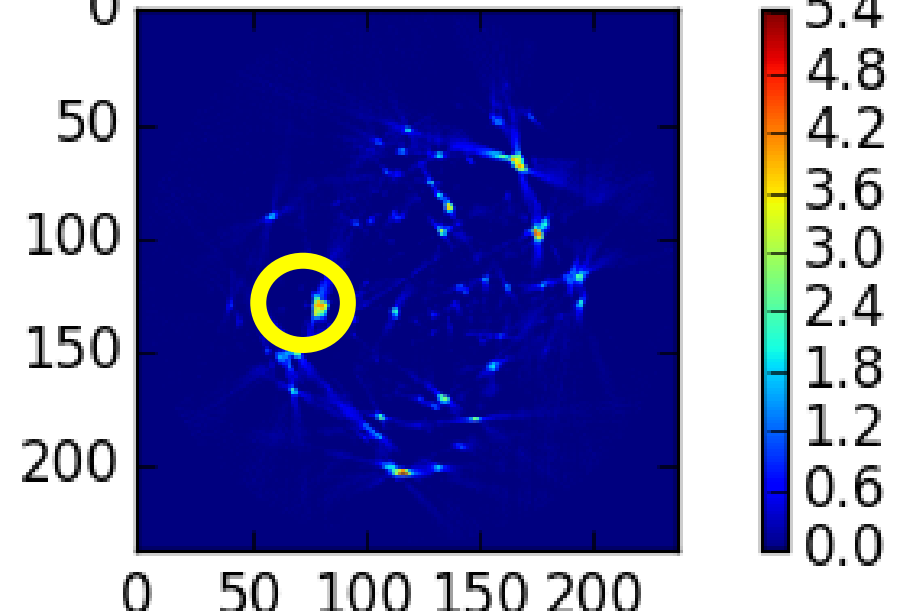


METEORITE from museum collection

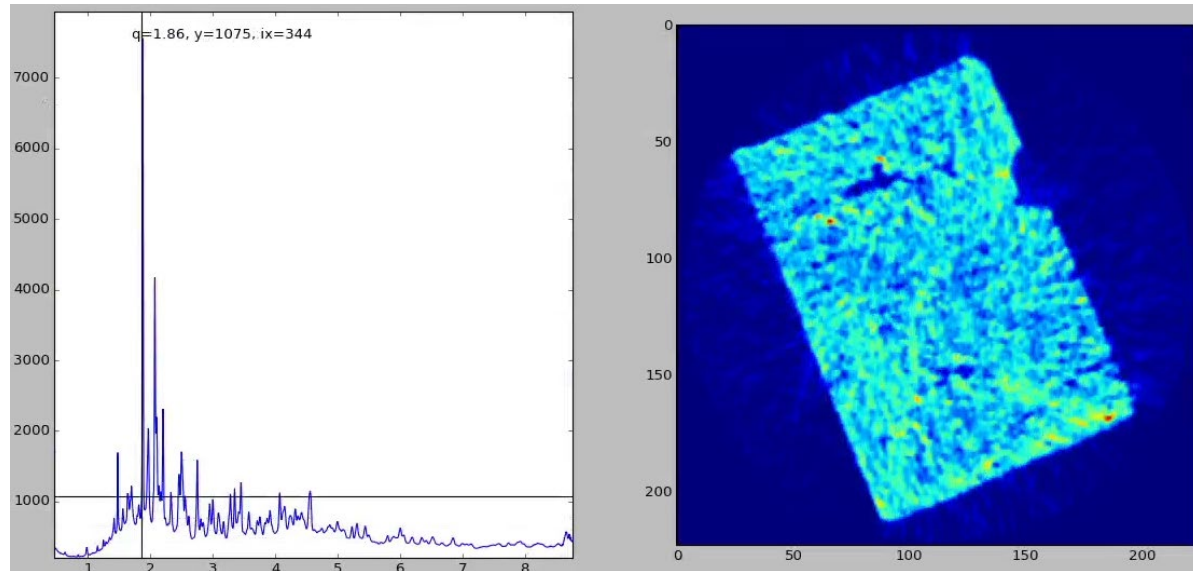
Channel = 146; $2\theta = 1.243$



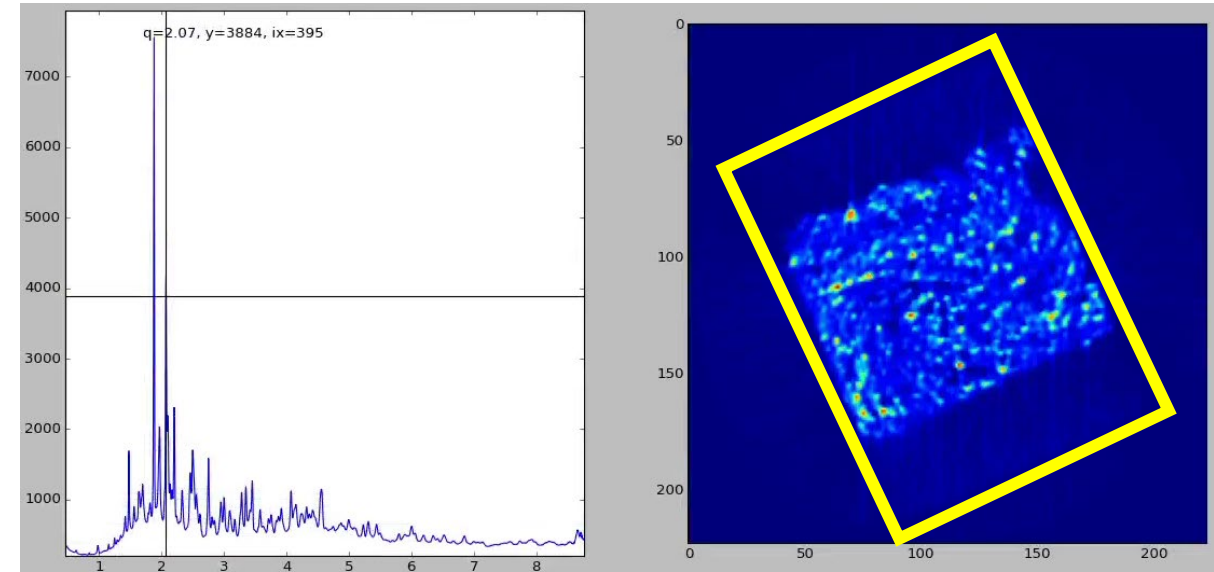
Channel = 667; $2\theta = 3.888$



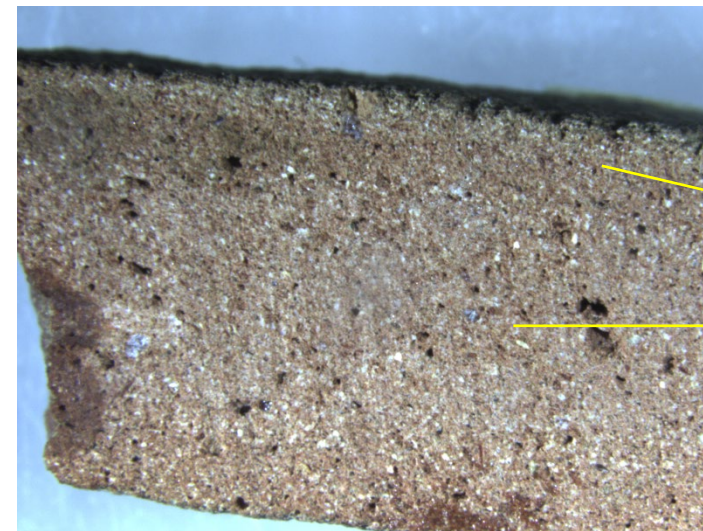
Archaeological sample: ceramic from northern Africa, Roman period (apx. 2000 year ago)



Quartz (SiO_2)

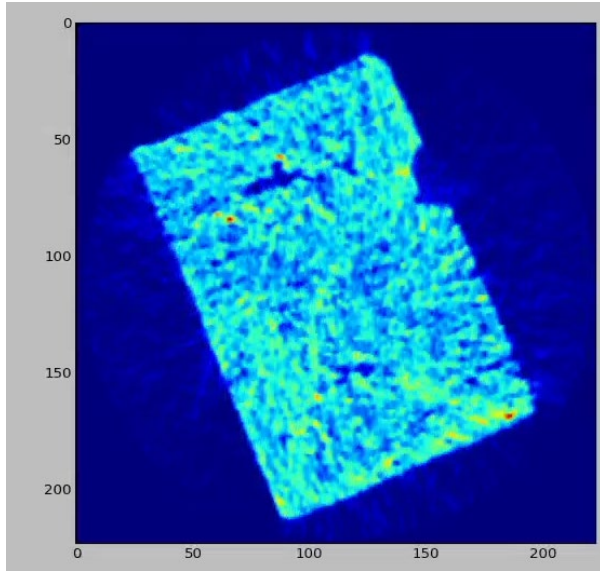


Calcite (CaCO_3)

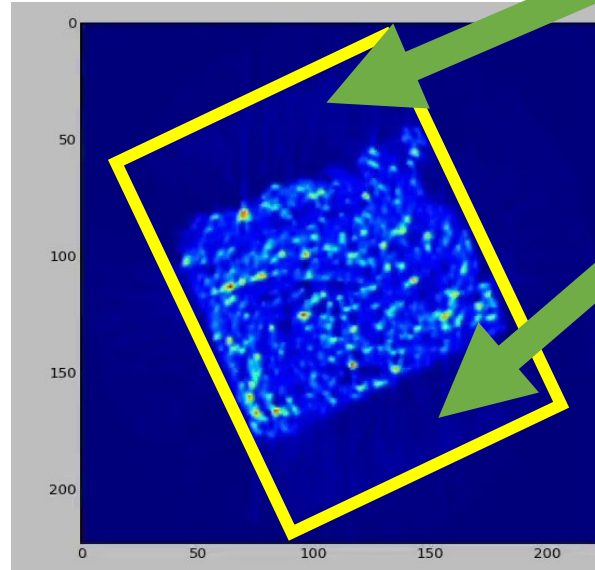


Different
granulometry
and calcite
distribution

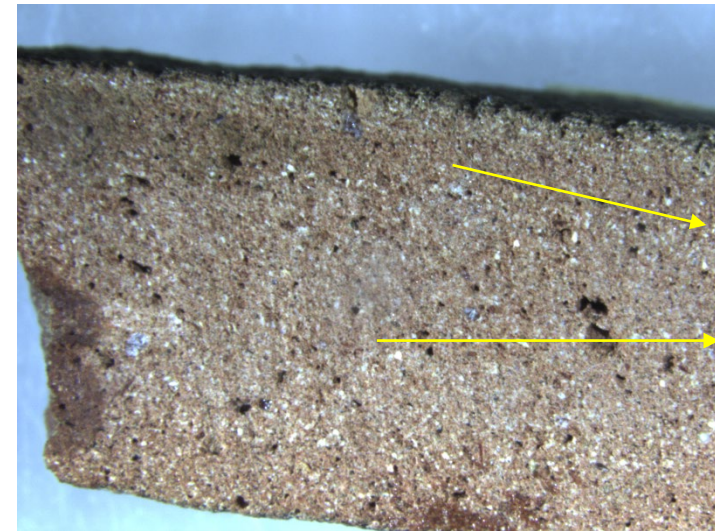
Archaeological sample: ceramic from northern Africa, Roman period (apx. 2000 year ago)



Quartz (SiO₂)



Missing calcite in external portion
of ceramic:
«Sandwich» preparation
With different clay composition



Different
granulometry
and calcite
distribution

**Single-crystal diffraction at the Extreme Conditions beamline
P02.2: procedure for collecting and analyzing high-pressure
single-crystal data**

André Rothkirch, G. Diego Gatta, Mathias Meyer, Sébastien Merkel,
Marco Merlini and Hanns-Peter Liermann

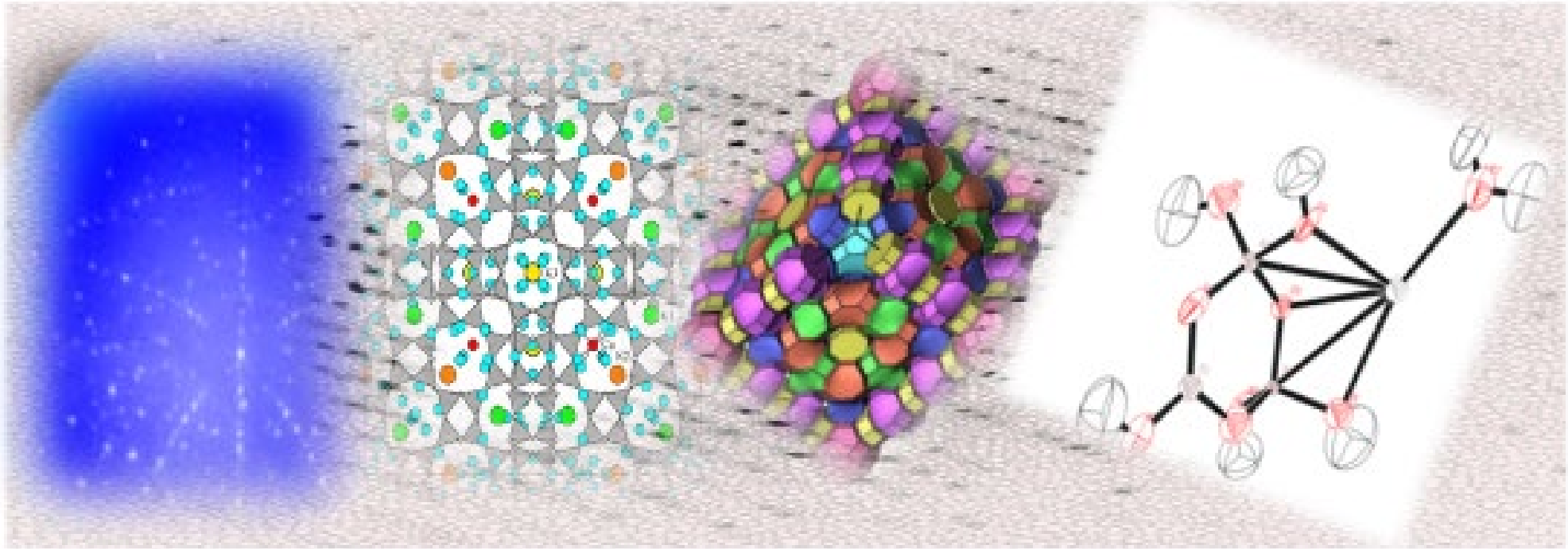
J. Synchrotron Rad. (2013). **20**, 711–720

PETRA III, DESY, is presented. A new data image format called ‘Esperanto’ is introduced that is supported by the commercial software package *CrysAlis^{Pro}* (Agilent Technologies UK Ltd). The new format acts as a vehicle to transform the most common area-detector data formats *via* a translator software. Such a conversion tool has been developed and converts tiff data collected on a Perkin Elmer detector, as well as data collected on a MAR345/555, to be imported into the *CrysAlis^{Pro}* software. In order to demonstrate the validity of the new

Commercial softwares (i.e. scientists and engineer working full time for software development, maintenance and upgrades) for single crystal data reduction from area detectors work much better than in-house written codes

XDS, CrysAlis, etc... are normally available at synchrotron beamlines and universities/research center

Single crystal X-ray diffraction is the primary technique for determining atomic-scale structures of materials.



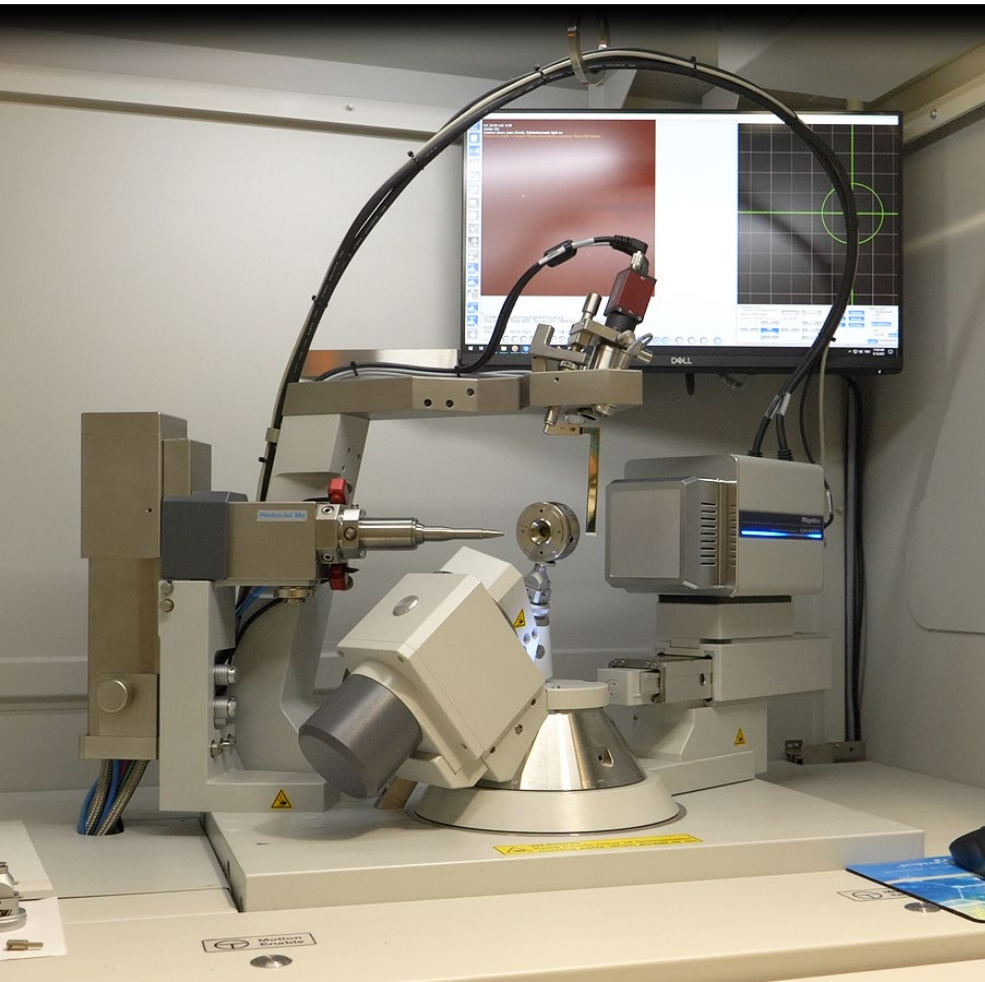
It provides precise information on the arrangement of atoms within a crystal, which is essential for understanding material properties.

High pressure and temperature can induce new atomic arrangements.

These conditions are critical for discovering new phases and structures, especially those that are unquenchable and exist only under these non ambient conditions.



DIAMOND ANVIL CELL



Many structures formed at high pressures are unquenchable, meaning they revert to their original form when pressure is released, making in situ studies essential for accurate structure determination.

The Development of the Diamond Anvil Cell (DAC)

The DAC was developed in 1958, revolutionizing high-pressure research.

Diamond anvil cell, 50th birthday

William A. Bassett*

Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, NY, USA

(Received 4 November 2008; final version received 4 November 2008)

The year 2008 marked the fiftieth birthday of the diamond anvil cell. Its birth took place when Alvin Van Valkenburg, while working with his colleagues, Charles E. Weir, Ellis R. Lippincott, and Elmer N. Bunting, first realized that he could look right through one of the diamond anvils and see a sample while it was at high pressure. In the following years, these scientists and many others adapted the diamond anvil cell to a wide variety of analytical techniques that have provided an impressive amount of information about materials at high pressures and high temperatures. But, virtually all of those techniques start with looking into the diamond anvil cell.

Keywords: diamond anvil cell; high pressure; high temperature; history



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High Pressure X-Ray Crystallography With the Diamond Cell at NIST/NBS

Gasper J. Piermarini

National Institute of Standards and
Technology,
Gaithersburg, MD 20899-8522

gasper.piermarini@nist.gov

Scientists in the Crystallography Section at NIST/NBS made several outstanding contributions which greatly promoted the development and advancement of high pressure x-ray crystallography during the second-half of the 20th century. These milestone achievements or “firsts” included: (1) the invention of the lever-arm type diamond anvil cell (DAC) in 1958; (2) the development of DAC technology for powder x-ray diffraction at high pressure in 1960; (3) the introduction of DAC methodology for single crystal x-ray diffraction at high pressure in 1964; (4) the invention of the optical fluorescence ruby method of pressure measurement in 1971; and (5) the discovery of hydrostatic pressure-transmitting media useful to unprecedented pressures for that time.

These achievements provided the spark that ignited the explosion of activity in high pressure research that occurred in laboratories throughout the world during the latter part of the 20th century. It is still going on, unabated, today. An estimated 5000 DACs were built during the last 40 years.

Key words: crystallography; diamond anvil cell (DAC); high pressure; hydrostaticity; polycrystalline; ruby pressure measurement; single crystal.

Accepted: August 22, 2001

Available online: <http://www.nist.gov/jres>

High Pressure Diamond

Volume 106

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Gaithersburg, MD 20899-8522

gasper.piermarini@nist.gov

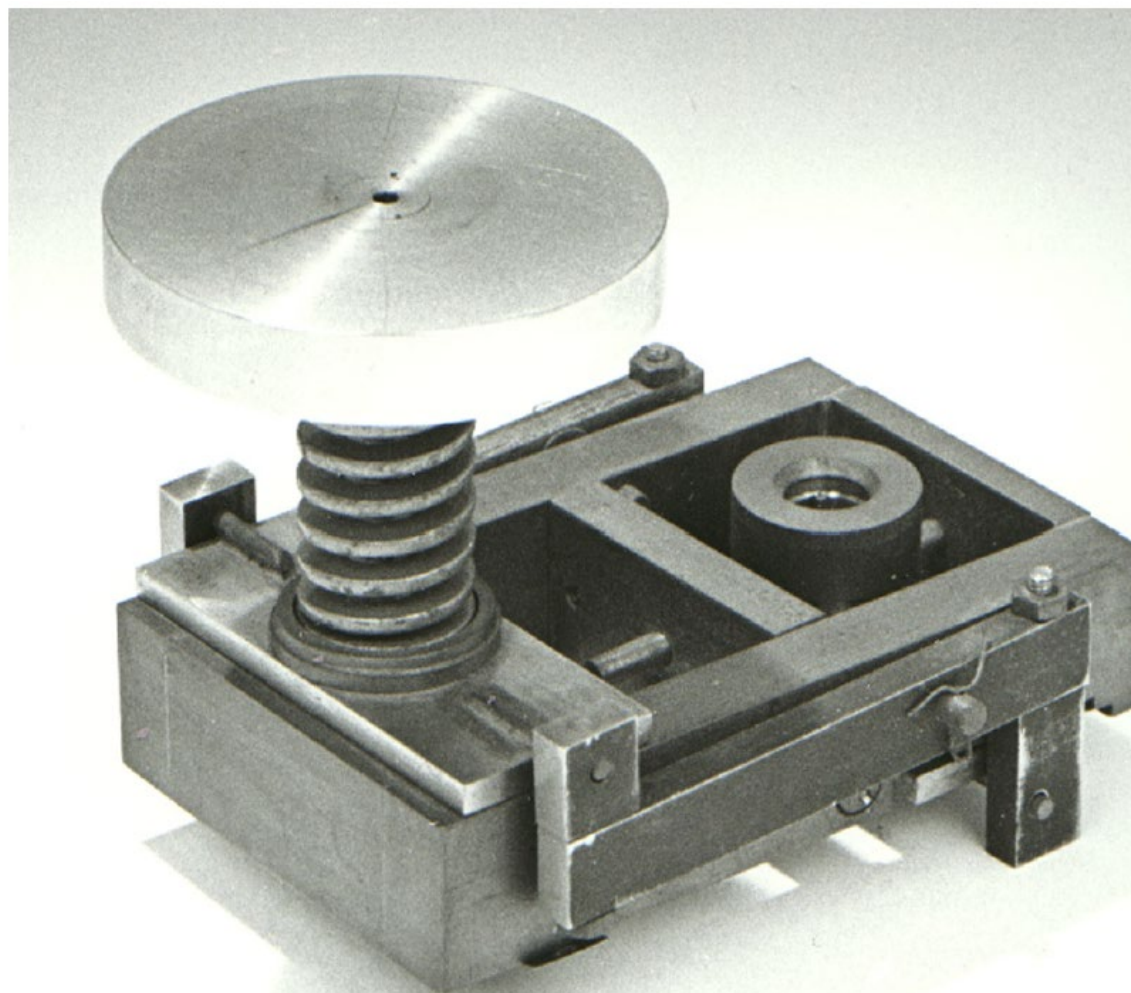


Fig. 2. The original diamond anvil pressure cell, now on display in the NIST Gaithersburg Museum. The unrefined instrument was handmade by C. E. Weir at NBS in 1957-58.

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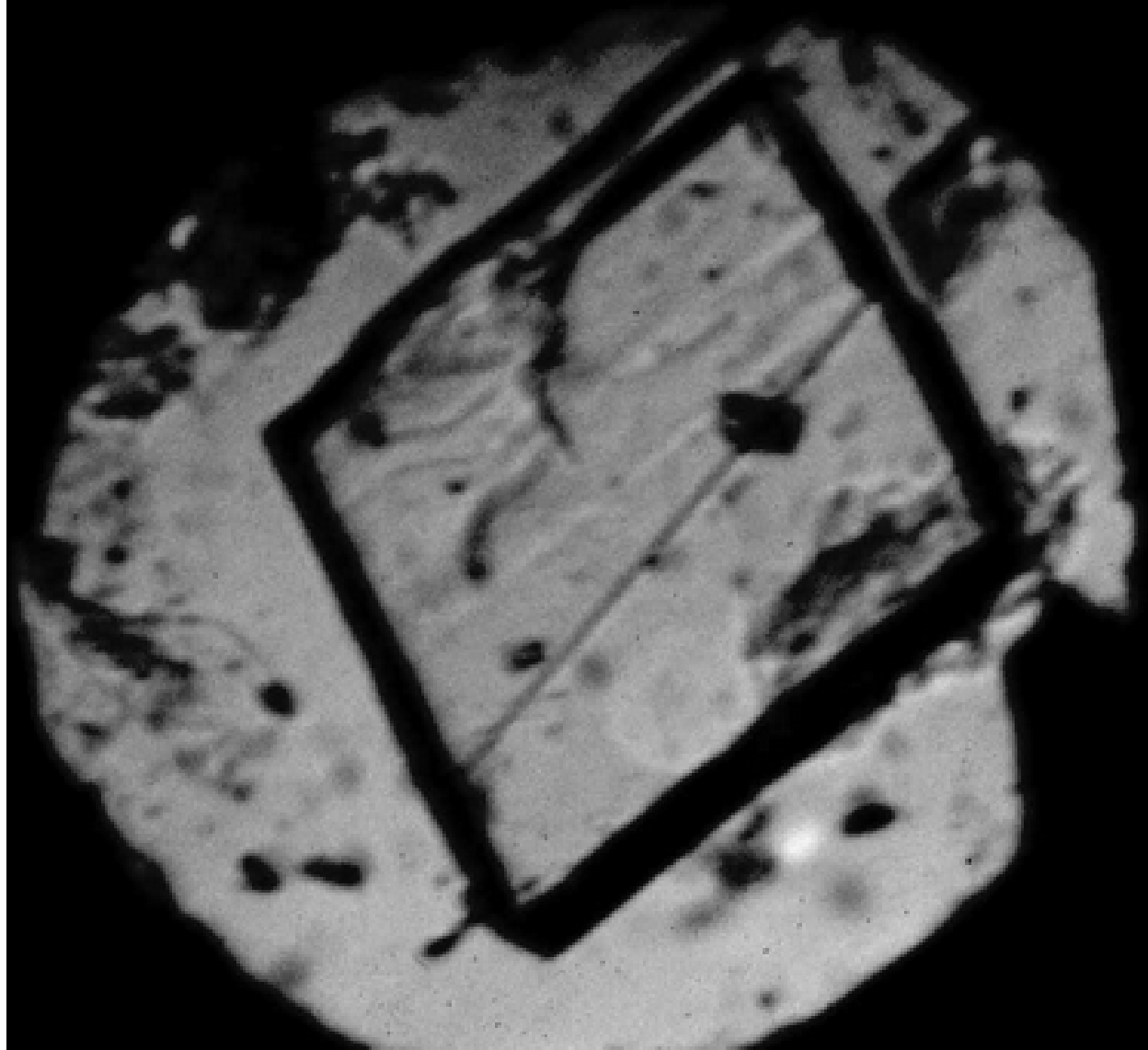
Figure 6. Alvin Van Valkenburg seated at his microscope preparing to examine a sample at high pressures in his diamond anvil cell, ca. 1964 (Courtesy of Robert Hazen and Eric Van Valkenburg).

History:
Optical view
of single
crystal to
single crystal
transition

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Diamond anvil cell, 50th birthday

William A. Bassett*



Becke line in CaCO_3

CaCO_3 – CaCO_3 -II phase transition

Single crystal to single crystal

@ 1.5 GPa

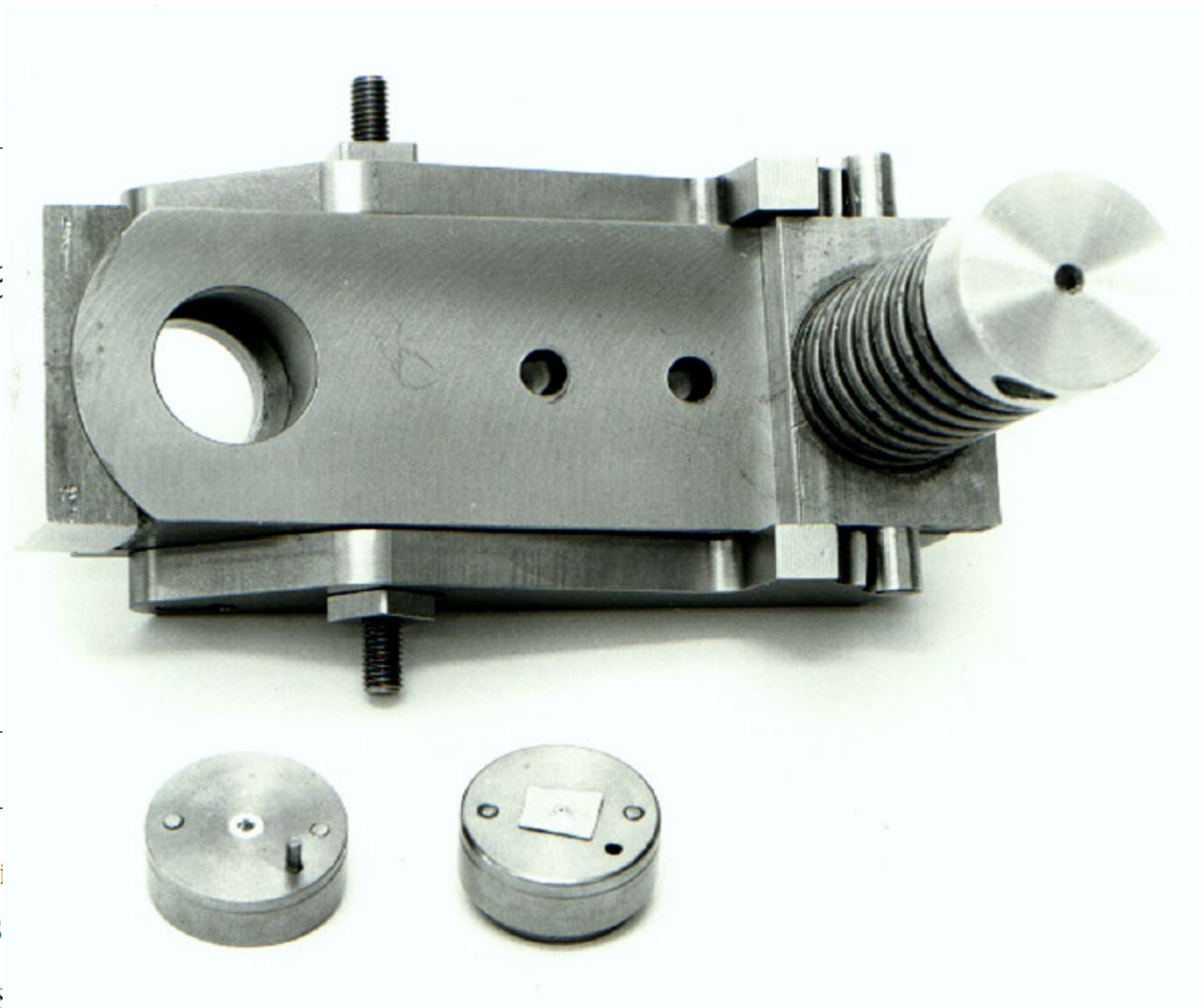


Fig. 12. The original NBS Be diamond cell (disassembled) made in 1964 was designed to be used with the modified Buerger precession camera for high pressure single crystal x-ray diffraction studies.



Fig. 11. A photograph of C. E. Weir examining two precession films of ice VI, from “Crystal Structures at High Pressures,” a movie produced at NBS in 1970. The 40 minute color film describes the development of the single crystal DAC technique for high pressure studies.

Table 1. Observed and calculated d spacings for iceVI at 0.9 GPa and RT [8]

Obs.	d - spacing (Å)		hkl
	Obs.	Calc.	
4.3	4.3	4.3	111* ^a
3.6	3.6	3.6	012
3.4	3.5	3.5	210
3.12	3.08	3.08	020
2.91	2.93	2.93	021*
2.75	2.75	2.75	121
2.63	2.67	2.67	301
2.51	2.51	2.51	022
2.43	2.42	2.42	203
2.21	2.22	2.22	004*
2.10	2.09	2.09	400
2.01	2.00	2.00	031*
1.97	1.97	1.97	204
1.85	1.85	1.85	230
1.75	1.76	1.76	124
1.64	1.64	1.64	205
1.56	1.57	1.57	502*
1.48	1.48	1.48	006
1.44	1.44	1.44	142*
1.41	1.42	1.42	513
1.37	1.37	1.37	424
1.34	1.34	1.34	035
1.30	1.30	1.30	612
1.26	1.26	1.26	107
1.21	1.21	1.21	151
1.14	1.14	1.14	712
1.104	1.104	1.104	108
1.084	1.081	1.081	615*
1.050	1.049	1.049	535*
1.010	1.009	1.009	642

^a Those indices marked with an asterisk represent multiple lines and only one possible index is given. These data represent the first ever obtained *in situ* from a single crystal under high pressure.

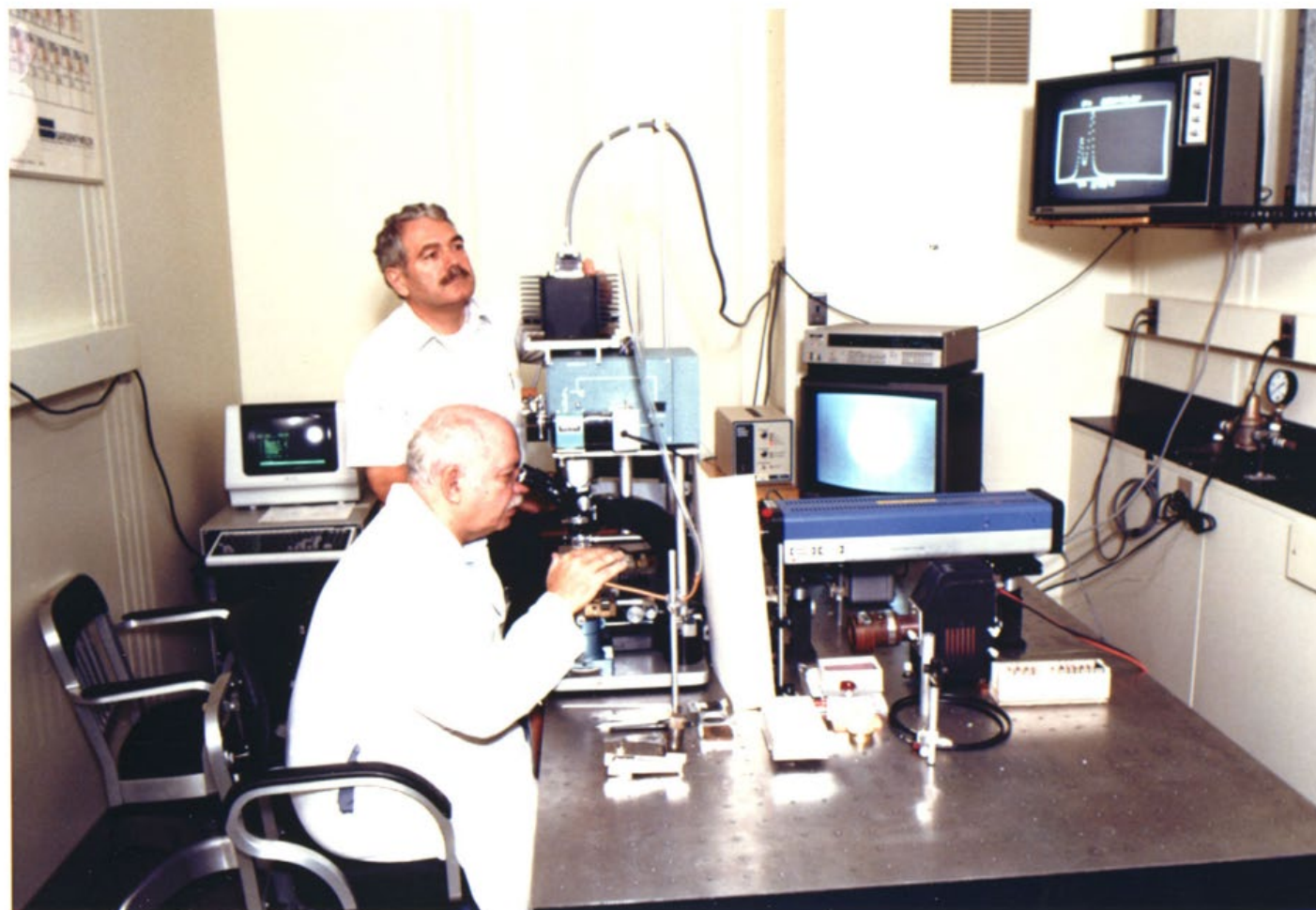
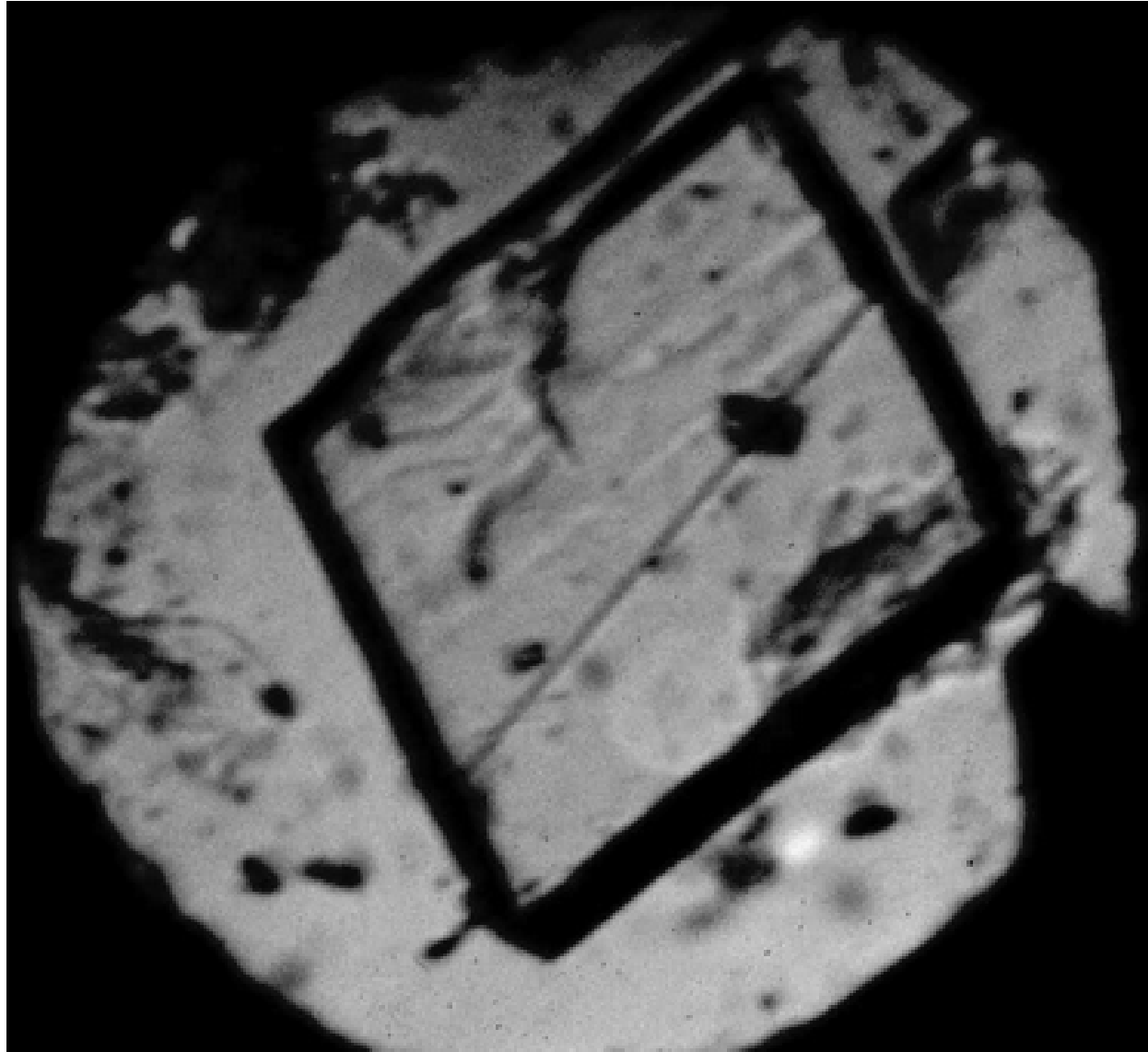


Fig. 24. A photograph of the pressure measuring system with a DAC mounted on the microscope stage. In the initial stages of its development, a photomultiplier tube and strip chart recorder were used to measure the fluorescence intensity. Also, a video camera was incorporated in the system to record pressure-induced phenomena on materials. In the improved version of the instrument shown here, with Block and Piermarini, a linear diode array, has replaced the photomultiplier tube and the pressure (wavelength) is determined utilizing computer software. The R-line intensity is partially displayed on the monitor in the upper right of the photograph.

Diamond anvil cell, 50th birthday

William A. Bassett*



Becke line in CaCO_3

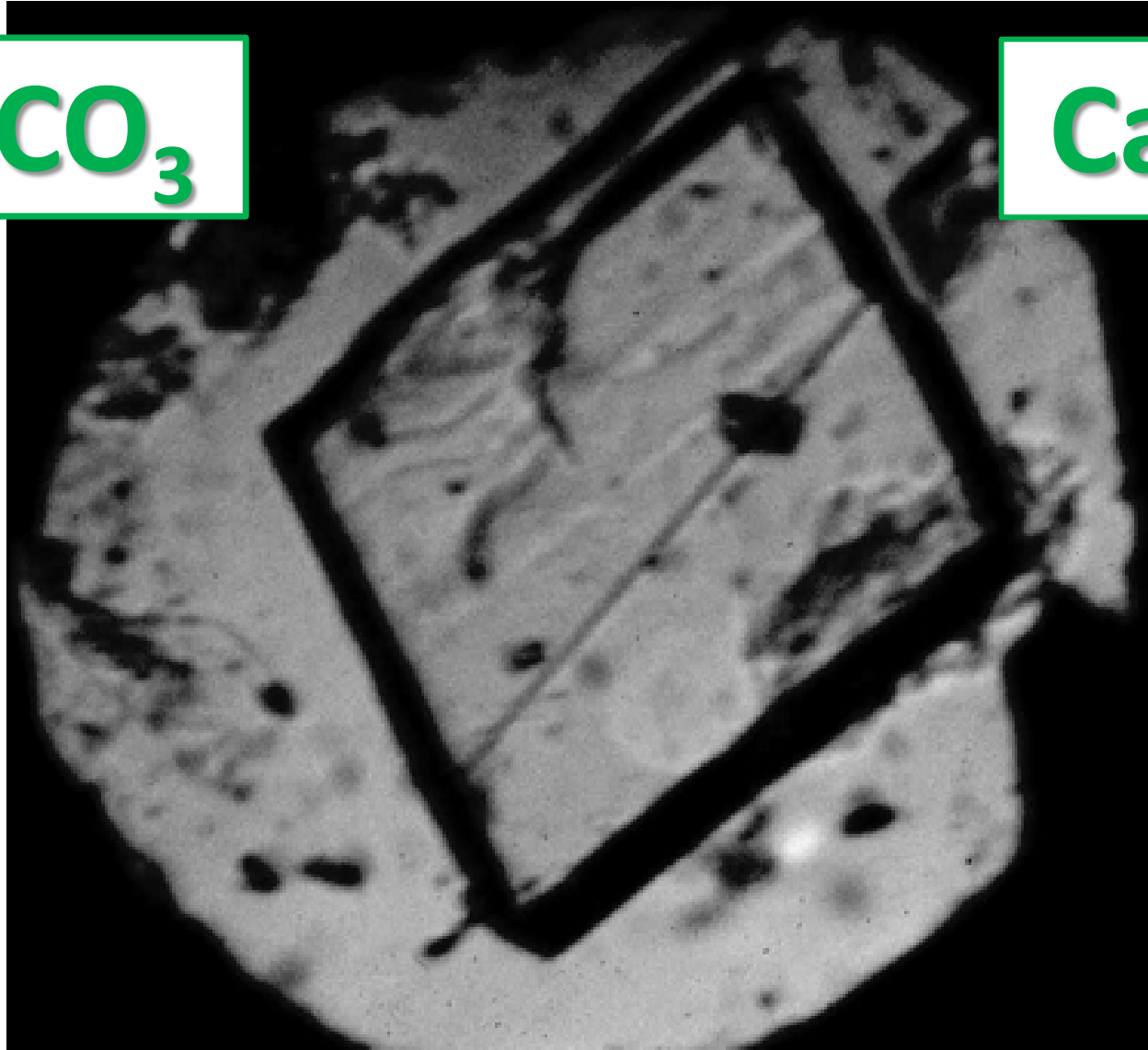
CaCO_3 – CaCO_3 -II phase transition

Single crystal to single crystal

@ 1.5 GPa

CaCO_3

$\text{CaCO}_3\text{-II}$

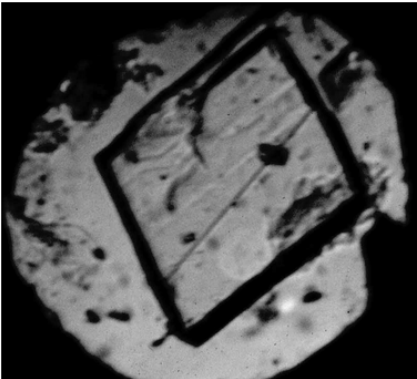


Becke line in CaCO_3

CaCO_3 – $\text{CaCO}_3\text{-II}$ phase transition

Single crystal to single crystal

@ 1.5 GPa



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Diamond anvil cell, 50th birthday

William A. Bassett*

Powder X-Ray diffraction: low resolution in '60 / '70 for ab-initio experimental structural determination

Single crystal diffraction with piston DAC only on Buerger precession camera

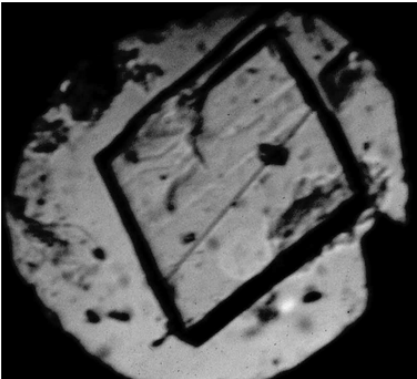


Leo Merrill (PhD student – advisor prof. William Bassett)

1969

Miniaturized Diamond Anvil Cell for single crystal diffraction
(the “Merrill-Basset” cell...)

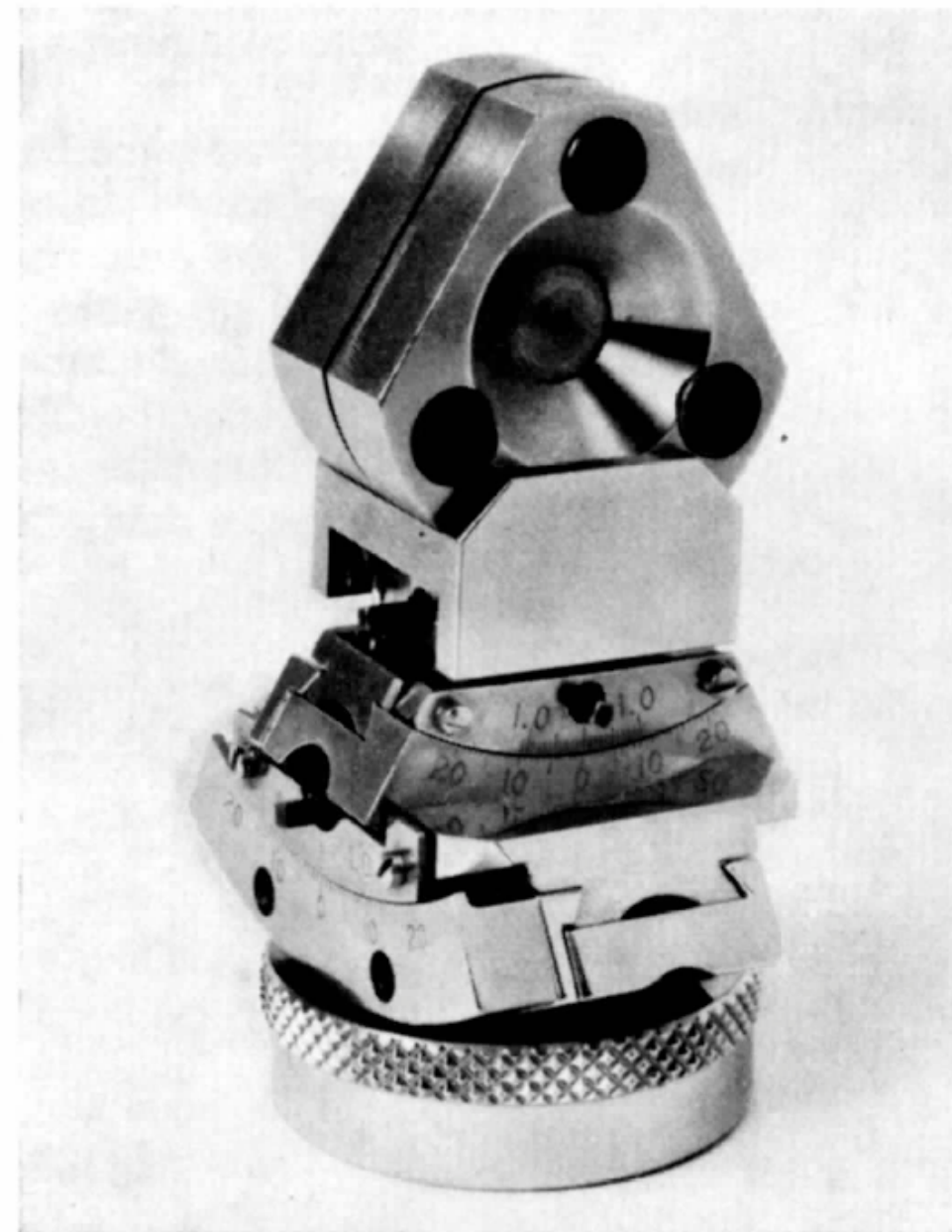
Designed for structure determination of calcite-II structure

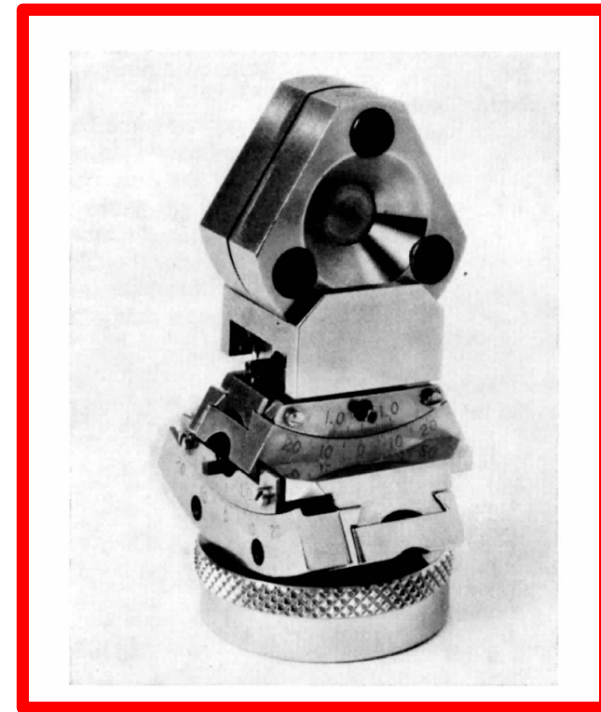
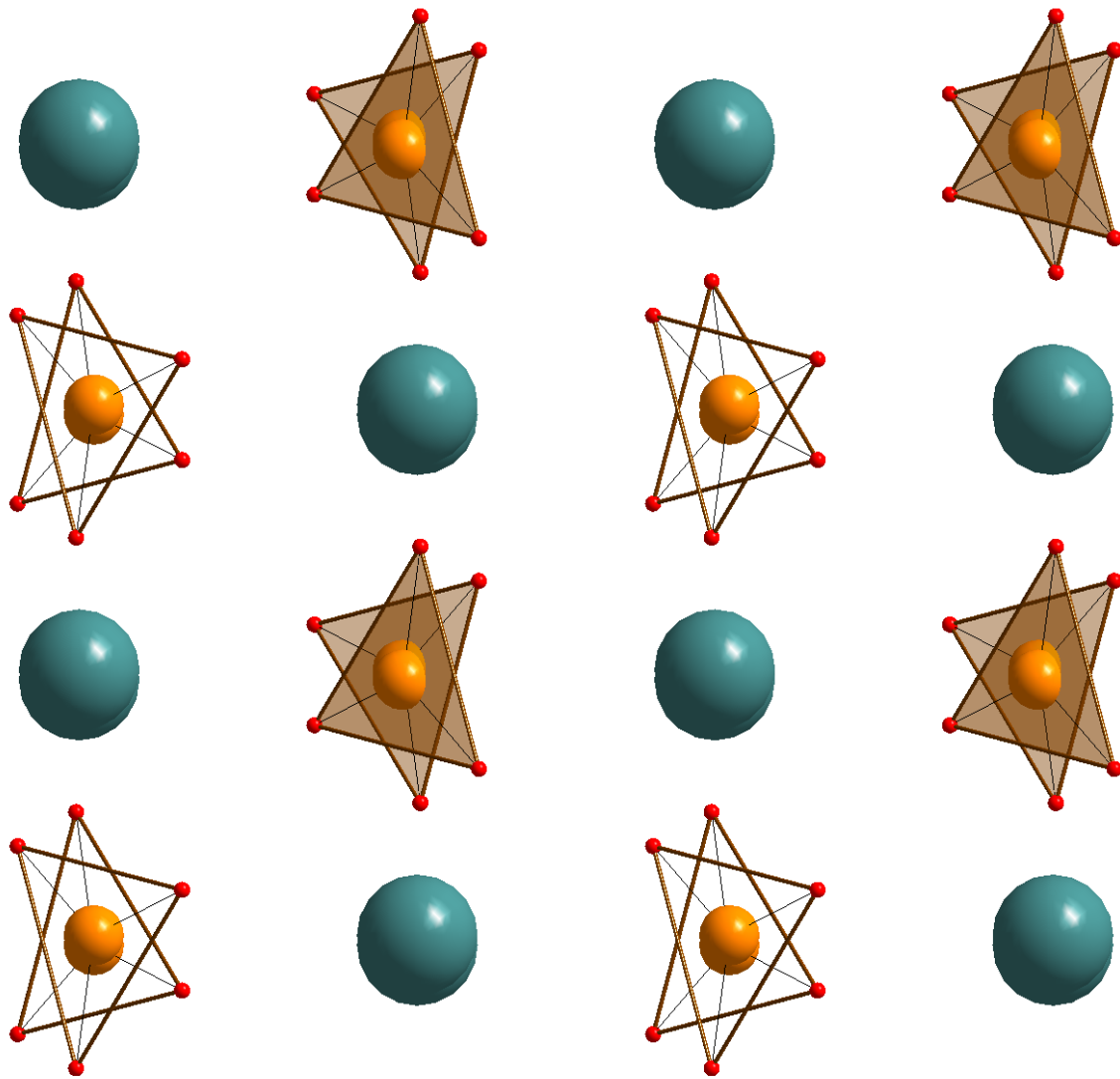


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Diamond anvil cell, 50th birthday

William A. Bassett*





1975: CaCO₃-II structure determination

Merrill-Basset DAC

Distortion of calcite structure;

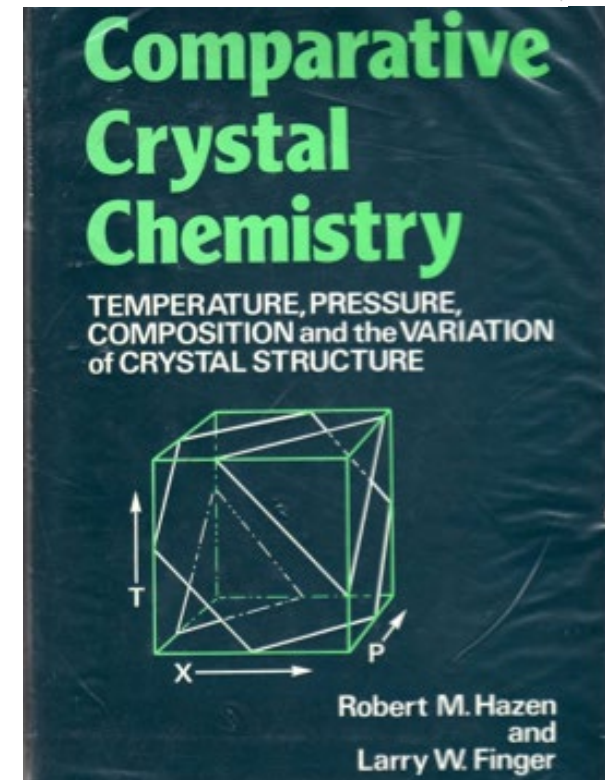
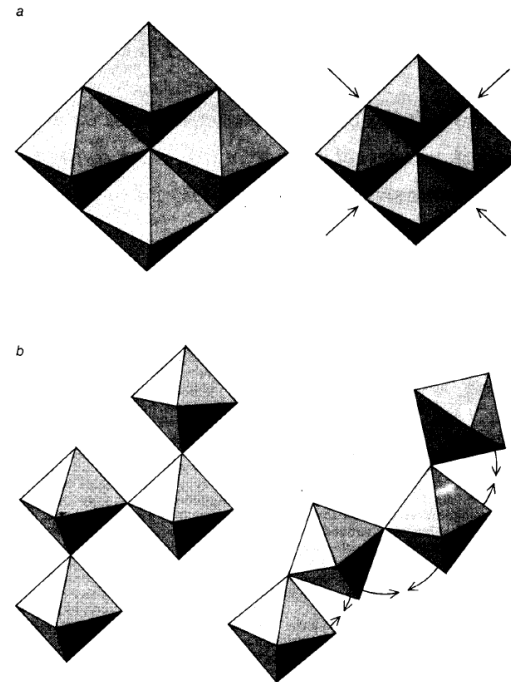
Tilted CO₃ groups

What happens to the atomic structure of a crystal when the external pressure is increased? In the broadest sense the answer is obvious: the individual atoms move closer together, reducing the crystal's volume. It is only in the past few years, however, that investigators have begun to analyze in detail the various ways in which compression affects particular arrangements of atoms. The gain in understanding has come from the marriage of two experimental tools. One, the diamond-anvil high-pressure cell, is a fairly recent addition to the laboratory; the other, the X-ray diffractometer, has been a mainstay of crystallographic research for decades.

Crystals at High Pressure

X-ray studies of crystals compressed between a pair of gem-quality diamonds reveal a range of responses to increased pressure. Changes in atomic structure are best viewed in terms of polyhedral geometry

by Robert M. Hazen and Larry W. Finger



Single-crystal x-ray diffraction of n -H₂ at high pressure

R. M. Hazen, H. K. Mao, L. W. Finger, and R. J. Hemley

*Geophysical Laboratory, Carnegie Institution of Washington, 2801 Upton Street N.W.,
Washington, D.C. 20008-3898*

(Received 15 December 1986; revised manuscript received 26 May 1987)

X-ray diffraction from a single crystal of solid n -H₂ has been obtained at high pressure in a diamond-anvil cell, and the crystal structure has been determined. Nineteen diffraction maxima, corresponding to the hexagonal-close-packed structure ($P6_3/mmc$, $Z=2$), were observed. Unit-cell dimensions at 5.40 ± 0.03 GPa and 300 ± 1 K are $a = 2.659 \pm 0.002$ Å, $c = 4.334 \pm 0.003$ Å, and $V = 26.55 \pm 0.05$ Å³. The structure determination and volume measurement provide the most accurate checks to date on the equation of state and phase diagram of hydrogen in this pressure range.

4 MARCH 1988

SCIENCE, VOL. 239

Synchrotron X-ray Diffraction Measurements of Single-Crystal Hydrogen to 26.5 Gigapascals

H. K. MAO, A. P. JEPHCOAT, R. J. HEMLEY, L. W. FINGER, C. S. ZHA,
R. M. HAZEN, D. E. COX

The crystal structure and equation of state of solid hydrogen have been determined directly to 26.5 gigapascals at room temperature by new synchrotron x-ray diffraction techniques. Solid hydrogen remains in the hexagonal close-packed structure under these pressure-temperature conditions and exhibits increasing structural anisotropy with pressure. The pressure-volume curve determined from the x-ray data represents the most accurate experimental measurement of the equation of state to date in this pressure range. The results remove the discrepancy between earlier indirect determinations and provide a new experimental constraint on the molecular-to-atomic transition predicted at higher pressures.

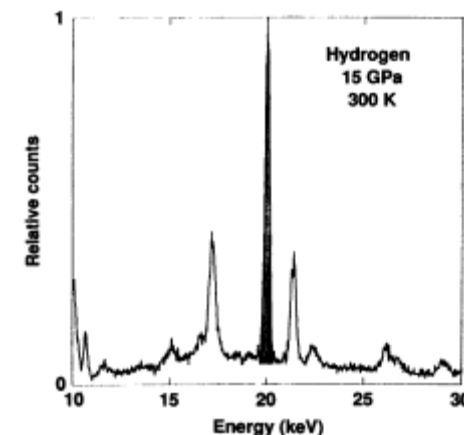
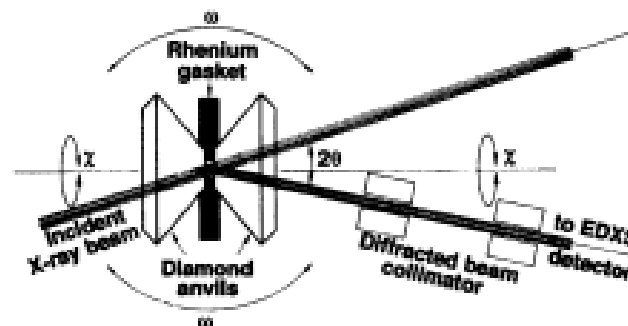
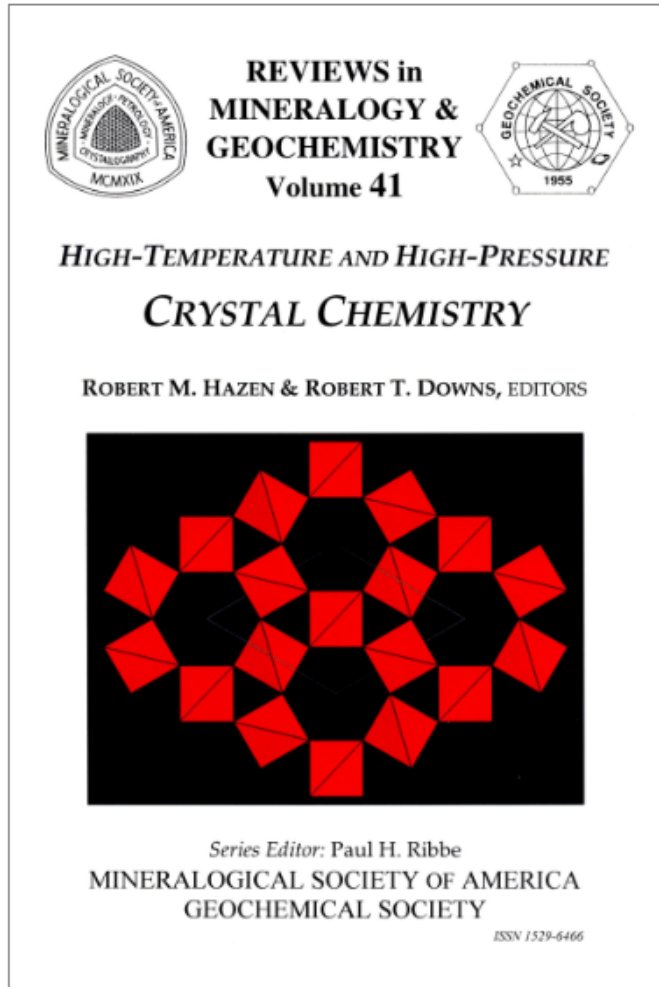


Fig. 2. A representative energy-dispersive x-ray diffraction spectrum for solid hydrogen [(101) reflection] at high pressure.

The Merrill-Bassett DAC became a standard tool for laboratory-based high-pressure research. It was used for accurate equation of state determinations using laboratory X-ray sources.

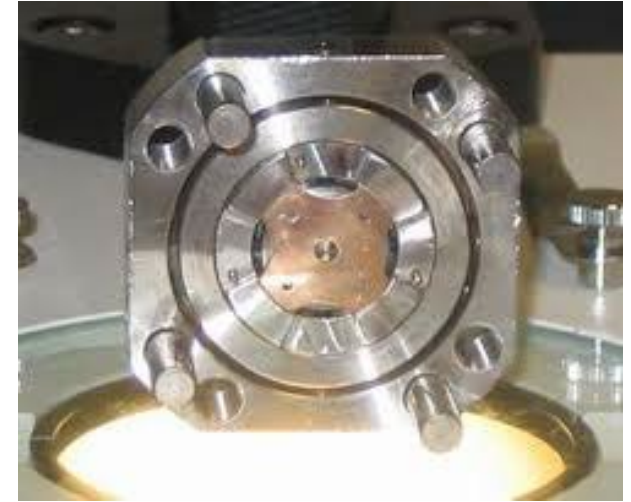


2

Equations of State

R. J. Angel

*Bayerisches Geoinstitut
Universität Bayreuth
D95440 Bayreuth, Germany*



ETH-DAC (Miletich)

INTRODUCTION

Diffraction experiments at high pressures provide measurement of the variation of the unit-cell parameters of the sample with pressure and thereby the variation of its volume (or equivalently its density) with pressure, and sometimes temperature. This last is known as the 'Equation of State' (EoS) of the material. It is the aim of this chapter to present a detailed guide to the methods by which the parameters of EoS can be obtained from experimental compression data, and the diagnostic tools by which the quality of the results can be assessed. The chapter concludes with a presentation of a method by which the uncertainties in EoS parameters can be predicted from the uncertainties in the measurements of pressure and temperature, thus allowing high-pressure diffraction experiments to be designed in advance to yield the required precision in results.

Determining complex crystal structures from high pressure single-crystal diffraction data collected on synchrotron sources

M. I. McMahon*, I. Loa, G. W. Stinton and L. F. Lundegaard

SUPA, School of Physics and Astronomy, and Centre for Science at Extreme Conditions, The University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, UK

The introduction of angle-dispersive X-ray powder-diffraction methods in the late 1980s and early 1990s changed all of this.[4,5] The ability to determine and Rietveld-refine crystal structures from X-ray powder-diffraction data revolutionised high pressure structural research,[6] and such studies have since been performed to pressures in excess of 300 GPa.[7–9] However, by the end of the 1990s, it was clear that the structural complexity revealed by numerous angle-dispersive diffraction studies was beyond that solvable using powder methods, necessitating a return to single-crystal techniques in order to solve the most complex structural forms. The subsequent use of such methods was the key to identifying the existence of incommensurate crystal structures at high pressures in Ba [10] and Te,[11] and to determining the extremely complex structural forms found in Cs, Rb and Ga at high pressures.[12–14]

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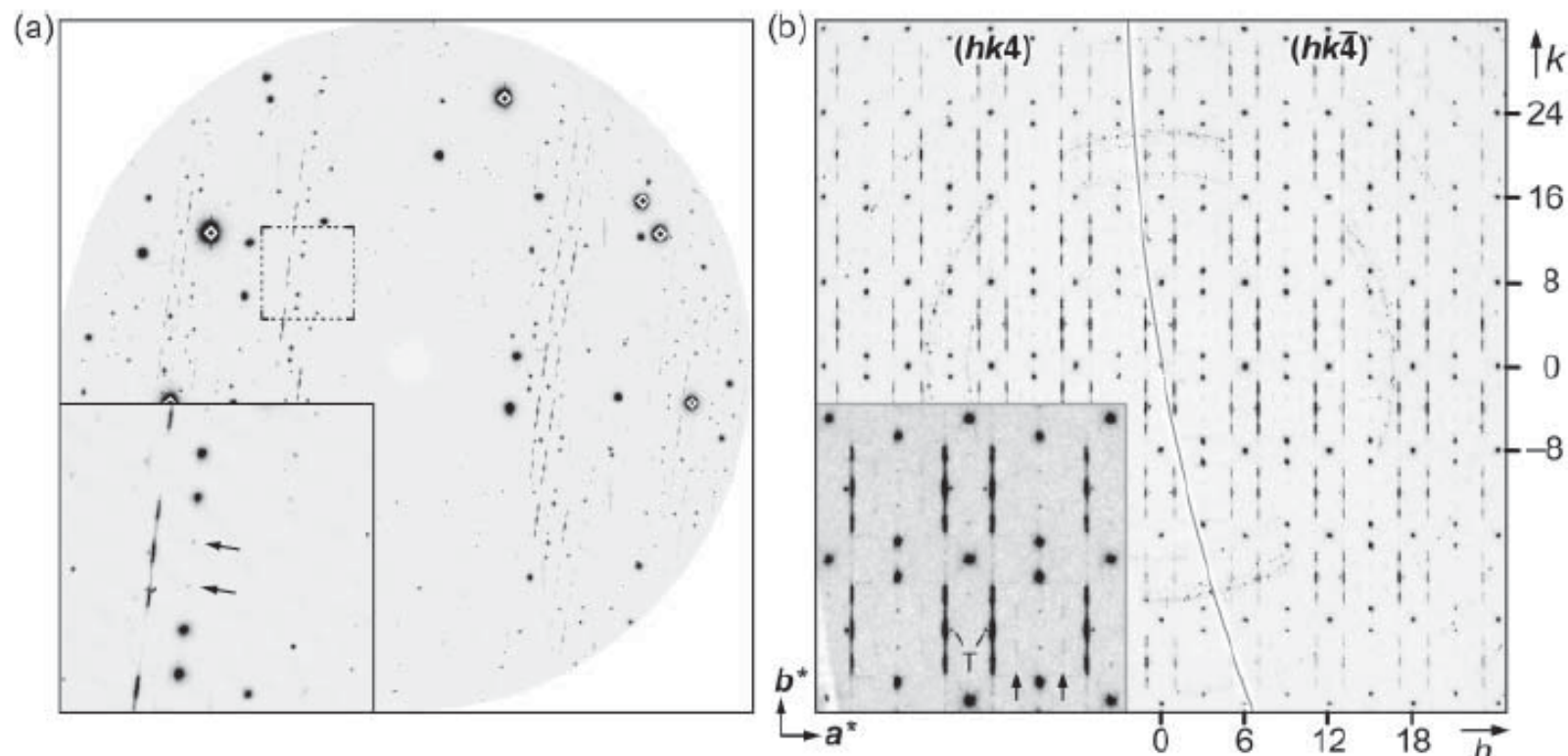
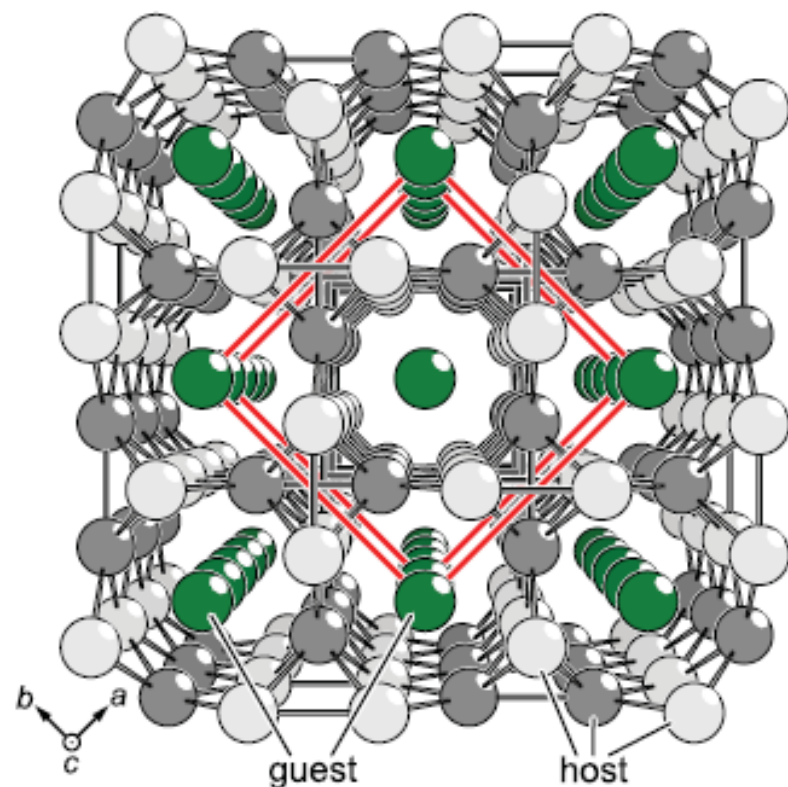
Self-Hosting Incommensurate Structure of Barium IV

R. J. Nelves, D. R. Allan, M. I. McMahon, and S. A. Belmonte

Department of Physics and Astronomy, The University of Edinburgh, Edinburgh EH9 3JZ, United Kingdom

(Received 11 June 1999)

The structure of phase IV of barium has been solved from single-crystal and powder diffraction x-ray data. It is composed of a tetragonal “host,” with “guest” chains in channels along the c axis of the host. These chains form two different structures, one well crystallized and the other highly disordered and giving rise to strong diffuse scattering. The guest structures are incommensurate with the host.



Evolution of Single Crystal Diffraction Techniques: Transition from laboratory to synchrotron sources for single crystal diffraction

APS (USA)

High Pressure Research, 2013

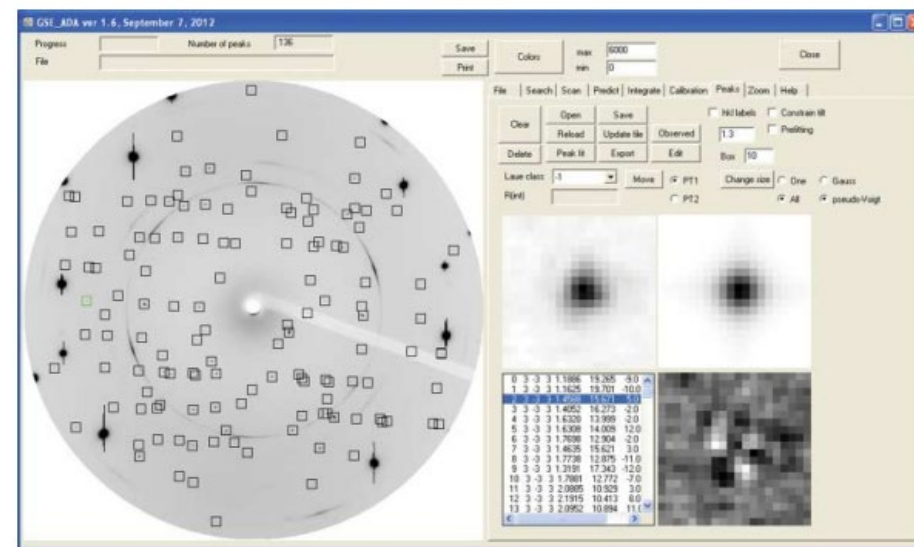
<http://dx.doi.org/10.1080/08957959.2013.806504>



High pressure single-crystal micro X-ray diffraction analysis with GSE_ADA/RSV software

Przemyslaw Dera^{a,b*}, Kirill Zhuravlev^a, Vitali Prakapenka^a, Mark L. Rivers^a,
Gregory J. Finkelstein^c, Ognjen Grubor-Urosevic^d, Oliver Tschauner^d, Simon M. Clark^e
and Robert T. Downs^f

^aCenter for Advanced Radiation Sources, Argonne National Laboratory, University of Chicago, Argonne, IL, USA; ^bSchool of Ocean and Earth Science and Technology, Hawaii Institute of Geophysics and Planetology, University of Hawaii at Manoa, Honolulu, HI, USA; ^cDepartment of Geosciences, Princeton University, Princeton, NJ, USA; ^dHigh Pressure Science and Technology Center, University of Nevada at Las Vegas, Las Vegas, NV, USA; ^eDepartment of Earth and Planetary Sciences, Macquarie University, North Ryde, Australia; ^fGeology Department, University of Arizona, Tucson, AZ, USA





Structure of siderite FeCO_3 to 56 GPa and hysteresis of its spin-pairing transition

Barbara Lavina,¹ Przemyslaw Dera,² Robert T. Downs,³ Wenge Yang,^{4,5} Stanislav Sinogeikin,⁴ Yue Meng,⁴ Guoyin Shen,⁴ and David Schiferl¹

¹High Pressure Science and Engineering Center and Department of Physics and Astronomy, University of Nevada, Las Vegas, Nevada 89154, USA

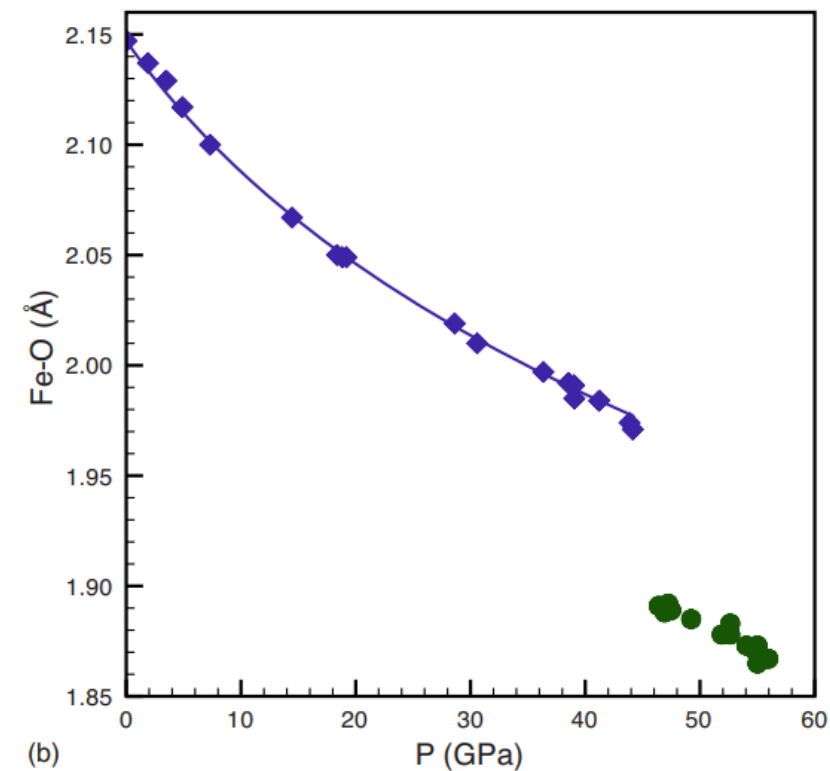
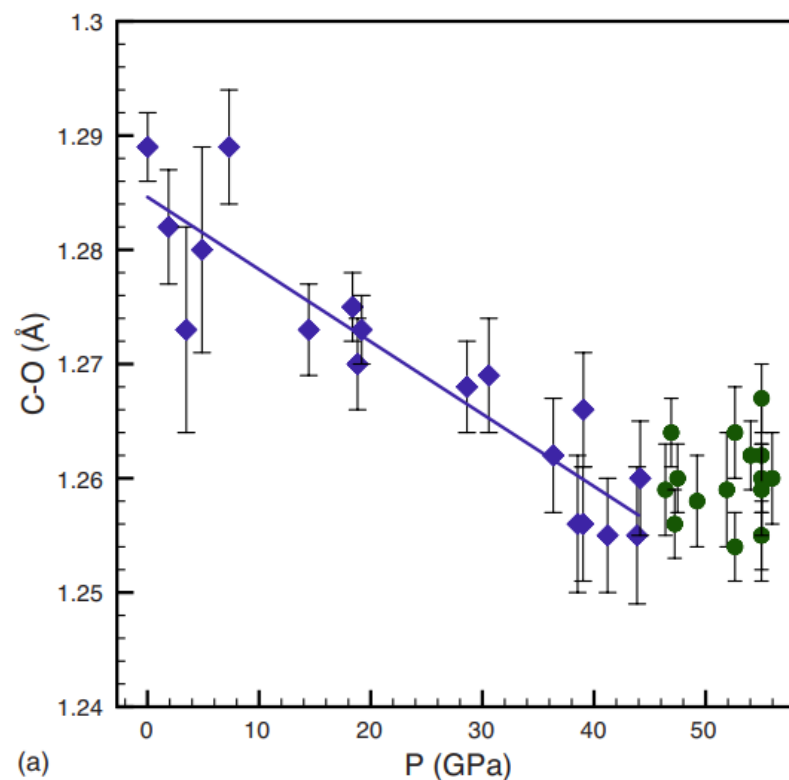
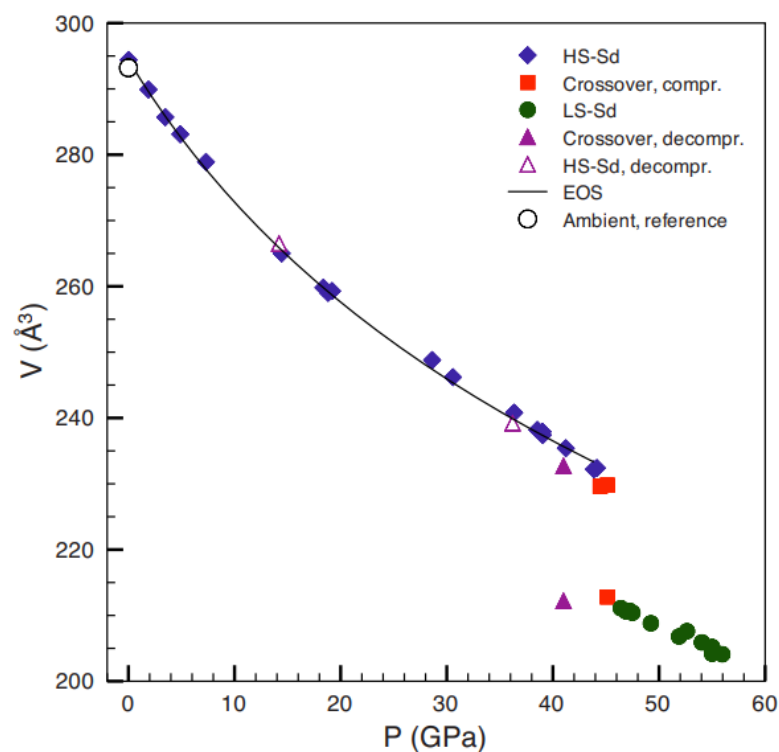
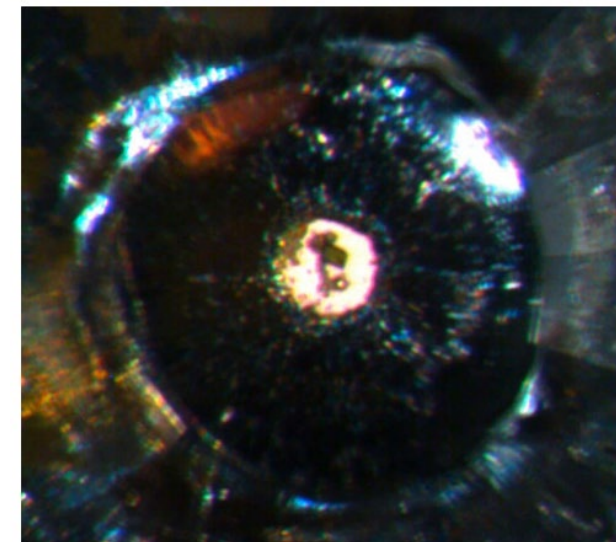
²GSECARS, University of Chicago, Building 434A, 9700 South Cass Avenue, Argonne, Illinois 60439, USA

³Geosciences, University of Arizona, Tucson, Arizona 85721-0077, USA

⁴HPCAT, Carnegie Institution of Washington, Building 434E, 9700 South Cass Avenue, Argonne, Illinois 60439, USA

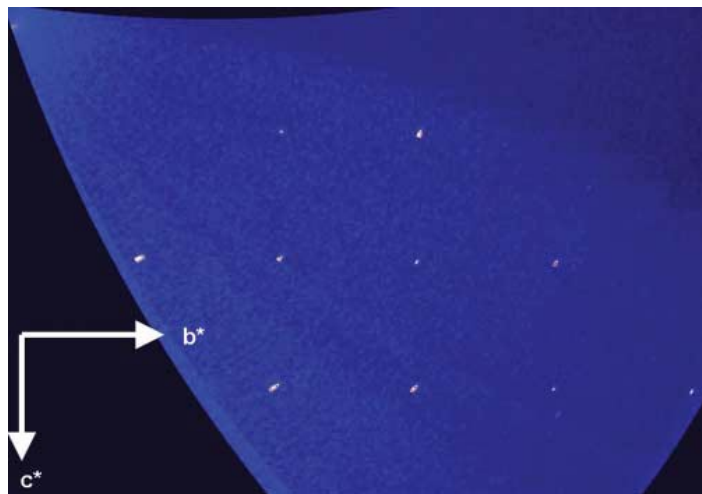
⁵HPSynC, Carnegie Institution of Washington, Building 401, 9700 South Cass Avenue, Argonne, Illinois 60439, USA

(Received 20 May 2010; published 23 August 2010)



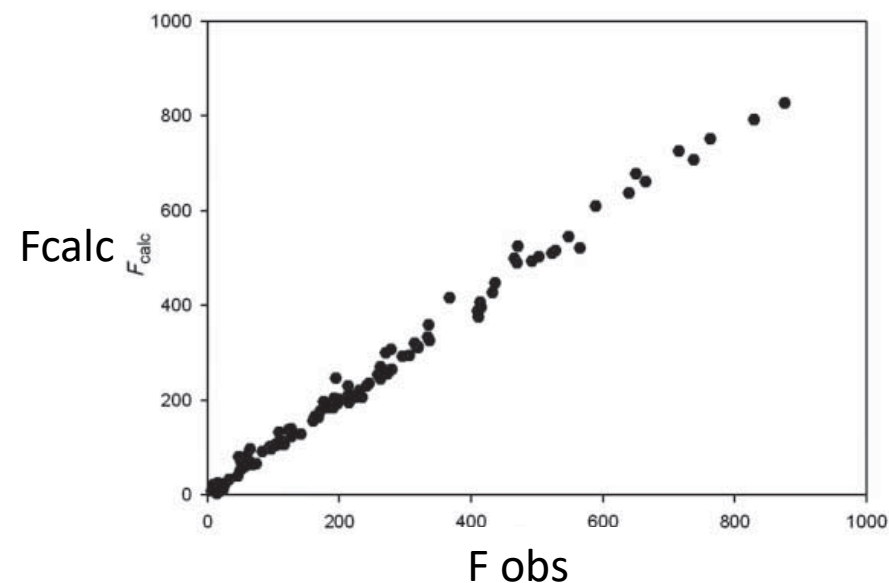
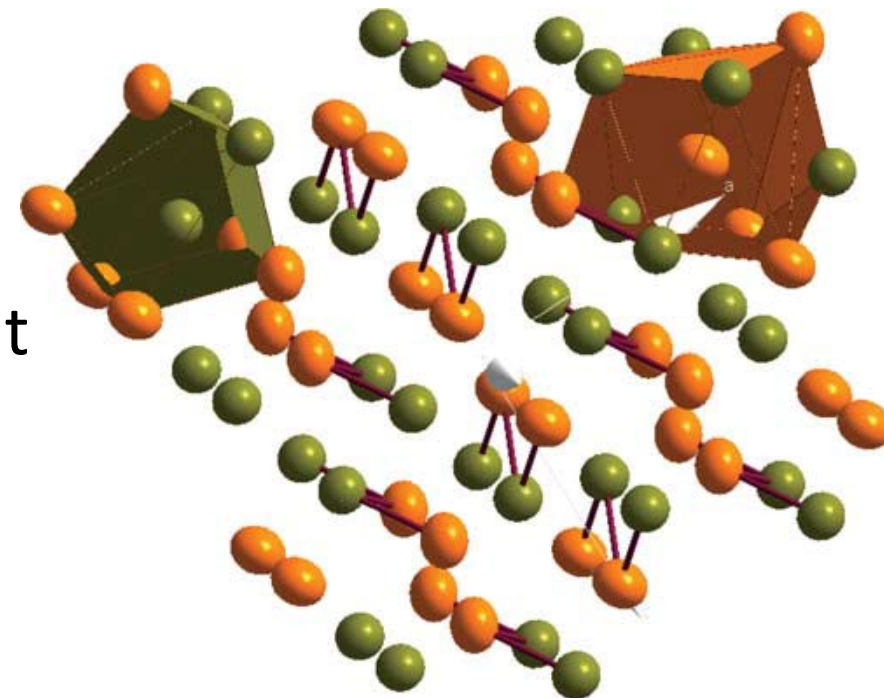
Na oP8 structure determined at 118 GPa

ESRF (GRENOBLE)



MnP type structure

Single atomic species, but
binary compound type
structure



High Pressure Research, 2013

<http://dx.doi.org/10.1080/08957959.2013.831088>



Single-crystal diffraction at megabar conditions by synchrotron radiation

Marco Merlini^{a*} and Michael Hanfland^b

^aDipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23,
20133 Milano, Italy; ^bESRF, European Synchrotron Radiation Facility, 6 Rue Jules Horowitz,
38000 Grenoble, France

LETTER

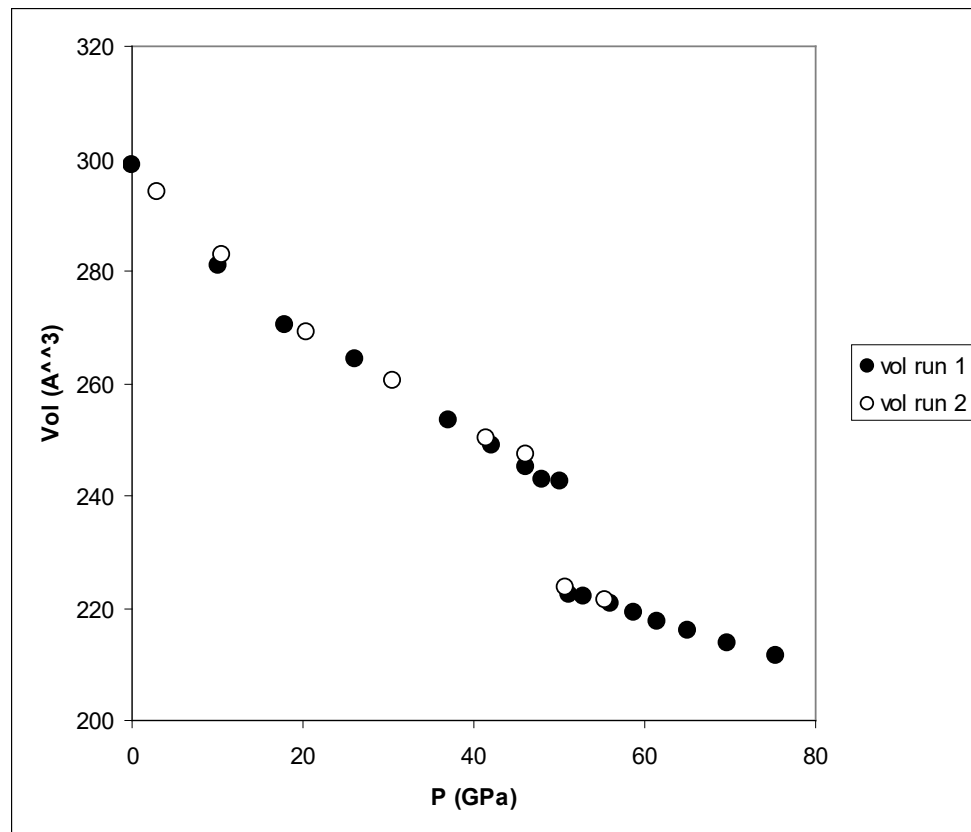
Fe³⁺ spin transition in CaFe₂O₄ at high pressure

MARCO MERLINI,^{1,2,*} MICHAEL HANFLAND,¹ MAURO GEMMI,² SIMO HUOTARI,¹
LAURA SIMONELLI,¹ AND PIERRE STROBEL³

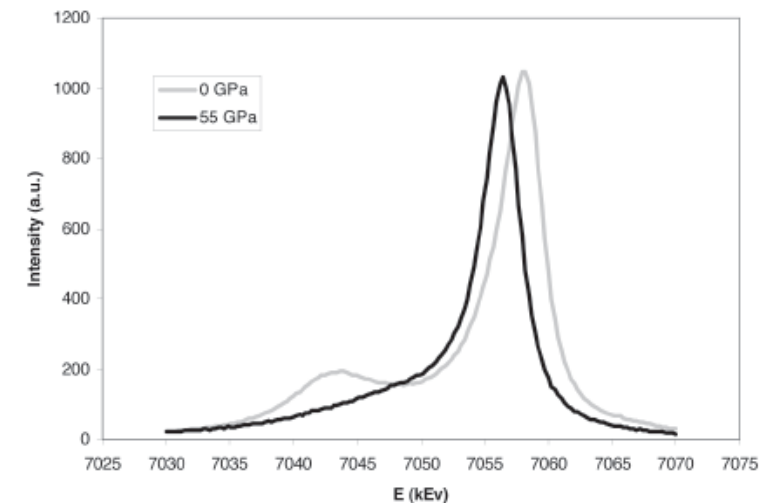
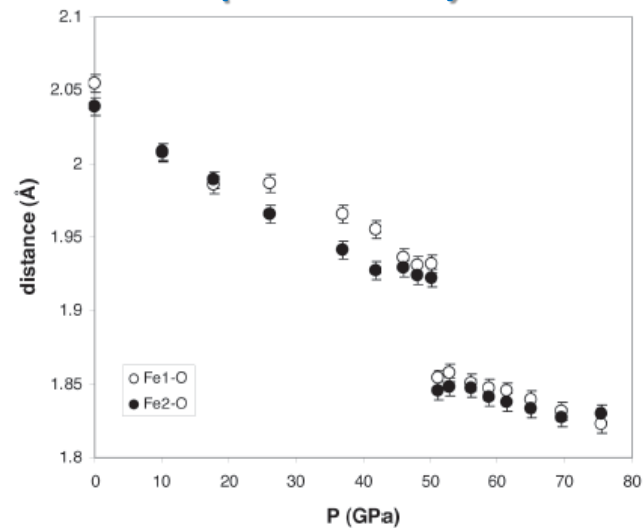
¹ESRF—European Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP220, 38043 Grenoble CEDEX, France

²Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23, 20133 Milano, Italy

³Institut Néel, CNRS and Université Joseph Fourier, BP166, 38042 Grenoble Cedex 9, France

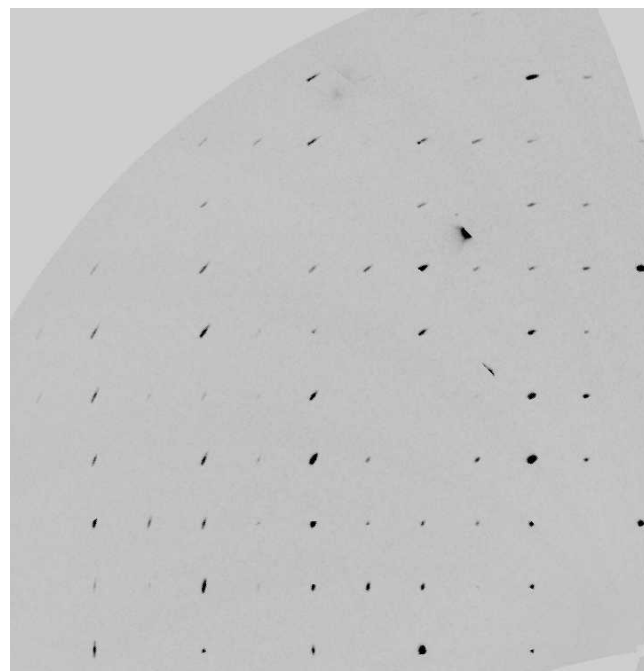


ESRF (GRENOBLE)

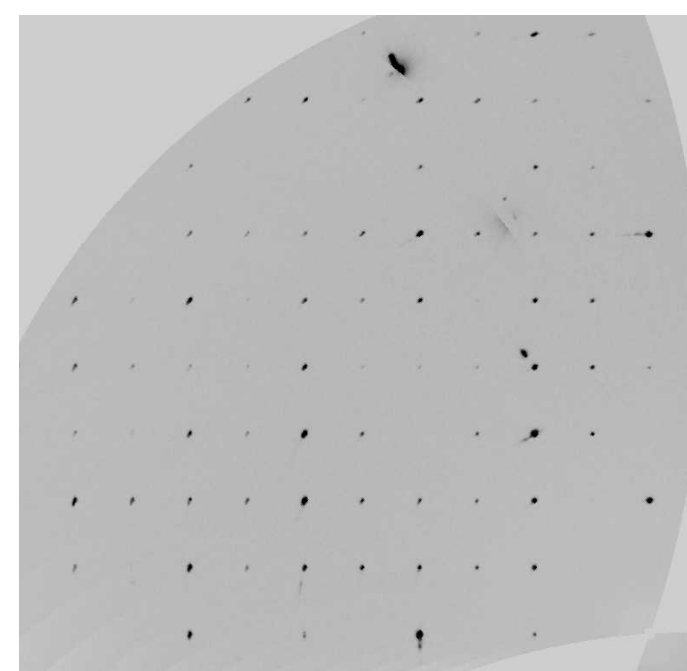


Reciprocal space reconstruction – hk0

P=10 GPa



P=60 GPa

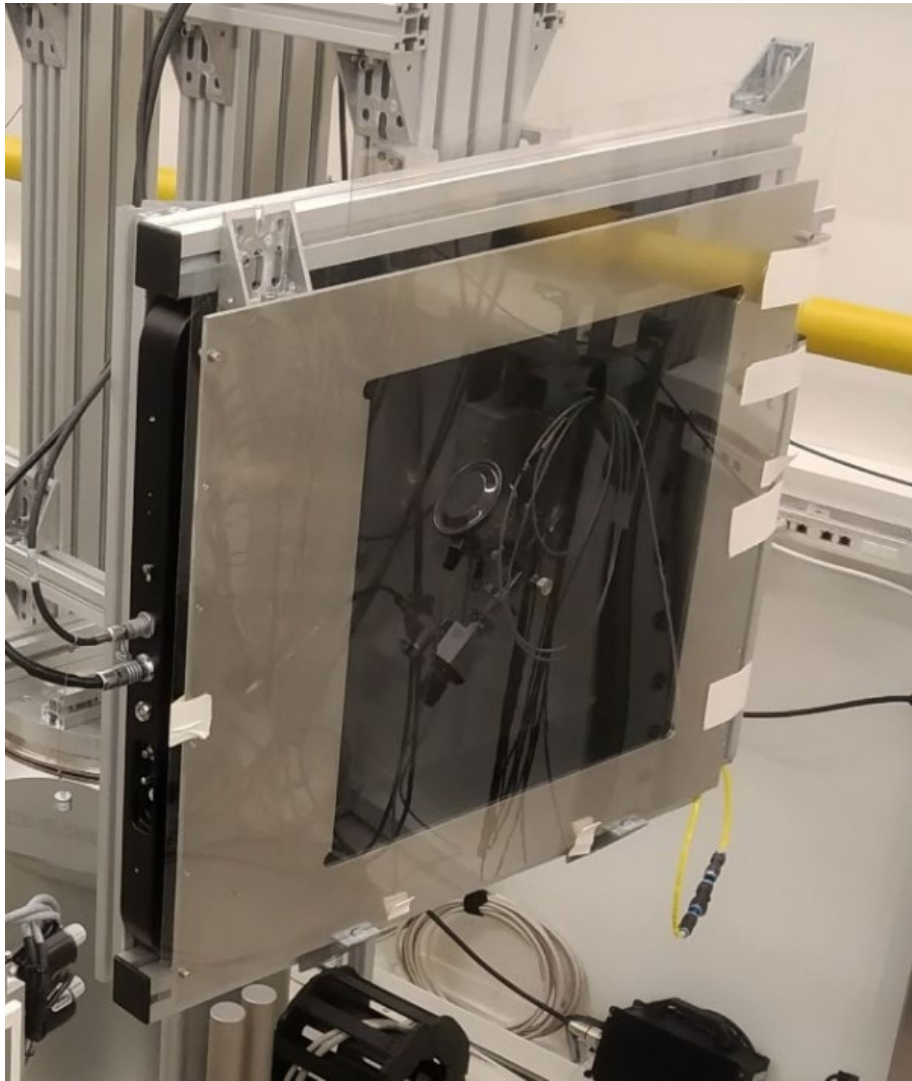


Beamline and Detector Advancements

Evolution of beamlines and detectors has enhanced data quality.

- Mar345 (image plate detector)
- MarCCD (charge-coupled device)
- Flat panel detectors (e.g., Mar555, Perkin-Elmer)
- New generation detectors like Pilatus

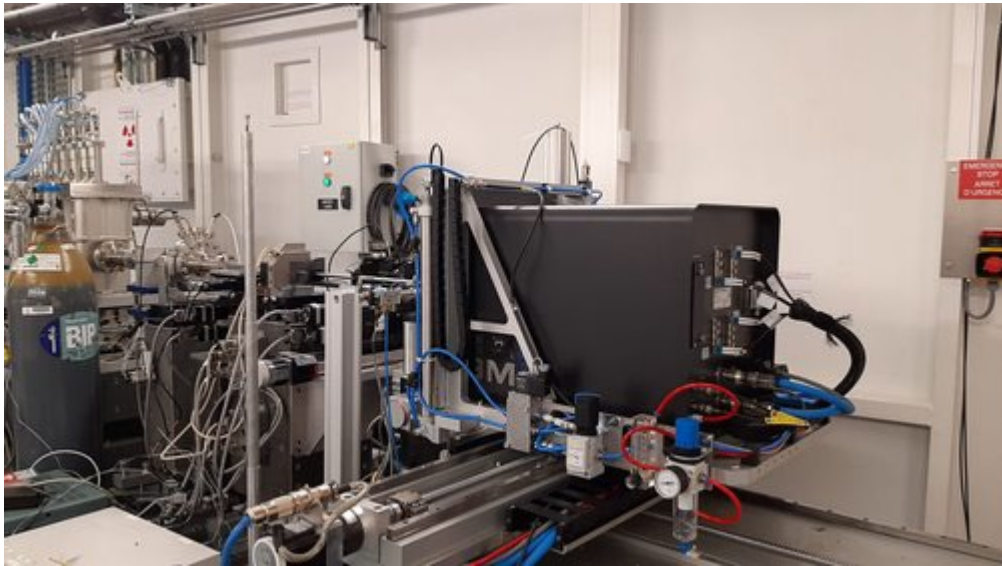




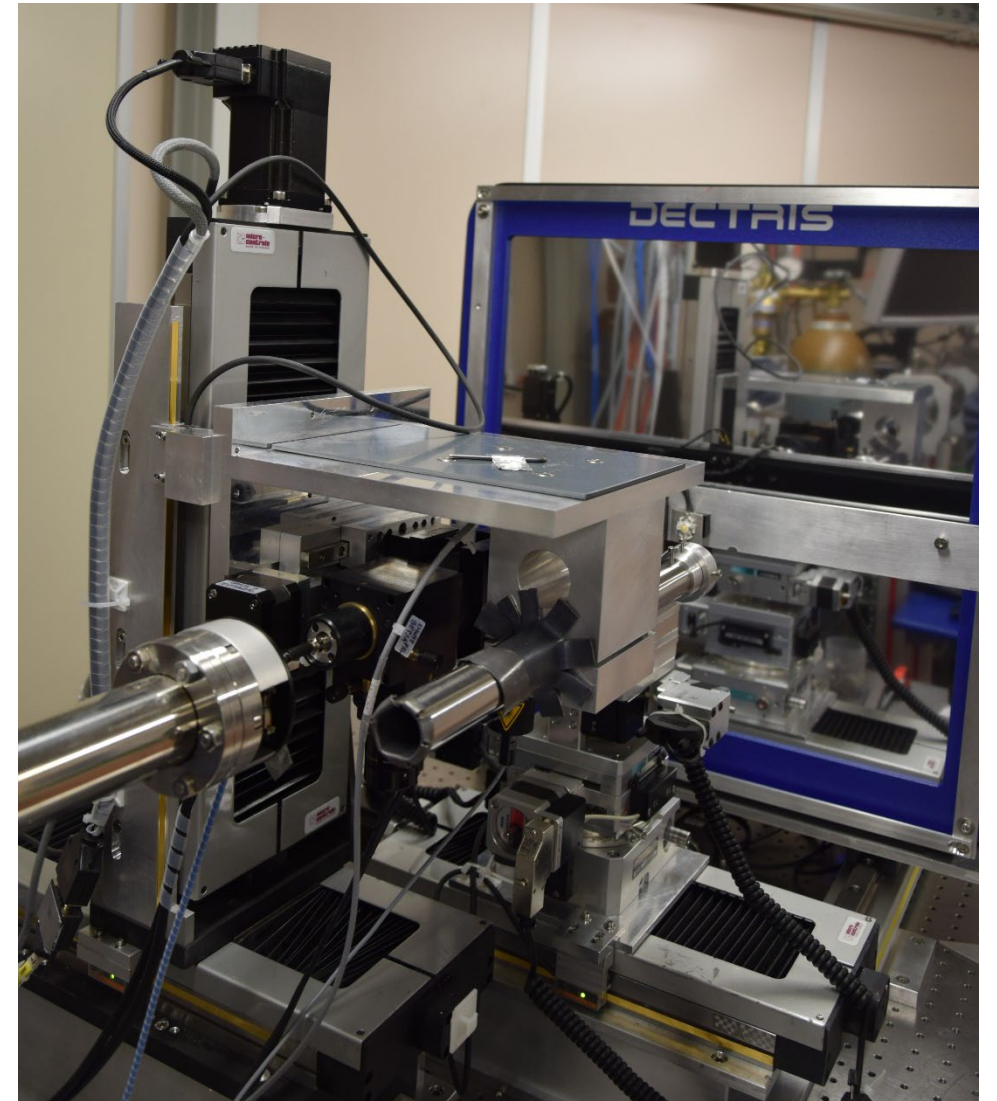
Petra-III (Hamburg) – flat panel detector



Esrf (Grenoble) – flat panel detector



Esrf, ID15b – Dectris (CdTe)



Elettra, XPRESS – Dectris (Silicon)

Example of contribution of single crystal diffraction at synchrotron to determine structure after multiple phase transition

CaCO₃-III: impossible to index completely the X-ray powder pattern

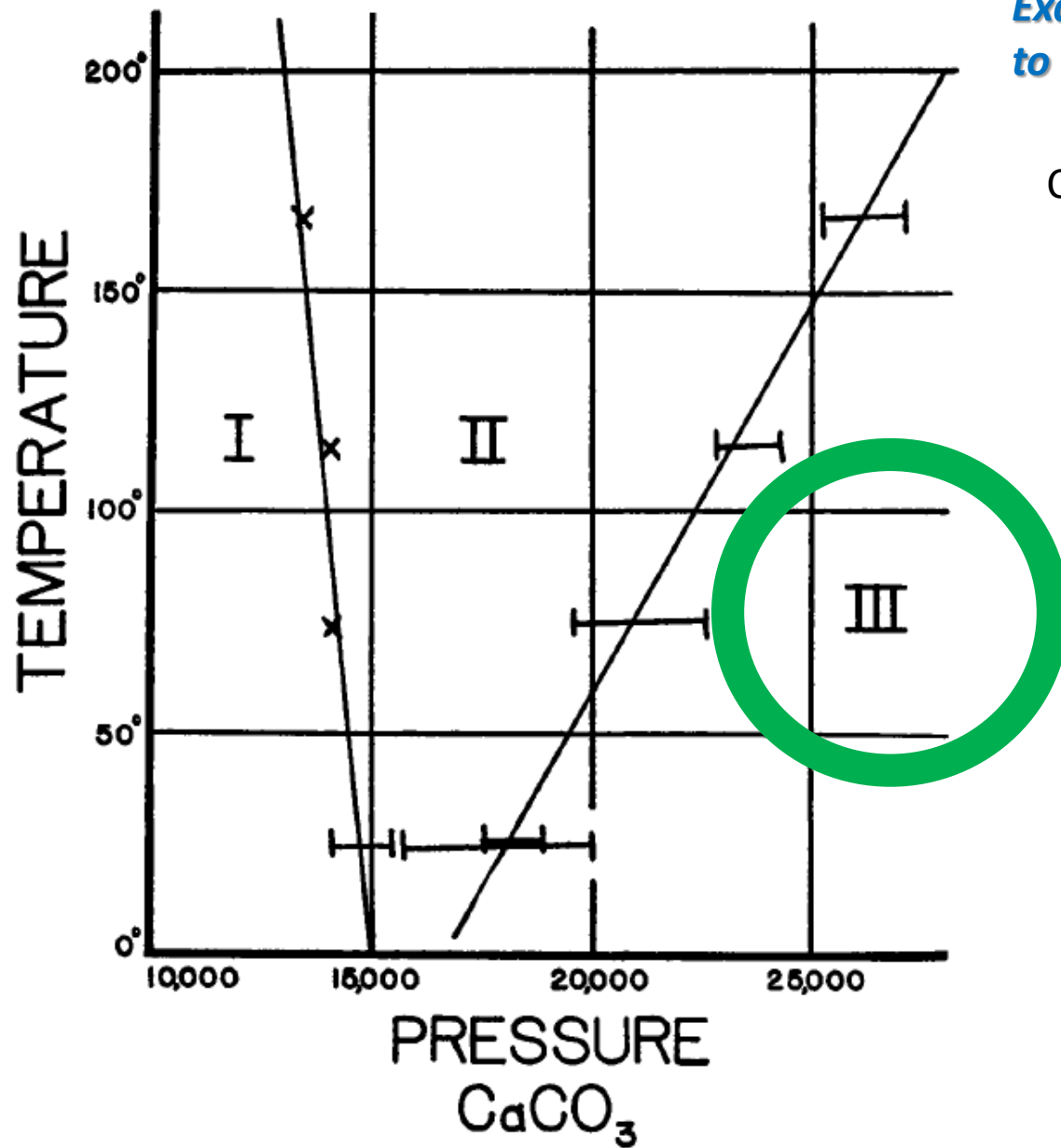


Fig. 1. The phase diagram of CaCO₃, temperature in degrees Centigrade against pressure in kilograms per square centimeter.

Bridgman, 1939
Davis, 1964
Merrill & Bassett, 1972
Liu & Mernagh, 1990
Fiquet et al., 1994
Smyth & Ahrens, 1997
Suito et al., 2001
Catalli & Williams, 2005
Hagiya et al., 2005

Even the determination of the unit cell was controversial (without structure determination)

Crystal structure determination in 2012:

New generation of x-ray detectors at synchrotron sources

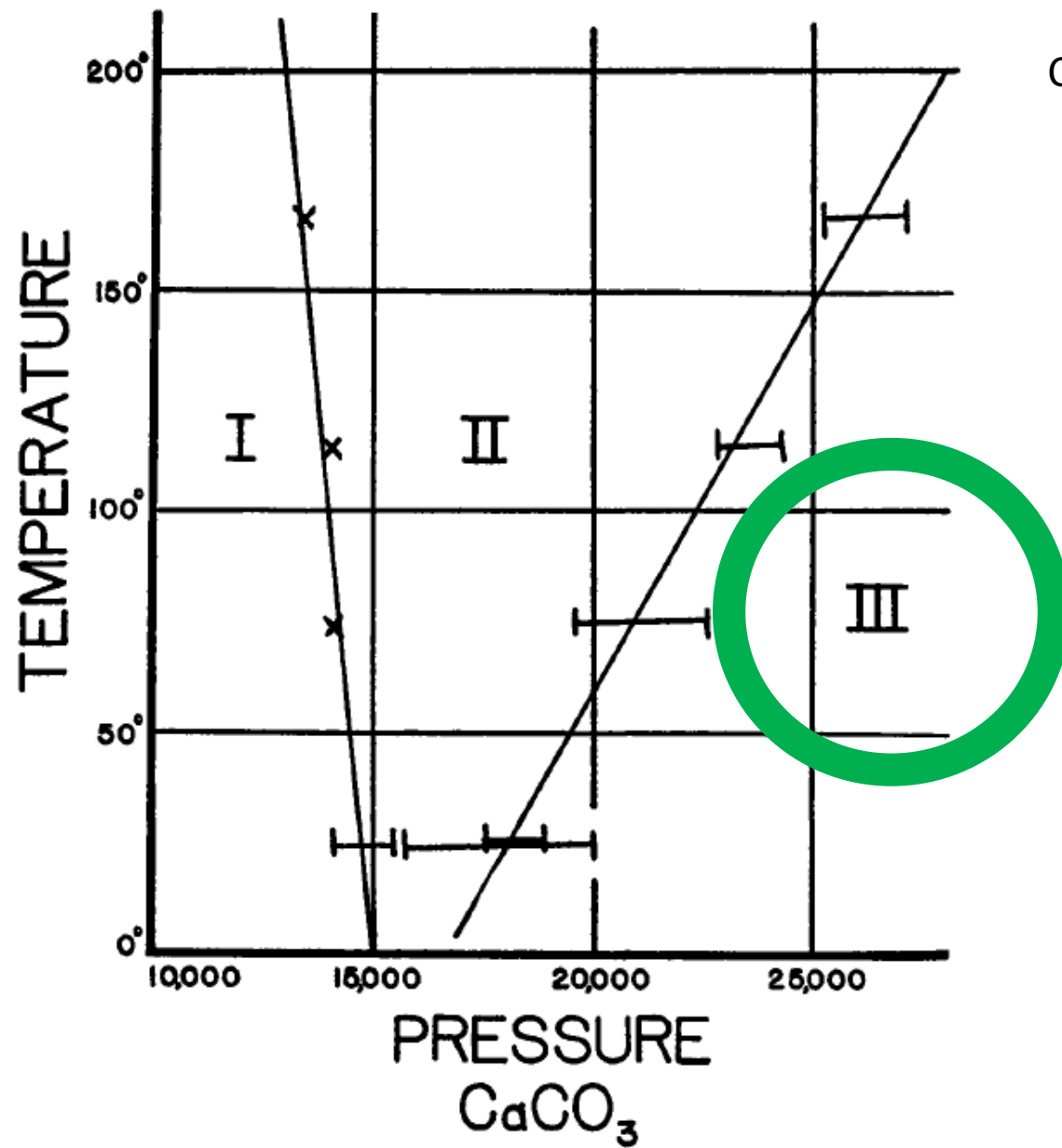


Fig. 1. The phase diagram of CaCO₃, temperature in degrees Centigrade against pressure in kilograms per square centimeter.

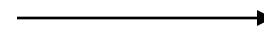
CaCO₃-III: impossible to index completely the X-ray powder pattern



Crystal structure determination in 2012:

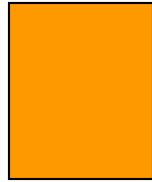
New generation of x-ray detectors at synchrotron sources

Microdiffraction from polycrystal sample



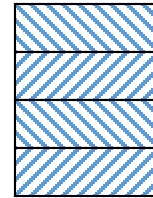
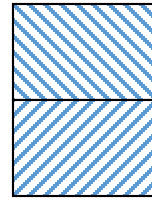
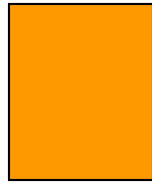
Phase transitions,
chemical reactions

1-



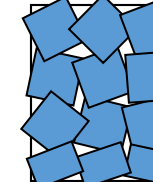
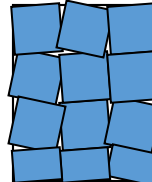
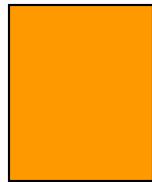
2nd order transition (i.e. martensitic)

2-



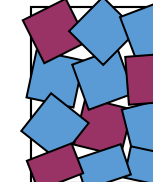
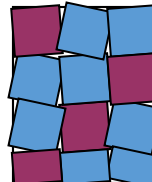
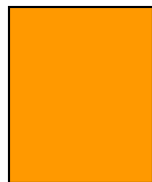
As 1) with twinning

3-



1st order, with volume discontinuity

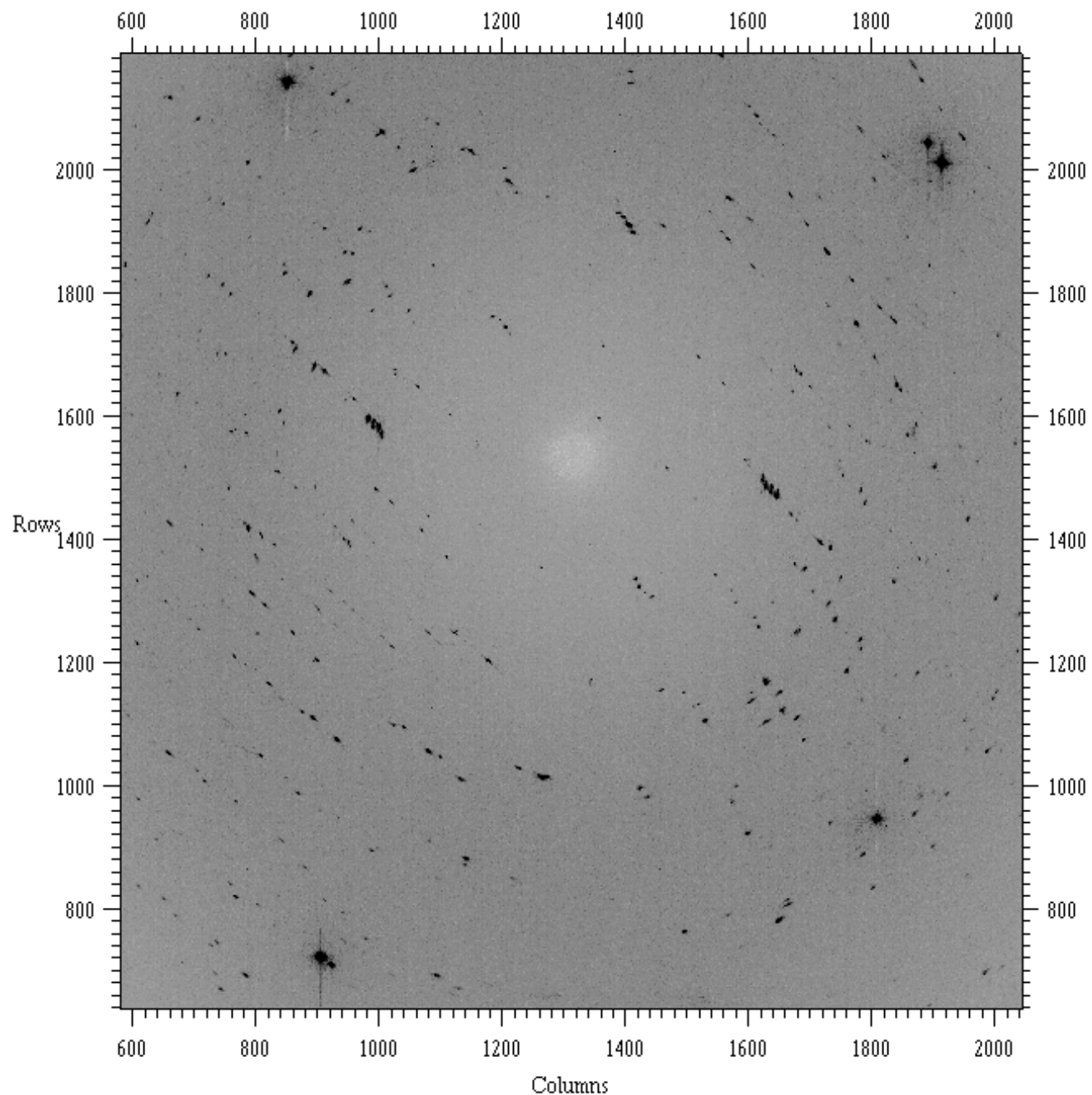
4-



Decomposition, chemical reactions

3-4) : single crystal domain size very small; Most interesting for Earth's mantle mineralogy

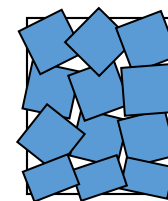
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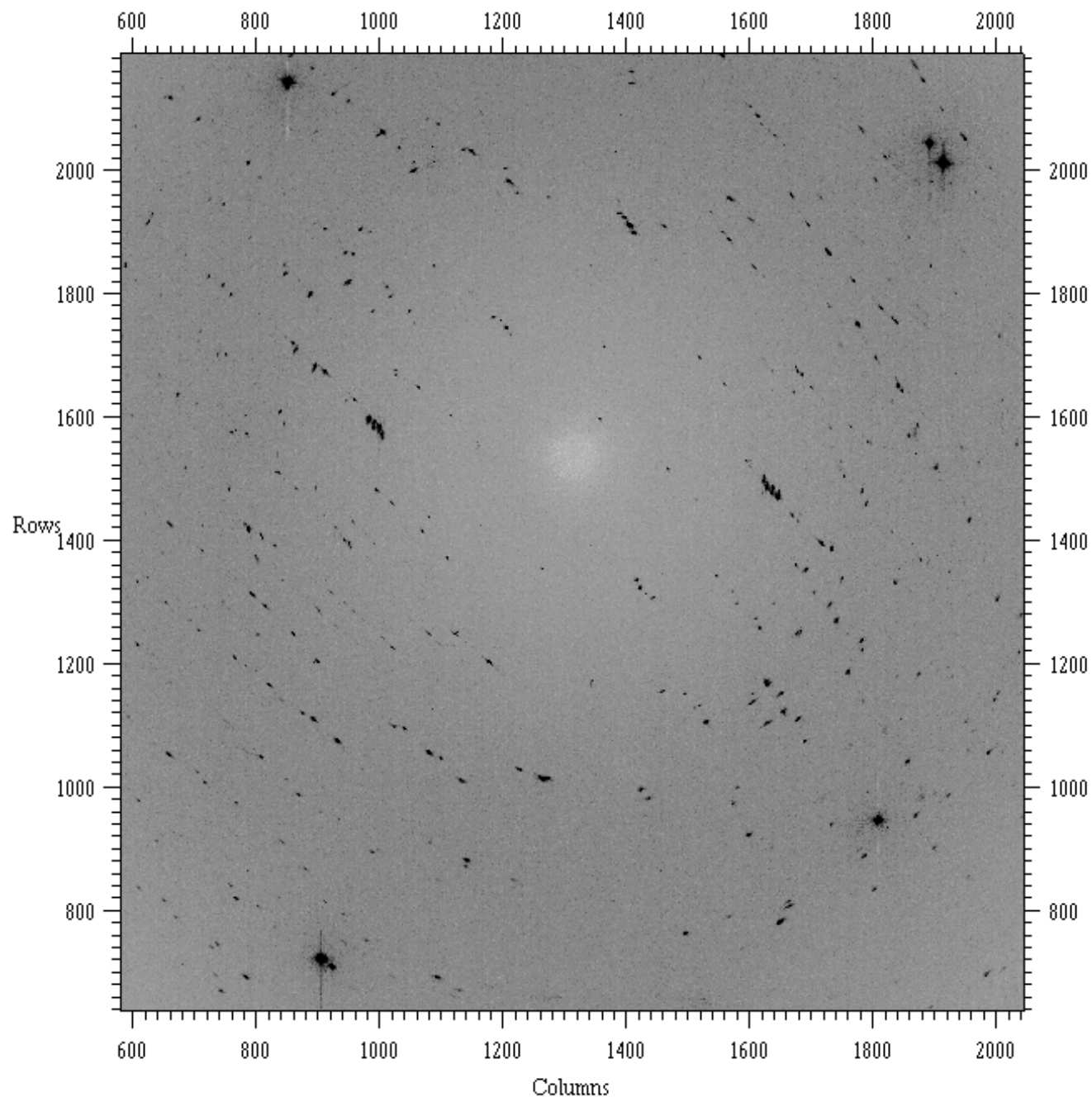
CaCO₃-III Multiple domains

Possibility to identify a crystal lattice for main domain and integrate intensity with resonable peak separation from nearly overlapping ones

Possible use of merged diffractions from different domain with different crystallographic orientation for structure solution (increase of reciprocal space coverage)



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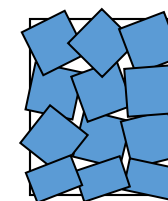


CaCO₃-III

Multiple domains

Possibility to identify a crystal lattice for main domain and integrate intensity with resonable peak separation from nearly overlapping ones

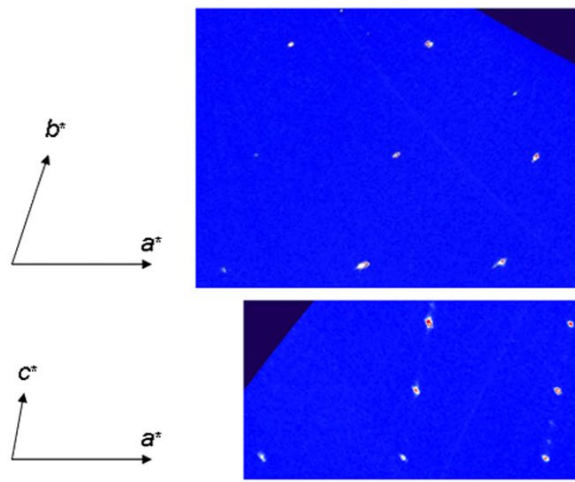
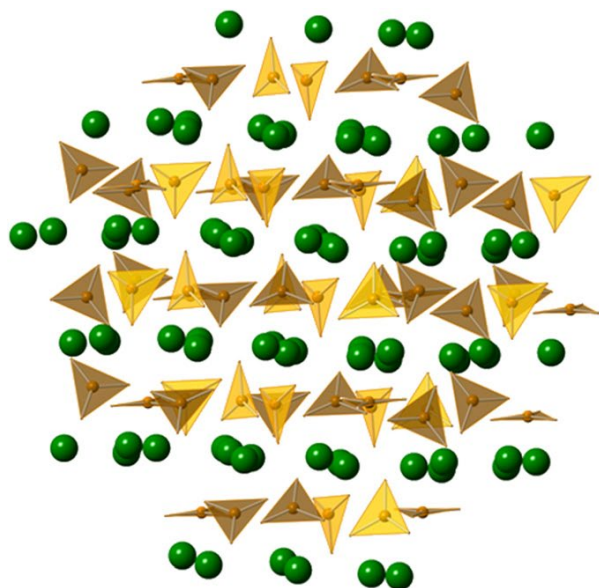
Possible use of merged diffractions from different domain with different crystallographic orientation for structure solution (increase of reciprocal space coverage)



Triclinic CaCO_3 -III

$a=6.281(1) \text{ \AA}$ $b=7.507(2) \text{ \AA}$ $c=12.516(3) \text{ \AA}$ $\alpha=93.76(2)^\circ$ $\beta=98.95(2)^\circ$ $\gamma=106.49(2)^\circ$

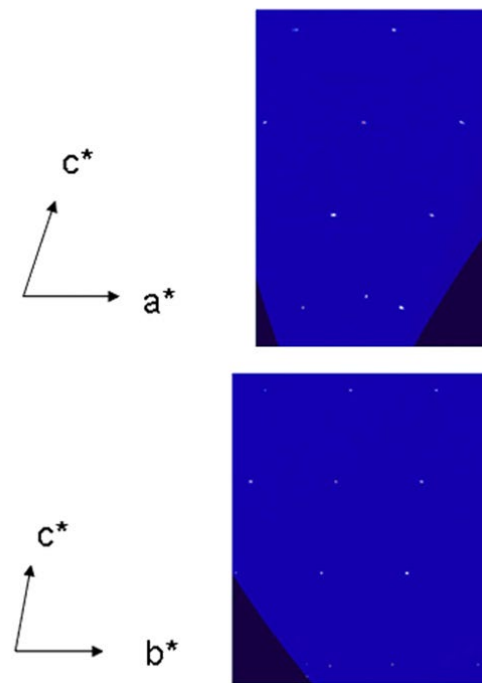
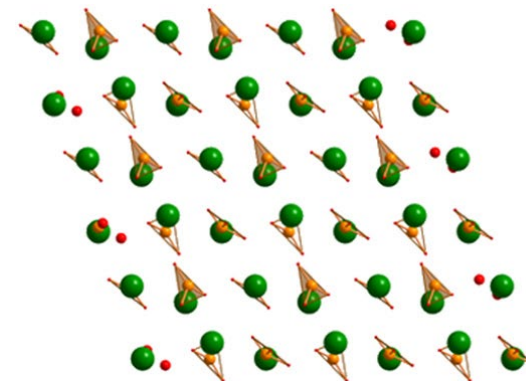
$Z=10$ (50 atoms in the unit cell)



Triclinic (pseudo monoclinic) CaCO_3 -IIIb

$a=6.144(3) \text{ \AA}$ $b=6.3715(14) \text{ \AA}$ $c=6.3759(15) \text{ \AA}$ $\alpha=93.84(2)^\circ$ $\beta=107.34(3)^\circ$ $\gamma=107.16(3)^\circ$

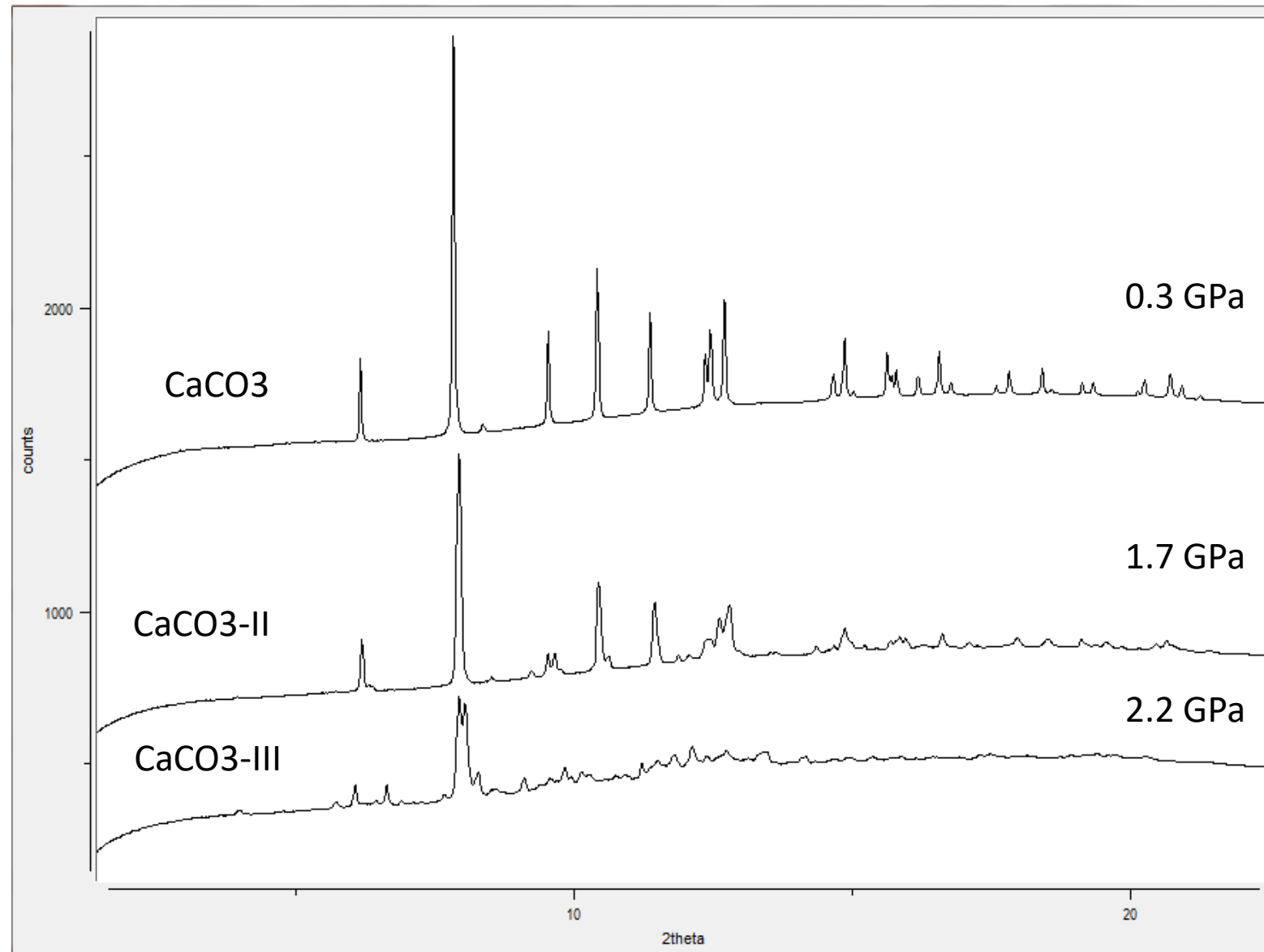
$Z=4$ (20 atoms in the unit cell)



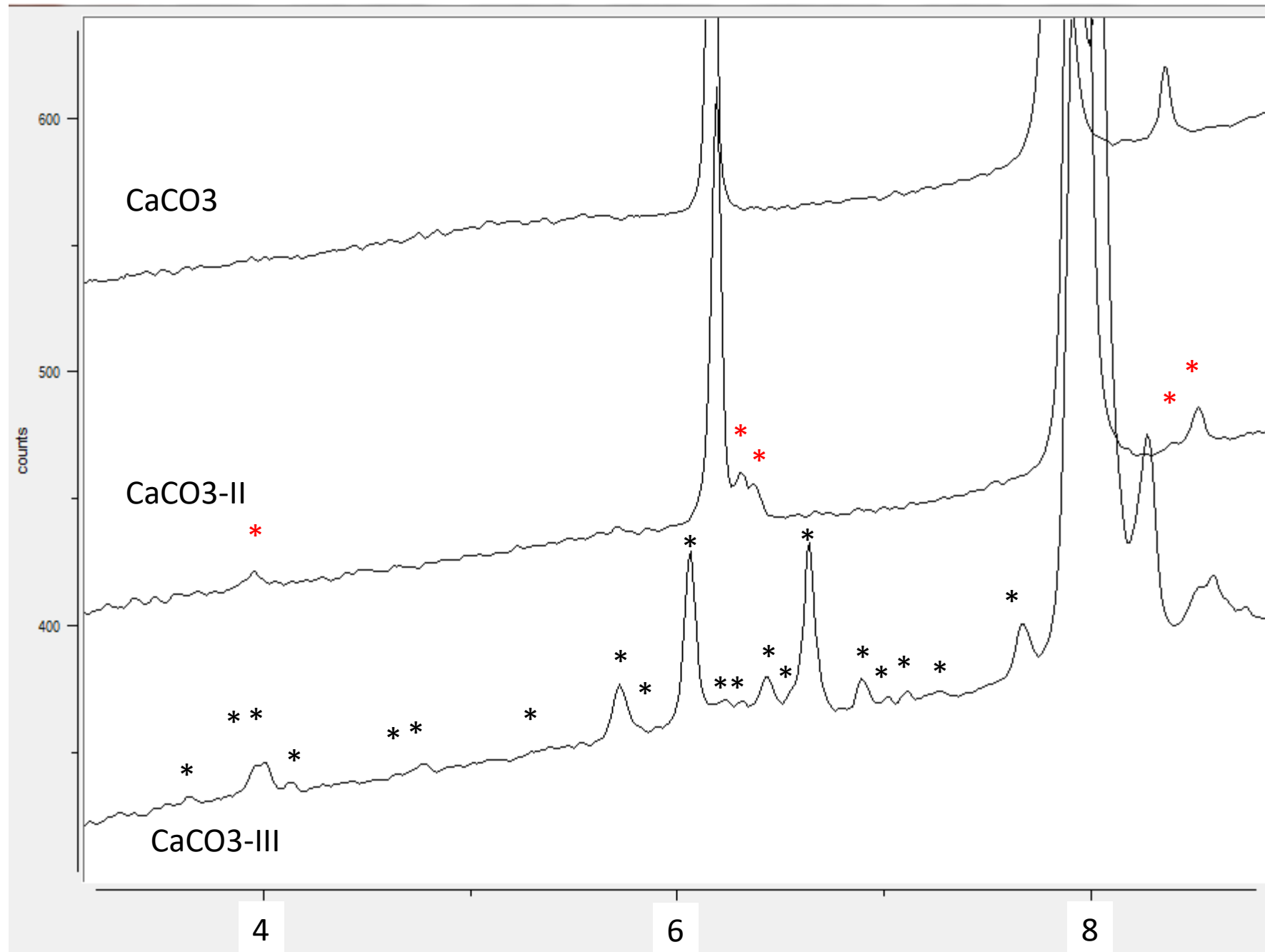
Two different
structures
observed in the
2-10 GPa range

High-resolution and high-flux X-ray synchrotron diffraction of CaCO_3 at high pressure

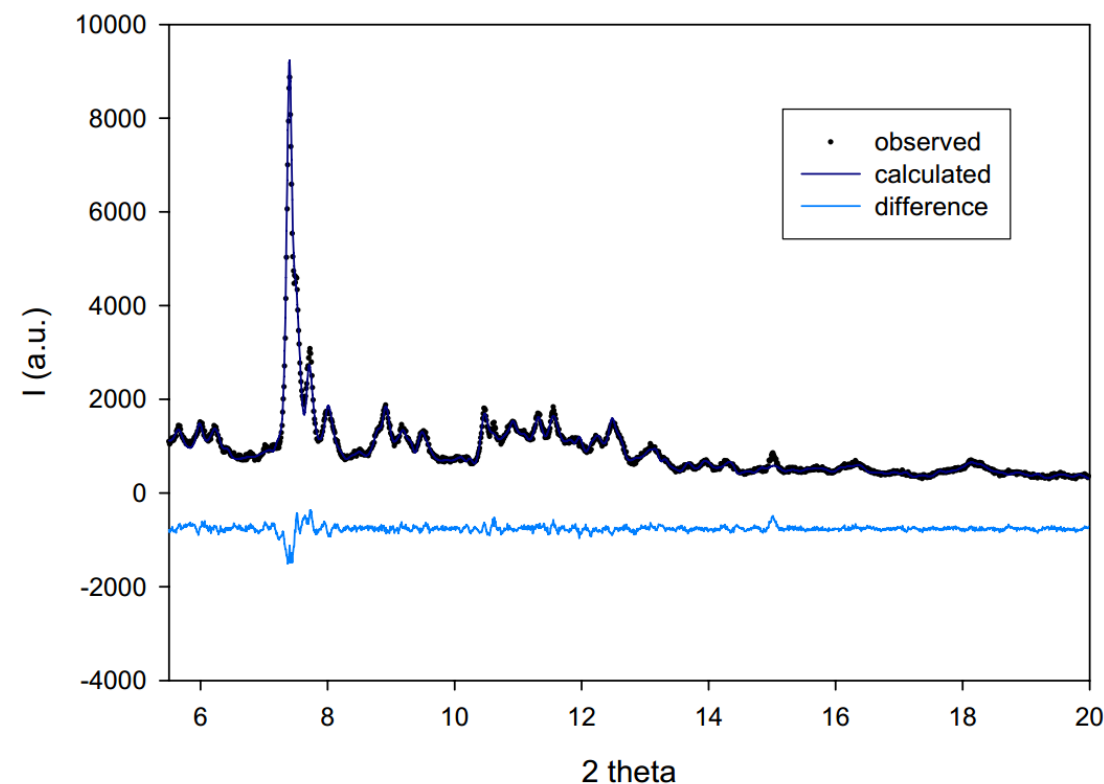
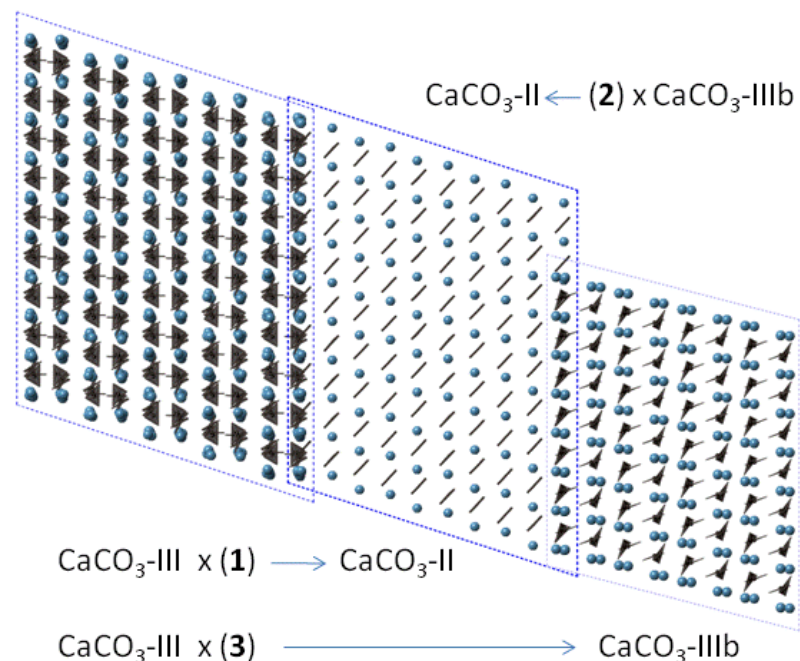
Data collected at ID09A beamline (ESRF – Grenoble, France), june 2015



Very complex X-ray powder pattern of CaCO₃-III, with large number of weak diffraction peaks



High resolution powder diffraction with multianvil press on CaCO_3
 The two determined structures can index «completely» the XRPD



Rietveld (not Le Bail) fit of “CaCO₃-III”
 Using both CaCO₃-III and CaCO₃-IIIb
 phase, resulting in apx 50 % (wt) each.
 -No extra peaks
 -Possible coexistence of these phases

Mineralogical Magazine, 2014, Vol. 78(2), pp. 225–233

Evidence of interspersed co-existing CaCO₃-III and
 CaCO₃-IIIb structures in polycrystalline CaCO₃ at high
 pressure

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² ESRF, European Synchrotron Radiation Facility, 6 rue Jules Horowitz, 38043 Grenoble cedex, France

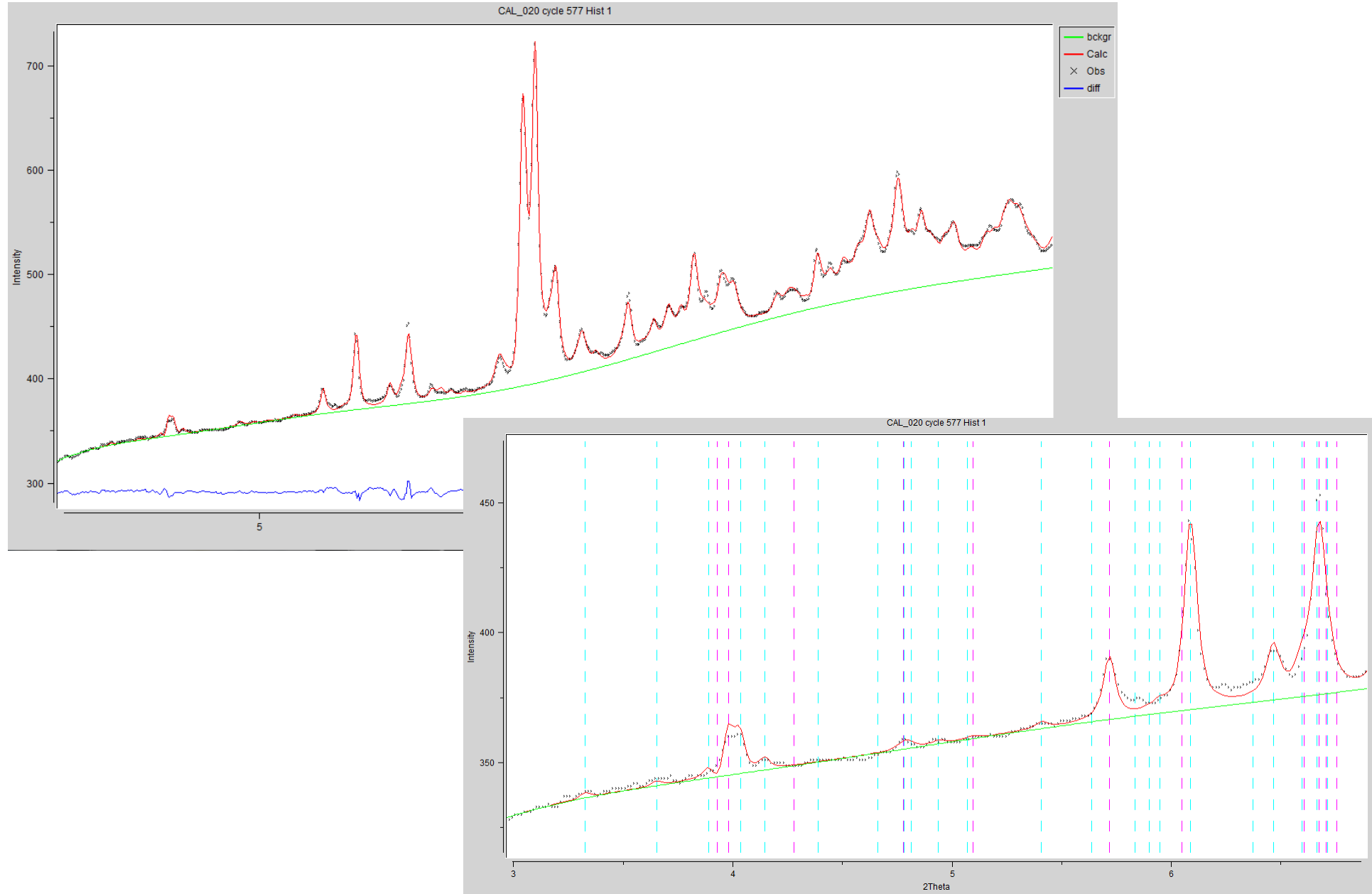
³ Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, UK

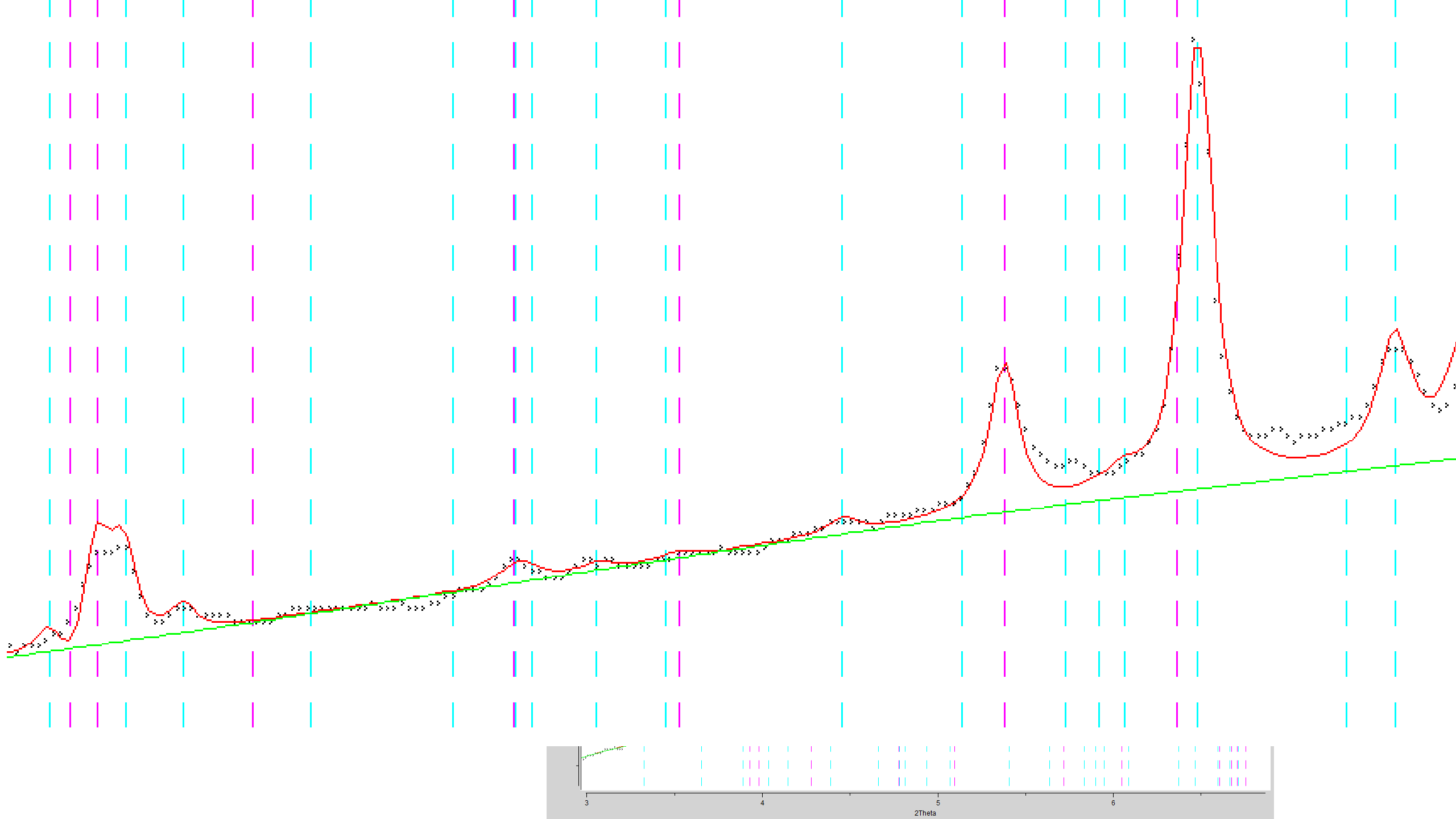
[Received 20 October 2013; Accepted 30 November 2013; Associate Editor: S.J. Mills]



Rietveld fit using CaCO₃-III and CaCO₃-IIIb simultaneously. Apx. 50% phase proportion

Almost impossible to determine ab-initio unit cell with powder data only





Single crystal diffraction after multiple phase transition at HP can be successfully applied for complex structure determination

American Mineralogist, Volume 100, pages 1821–1833, 2015

High-pressure phases of cordierite from single-crystal X-ray diffraction to 15 GPa

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²Hawaii Institute of Geophysics & Planetary Science, School of Ocean and Earth Science and Technology, University of Hawaii,
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³GSECARS, University of Chicago, Building 434A, 9700 South Cass Avenue, Argonne, Illinois 60439, U.S.A.

TABLE 2. Unit-cell parameters and volumes of cordierite phases

Run no.	Structure	Au a (Å)	P (GPa)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)
1 ^a	Cordierite	N/A	0	17.0508(6)	9.7129(3)	9.3357(3)	90	90	90	1546.11(9)
2	Cordierite	4.0678(6)	1.37(7)	17.055(5)	9.6916(5)	9.3100(5)	90	90	90	1538.8(5)
3 ^a	Cordierite II	4.02450(13)	7.52(3)	15.567(3)	9.6235(4)	9.0658(6)	89.963(5)	86.252(10)	90.974(8)	1355.0(2)
2	Cordierite II	4.0195(6)	8.30(10)	15.504(2)	9.589(3)	9.0414(5)	89.92(2)	86.153(6)	90.97(2)	1340.9(3)
2 ^a	Cordierite III (P1)	3.9797(8)	15.22(15)	8.5191(19)	8.2448(3)	9.1627(4)	85.672(4)	85.986(7)	70.839(10)	605.48(14)
2	Cordierite III (C1)	3.9797(8)	15.22(15)	13.6619(8)	9.718(2)	9.1627(4)	89.847(7)	84.883(5)	91.977(9)	1211.0(3)

^a Crystal structure refined at this pressure step.

TABLE 5. Atomic parameters of cordierite III at 15.22(15) GPa

Site	Coord. no.	x/a	y/b	z/c	Occ.	U _{eq}
Mg1A/	Mg1A, Mg1E/	5	0.610(4)	0.736(3)	0.7700(13)	0.959/
Fe1A	Fe1A, Fe1E	6	0.228(4)	0.387(2)	0.7359(12)	0.041
Mg1B/	Mg1B, Mg1F/	5	0.423(4)	0.200(3)	0.2260(13)	0.041
Fe1B	Fe1B, Fe1F	6	0.791(4)	0.552(2)	0.2637(13)	0.959/
Mg1C/	Mg1C, Mg1G/	5	0.093(4)	0.000(3)	0.0000(13)	0.041
Fe1C	Fe1C, Fe1G	6	0.907(4)	0.999(3)	0.9999(13)	0.959/
Mg1D/	Mg1D, Mg1H/	5	0.093(4)	0.000(3)	0.0000(13)	0.041
Fe1D	Fe1D, Fe1H	6	0.907(4)	0.999(3)	0.9999(13)	0.959/
Al1A	Al1A, Al1E	5	0.093(4)	0.000(3)	0.0000(13)	0.041
Al1B	Al1B, Al1F	6	0.907(4)	0.999(3)	0.9999(13)	0.959/
Al1C	Al1C, Al1G	5	0.093(4)	0.000(3)	0.0000(13)	0.041
Al1D	Al1D, Al1H	6	0.907(4)	0.999(3)	0.9999(13)	0.959/
Al2A	Al2A, Al2E	4	0.325(3)	0.5725(14)	0.9274(9)	1
Al2B	Al2B, Al2F	4	0.131(3)	0.303(14)	0.0725(9)	1
Al2C	Al2C, Al2G	4	0.393(4)	0.6644(18)	0.5720(10)	1
Al2D	Al2D, Al2H	4	0.426(4)	0.7254(17)	0.4309(11)	1
Si1A	Si1A, Si1C	6	0.025(4)	0.3338(17)	0.7336(11)	0.0111(8)
Si1B	Si1B, Si1D	6	0.401(4)	0.5812(18)	0.2514(11)	0.0111(8)
Si2A	Si2A, Si2E	4	0.040(2)	0.7359(11)	0.9390(7)	1
Si2B	Si2B, Si2F	4	0.085(19)	0.2252(11)	0.0718(7)	1
Si2C	Si2C, Si2G	4	0.265(4)	0.0490(18)	0.5453(12)	1
Si2D	Si2D, Si2H	4	0.756(4)	0.8894(18)	0.4550(12)	1
Si3A	Si3A, Si3E	5	0.042(4)	0.0447(19)	0.9915(11)	0.0116(5)
Si3B	Si3B, Si3F	5	0.383(4)	0.8976(18)	0.0136(10)	0.0116(5)
Si3C	Si3C, Si3G	5	0.934(4)	0.3394(17)	0.5116(10)	0.0116(5)
Si3D	Si3D, Si3H	5	0.074(4)	0.0118(17)	0.4898(10)	0.0116(5)
Ch1A*	N/A	0.993(3)	0.898(14)	0.759(9)	0.78	0.16(3)
Ch1B*	Ch1B, Ch1D	1	0.123	0.940(15)	0.219(9)	0.78
O1A	O1A, O1I	5	0.564(8)	0.570(3)	0.659(9)	0.0078(2)
O1B	O1B, O1J	5	0.427(7)	0.402(4)	0.839(3)	1
O1C	O1C, O1K	5	0.555(8)	0.271(4)	0.596(3)	1
O1D	O1D, O1L	5	0.722(8)	0.416(4)	0.905(3)	1
O1E	O1E, O1M	5	0.630(9)	0.520(4)	0.155(2)	0.0078(2)
O1F	O1F, O1N	5	0.307(7)	0.509(4)	0.310(3)	0.0078(2)
O1G	O1G, O1O	5	0.467(8)	0.363(3)	0.338(3)	0.0078(2)
O1H	O1H, O1P	5	0.445(8)	0.687(4)	0.403(3)	1
O2A	O2A, O2E	4	0.113(7)	0.851(4)	0.627(3)	1
O2B	O2B, O2F	4	0.141(5)	0.642(3)	0.8608(16)	1
O2C	O2C, O2G	4	0.892(5)	0.254(3)	0.1289(16)	1
O2D	O2D, O2H	4	0.706(8)	0.078(4)	0.313(3)	1
O3A	O3A, O3I	5	0.585(9)	0.140(3)	0.830(3)	1
O3B	O3B, O3J	5	0.824(8)	0.232(3)	0.687(3)	1
O3C	O3C, O3K	5	0.018(8)	0.462(3)	0.631(3)	1
O3D	O3D, O3L	5	0.516(7)	0.945(4)	0.883(3)	1
O3E	O3E, O3M	5	0.509(8)	0.880(4)	0.124(3)	1
O3F	O3F, O3N	5	0.571(9)	0.804(5)	0.173(3)	0.0101(8)
O3G	O3G, O3O	5	0.007(8)	0.467(4)	0.372(3)	1
O3H	O3H, O3P	5	0.174(8)	0.623(5)	0.315(3)	0.0101(8)
O4A	O4A, O4I	5	0.838(9)	0.644(4)	0.8314(17)	1
O4B	O4B, O4J	5	0.056(7)	0.337(4)	0.889(3)	1
O4C	O4C, O4K	5	0.305(7)	0.168(4)	0.6567(19)	0.0089(8)
O4D	O4D, O4L	5	0.327(8)	0.903(3)	0.065(3)	0.0089(8)
O4E	O4E, O4M	5	0.187(6)	0.289(4)	0.1855(18)	0.0089(8)
O4F	O4F, O4N	5	0.060(7)	0.588(4)	0.112(3)	0.0089(8)
O4G	O4G, O4O	5	0.389(8)	0.036(5)	0.339(3)	0.0089(8)
O4H	O4H, O4P	5	0.690(7)	0.792(4)	0.333(2)	0.0089(8)
O5A	O5A, O5E	4	0.214(7)	0.037(4)	0.981(3)	1
O5B	O5B, O5F	4	0.836(7)	0.016(4)	0.015(2)	0.0167(14)
O5C	O5C, O5G	4	0.096(9)	0.127(5)	0.500(3)	1
O5D	O5D, O5H	4	0.948(9)	0.809(5)	0.498(3)	0.0167(14)
O5A	O5A, O5E	4	0.252(7)	0.573(4)	0.587(3)	1
O5B	O5B, O5F	4	0.409(7)	0.717(4)	0.912(3)	0.0094(11)
O5C	O5C, O5G	4	0.598(7)	0.222(4)	0.081(3)	0.0094(11)
O5D	O5D, O5H	4	0.736(7)	0.391(4)	0.415(3)	0.0094(11)

Note: All atoms are in Wyckoff position 1a.

* Refined as oxygen.

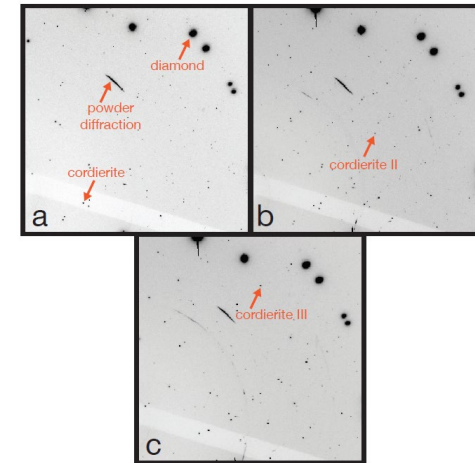


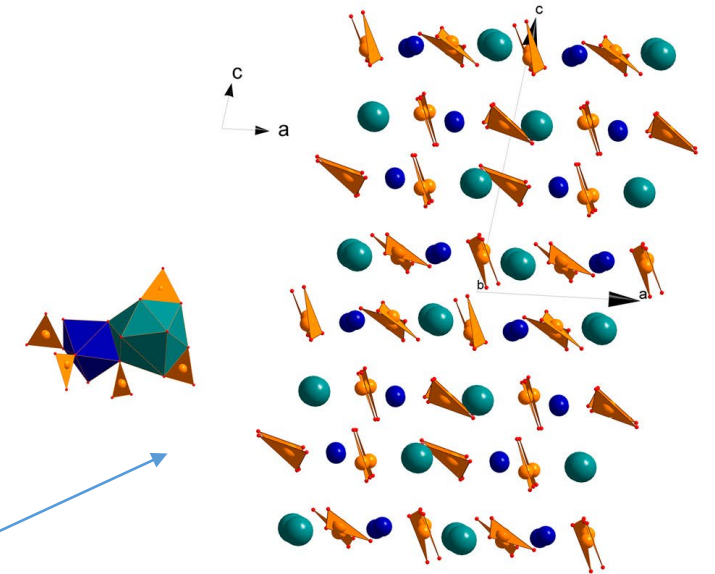
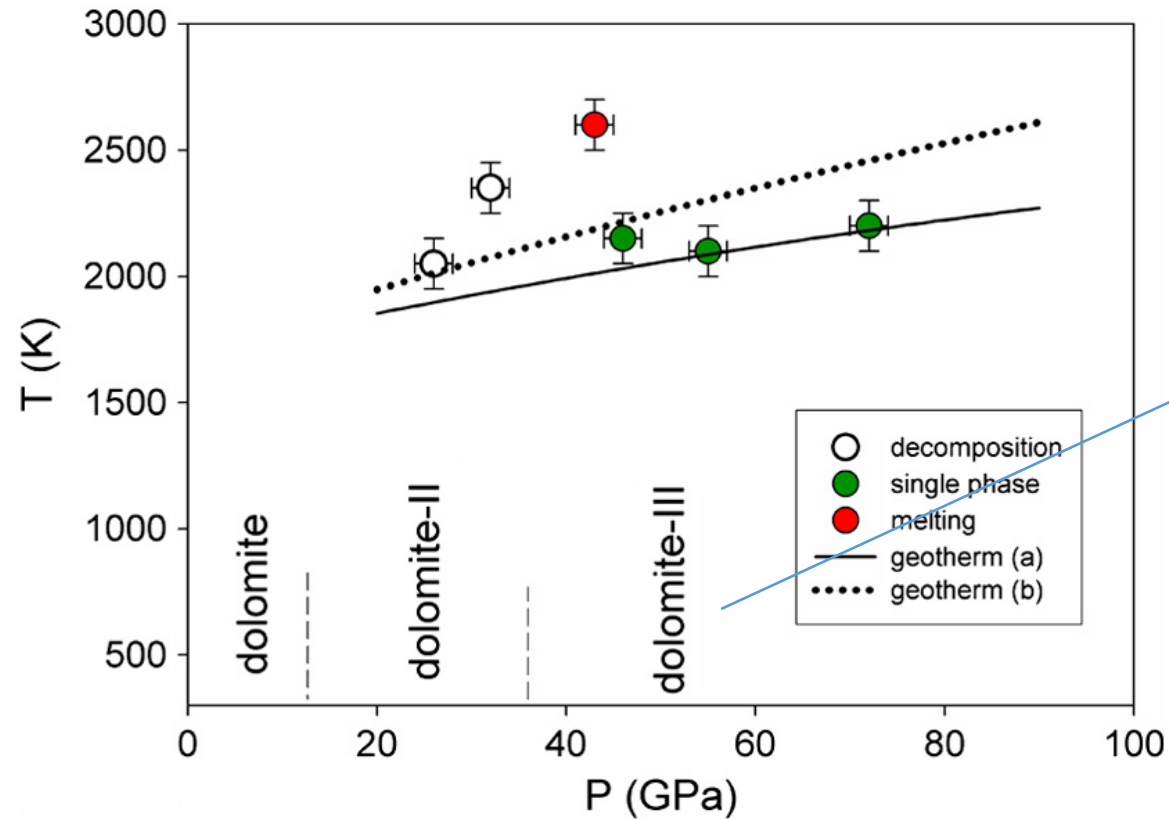
TABLE 4. Atomic parameters of cordierite II at 7.52(3) GPa

Site	Coord. no.	x/a	y/b	z/c	Occ.	U _{eq}
Mg1A/	6	0.7102(16)	0.1491(14)	0.815(3)	0.959/	0.0081(6)
Fe1A	6	0.8481(12)	0.6506(12)	0.8172(17)	0.041	0.0081(6)
Mg1B/	6	0.8555(17)	0.5431(16)	0.319(3)	0.959/	0.0081(6)
Fe1B	6	0.6862(15)	0.0348(15)	0.338(3)	0.041	0.0081(6)
Mg1C/	6	0.8555(17)	0.5431(16)	0.319(3)	0.959/	0.0081(6)
Fe1C	6	0.6862(15)	0.0348(15)	0.338(3)	0.041	0.0081(6)
Mg1D/	6	0.8555(17)	0.5431(16)	0.319(3)	0.959/	0.0081(6)
Fe1D	6	0.6862(15)	0.0348(15)	0.338(3)	0.041	0.0081(6)
Mg1E/	6	0.1850(16)	0.5277(16)	0.855(3)	0.959/	0.0081(6)
Fe1E	6	0.3675(15)	0.0403(16)	0.818(3)	0.041	0.0081(6)
Mg1F/	6	0.3309(16)	0.9345(13)	0.368(3)	0.959/	0.0081(6)
Fe1F	6	0.3309(16)	0.9345(13)	0.368(3)	0.041	0.0081(6)
Mg1G/	6	0.3309(16)	0.9345(13)	0.368(3)	0.959/	0.0081(6)
Fe1G	6	0.3309(16)	0.9345(13)	0.368(3)	0.041	0.0081(6)
Mg1H/	6	0.2149(12)	0.4316(12)	0.3193(17)	0.959/	0.0081(6)
Fe1H	6	0.2149(12)	0.4316(12)	0.3193(17)	0.041	0.0081(6)
Al1A	4	0.790(15)	0.8273(15)	0.844(3)	1	0.0055(6)
Al1B	5	0.8504(14)	0.3196(11)	0.806(3)	1	0.0055(6)
Al1C	4	0.7776(12)	0.2792(11)	0.3365(18)	1	0.0055(6)
Al1D	4	0.7629(15)	0.7862(14)	0.333(3)	1	0.0055(6)
Al1E	4	0.2752(14)	0.2908(14)	0.845(3)	1	0.0055(6)
Al1F	4	0.2707(12)	0.7842(11)	0.8460(19)	1	0.0055(6)
Al1G	5	0.1920(14)	0.7426(11)	0.364(3)	1	0.0055(6)
Al1H	4	0.3318(15)	0.2476(15)	0.336(3)	1	0.0055(6)
Al1I	4	0.5029(14)	0.2187(13)	0.015(3)	1	0.0016(5)
Al1J	4	0.5462(14)	0.8602(13)	0.157(3)	1	0.0016(5)
Al1K	4	0.5918(14)	0.2267(14)	0.621(3)	1	0.0016(5)
Al1L	4	0.4517(14)	0.8516(14)	0.556(3)	1	0.0016(5)
Al1M	4	0.9475(12)	0.7212(13)	0.0447(19)	1	0.0016(5)
Al1N	4	0.0862(12)	0.3566(13)	0.1432(19)	1	0.0016(5)
Al1O	4	0.0550(15)	0.7023(14)	0.649(3)	1	0.0016(5)
Al1P	4	0.9882(15)	0.3702(14)	0.521(3)	1	0.0016(5)
Al1Q	5	0.5417(16)	0.9637(15)	0.821(3)	1	0.0114(8)
Al1R	5	0.0394(14)	0.6154(14)	0.318(3)	1	0.0114(8)
Al1S	5	0.0098(14)	0.4544(14)	0.856(3)	1	0.0114(8)
Al1T	5	0.5069(16)	0.1128(15)	0.345(3)	1	0.0114(8)
Al1U	4	0.3801(12)	0.4533(12)	0.0616(18)	1	0.0093(6)
Al1V	4	0.6755(12)	0.6263(12)	0.1169(18)	1	0.0093(6)
Al1W	4	0.7308(16)	0.4575(15)	0.608(3)	1	0.0093(6)
Al1X	4	0.3185(16)	0.6196(15)	0.554(3)	1	0.0093(6)
Al1Y	4	0.8293(11)	0.9672(11)	0.0394(18)	1	0.0093(6)
Al1Z	4	0.2344(11)	0.1161(11)	0.1068(18)	1	0.0093(6)
Al1AA	4	0.1804(15)	0.9504(14)	0.629(3)	1	0.0093(6)
Al1AB	4	0.8672(15)	0.1294(14)	0.538(3)	1	0.0093(6)
Al1AC	4	0.3594(16)	0.7758(14)	0.114(3)	1	0.0103(6)
Al1AD	4	0.6804(15)	0.2994(14)	0.070(3)	1	0.0103(6)
Al1AE	4	0.6308(16)	0.7460(14)	0.571(3)	1	0.0103(6)
Al1AF	4	0.4194(16)	0.3358(14)	0.590(3)	1	0.0103(6)
Al1AG	4	0.9143(15)	0.2611(14)	0.104(3)	1	0.0103(6)
Al1AH	4	0.1289(15)	0.8211(14)	0.069(3)	1	0.0103(6)
Al1AI	4	0.1738(15)	0.2618(13)	0.580(3)	1	0.0103(6)
Al1AJ	4	0.8797(14)	0.8206(13)	0.578(3)	1	0.0103(6)
Al1AK	N/A	0.524(9)	0.594(9)	0.757(14)	0.78	0.156(16)
Al1AL	N/A	0.454(9)	0.518(9)	0.264(13)	0.78	0.156(16)
Al1AM	N/A	0.980(9)	0.033(10)	0.773(15)	0.78	0.156(16)
Al1AN	N/A	0.011(9)	0.965(9)	0.227(14)	0.78	0.156(16)
Al1AO	N/A	0.599(3)	0.083(3)	0.723(5)	1	0.0065(10)
Al1AP	N/A	0.932(3)	0.586(3)	0.946(4)	1	0.0065(10)
Al1AQ	N/A	0.950(3)	0.384(3)	0.696(5)	1	0.0065(10)
Al1AR	N/A	0.561(3)	0.890(3)	0.988(5)	1	0.0065(10)
Al1AS	N/A	0.578(3)	0.981(3)	0.270(5)	1	0.0065(10)
Al1AT	N/A	0.471(3)	0.180(3)	0.179(5)	1	0.0065(10)
Al1AU	N/A	0.962(3)	0.501(3)	0.435(4)	1	0.0065(10)
Al1AV	N/A	0.078(3)	0.689(3)	0.477(5)	1	0.0065(10)
Al1AW	N/A	0.079(3)	0.568(3)	0.755(4)	1	0.0065(10)

TABLE 4.—CONTINUED

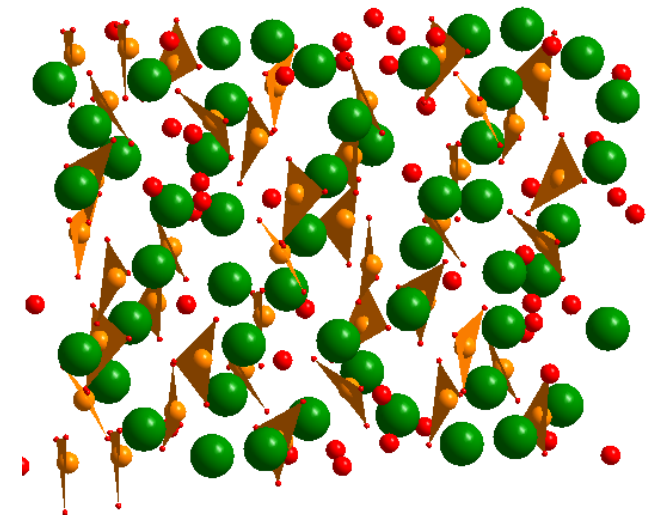
Site	Coord. no.	x/a	y/b	z/c	Occ.	U _{eq}
O1J	6	0.471(3)	0.097(3)	0.914(5)	1	0.0065(10)
O1K	6	0.450(3)	0.898(3)	0.716(5)	1	0.0065(10)
O1L	6	0.087(3)	0.414(3)	0.966(5)	1	0.0065(10)
O1M	6	0.100(3)	0.486(3)	0.254(4)	1	0.0065(10)
O1N	6	0.948(3)	0.652(3)	0.198(5)	1	0.0065(10)

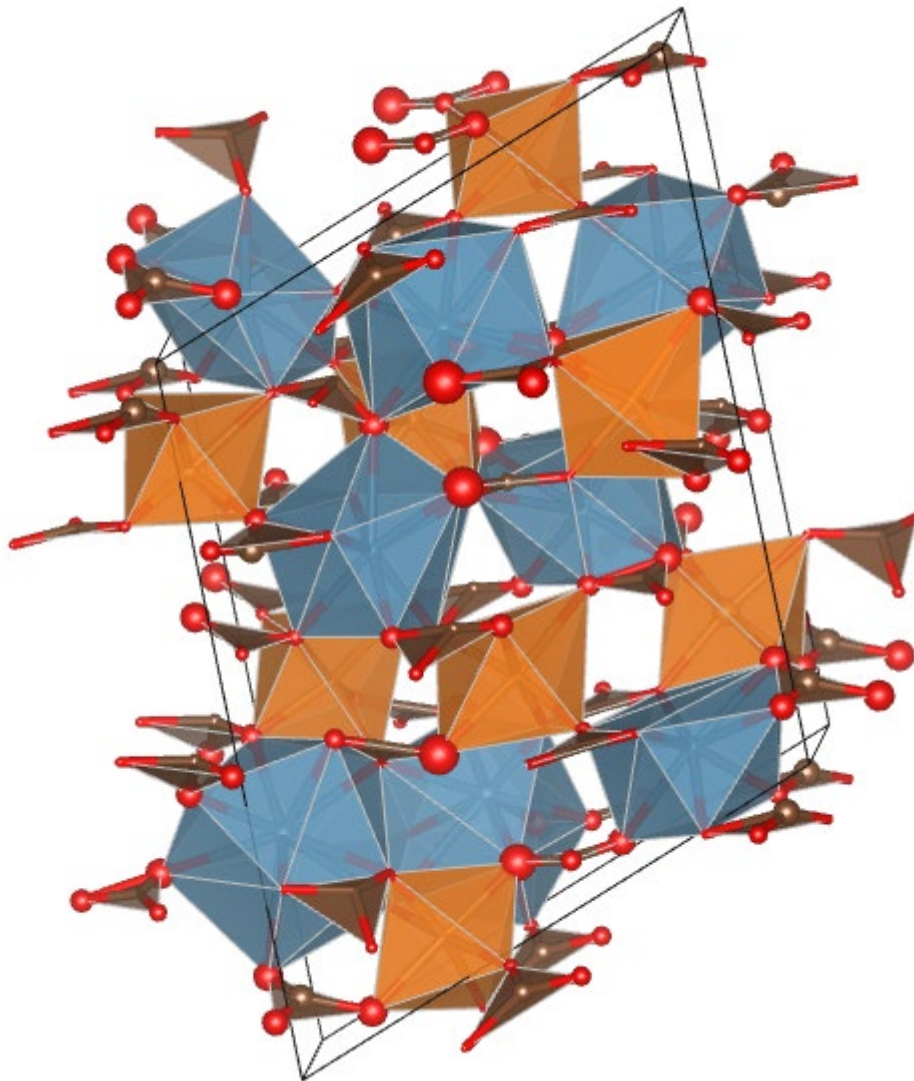
Study of the structural evolution of dolomite $\text{Ca}(\text{Mg,Fe})(\text{CO}_3)_2$ at extreme pressures



Merlini et al., PNAS, 2012

The compression of dolomite transform the structure into a denser structure with tilted carbonate groups and the possibility to create complex superstructures, with large unit cell parameters – similar to CaCO_3 -III





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Lattice type      P
Space group name  P 1
Space group number 1
Setting number    1

Lattice parameters

      a      b      c      alpha      beta      gamma
4.46270 11.23900 13.70600 111.1000  91.4400  89.6400

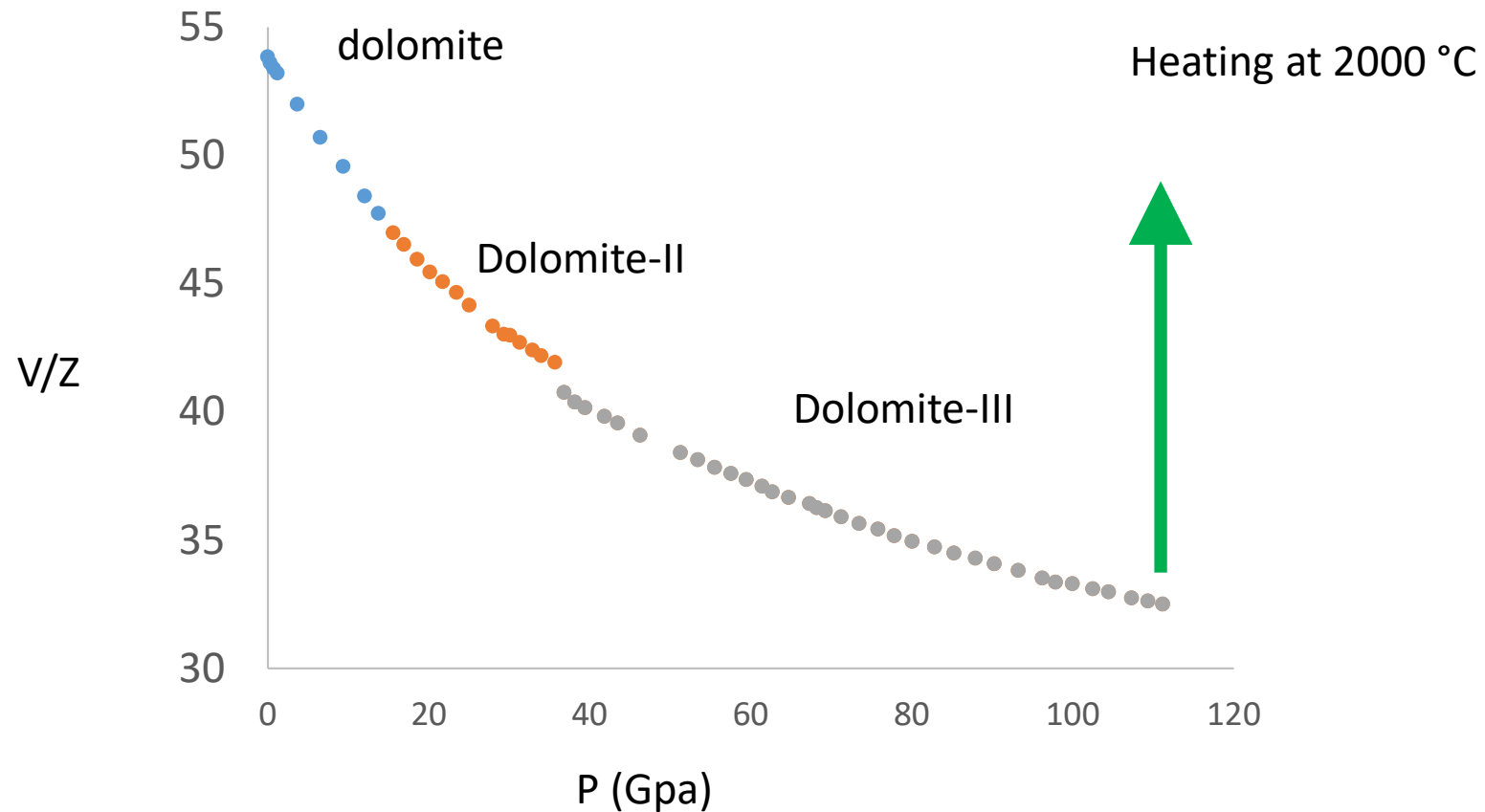
Unit-cell volume = 641.146150 Å3

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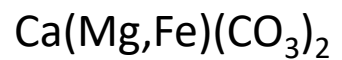
Dolomite $\text{CaMg}(\text{CO}_3)_2$ at 1 Mbar

P1, 80 atoms in the unit cell

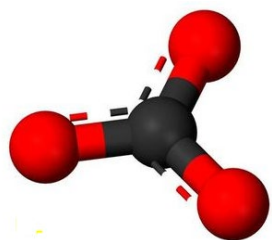
At Mbar pressures, change in crystal chemistry. sp^2 to sp^3 hybridization of carbon in C-O bonds and formation of tetrahedral groups



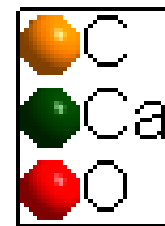
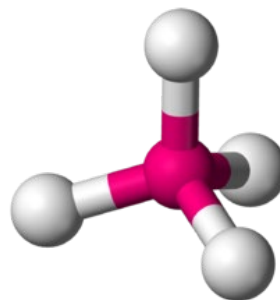
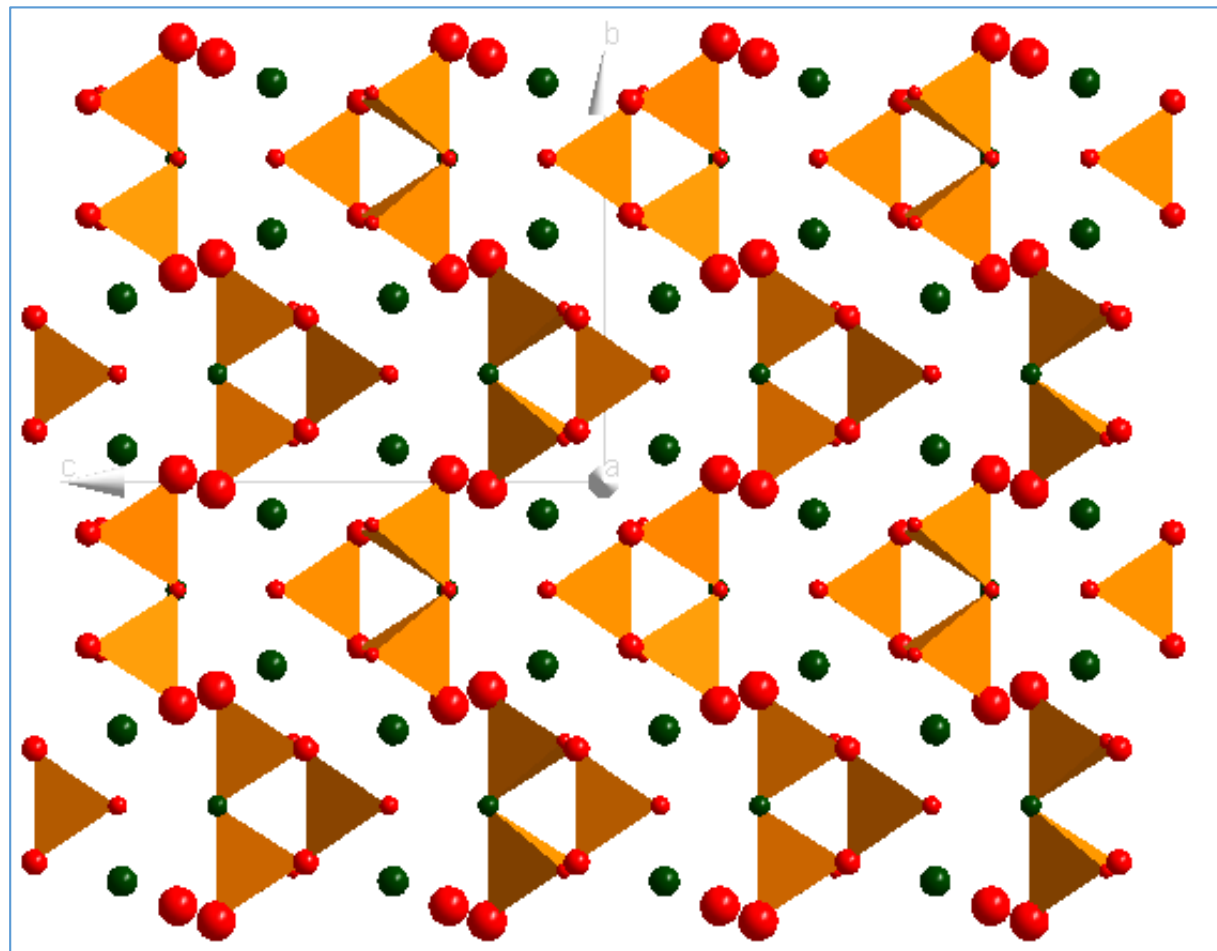
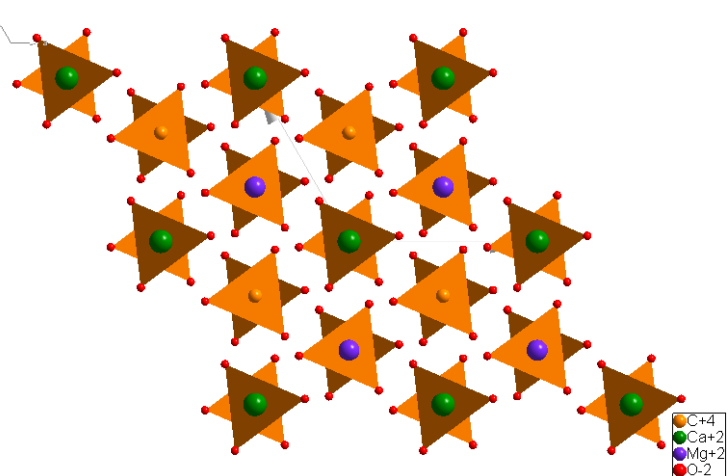
Dolomite at core/mantle boundary, 115 GPa after heating at mantle temperatures



New unpredicted structures
with ring-carbonate
tetrahedral groups

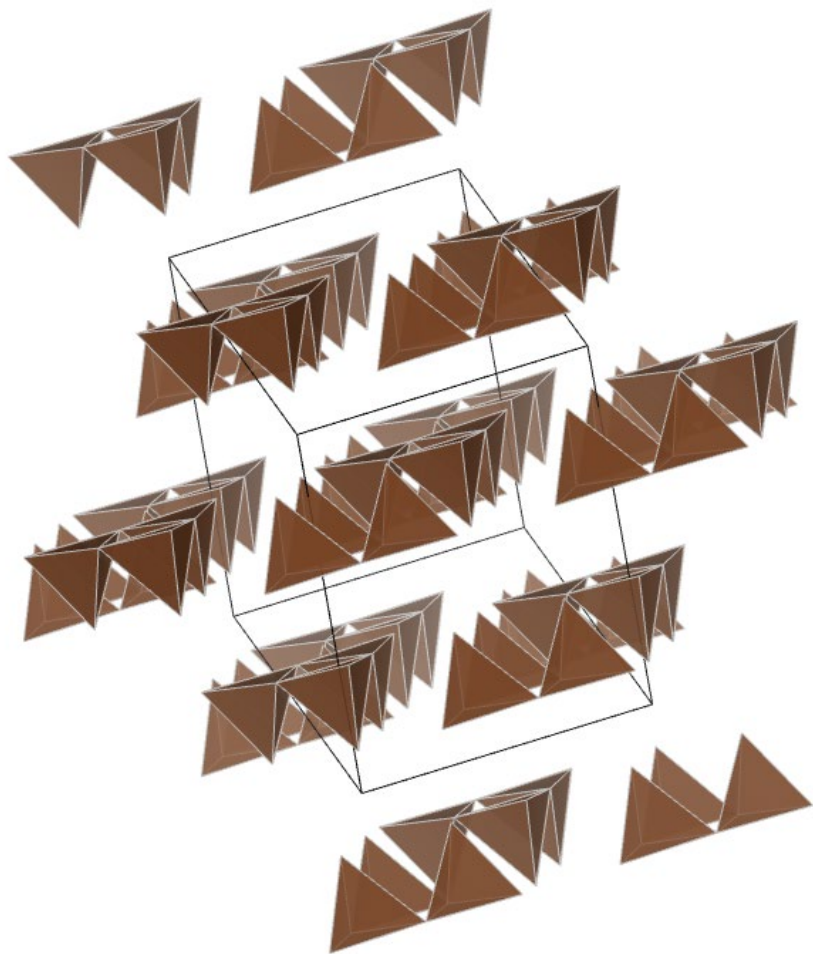


Dolomite ambient pressure

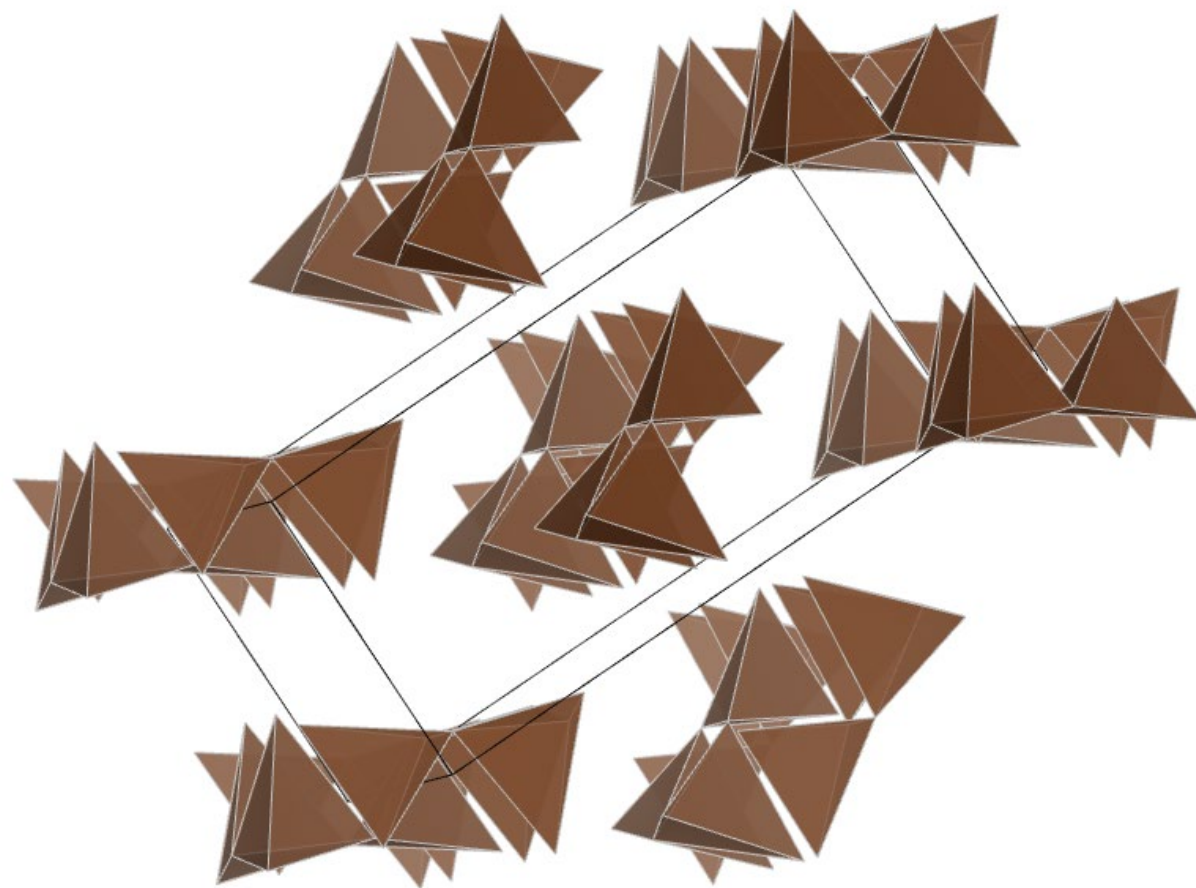


Merlini et al., 2017

Fe-magnesite-II (Chariton et al., 2020)

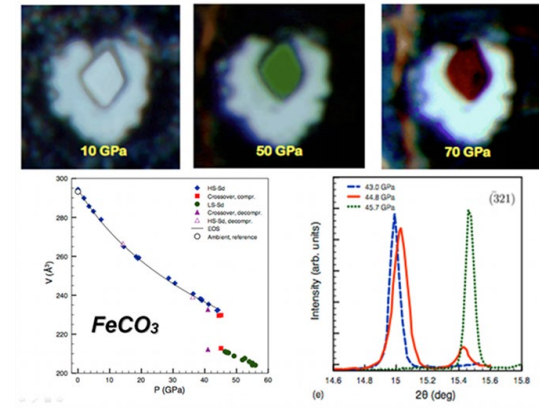


Dolomite-IV (Merlini et al., 2017)

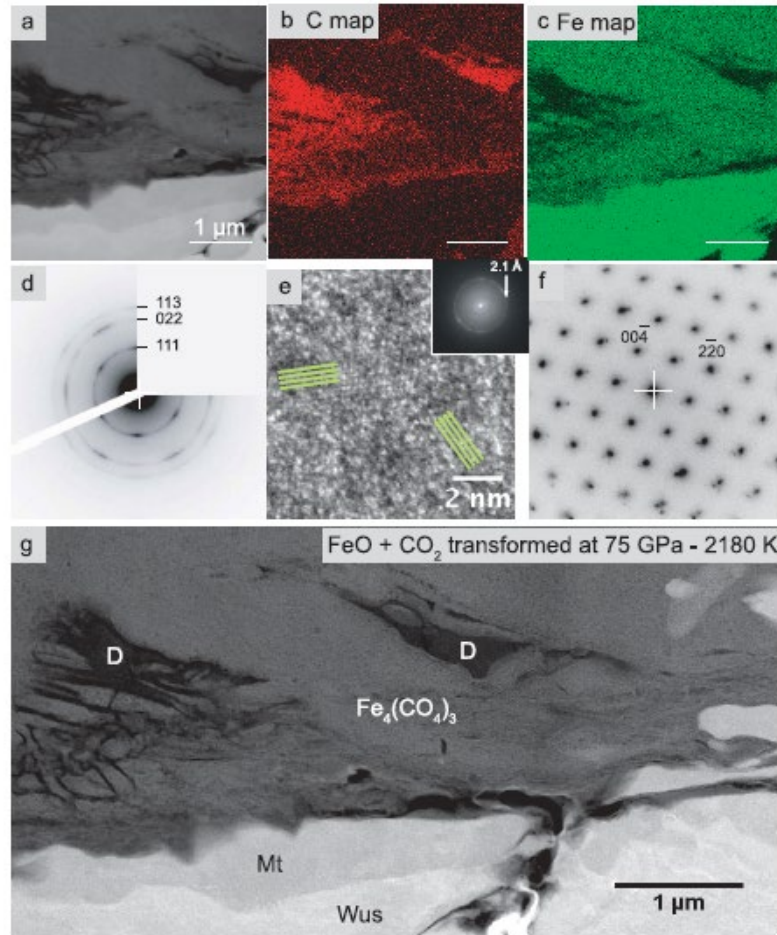


FeCO₃ siderite

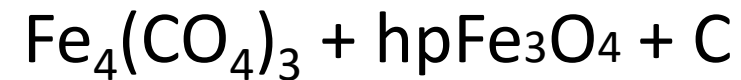
HP - low T: isosymmetric transition (high-low spin Fe)



Lavina et al., 2010

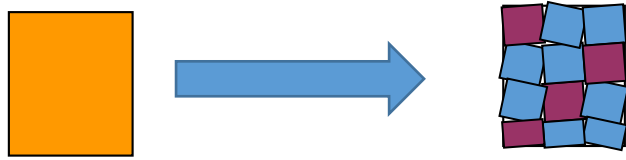


HP - high T: red-ox reactions; new Fe³⁺ carbonates

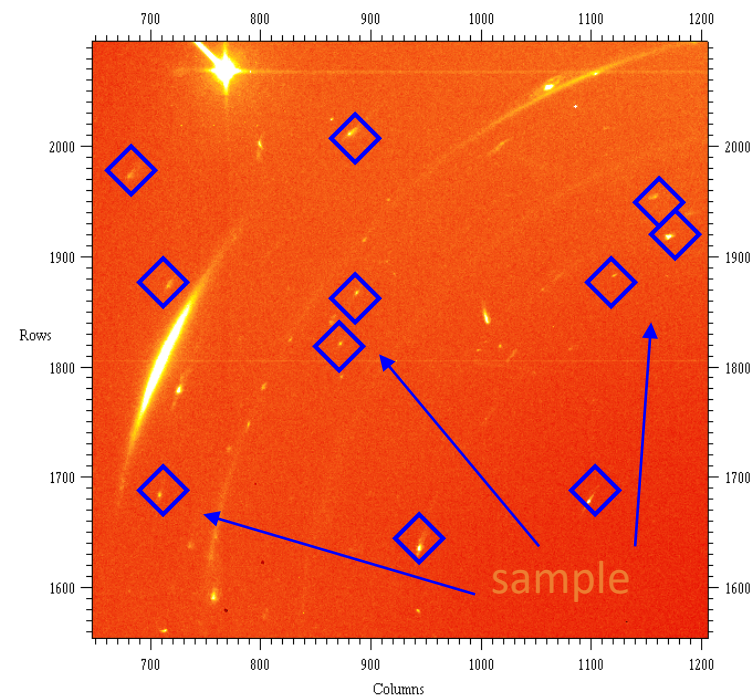
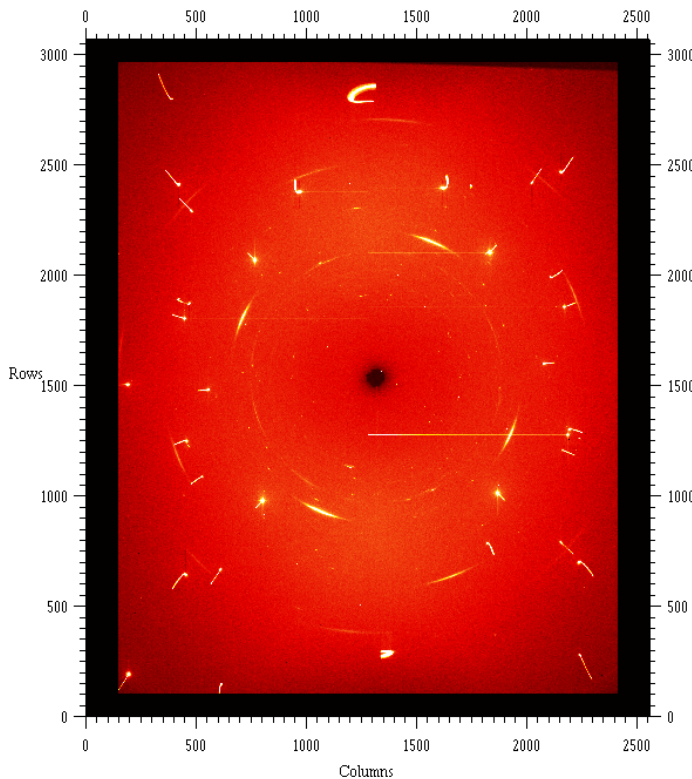


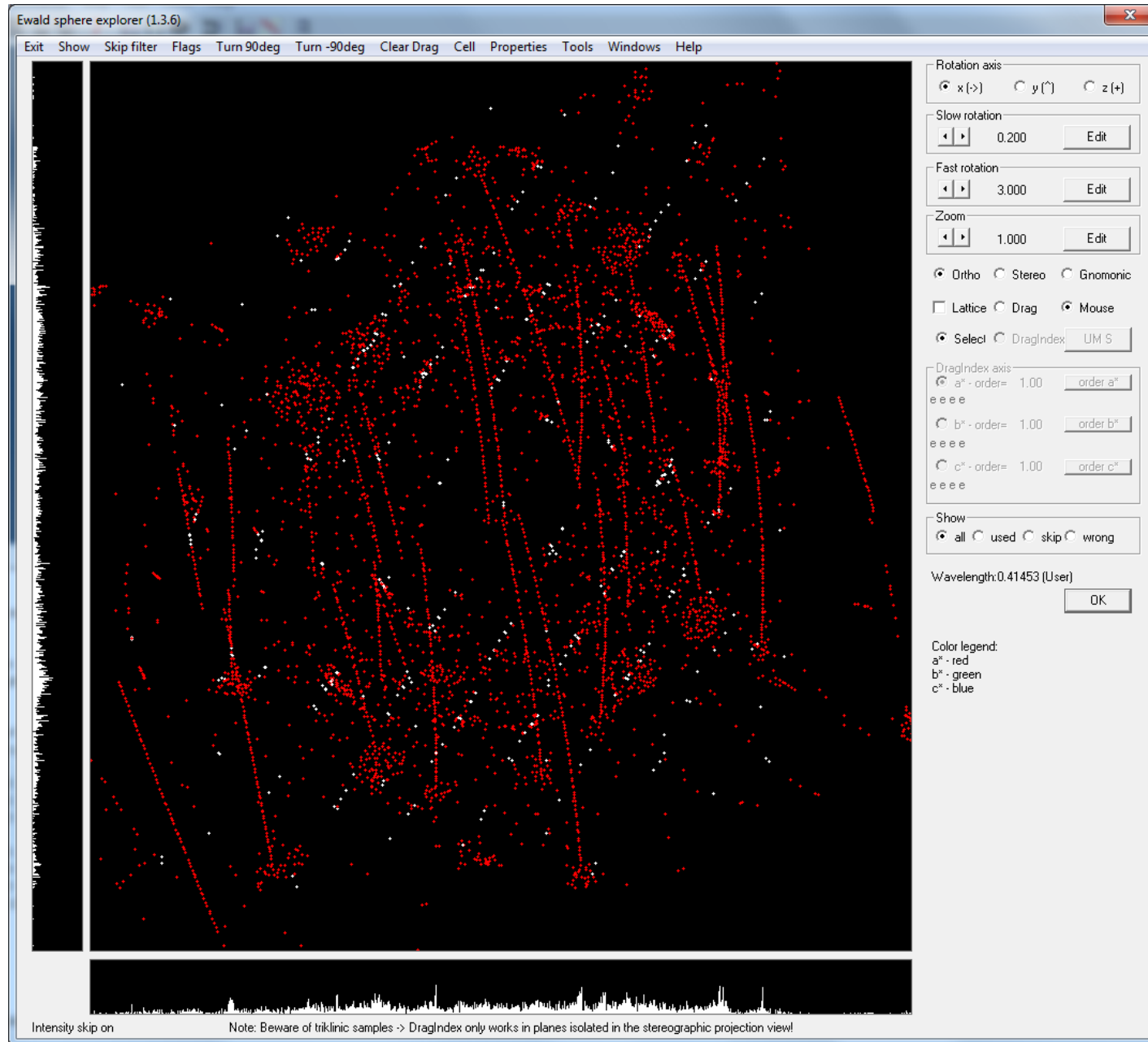
Boulard et al., JGR 2012

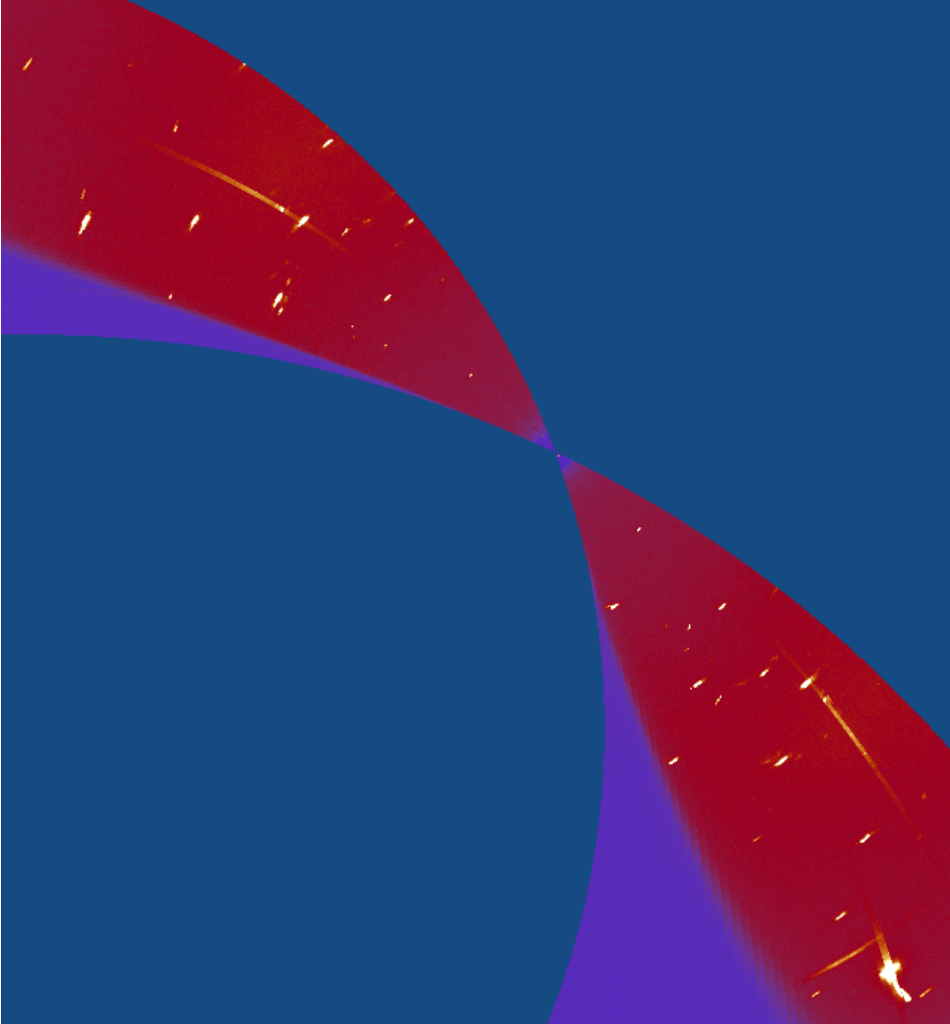
Stabilization of $(\text{Mg,Fe})\text{CO}_3$ at mantle pressures and temperatures: 130 GPa annealing at 2700 K



Chemical reaction with formation of multidomain sample;
Single crystal data for the larger domains







Unit cell dimensions

$$a = 9.822(3) \text{ \AA}$$

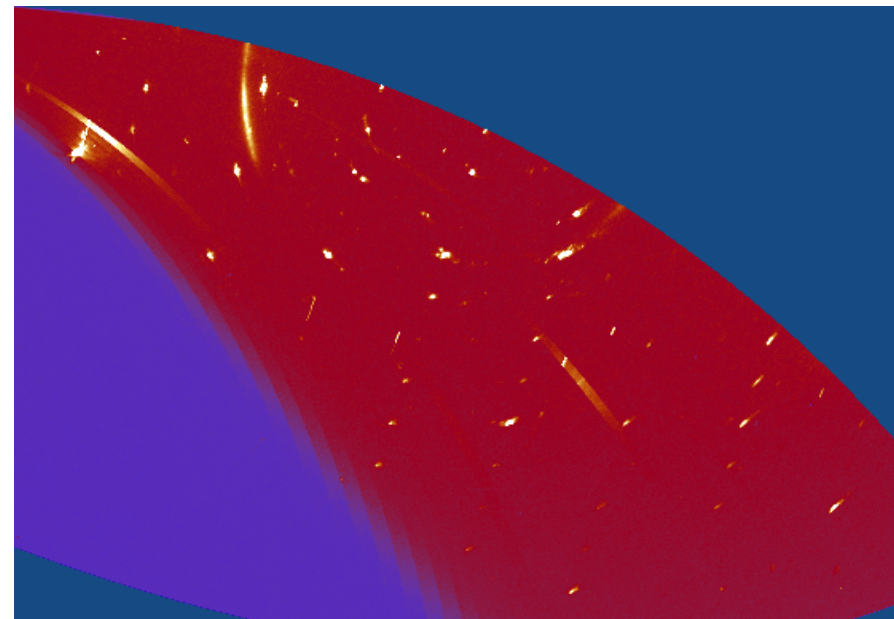
$$b = 3.9023(13) \text{ \AA}$$

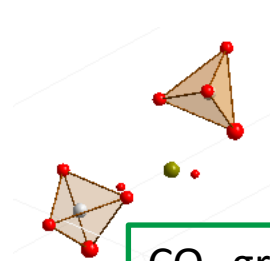
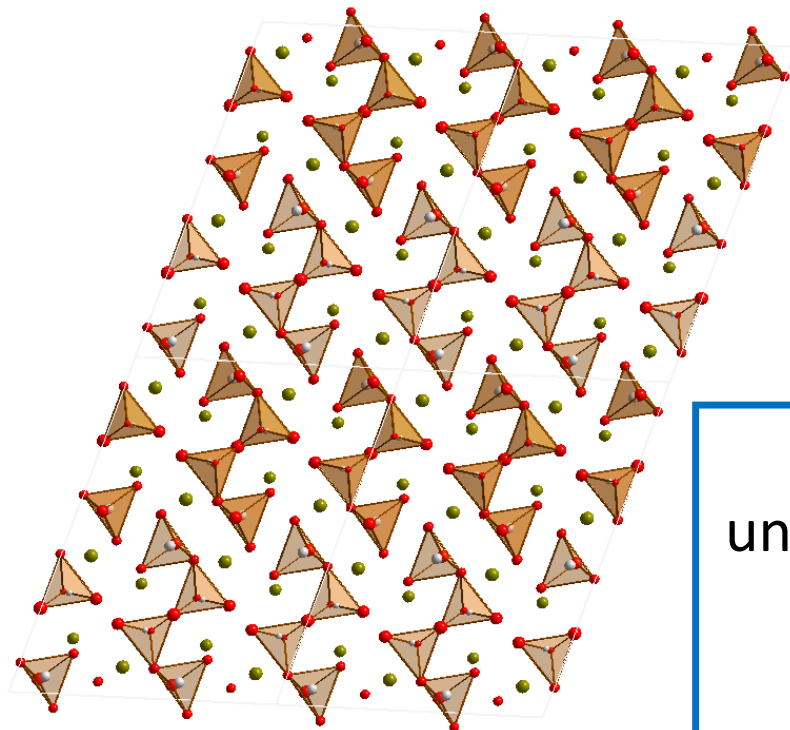
$$c = 13.154(5) \text{ \AA}$$

$$\text{beta} = 108.02(3)^\circ$$

Cell volume $479.44(30) \text{ \AA}^3$

Then..... Structure solution!

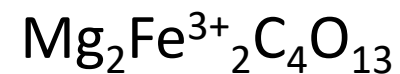




P= 130 GPa

CO₄ groups – truncated tetrahedral chains

Carbonate with new chemical formula,
unknown at low pressure, with trivalent iron



C 1 2/c 1 (no. 15)

Unit cell dimensions $a = 9.822(3) \text{ \AA}$

$b = 3.9023(13) \text{ \AA}$

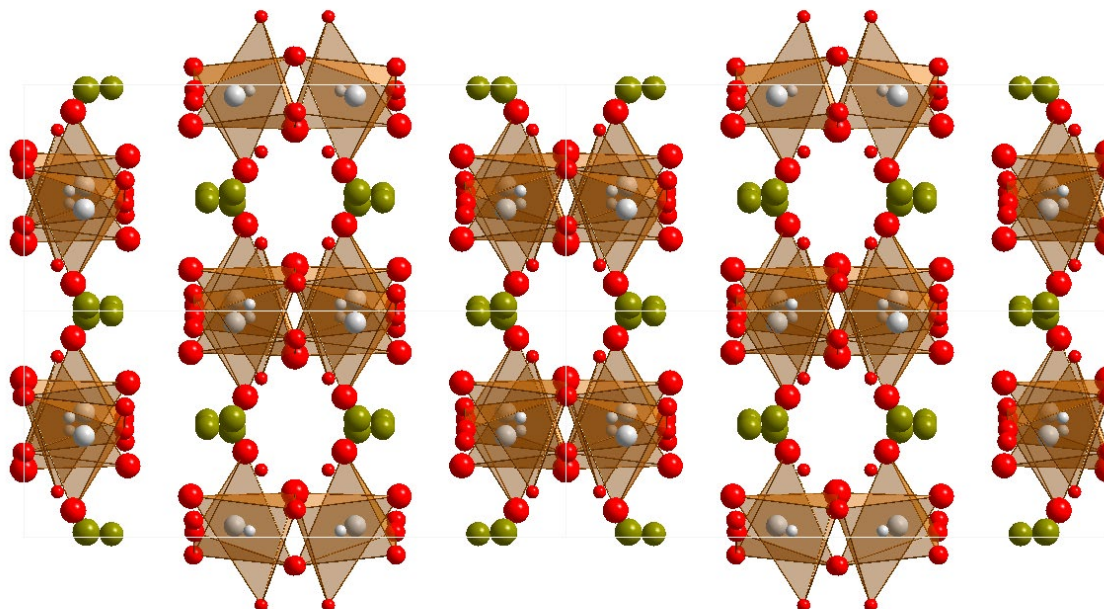
$c = 13.154(5) \text{ \AA}$

$\beta = 108.02(3)^\circ$

Cell volume $479.44(30) \text{ \AA}^3$

Z=8

Atoms in the unit cell: 168



Crystal data

Formula sum $\text{C}_4\text{Fe}_2\text{Mg}_2\text{O}_{13}$
Crystal system monoclinic
Space group $C 1 2/c 1$ (no. 15)
Unit cell dimensions $a = 9.822(3) \text{ \AA}$
 $b = 3.9023(13) \text{ \AA}$
 $c = 13.154(5) \text{ \AA}$
 $\beta = 108.02(3)^\circ$
Cell volume $479.44(30) \text{ \AA}^3$
Z 16
Pearson code mC84
Formula type N4O4P13
Wyckoff sequence $f^{10}e$

Fe1	O7	1.746
	O3	1.802
	O6	1.886
	O5	1.907
	O4	1.922
Fe2	O7	1.950
	O1	2.076
	O6	1.831
	O1	1.928
	O3	1.962
	O5	1.984
	O2	1.985
	O7	2.024
	O1	2.046
	O5	2.056
	O3	2.257

Atomic coordinates and isotropic displacement parameters (in $\text{\AA}^2$)

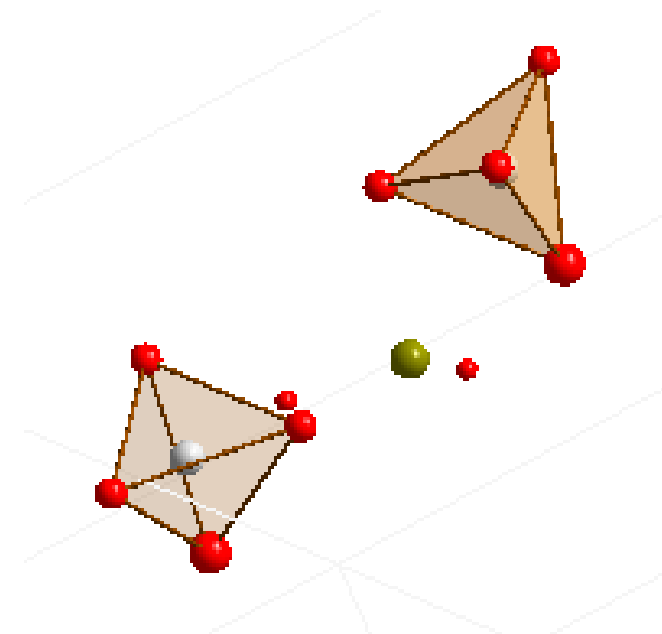
Atom	Wyck.	Occ.	x	y	z	U
Mg1	8f	0.299	0.88478	-0.02538	0.41144	0.0217
Mg2	8f	0.261	0.66154	-0.48586	0.33561	0.0173
O1	8f		0.80537	0.30718	0.28354	0.0159
O2	4e		1/2	-0.19830	1/4	0.0185
O3	8f		0.93831	0.80183	0.30257	0.0064
O4	8f		1.00092	-0.37512	0.58752	0.0073
O5	8f		0.81759	-0.52368	0.62268	0.0106
O6	8f		0.81245	-0.42400	0.45742	0.0089
O7	8f		0.91026	-0.87915	0.54143	0.0181
C1	8f		0.88391	-0.55002	0.54753	0.0064
C2	8f		1.08276	-0.46856	0.69702	0.0068
Fe1	8f	0.701	0.88478	-0.02538	0.41144	0.0217
Fe2	8f	0.739	0.66154	-0.48586	0.33561	0.0173

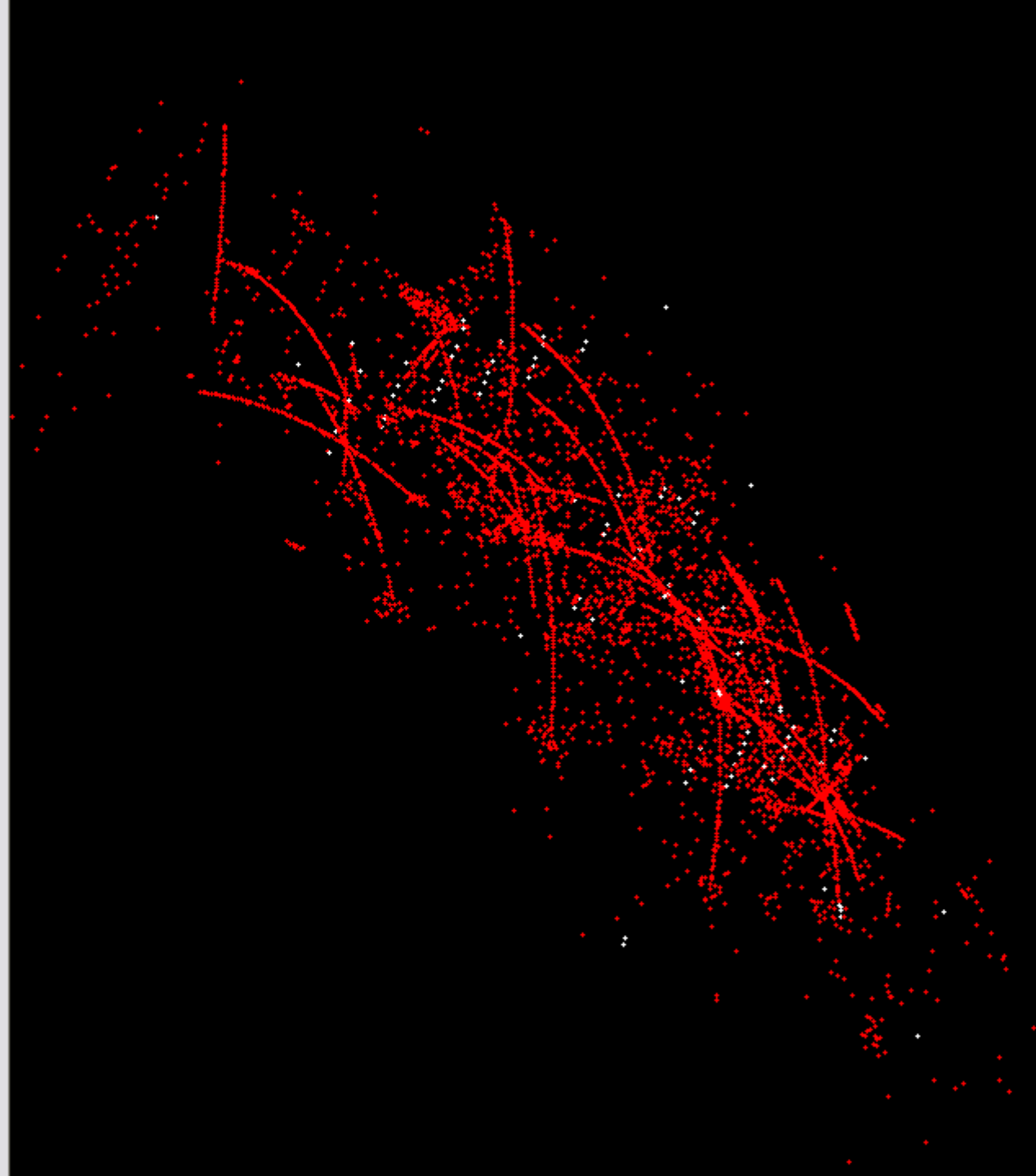
Refinement without
constraints

ADPs refinement
with sensible values

Tetrahedrally coordinated CO4 carbon unit

C1	O4	1.236
	O7	1.305
	O6	1.308
	O5	1.351
C2	O1	1.183
	O3	1.291
	O2	1.361
	O4	1.515





0.200 Edit

Fast rotation
◀ ▶ 3.000 Edit

Zoom
◀ ▶ 0.800 Edit

☒ Ortho ☐ Stereo ☐ Gnomonic

☐ Lattice ☐ Drag ☒ Mouse

☒ Select ☐ DragIndex UM S

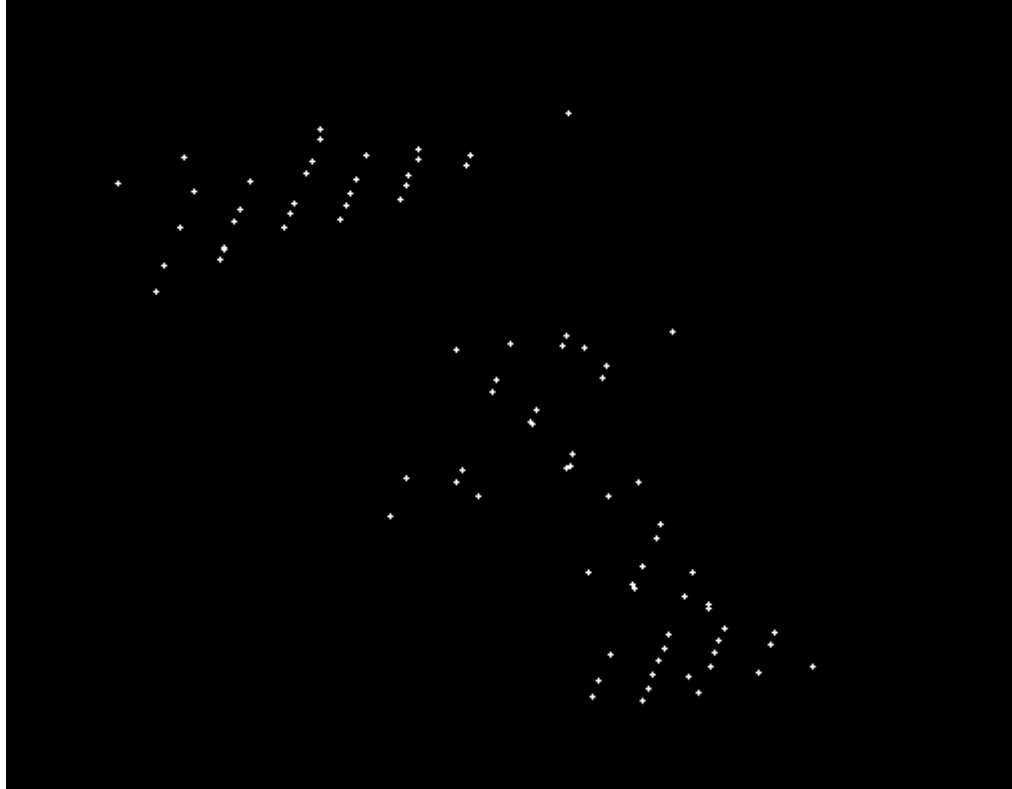
DragIndex axis
☒ a* - order= 1.00 order a*
e e e e
☐ b* - order= 1.00 order b*
e e e e
☐ c* - order= 1.00 order c*
e e e e

Show
☒ all ☐ used ☐ skip ☐ wrong

Wavelength: 0.41453 (User)

OK

Color legend:
a* - red
b* - green
c* - blue



Unit cell dimensions

$$a = 19.2330(18) \text{ \AA}$$

$$b = 2.5820(13) \text{ \AA}$$

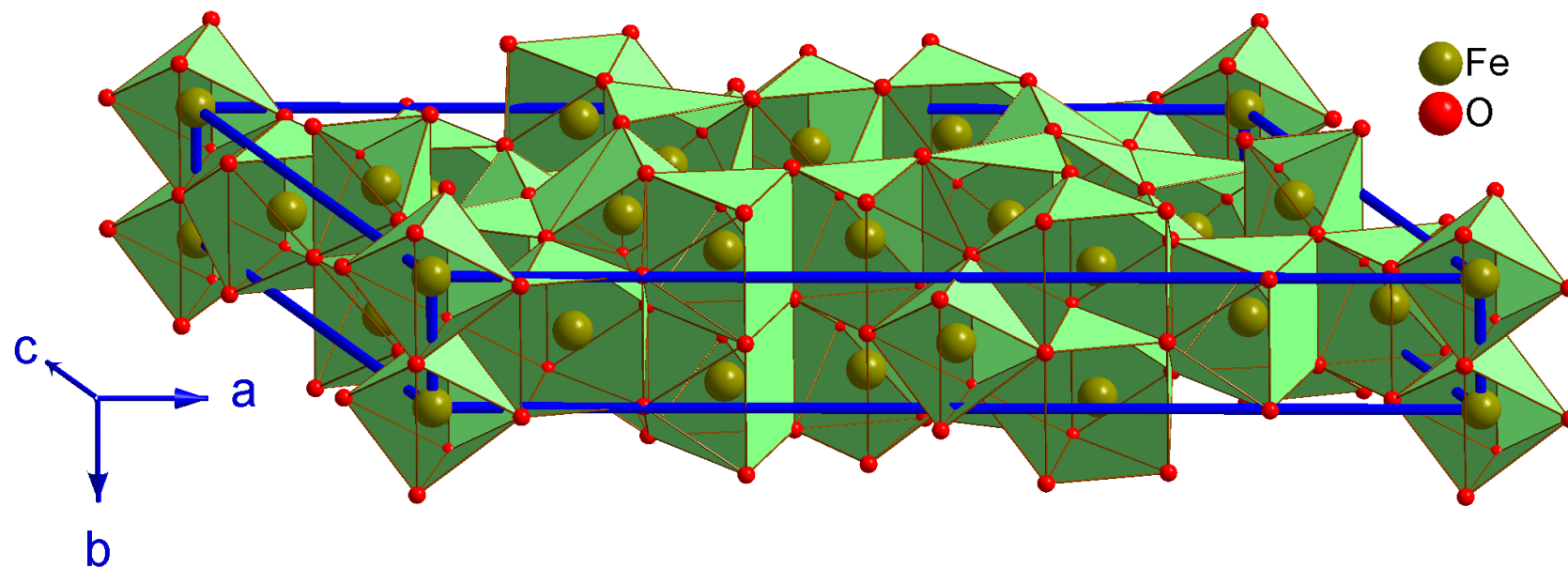
$$c = 9.550(11) \text{ \AA}$$

$$\beta = 118.39(3)^\circ$$

Cell volume $417.21(50) \text{ \AA}^3$

No idea about chemical composition:
an other carbonate? A decomposition product? Mg rich? Fe rich?

Second phase: new class of iron oxide, Fe₁₃O₁₉



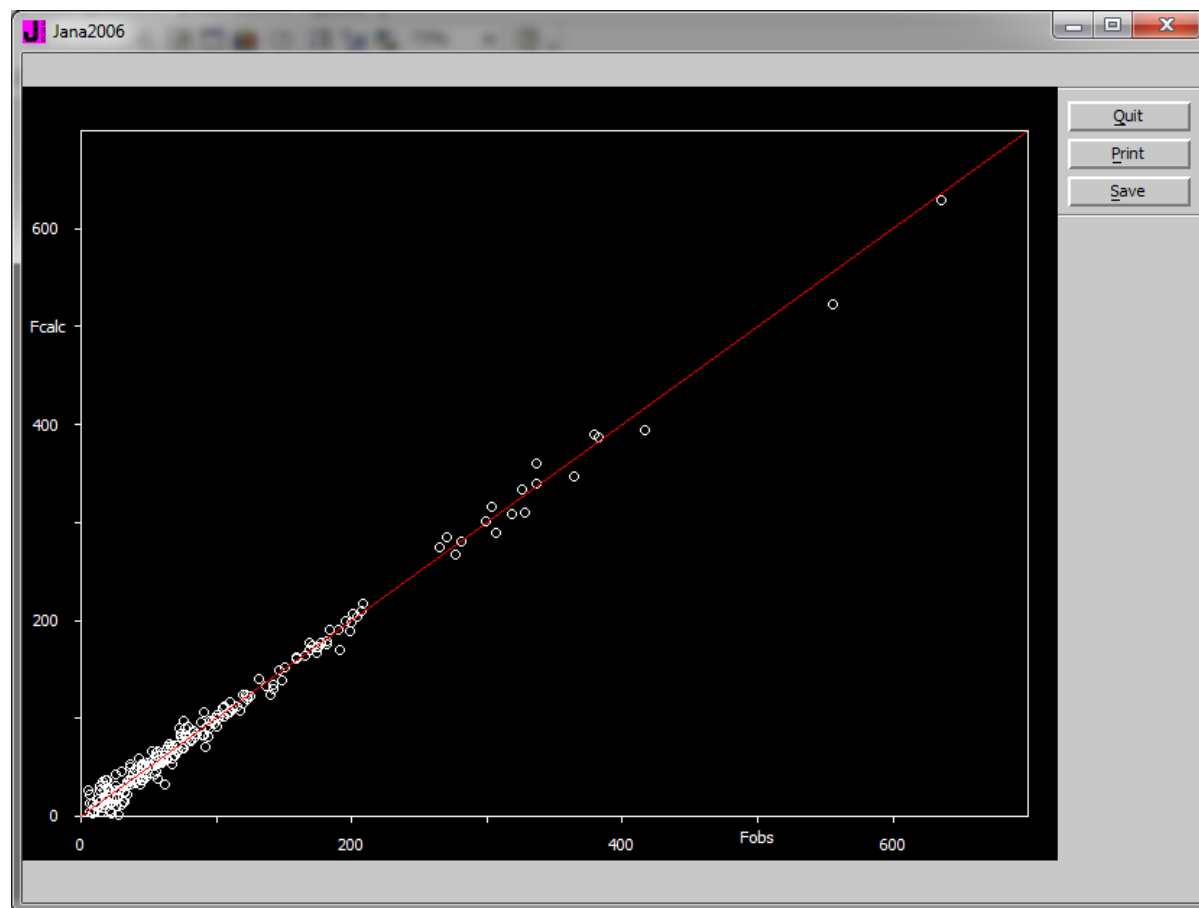
Crystal data

Formula sum	Fe _{13.25} O _{4.75}
Crystal system	monoclinic
Space group	C1 2/m 1 (no. 12)
Unit cell dimensions	$a = 19.2330(18) \text{ \AA}$ $b = 2.5820(13) \text{ \AA}$ $c = 9.550(11) \text{ \AA}$ $\beta = 118.39(3)^\circ$
Cell volume	$417.21(50) \text{ \AA}^3$
Z	8
Pearson code	mC64
Formula type	N13O19
Wyckoff sequence	i ¹ 'da

Atomic coordinates and isotropic displacement parameters (in $\text{\AA}^2$)

Atom	Wyck.	x	y	z	U
Fe1	4i	0.42673	-1/2	0.46077	0.0116
Fe2	4i	0.26499	0	0.36556	0.0096
Fe3	4i	0.46526	-1.00000	0.22941	0.0119
Fe4	4i	0.62638	-1.00000	0.34181	0.0127
Fe5	4i	0.35026	0	-0.06892	0.0118
Fe6	2a	1/2	-1/2	0	0.0177
Fe7	4i	0.31384	0	0.15739	0.0116
O1	2d	1/2	0	1/2	0.0156
O2	4i	0.40309	-1/2	0.26075	0.0090
O3	4i	0.29891	1/2	0.52089	0.0098
O4	4i	0.16083	0	0.22790	0.0082
O5	4i	0.45657	-1/2	0.66825	0.0155
O6	4i	0.37261	0	0.42921	0.0155
O7	4i	0.29676	-1/2	-0.00874	0.0099
O8	4i	0.24411	0	-0.22477	0.0046
O9	4i	0.57207	-1/2	-0.05633	0.0162
O10	4i	0.45524	0	-0.13134	0.0081

$\text{Fe}_{13}\text{O}_{19}$ @ 135 GPa



F calc vs Fobs

Independent reflections:

158

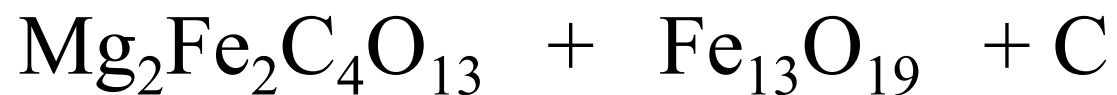
Refined parameters:

48

R obs:
5.2 %

R all

7.44 %



Fe^{3+}

oxidation

C^0

reduction

Red-ox reaction

American Mineralogist, Volume 100, pages 2001–2004, 2015

LETTER

The crystal structures of $\text{Mg}_2\text{Fe}_2\text{C}_4\text{O}_{13}$, with tetrahedrally coordinated carbon, and $\text{Fe}_{13}\text{O}_{19}$, synthesized at deep mantle conditions

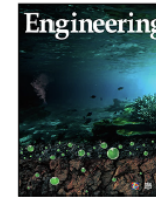
MARCO MERLINI^{1,*}, MICHAEL HANFLAND², ASHKAN SALAMAT³, SYLVAIN PETITGIRARD⁴ AND HARALD MÜLLER²

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⁴Bayerisches Geoinstitut, Universität Bayreuth, 95440, Germany



Research
Deep Matter & Energy—Review

Development of High-Pressure Multigrain X-Ray Diffraction for Exploring the Earth's Interior

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ted as an aggregate of thousands of individual single crystals. An accurate and efficient indexing algorithm is required to process such datasets. We have found that GrainSpotter [27], which is part of the FABLE package [28], is an efficient algorithm that can be readily applied to a rotation-scan dataset for indexing grains in an assemblage contained in a DAC [25,29,30]. In some cases, experienced crystallographers can index a few grains manually in a high-pressure rotation dataset and solve their crystal structures [6,31].

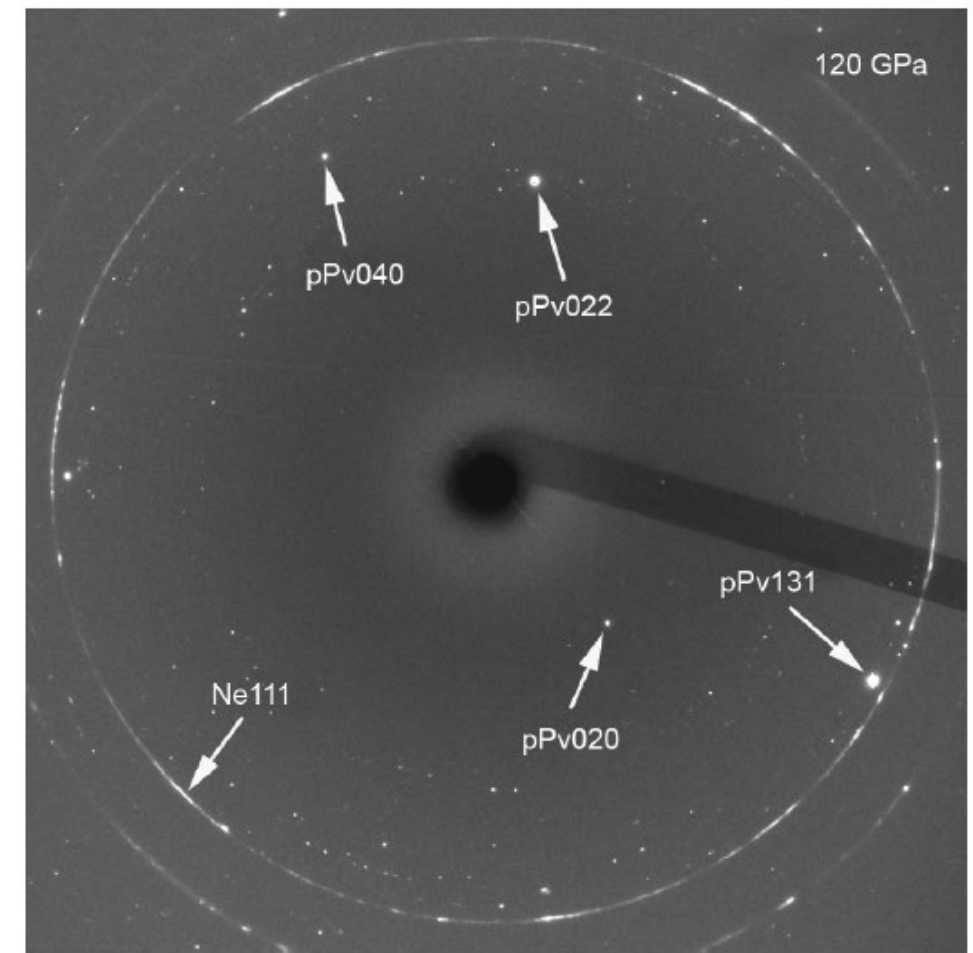


Fig. 1. A representative spotty powder XRD pattern of (Mg,Fe)SiO₃ pPv. The diffraction pattern was collected at a fixed ω angle at 120 GPa after temperature quenching from 2400 K, showing the spottiness of the XRD pattern. Ne: neon. Reproduced from Ref. [25] with permission of PNAS, © 2013.

5.5. Multigrain crystallography and three-dimensional grain mapping

H. F. POULSEN AND G. B. M. VAUGHAN

5.5.1. List of symbols

2θ : Bragg diffraction angle.

(x_l, y_l, z_l) : laboratory frame; x_l lies along the incident beam, y_l and z_l are perpendicular to the incident beam, laterally and vertically.

(x_b, y_b, z_b) : position of the origin of a scattering event in the laboratory frame; the centre of mass of a diffracting crystal.

ω : rotation around z_l

η : rotation around x_l

$(x_{\omega}, y_{\omega}, z_{\omega})$: rotated sample frame.

Ω, X, Θ : rotation matrices of a generalized goniometer.

Γ : total rotation matrix, $\Gamma = \Omega X \Theta$.

$(y_{\text{raw}}, z_{\text{raw}})$: detector coordinates on the face of the detector.

SC: spatial-distortion operator on the face of the detector.

$(y_{\text{det}}, z_{\text{det}})$: spatially corrected detector coordinates in the detector frame.

$(\varphi_x, \varphi_y, \varphi_z)$: right-handed detector tilts around (x_l, y_l, z_l) .

R^X, R^Y and R^Z : detector rotation matrices corresponding to rotations of φ_x, φ_y and φ_z , respectively.

R : total detector rotation matrix, $R^X R^Y R^Z$.

$[y_{\text{det}}(0), z_{\text{det}}(0)]$: pixel coordinates for the incident ray passing through $(x_l, y_l, z_l) = (0, 0, 0)$.

P_y, P_z : pixel sizes on the detector face along y and z .

G : scattering vector (G vector)

$G_l, G_{\omega}, G_y, G_s, G_c, G_{hkl}$: G vectors in the laboratory frame, ω frame, rotated frame, sample frame, Cartesian grain frame and reciprocal-lattice frame, respectively.

β_k : misorientation of a symmetry-equivalent direction with respect to the fundamental zone.

$g: U^{-1}$; sample rotation in Euler space.

5.5.2. Introduction

Conventionally, crystallography is based on either single-crystal or powder diffraction measurements. Such methods apply to two extremes of sample morphology: a homogeneous, mono-domain specimen, or an (ideally) mono-disperse and homogeneous powder comprising a huge number of isotropically oriented crystals. Unfortunately, the morphology of a sample is often a heterogeneous assembly of a finite number of poor crystals, perhaps even including several phases. While perturbative methods allow samples departing significantly from the ideal to be treated, many samples are still inappropriate for crystallographic characterization by these methods, leading to significant effort in sample preparation (see Chapter 2.10). In numerous cases, preparation of suitable single crystals is not possible, *e.g.* in relation to studies in extreme environments, studies involving first-order transitions or more generally cases where suitable crystallization conditions have not been found. In other cases, samples are extremely unstable, making it impossible to collect complete data sets. Structures are now routinely solved and refined from powder-diffraction data, but these structures are intrinsically less well determined than those from single crystals

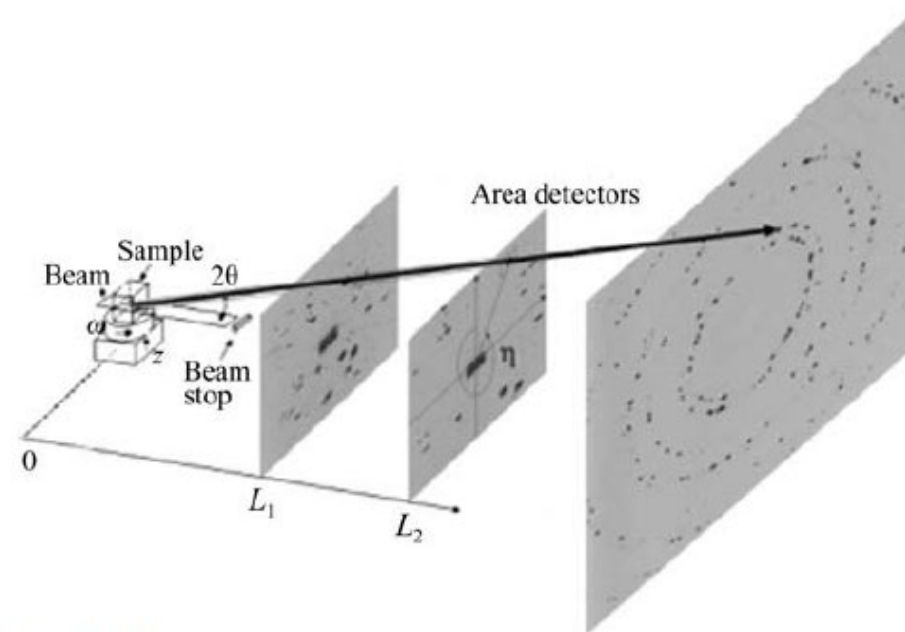


Figure 5.5.1

Sketch of the 3DXRD principle. The Bragg angle 2θ , the rotation angle ω and the azimuthal angle η are indicated for the diffracted beam arising from one grain of a coarse-grained specimen. The axes for the laboratory coordinate system are also shown.

Reliability of multigrain indexing for orthorhombic polycrystals above 1 Mbar: application to MgSiO_3 post-perovskite

Christopher Langrand,^{a,*} Nadège Hilairet,^a Carole Nisr,^b Mathieu Roskosz,^a Gábor Ribárik,^{c,d} Gavin B. M. Vaughan^e and Sébastien Merkel^{a,f}

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Keywords: three-dimensional X-ray diffraction; high pressure; microstructures; diamond anvil cells; multigrain crystallography; post-perovskite.

Supporting information: this article has supporting information at journals.iucr.org/j

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This paper describes a methodology for characterizing the orientation and position of grains of an orthorhombic polycrystalline material at high pressure in a diamond anvil cell. The applicability and resolution of the method are validated by simulations and tested on an experimental data set collected on MgSiO_3 post-perovskite at 135 GPa. In the simulations, ~95% of the grains can be indexed successfully with ~80% of the peaks assigned. The best theoretical average resolutions in grain orientation and position are 0.02° and $1.4\ \mu\text{m}$, respectively. The indexing of experimental data leads to 159 grains of post-perovskite with 30% of the diffraction peaks assigned with a $0.2\text{--}0.4^\circ$ resolution in grain orientation. The resolution in grain location is not sufficient for *in situ* analysis of spatial relationships at high pressure. The grain orientations are well resolved and sufficient for following processes such as plastic deformation or phase transformation. The paper also explores the effect of the indexing parameters and of experimental constraints such as rotation range and step on the validity of the results, setting a basis for optimized experiments.

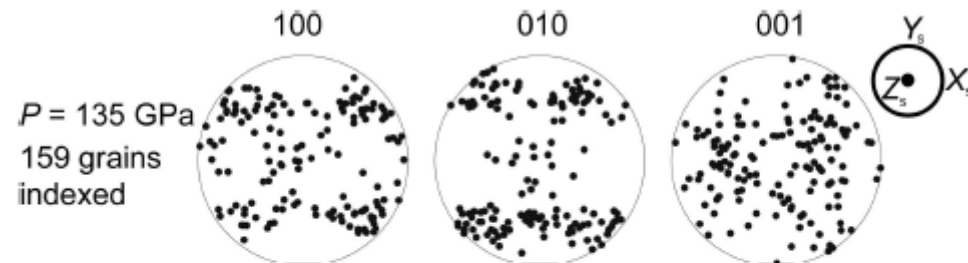


Figure 8

Experimental results: 100, 010 and 001 pole figures representing the orientation of the indexed MgSiO_3 pPv grains at 135 GPa. The compression axis of the DAC is along Y_s and the plane of the gasket is in X_sZ_s . Each dot represents the orientation of a single grain.

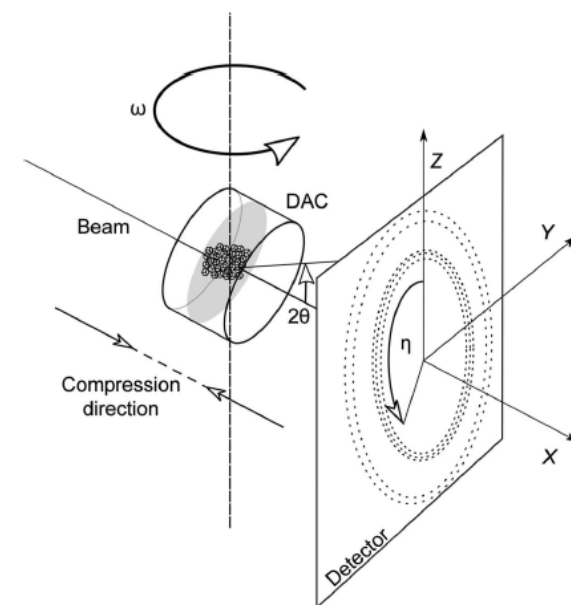


Figure 1

The setup for multigrain crystallography at high pressure. The sample is confined in a DAC in axial geometry with an ω rotation parallel to the Z direction. Diffraction patterns are collected on a flat panel detector orthogonal to the incoming X-ray beam. Images are collected over ω ranges $\Delta\omega = [-120^\circ; -65^\circ]$ and $[60^\circ; 115^\circ]$ and individually exposed while the DAC is rotated in steps of $\delta\omega = 0.5^\circ$. The grey area represents the transverse plane, the plane of the gasket, perpendicular to the compression direction.



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computer programs

Domain Auto Finder (DAFi) program: the analysis of single-crystal X-ray diffraction data from polycrystalline samples

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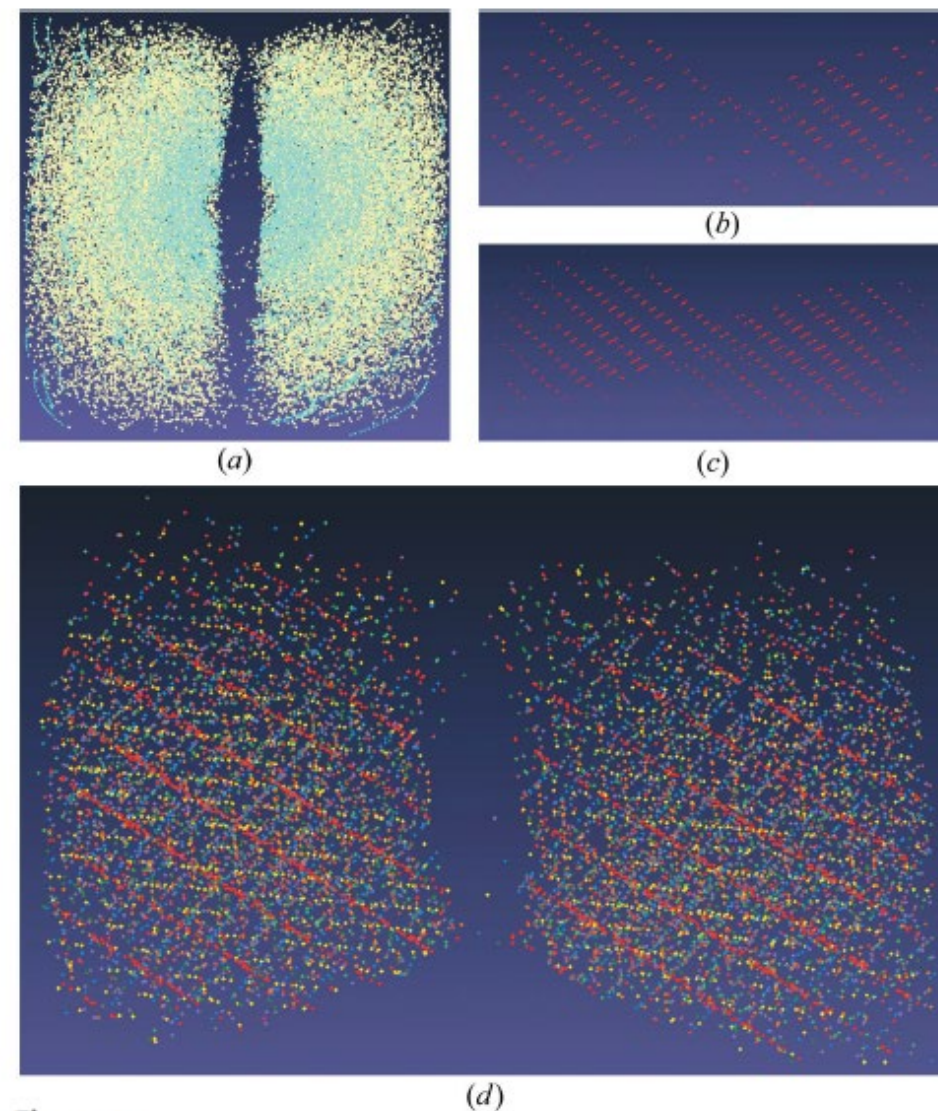
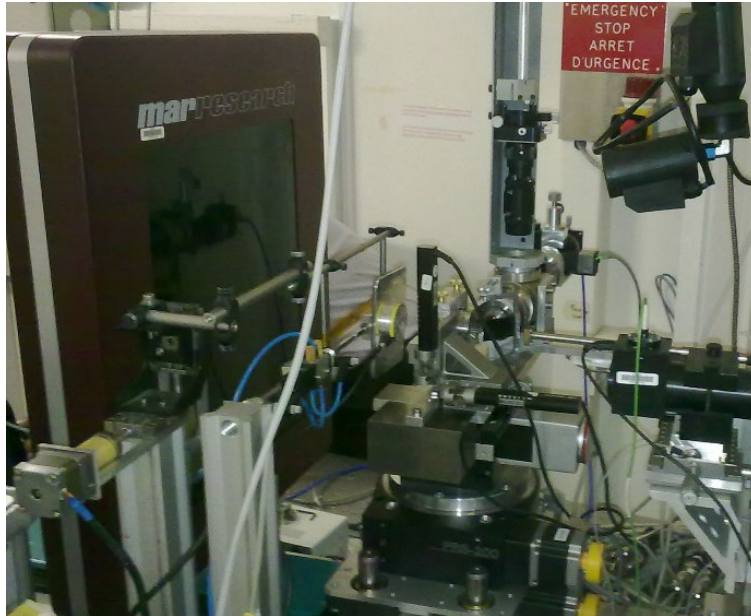


Figure 5

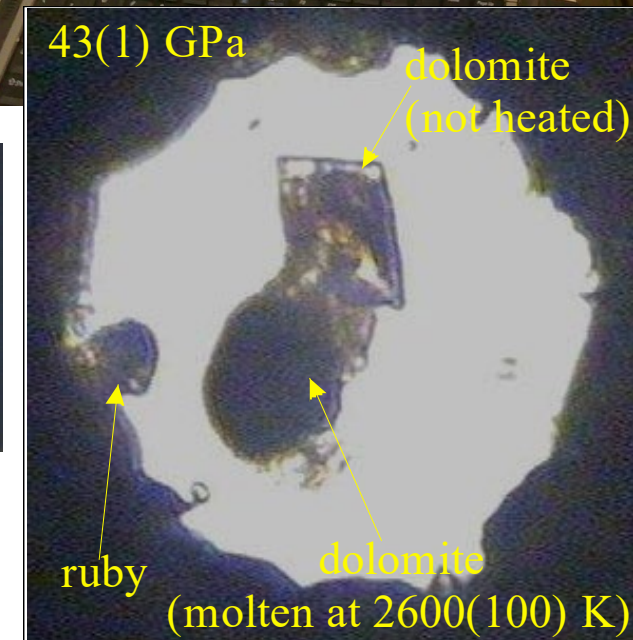
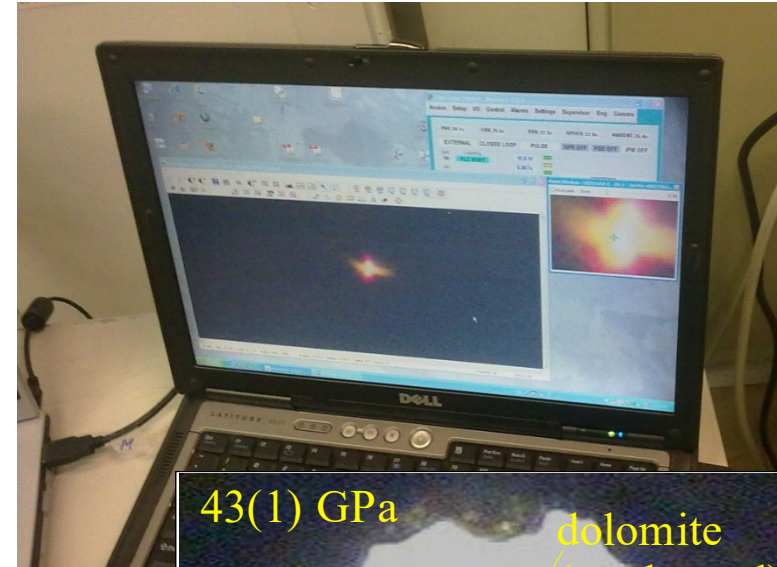
Reciprocal space representing SC-XRD data from a sample of $Y+N_2$ in a DAC: (a) all reflections (cyan reflections are those filtered after applying 'advanced filtering'); (b) reflections of group 1 belonging to the first Y_5N_{14} domain found by the *DAFi* program; (c) reflections of group 1 belonging to the Y_5N_{14} domain extended by *CrysAlis^{Pro}*; (d) reflections of ten groups (1 through 10) belonging to ten Y_5N_{14} domains marked by ten different colors.

2010: crystal structure determination *in-situ* at simultaneous high-pressure and high-temperature conditions of the deep Earth, with single crystal diffraction techniques, synchrotron radiation and portable laser heating system coupled with diamond anvil cell



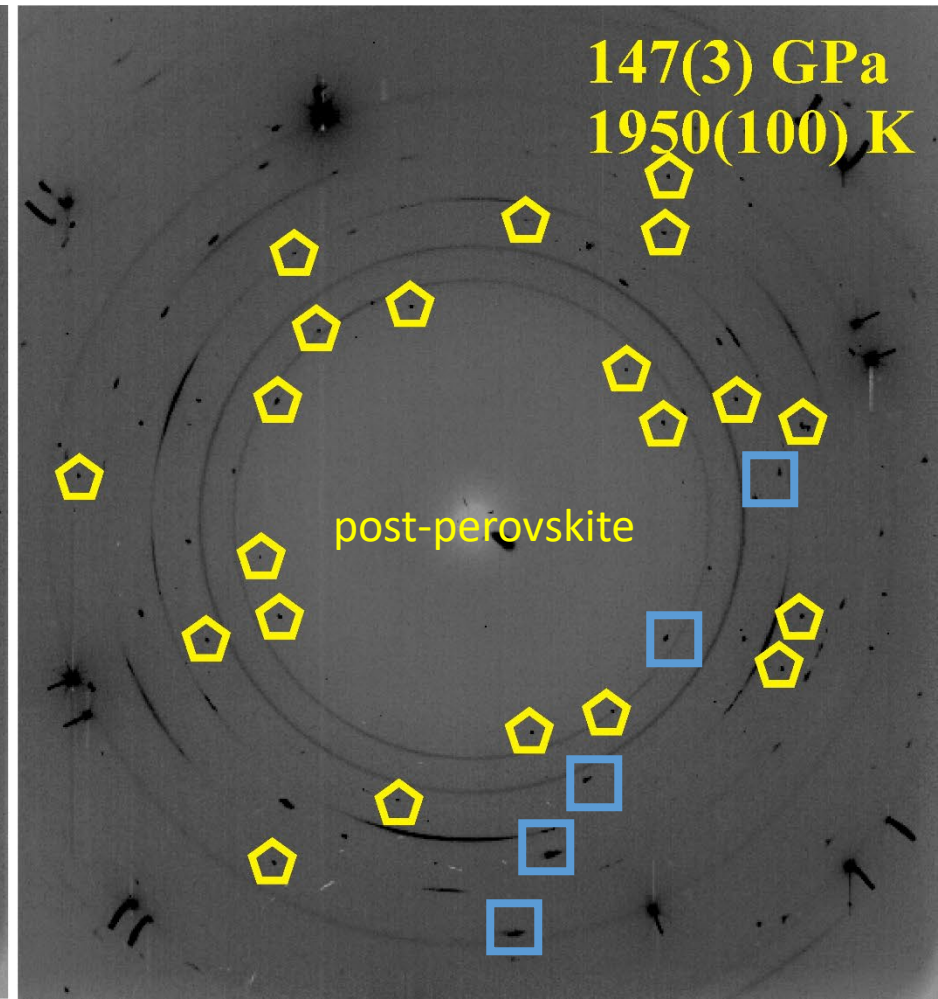
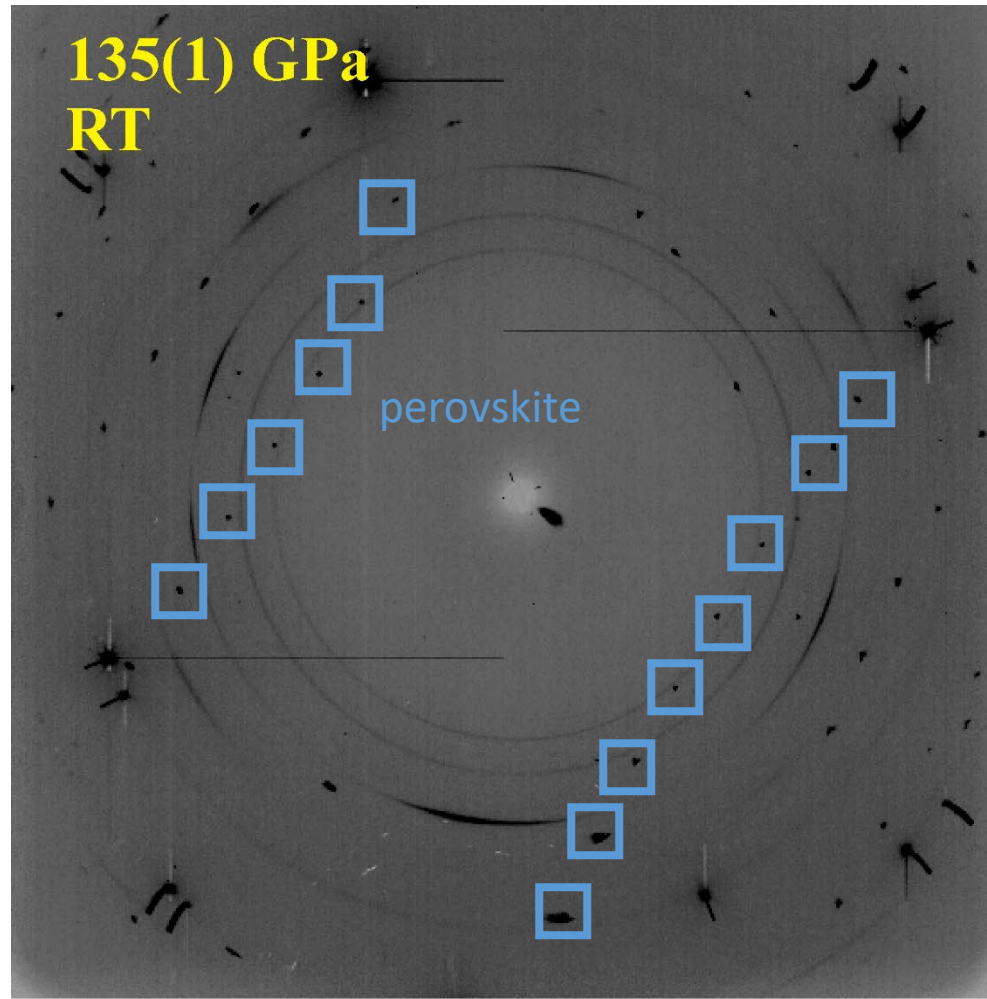
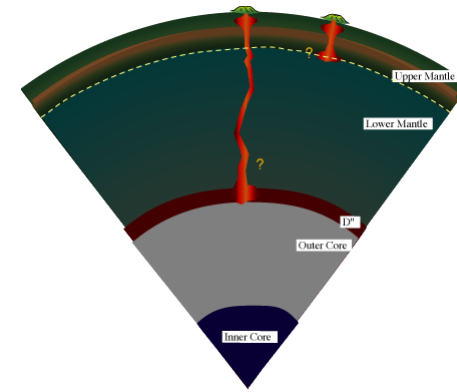
Compact laser heating devices which can rotate simultaneously with the diamond anvil cell to perform single crystal diffraction @ HP/HT

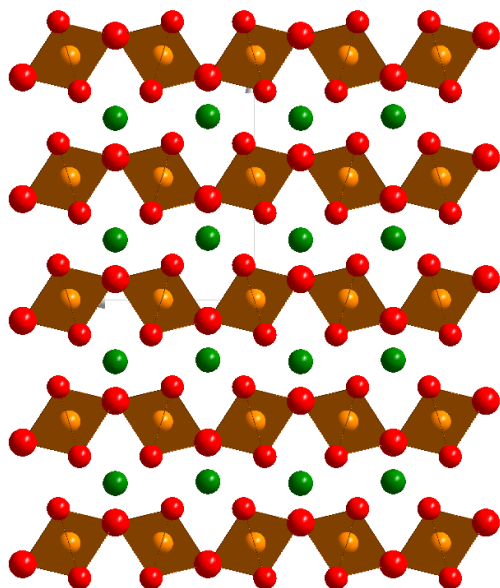
«Portable laser heating system for single crystal diffraction»
Dubrovinsky et al., HPR 2010



Single crystal diffraction at D'' conditions and growth of a single crystal of post-perovskite

5 (five!) minutes of experiment – in-situ single crystal diffraction and direct observation of the perovskite – post-perovskite transformation





2010: test experiment on
post-perovskite
State of art:
five minutes data
collection @ HT/HP;
structure solution and
refinement, using in-situ
data

Crystal data

Formula sum	$\text{Fe}_1\text{Mg}_1\text{O}_1\text{Si}_1$
Crystal system	orthorhombic
Space group	$C m c m$ (no. 63)
Unit cell	$a = 2.477(7) \text{ \AA}$ $b = 8.03(2) \text{ \AA}$ $c = 6.109(13) \text{ \AA}$
Cell volume	$121.51(50) \text{ \AA}^3$
Z	16
Pearson code	oC20

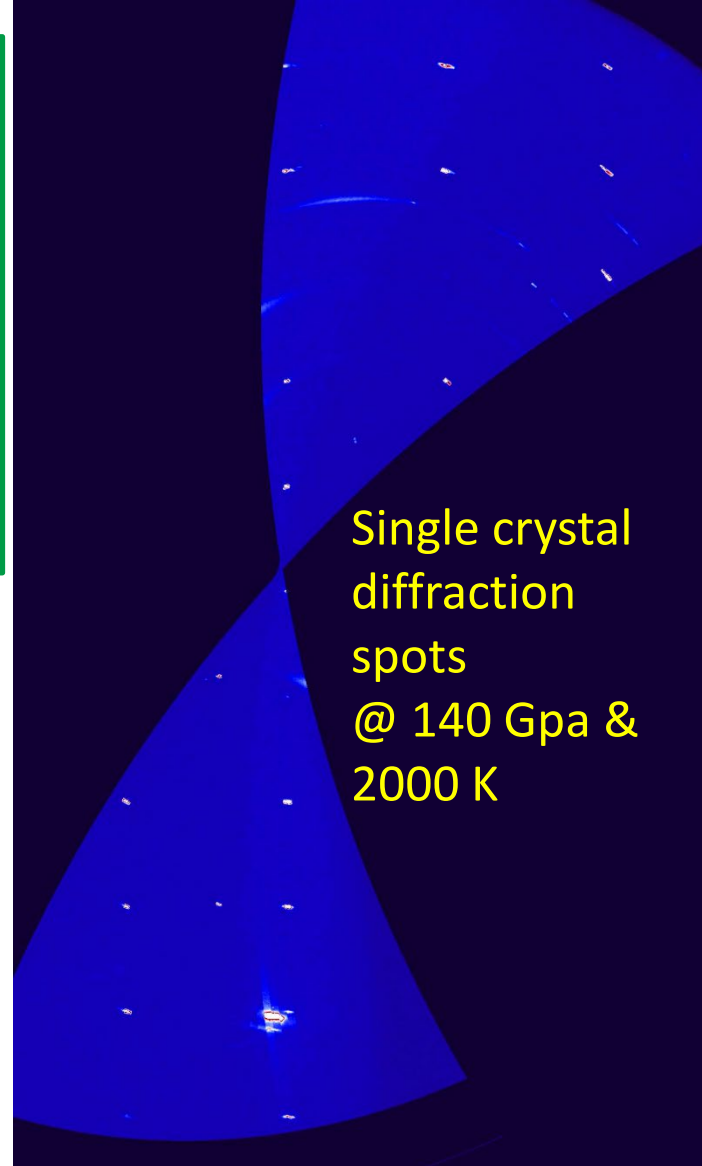
Post-perovskite,

Crystal structure at
140 GPa e 2000K

Atomic coordinates and isotropic displacement parameters (in $\text{\AA}^2$)

Atom	Wyck.	Occ.	x	y	z	U
Mg1	4c	0.703	0	0.25346	1/4	0.0149
Fe1	4c	0.297	0	0.25346	1/4	0.0149
Si	4a		0	0	0	0.0126
O1	4c		0	0.91453	1/4	0.0187
O2	8f		0	0.64244	0.44277	0.0130

Single crystal
diffraction
spots
@ 140 GPa &
2000 K



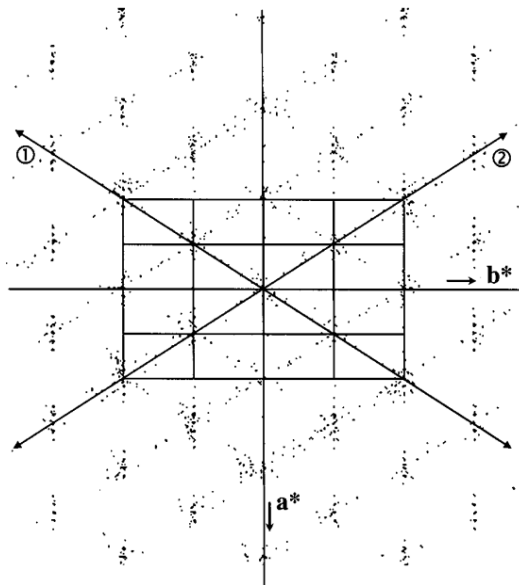


Figure 1
Projection of the reciprocal space of phase γ along c^* . Strong peaks are represented by dots; the satellite reflections are projected in the a^* , b^* plane. The peaks that can neither be indexed as a main reflection nor as satellites are mostly located along the dotted lines labelled '1' and '2' (in rings). This indicates the presence of two other domains of Na_2CO_3 .

research papers

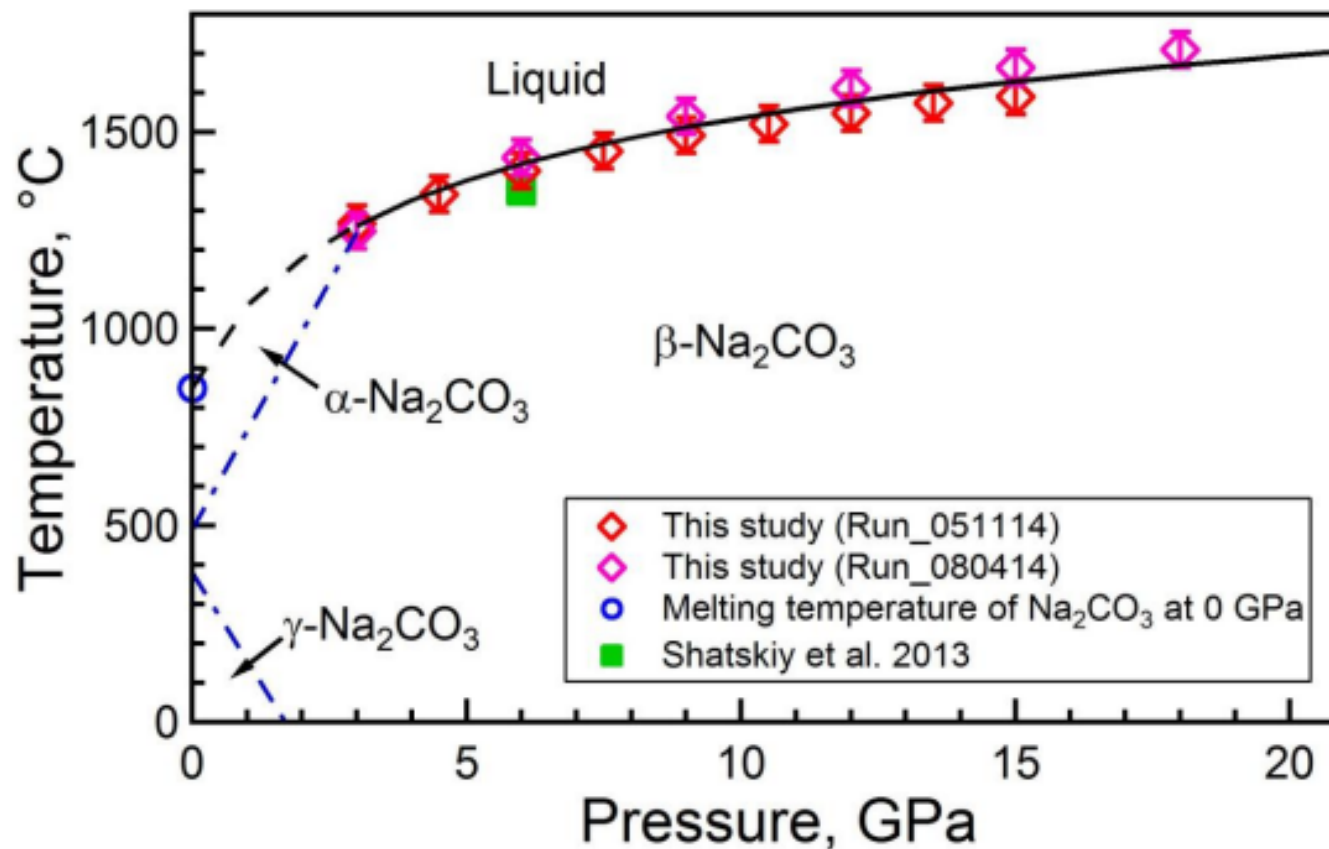


Figure 5.2 Melting curve of Na_2CO_3 . The blue dash-dot lines are phase boundaries between α - Na_2CO_3 , β - Na_2CO_3 and γ - Na_2CO_3 proposed by Shatskiy et al. (2013). The black solid curve is the polynomial fit of our data. The black dash line is the interpolated melting curve based on our data and ambient temperature melting temperature. The error bar of our data is ± 45 °C.

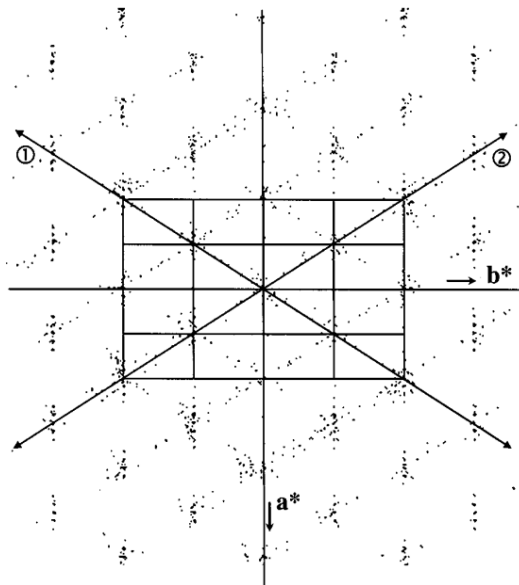


Figure 1
Projection of the reciprocal space of phase γ along c^* . Strong peaks are represented by dots; the satellite reflections are projected in the a^* , b^* plane. The peaks that can neither be indexed as a main reflection nor as satellites are mostly located along the dotted lines labelled '1' and '2' (in rings). This indicates the presence of two other domains of Na_2CO_3 .

research papers

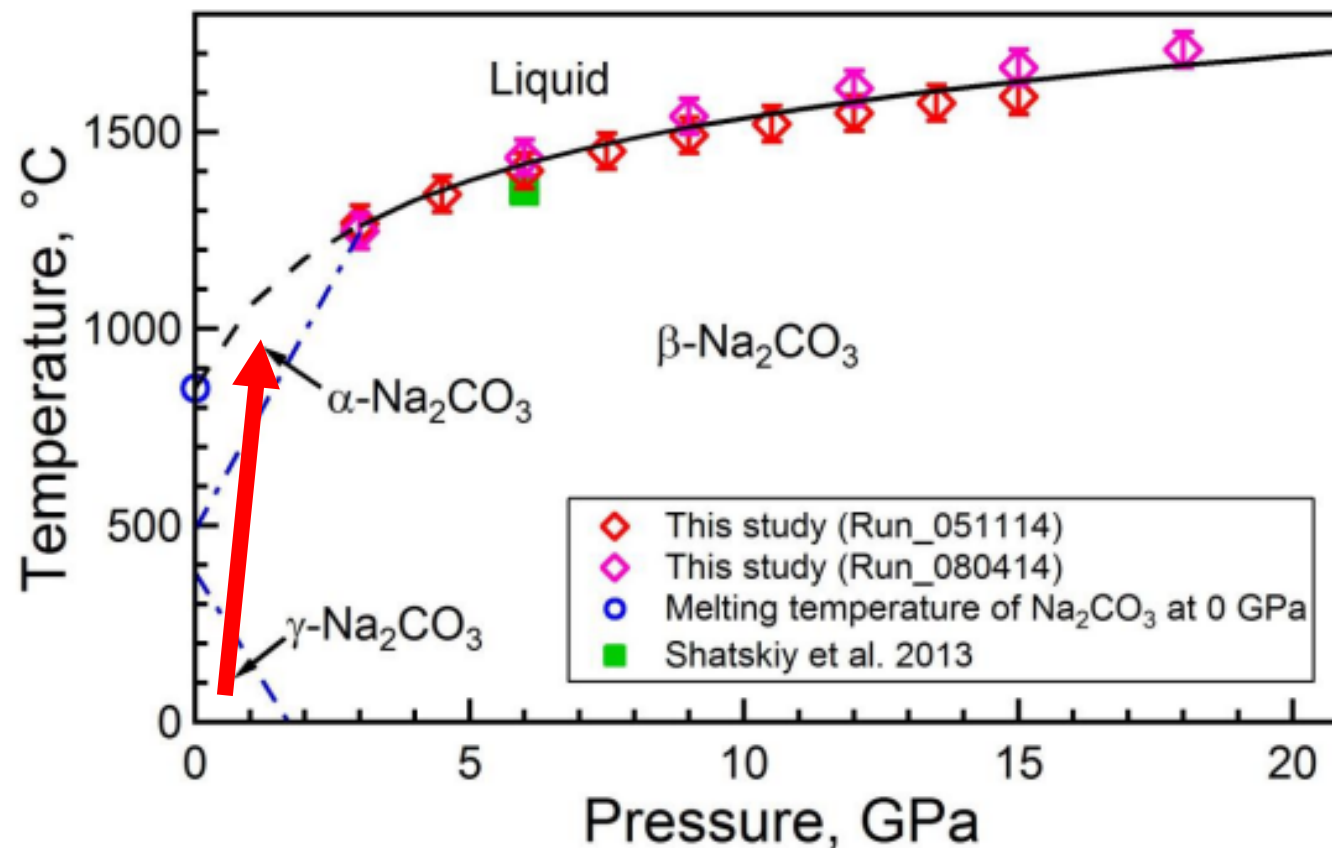
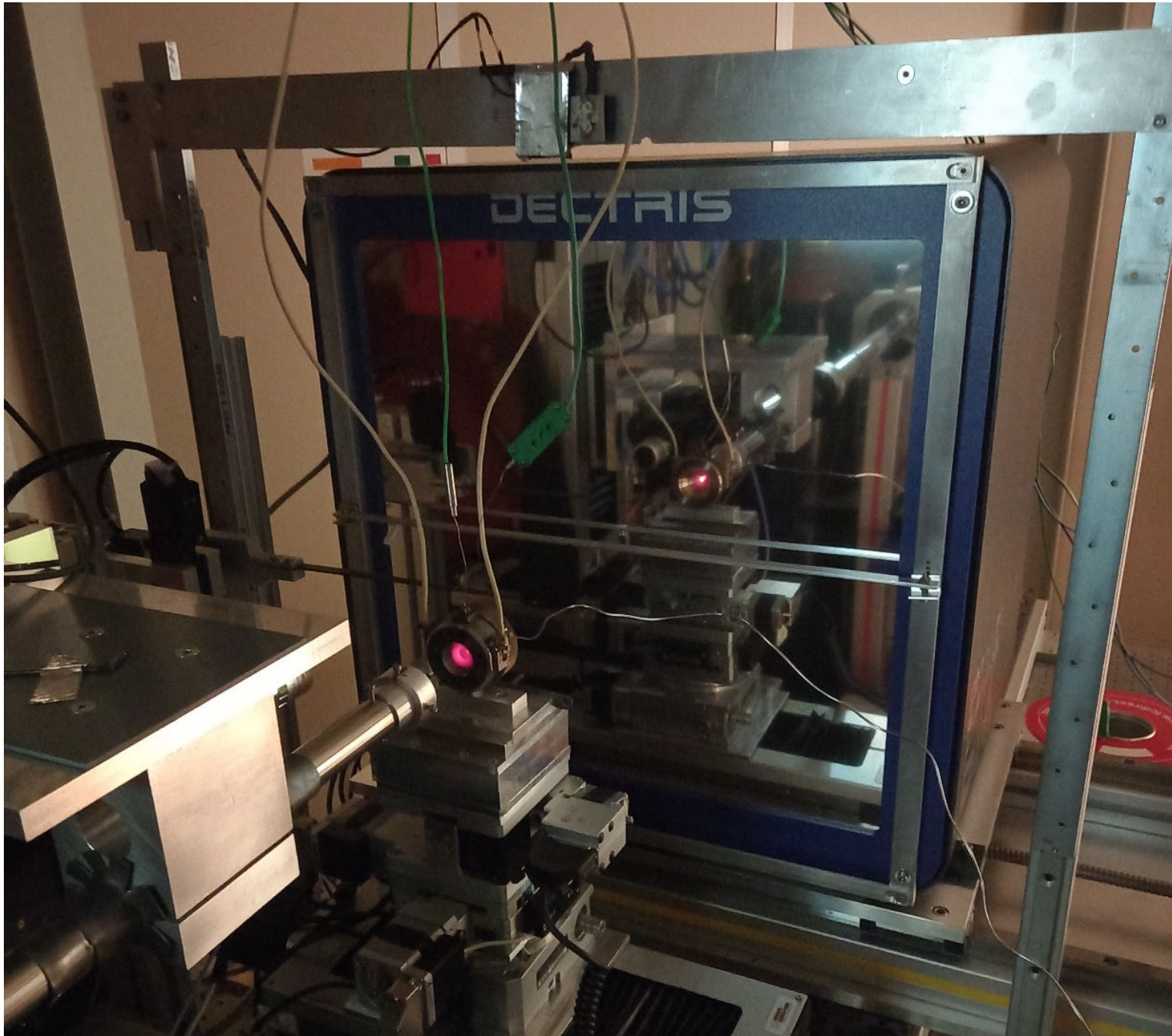
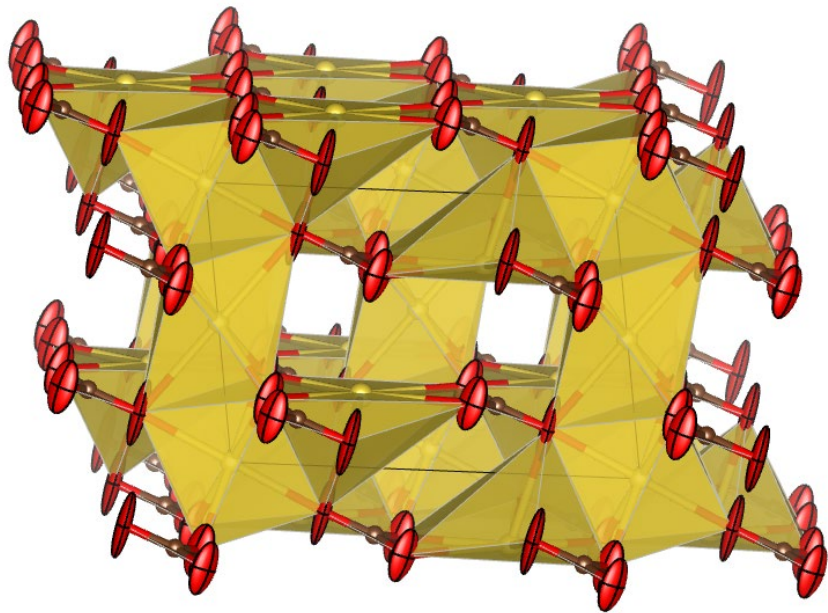
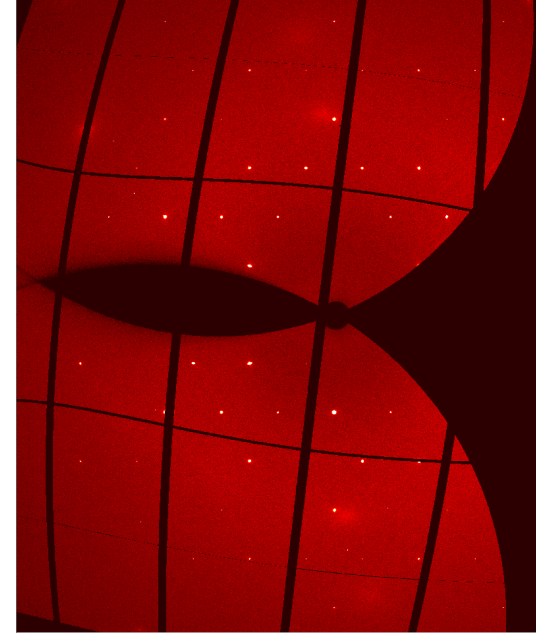
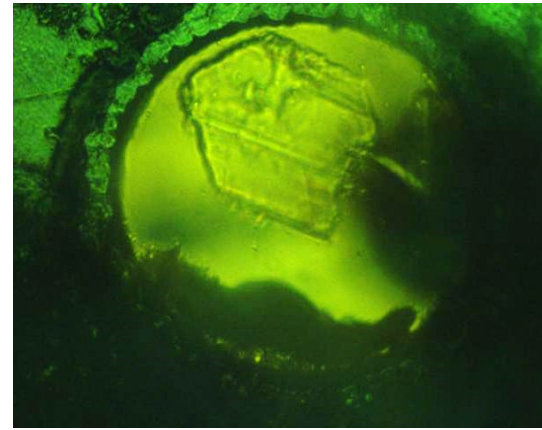
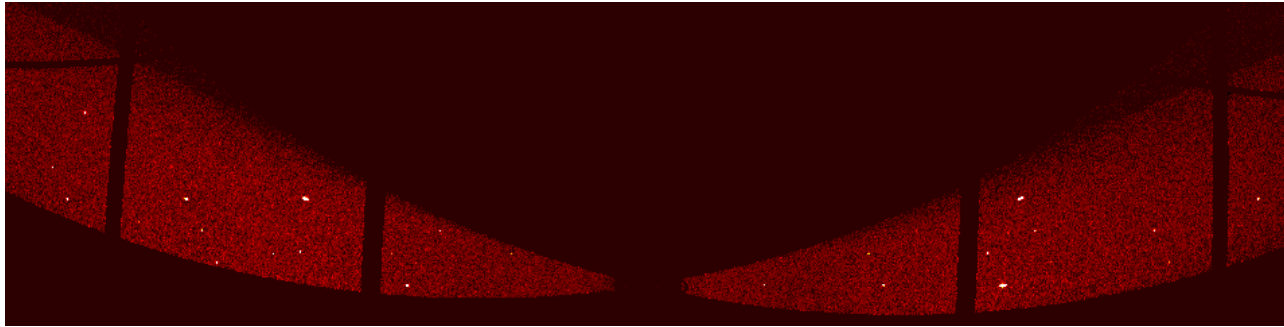


Figure 5.2 Melting curve of Na_2CO_3 . The blue dash-dot lines are phase boundaries between α - Na_2CO_3 , β - Na_2CO_3 and γ - Na_2CO_3 proposed by Shatskiy et al. (2013). The black solid curve is the polynomial fit of our data. The black dash line is the interpolated melting curve based on our data and ambient temperature melting temperature. The error bar of our data is $\pm 45^\circ\text{C}$.

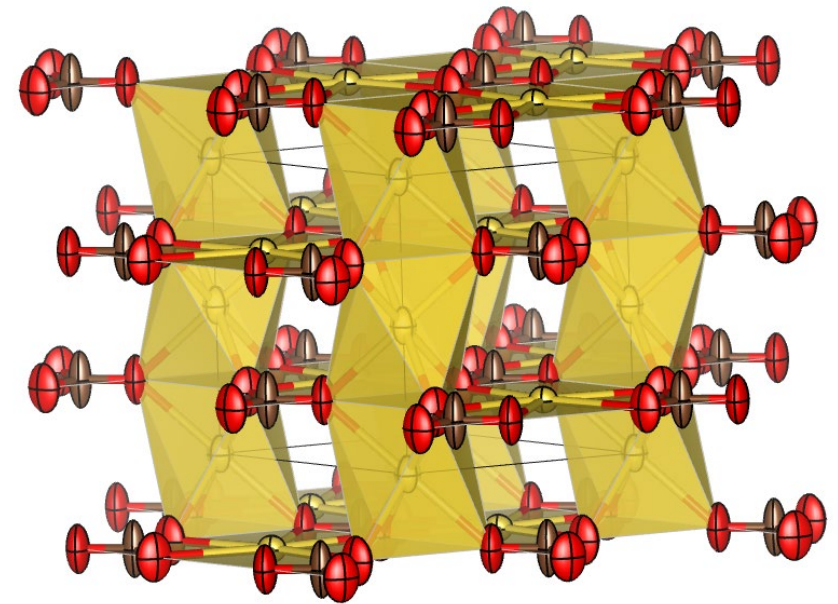


Resistively heated DAC – stable temperature and good quality of diffraction data

High-pressure and temperature studies of Na_2CO_3

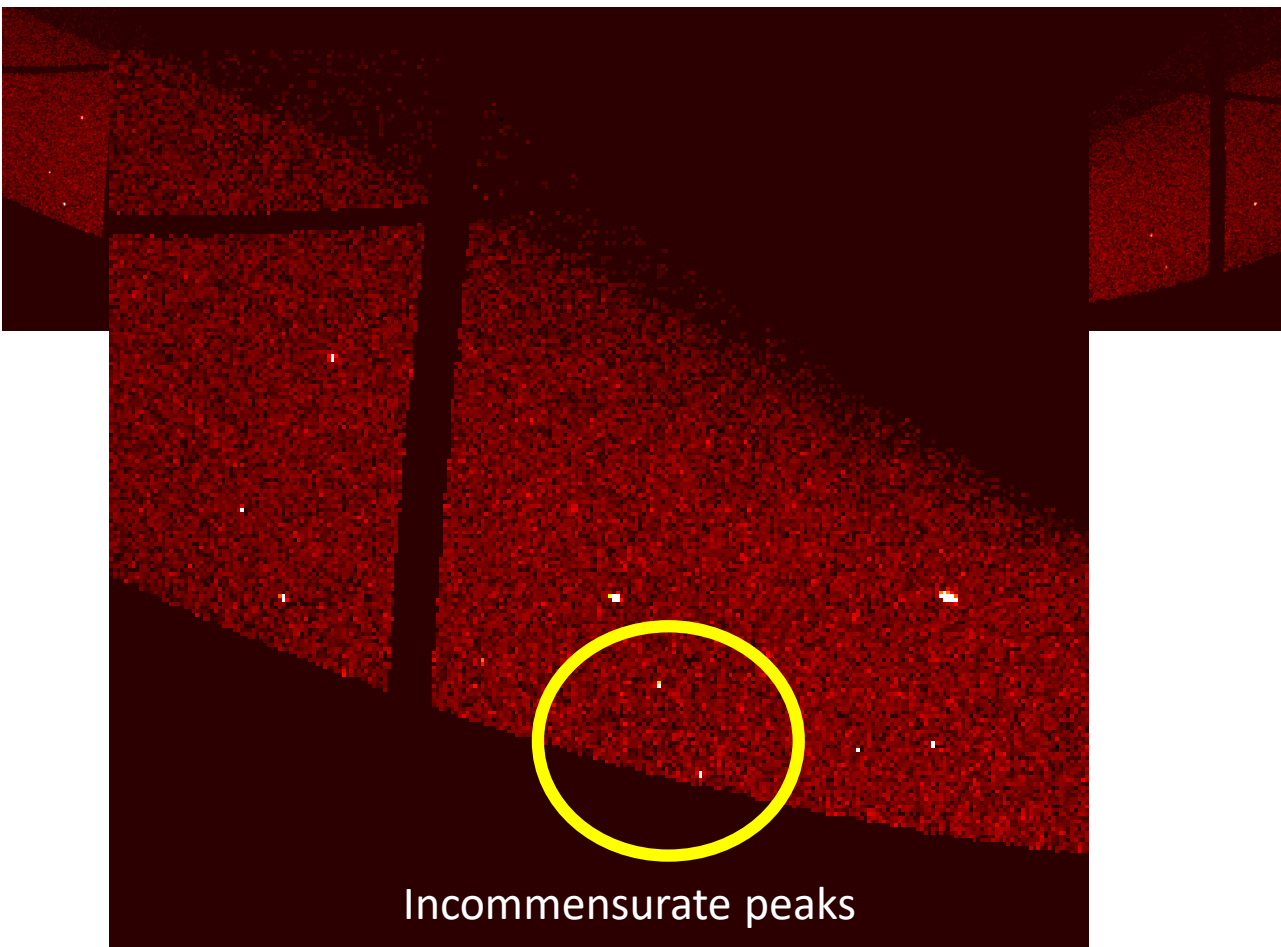


8.9839 (16) 5.2359 (4) 6.262 (9)
90.0 97.88 (5) 90.0
V = 291.8 (4)



5.2130 (5) 5.2130 (5) 6.437 (6)
90.0 90.0 120.0
V = 151.49 (16)

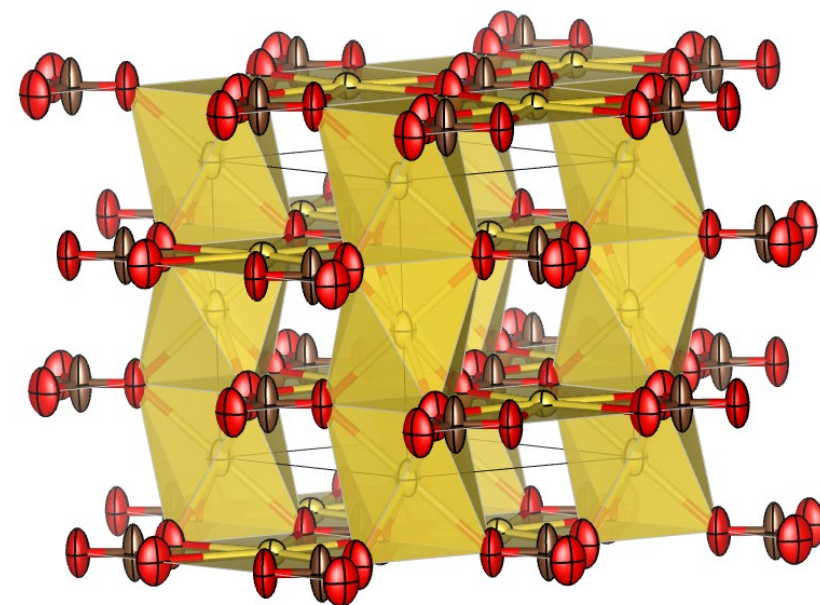
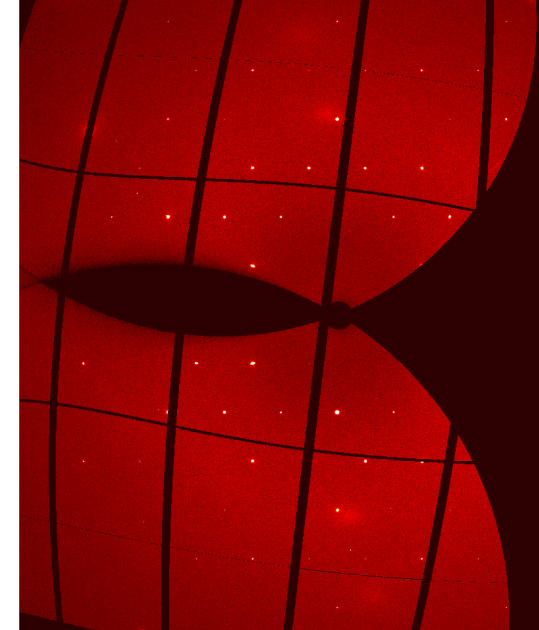
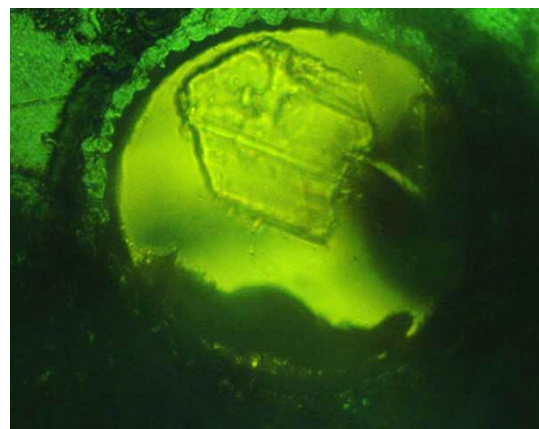
High-pressure and temperature studies of Na_2CO_3



Incommensurate peaks

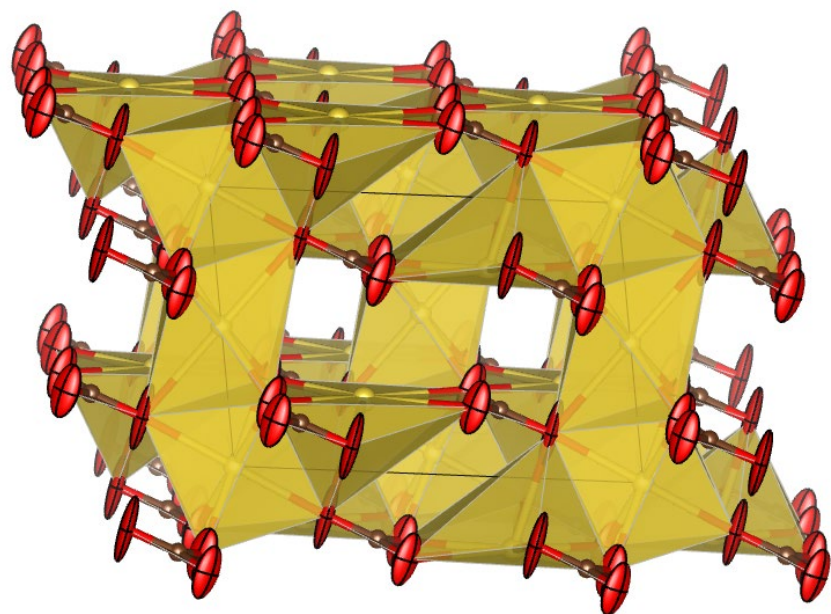
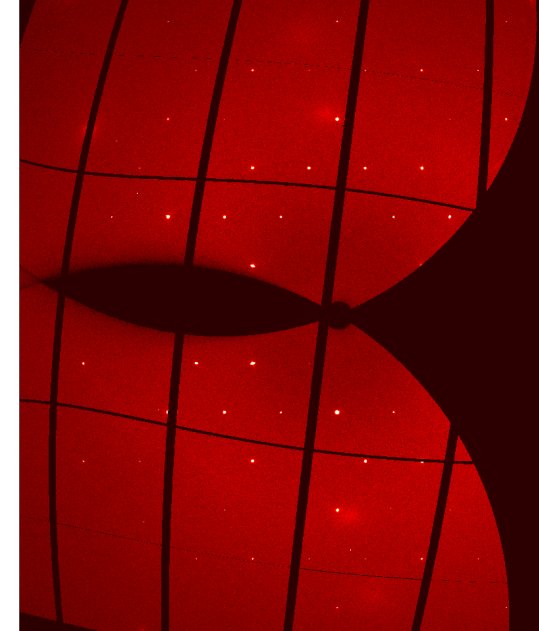
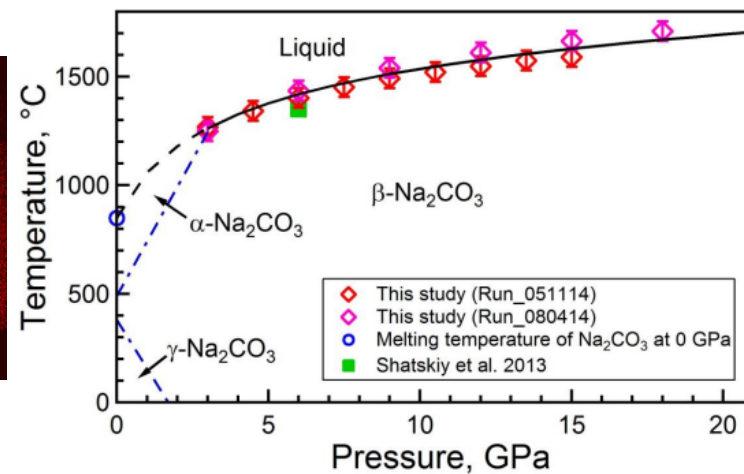
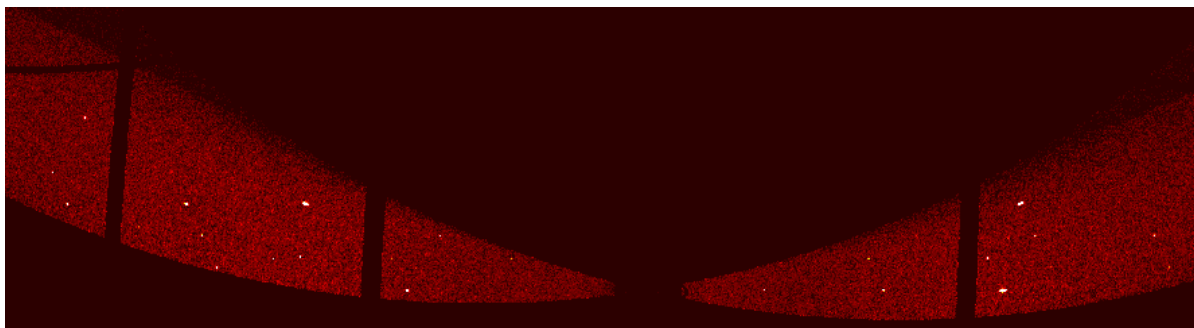


8.9839 (16) 5.2359 (4) 6.262 (9)
 90.0 97.88 (5) 90.0
 $V = 291.8 (4)$



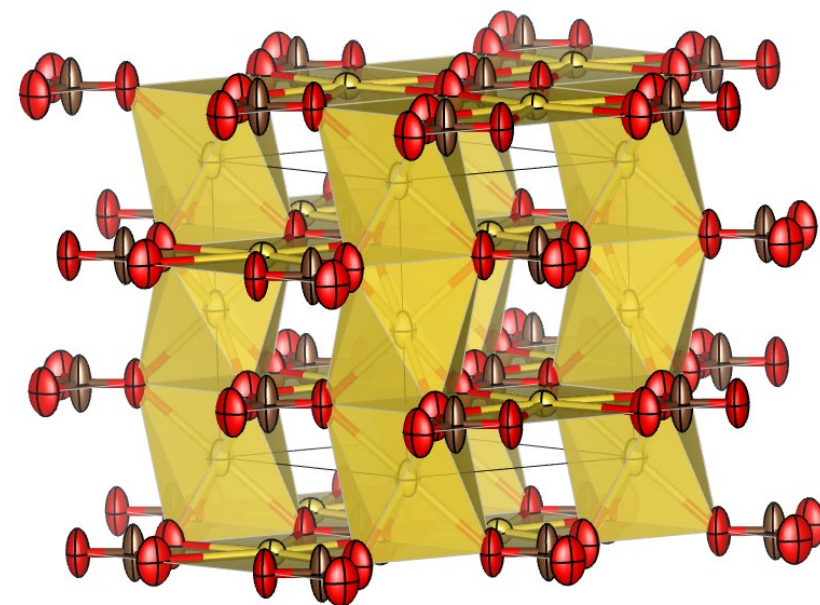
5.2130 (5) 5.2130 (5) 6.437 (6)
 90.0 90.0 120.0
 $V = 151.49 (16)$

High-pressure and temperature studies of Na_2CO_3



Beta-phase

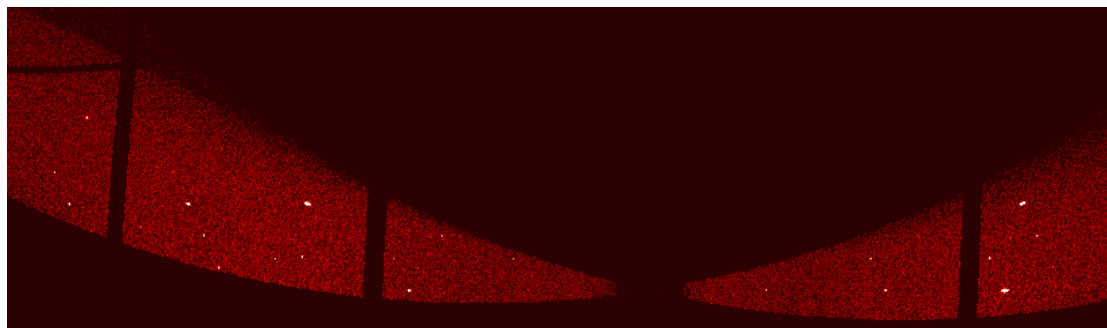
8.9839 (16) 5.2359 (4) 6.262 (9)
 90.0 97.88 (5) 90.0
 $V = 291.8 (4)$



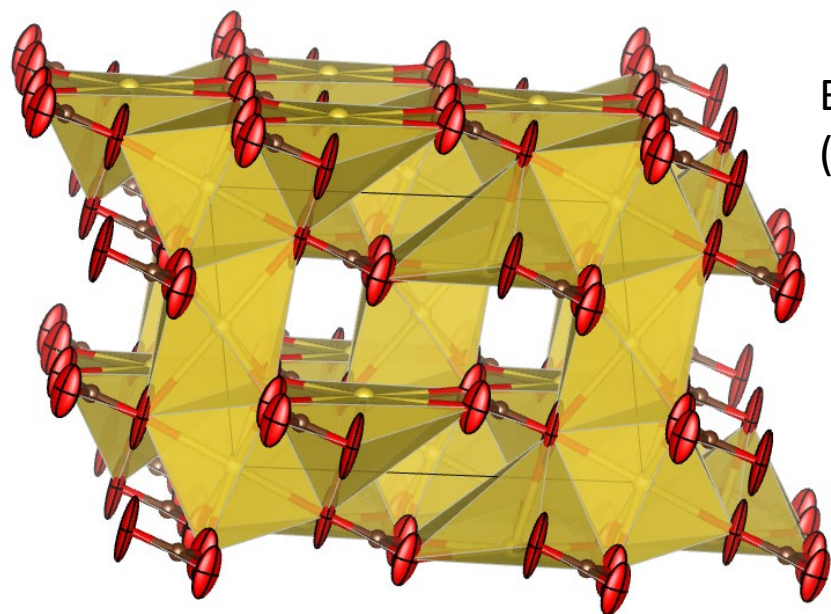
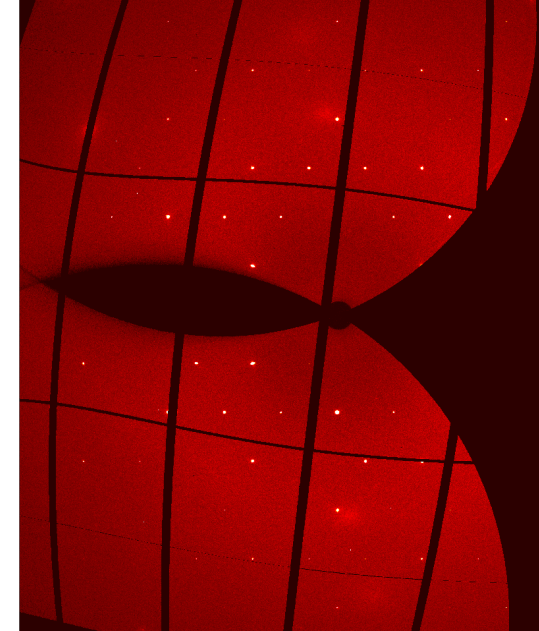
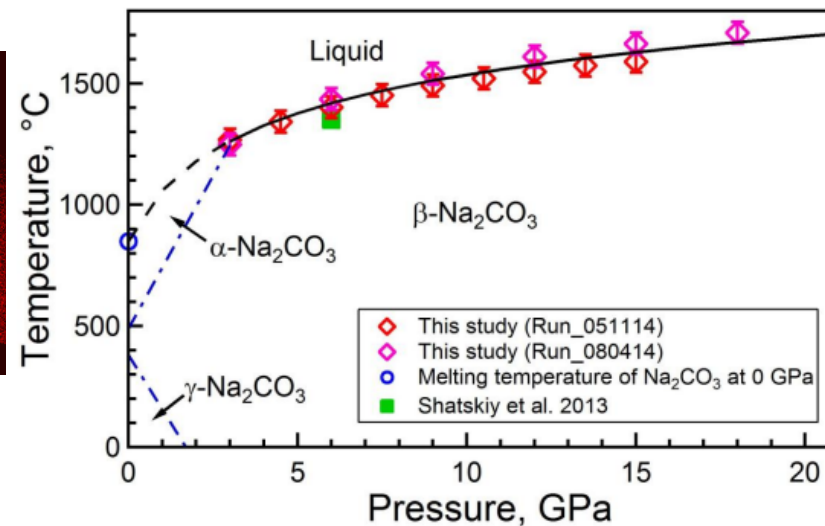
alpha-phase
 2 GPa – 800 °C

5.2130 (5) 5.2130 (5) 6.437 (6)
 90.0 90.0 120.0
 $V = 151.49 (16)$

High-pressure and temperature studies of Na_2CO_3

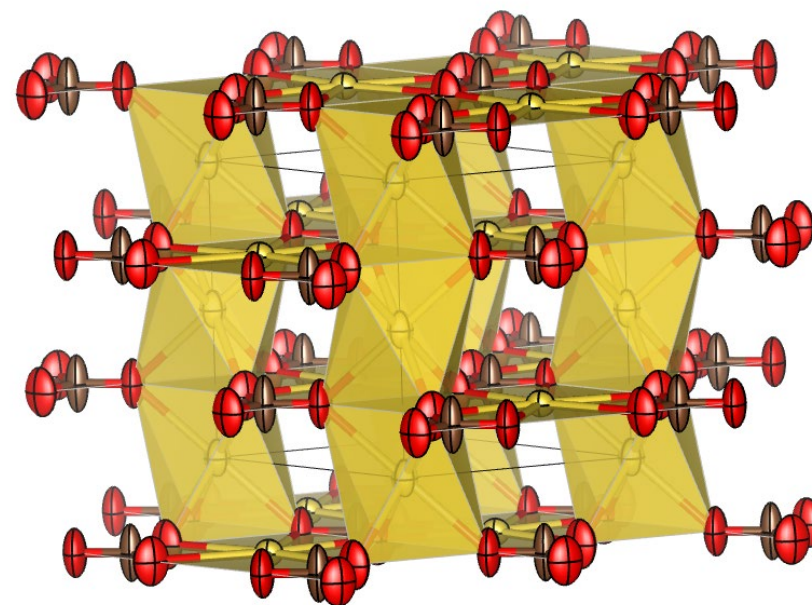


gamma, incommensurate (1 GPa)



Beta-phase
(1.5 GPa, 600 °C)

8.9839 (16) 5.2359 (4) 6.262 (9)
 90.0 97.88 (5) 90.0
 $V = 291.8 (4)$



alpha-phase
2 GPa – 800 °C

5.2130 (5) 5.2130 (5) 6.437 (6)
 90.0 90.0 120.0
 $V = 151.49 (16)$