2017 National School on Neutron and X-Ray Scattering

x-ray and neutron scattering & High Pressure Science

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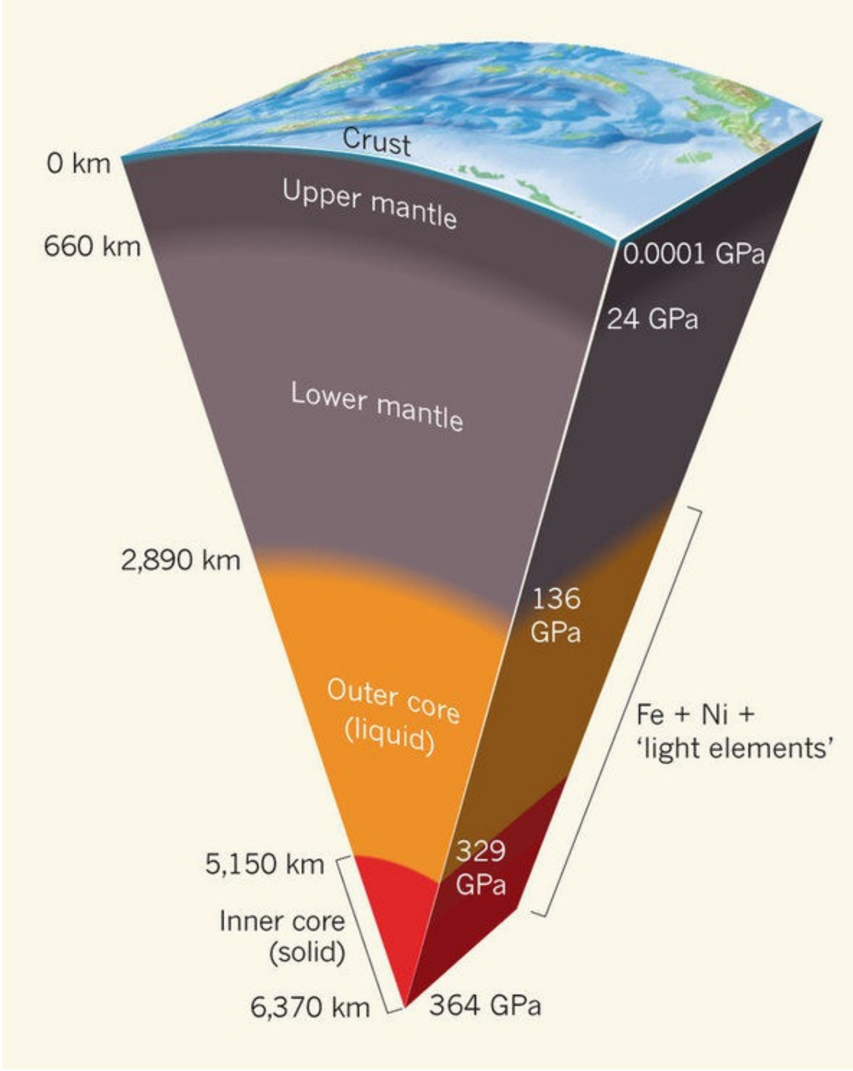
Outline

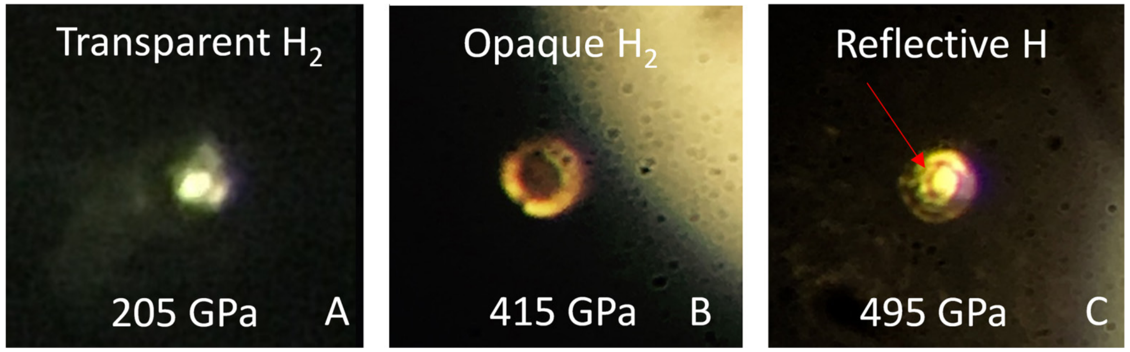
- high-pressure in the Universe
- significance of high-pressure research
- overview of pressure-generating devices
- high-pressure experiments and brilliance
- a very exotic world: some recent scientific highlights
- challenges of non-ambient experiments
- monochromatic high-pressure micro-diffraction and micro diffraction mapping of heterogenous samples: an example of problems and solutions in high pressure experiments

Pressure in the universe

- 10^{-17} Pa, intergalactic voids
- ~10^{-7} Pa, APS storage ring
- ~ 5 GPa graphite turns to diamond
- ~ 10 GPa, at ambient T, He, H, Ne are solids
- ~360 GPa Earth's center
- 500 GPa, hydrogen becomes a stiff metal
- 10^{13} Pa Jupiter interior
- 10^{16} Pa Sun's core
- 10^{34} Pa inside neutron star



Duffy, Nature, 2011



Metallic hydrogen
Dias & Silvera, Science, 2017

Geo & planetary science

The composition, structure and evolution of the environment we live in depends on processes occurring deep inside the Earth. For instance,

- the atmosphere and the oceans (at least in part) were originated from the planet outgassing;
- ores formation in most cases occur at some depths;
- volcanoes and earthquakes can originate at great depths.

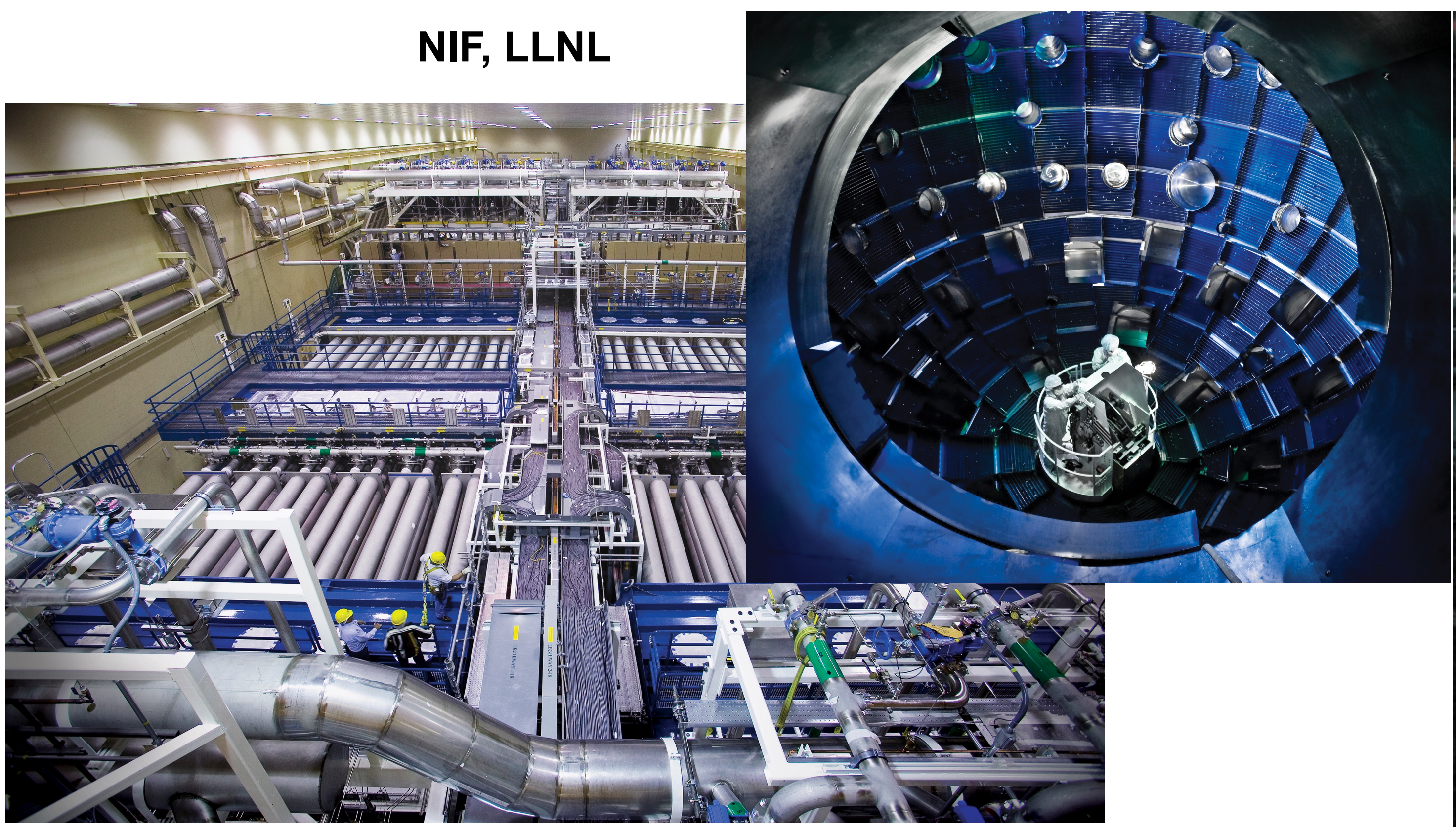
Large and small impacts are critical to planets formation and history.

Extraterrestrial planets differ in whole composition and size but also in differentiation history. In order to understand their nature we must learn what phases might constitute their interiors.

National Security

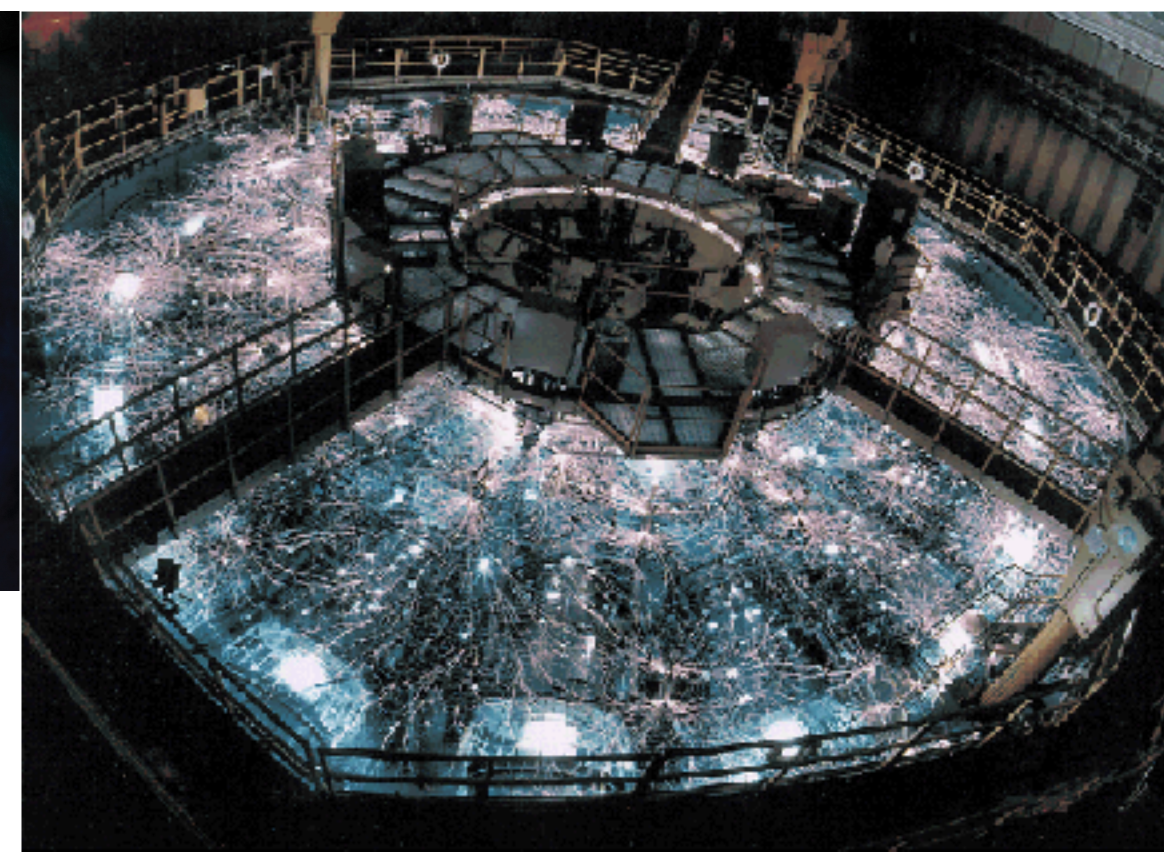
- “As a core part of the NNSA’s advanced science and technology portfolio, the Office of ICF is working to produce thermonuclear burn conditions in the laboratory, to develop laboratory capabilities that will create and measure extreme conditions of temperature, pressure, and radiation of relevance to nuclear weapons, and to conduct weapons-related research in these environments.” (nnsa.energy.gov)
- NNSA supports large scale facilities where high-pressure research is being conducted and scientific opportunities are available.

NIF, LLNL



NIF’s 192 laser beams routinely creating temperatures and pressures similar to those that exist only in the cores of stars and giant planets and inside nuclear weapons.https://lasers.llnl.gov/about

Z-pinch machine, SNL



Z has so much energy that it can melt diamond, and in melting diamond to a puddle, Z scientists have been able to understand the material’s various states – from solid to liquid, with a mixed state in-between.
http://www.sandia.gov/z-machine/

Material science

Pressure is a powerful tool to change properties and design materials. Areas of research include:

- superhard materials,
- superconductors & other materials with interesting electronic properties,
- high-energy-density materials and hydrogen storage,
- nuclear waste storage.

Biology and medicine

- pressure aided synthesis of pharmaceuticals
- food preservation
- life at high pressure

Fundamental Physics & Chemistry

Understanding the behavior of matter at extreme conditions broadens and deepens our fundamental physics and chemistry knowledge. By applying pressure we can add extremely high energy to a system, dramatically affecting all physical and chemical properties. High pressure studies include:

- equilibrium phase diagrams and metastability,
- deformation (from atomic scale to bulk) in hydrostatic and non-hydrostatic conditions,
- electrical and magnetic properties,
- bonding and chemistry at extremes conditions.

High Pressure generation: common devices

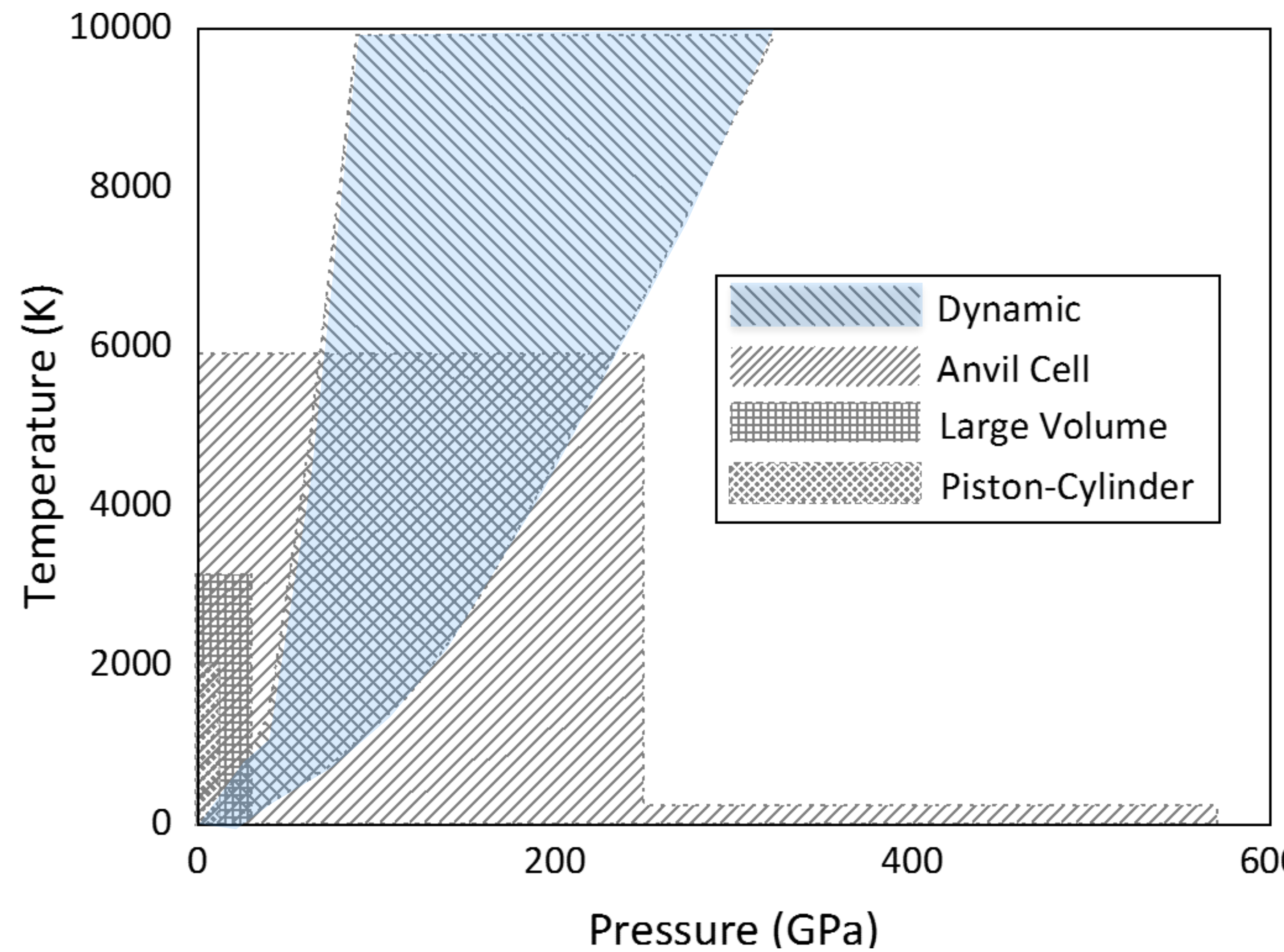
Static

- the diamond anvil cell, with 50+ years of history is by far the most common device
- large volume presses
- Paris-Edinburg cells

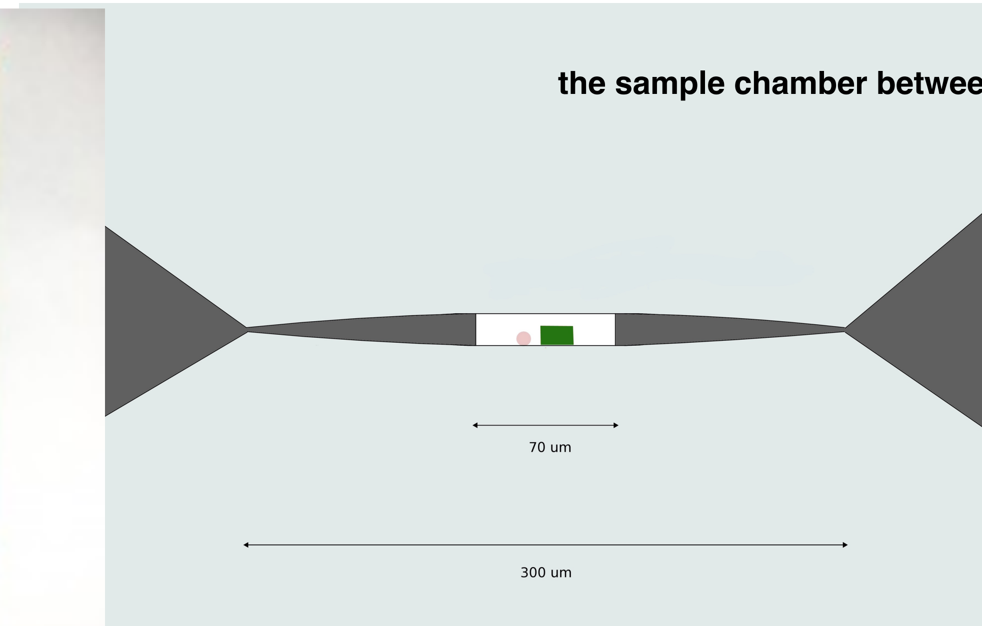
Dynamic

- gas guns, powder guns
- laser shock

Recio et al. 2016



The diamond anvil cell



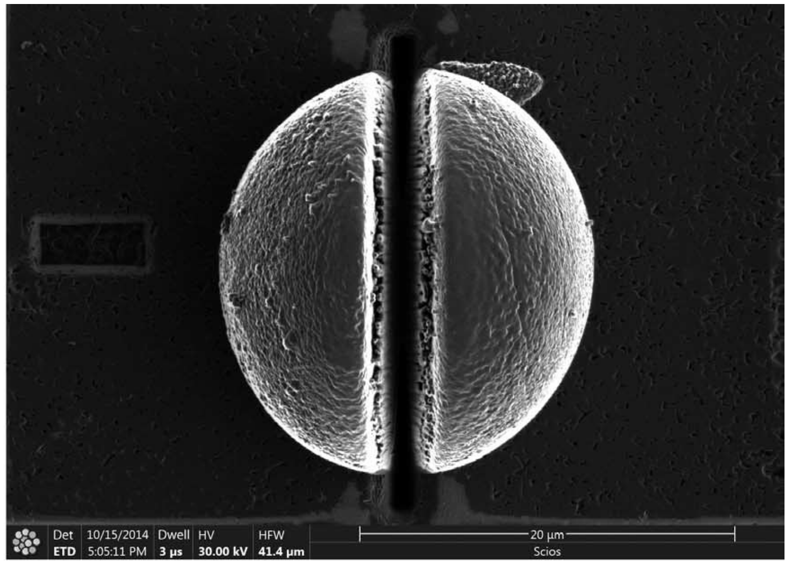
The DAC is a small device that can generate pressures up to 1000 GPa.

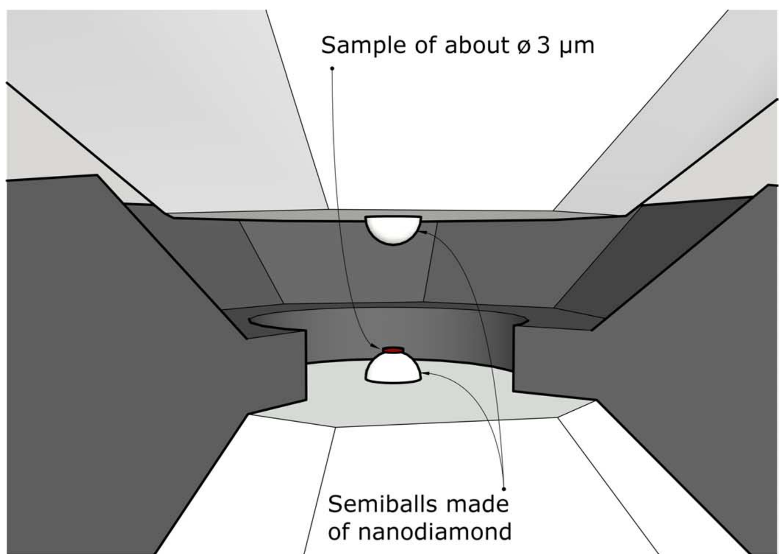
Temperatures range from few degrees K to several thousands degrees K

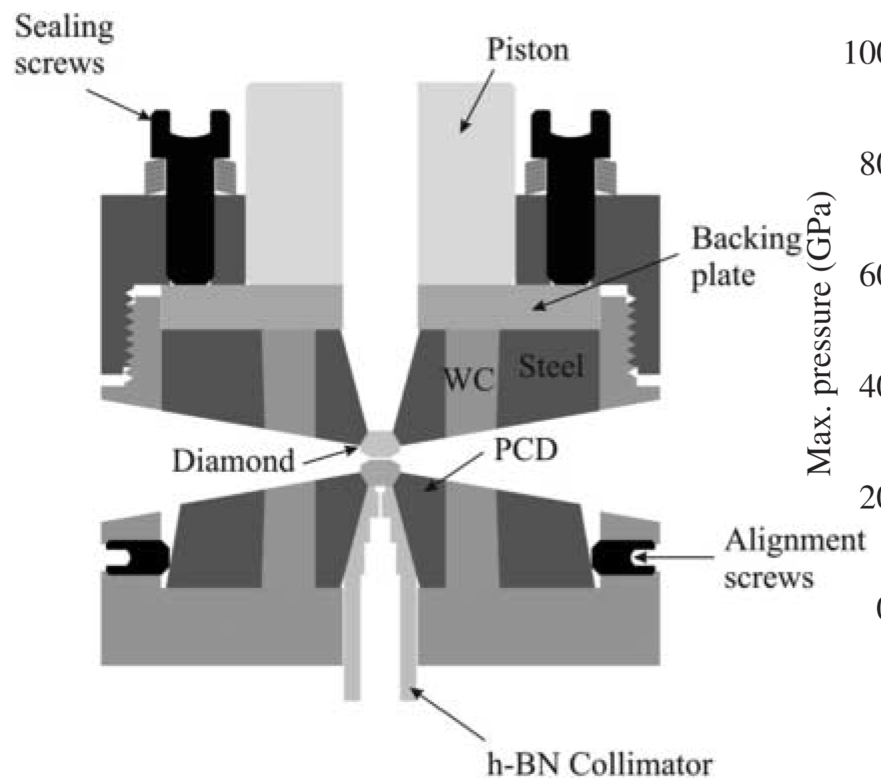
It is the most versatile instrument, with a range of designs that better suite experimental conditions and probing techniques.

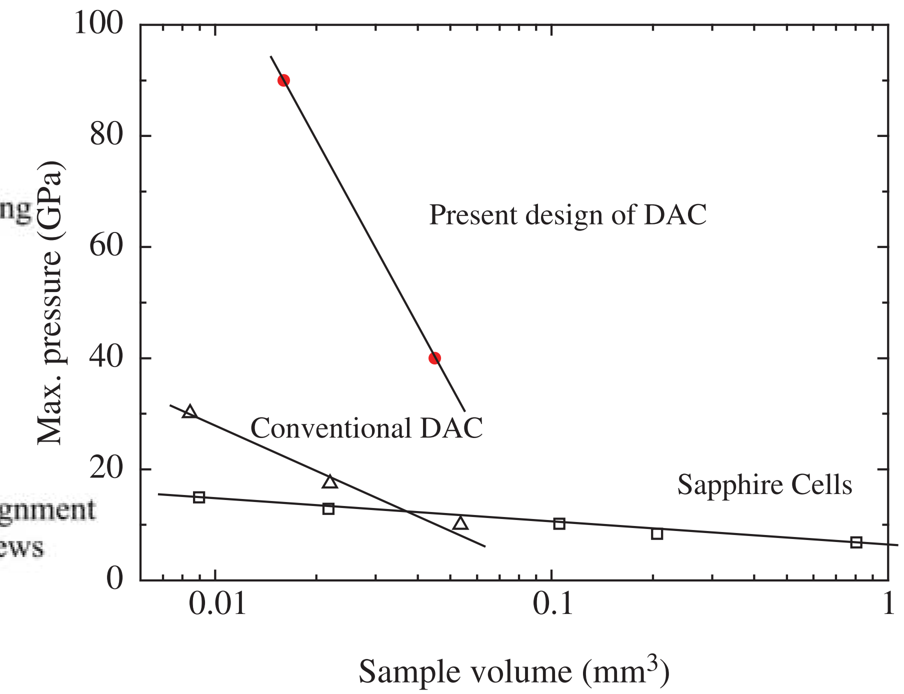
Several techniques are compatible exclusively with DACs.

The diamond anvil cell, recent breakthroughs









Record pressures were achieved by using a second stage nano diamond semi balls between two diamond anvils.
Dubrovinskaya et al, Sci. Adv., 2016

Much increased sample volume in DACs were developed for neutron experiments.

Boehler et al. High Pressure Res., 2013

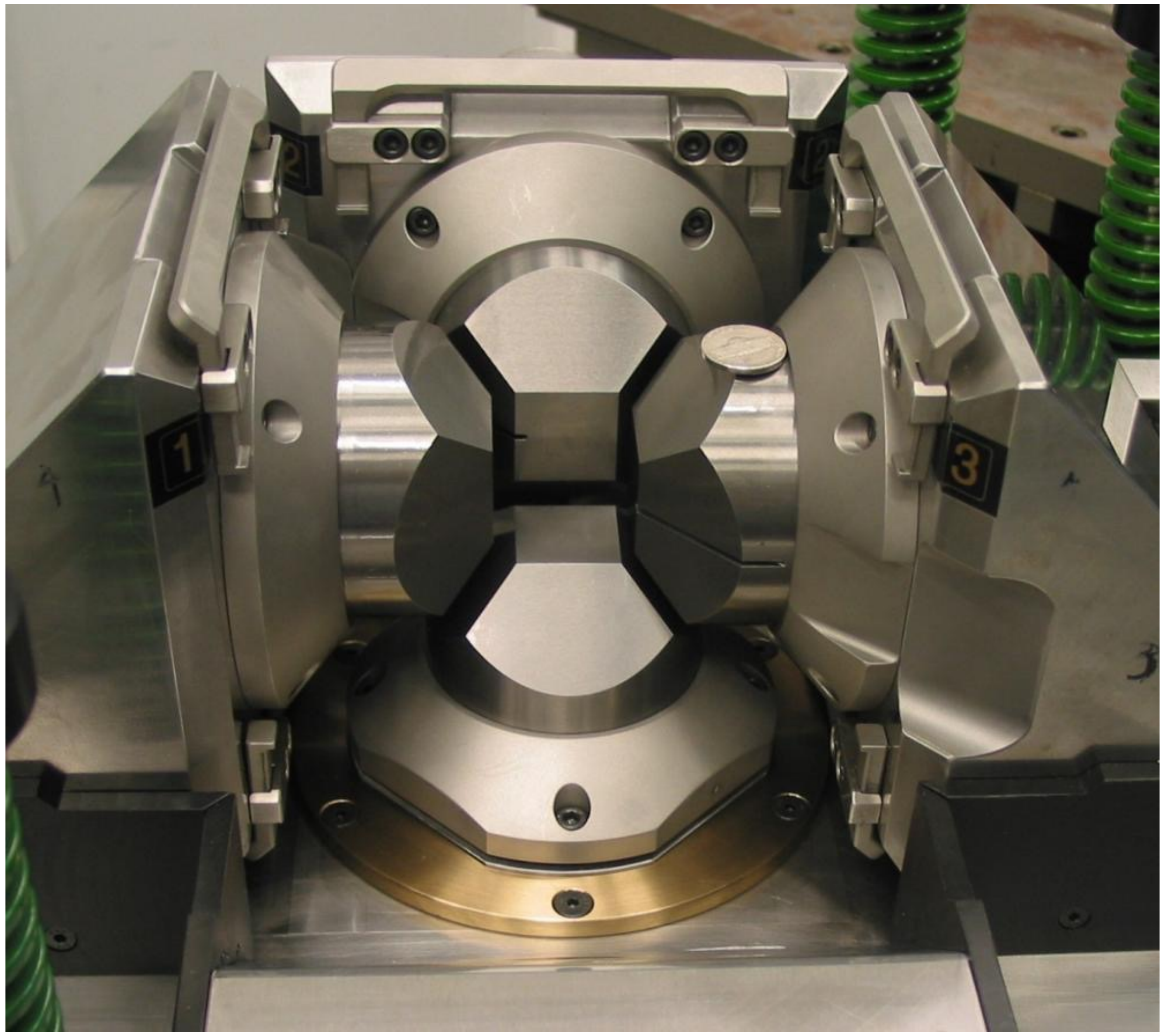
The multianvil press

These large devices can generate pressures of up to ~ 100 GPa.

Temperatures range from ambient to ~2000 K.

The sample is typically few mm large.

These presses are very suitable to high P-T studies, deformation of polycrystalline samples, synthesis of recoverable phases and studies of multiphase materials.

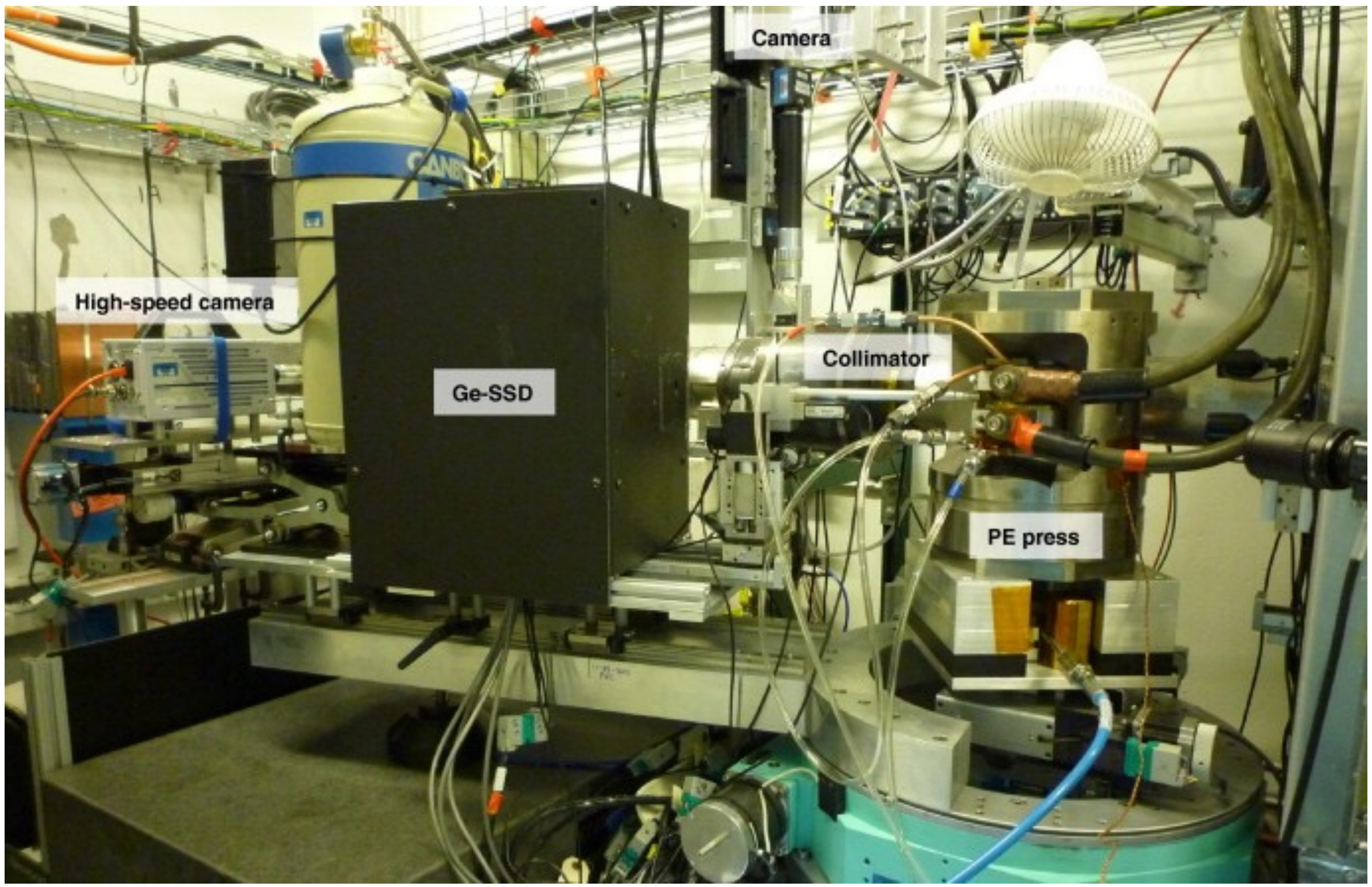


Multianvil press, GSECARS, APS

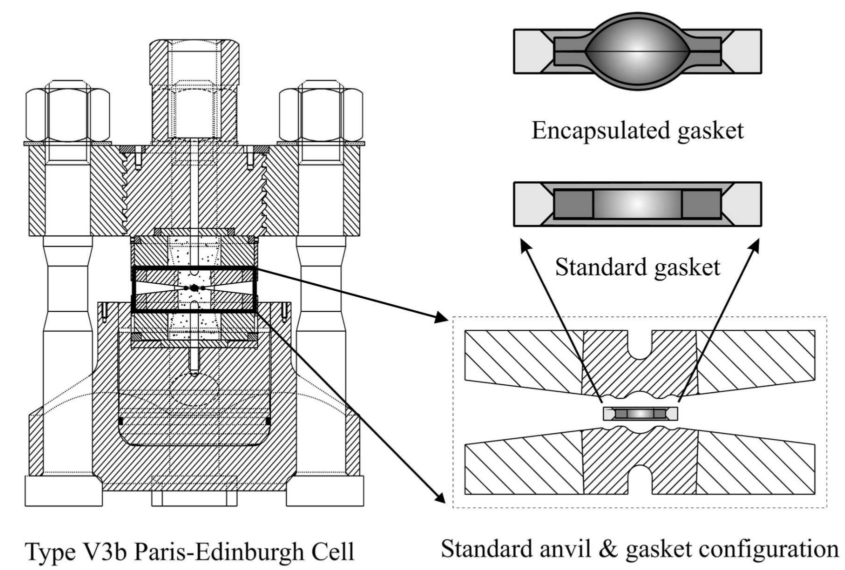
Paris-Edinburgh cell

The Paris-Edinburgh cell is the most common highP device at neutron sources as it provides relatively large samples in a relatively small device.

Max P ~ 40 GPa, max T ~ 2000 K



HPCAT, APS



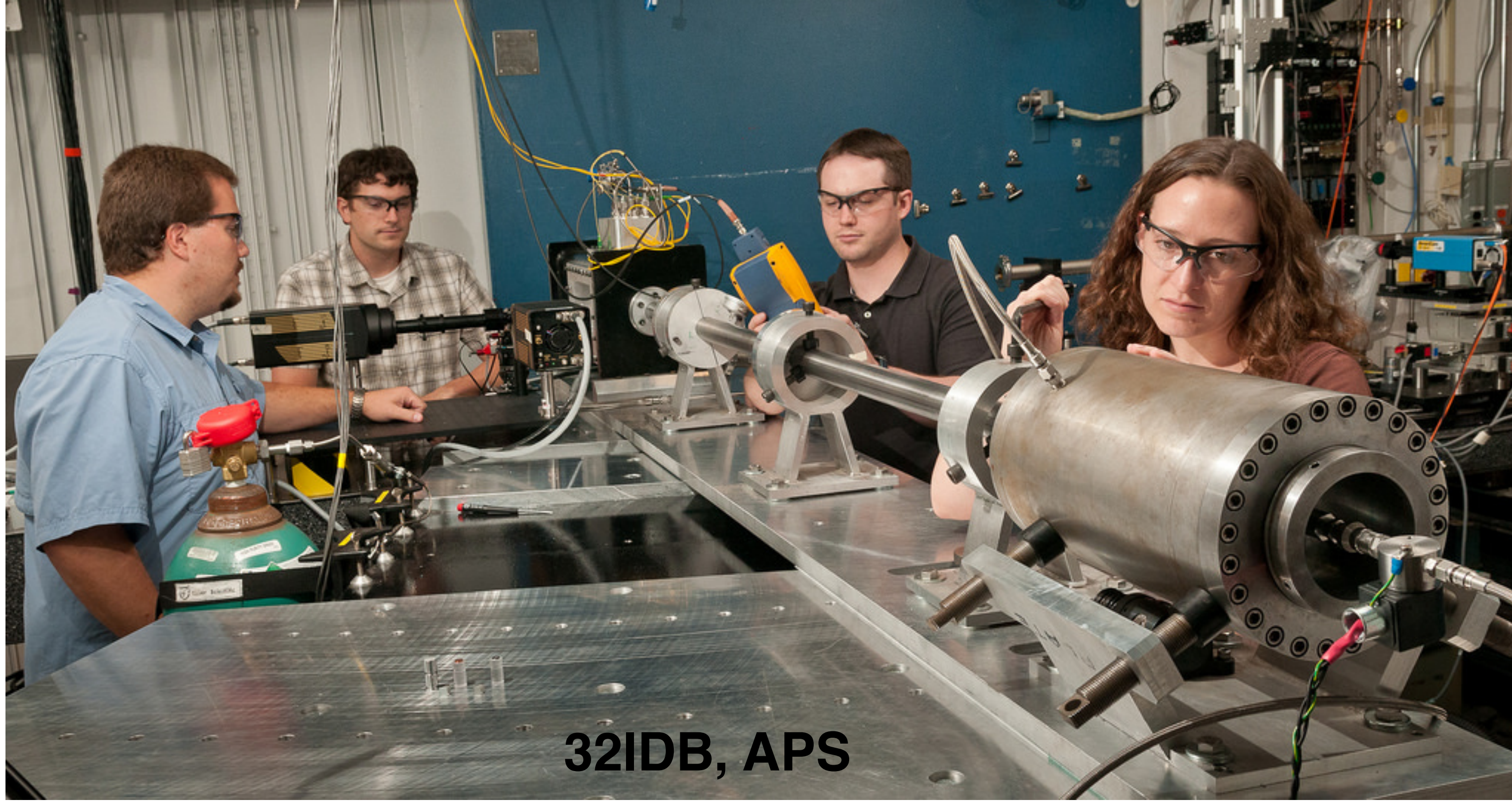
Marshall & Francis, J. Appl. Cryst.,2001

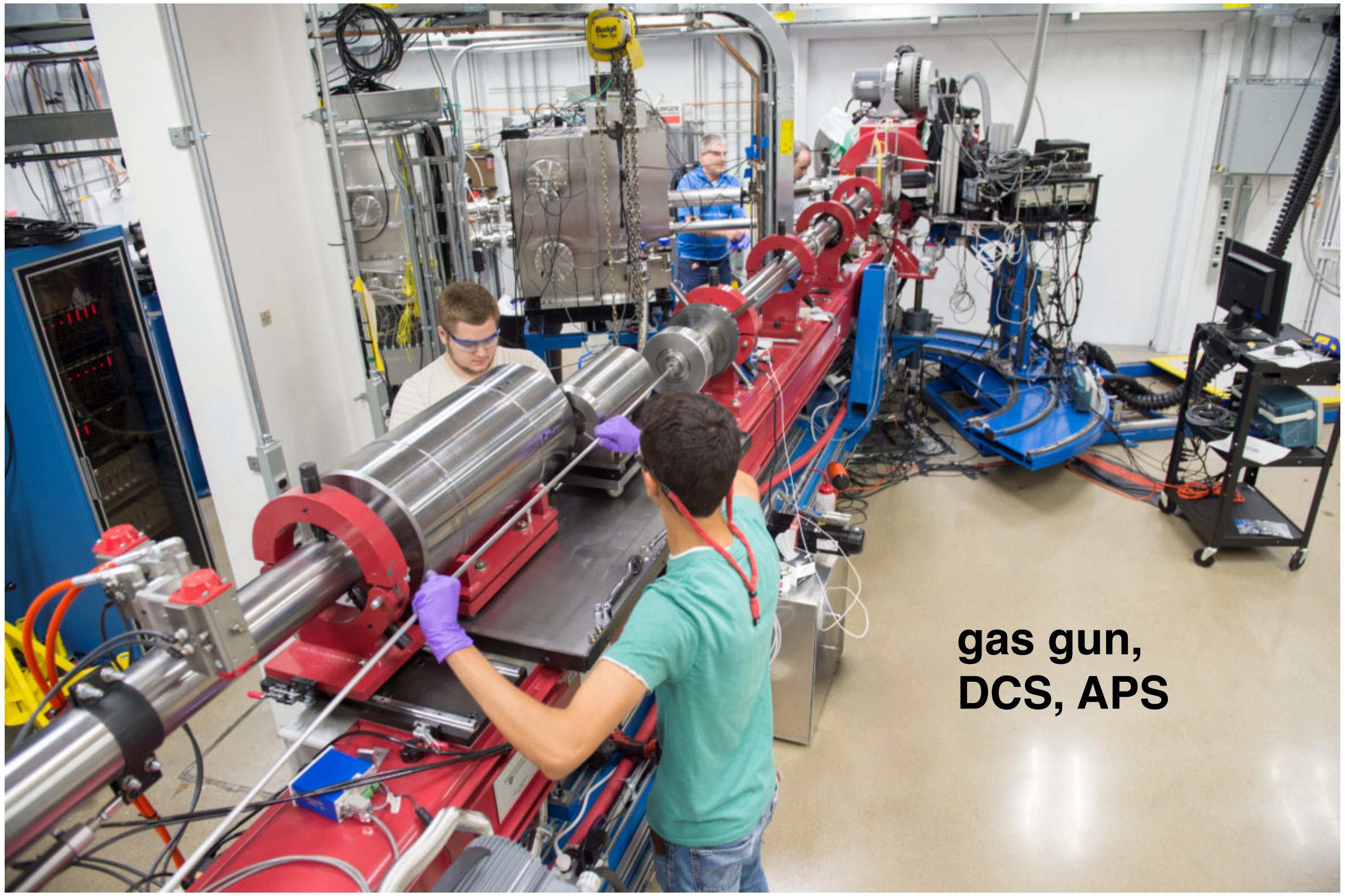
https://neutrons.ornl.gov/snap/sample

Shock compression

Shock compression can achieve the highest P-T conditions

Samples are relatively large but very short-lived





Both guns and laser driven shock devices will be available at the APS, allowing for a broad range of pressure, temperature and strain rate to be achieved.

High pressure & brilliant radiation

Samples under high pressure are:

- very small and/or,
- enclosed in bulky devices, access to samples is limited to semitransparent windows,
- in some case very short lived,
- often very **complex** (pressure gradients, multiphase, poorly crystallized)

High pressure & brilliant radiation

In addition to the general advantage of brilliant source, probing high-pressure samples in situ requires

- **high flux** for the beam to penetrate the device and for scattered radiation to travel out, obtain a reasonable signal from small samples or to collect data in short time,
- **highly focused** beam in order to reduce parasitic scattering,
- **tunable energy** allowing to play with the absorption of device components and optimize resolution (diffraction).

At high pressure you need all the brilliance you can get!!

High Pressure at the APS

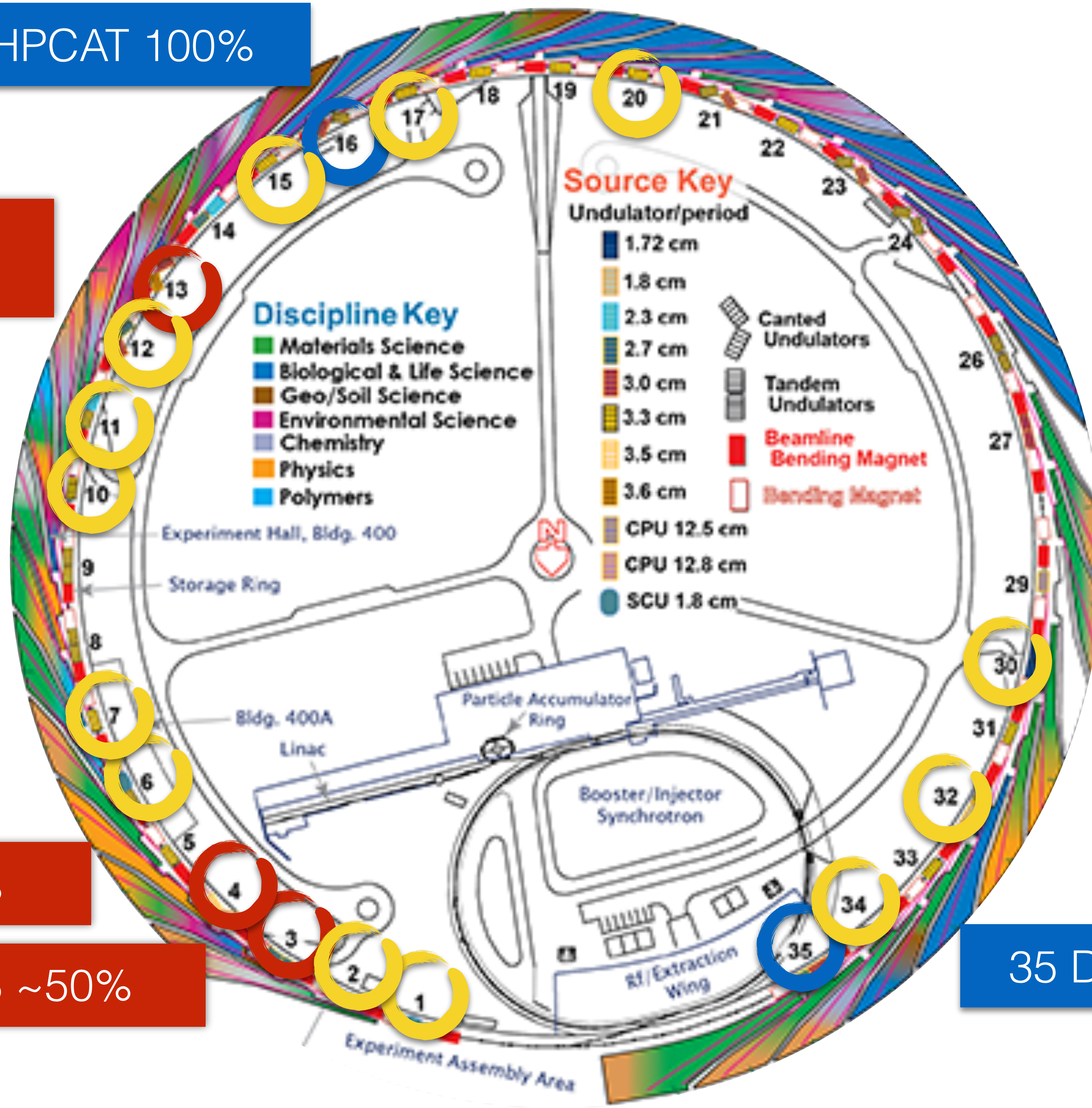
16 HPCAT 100%

13 GSECARS > 50%

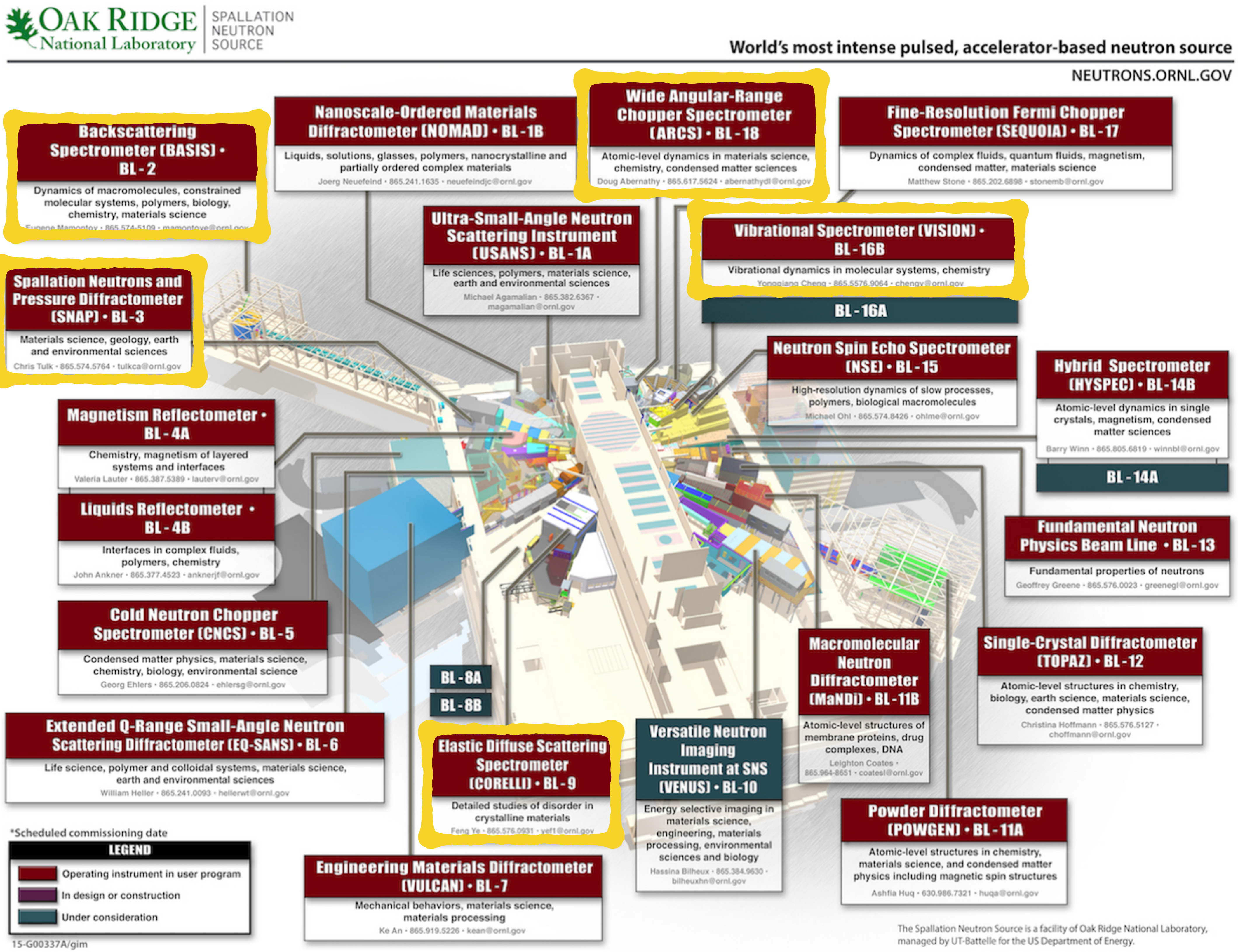
4 40%

3 ~50%

35 DCS 100%



100%
BL3-SNAP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In design or construction
Under consideration
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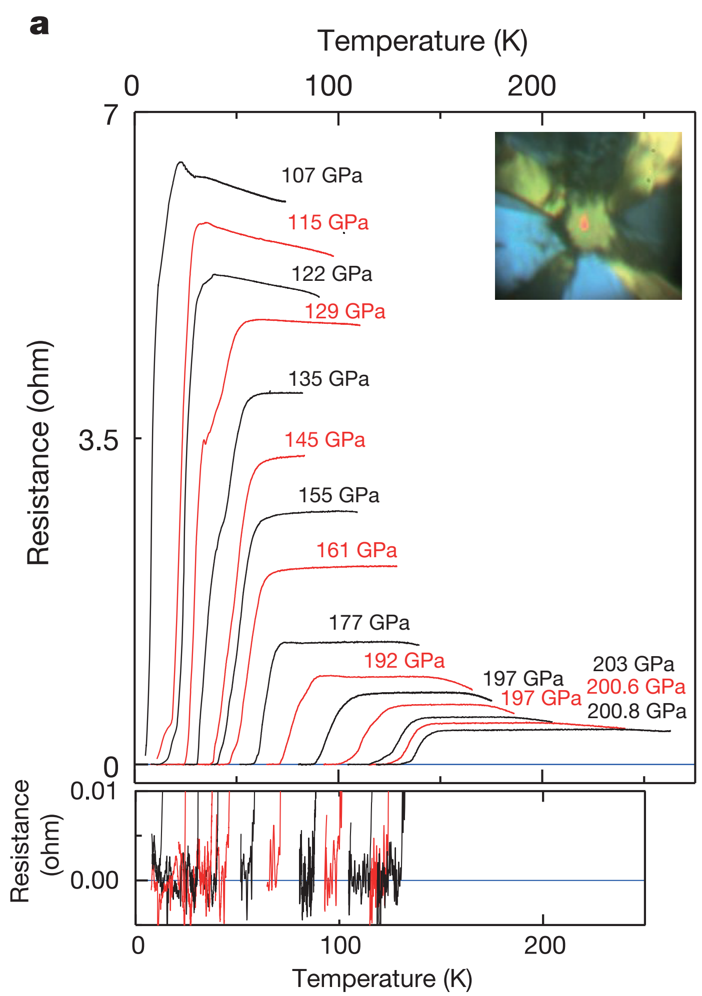
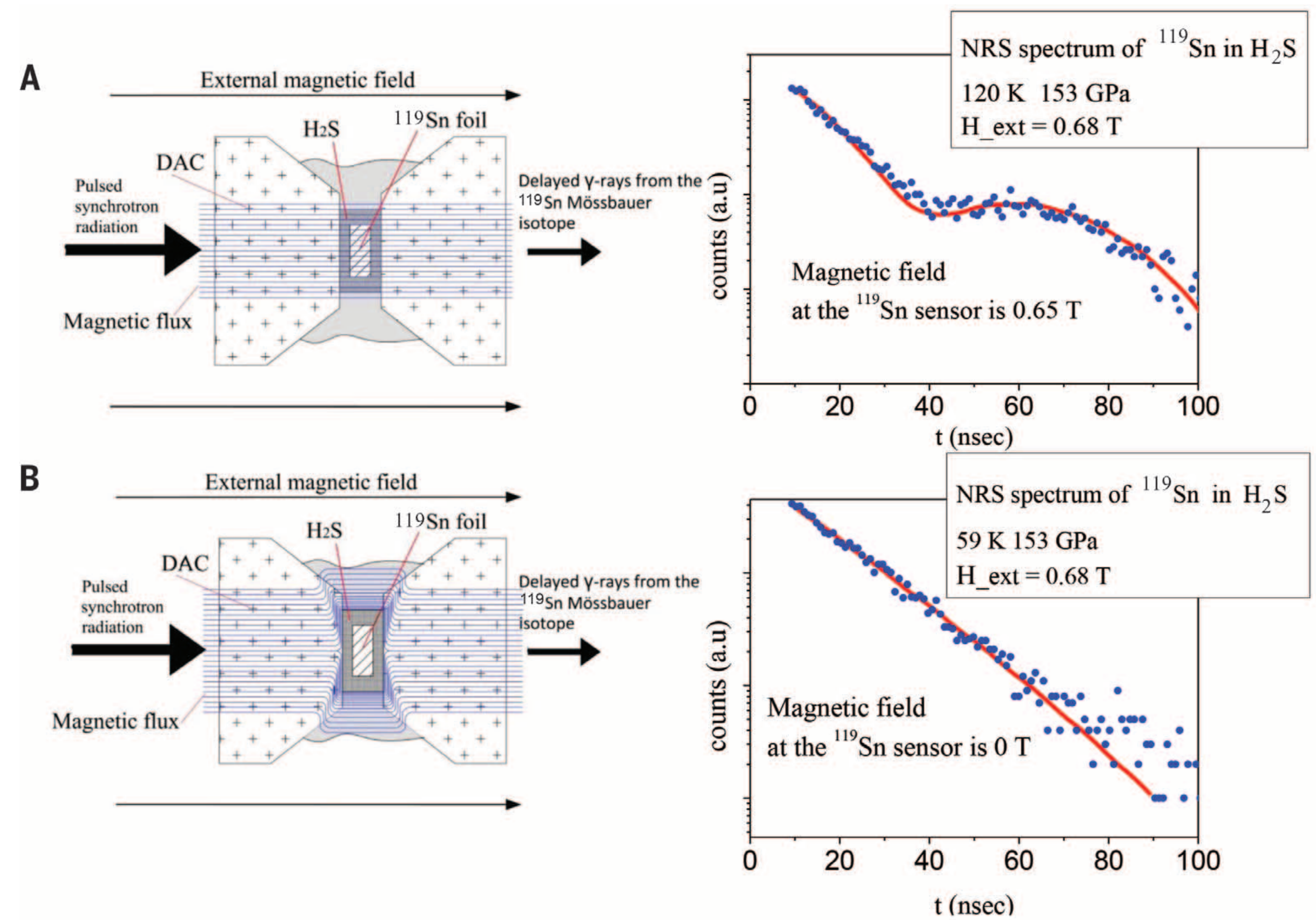
superconductivity



nuclear resonant scattering



The highest T superconductivity was measured at ~ 200 GPa in hydrogen sulphide

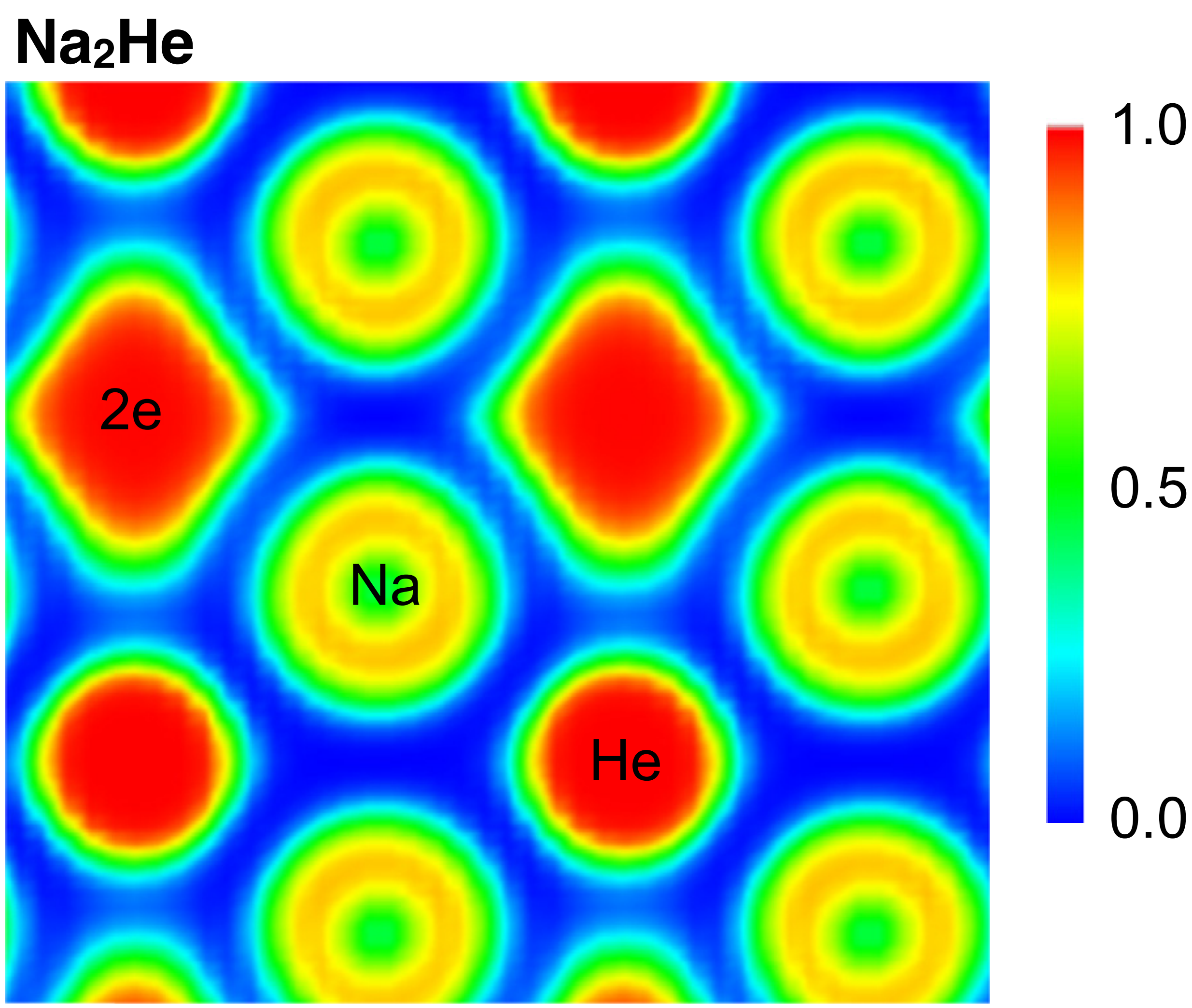
Drozdov et al., Nature, 2015

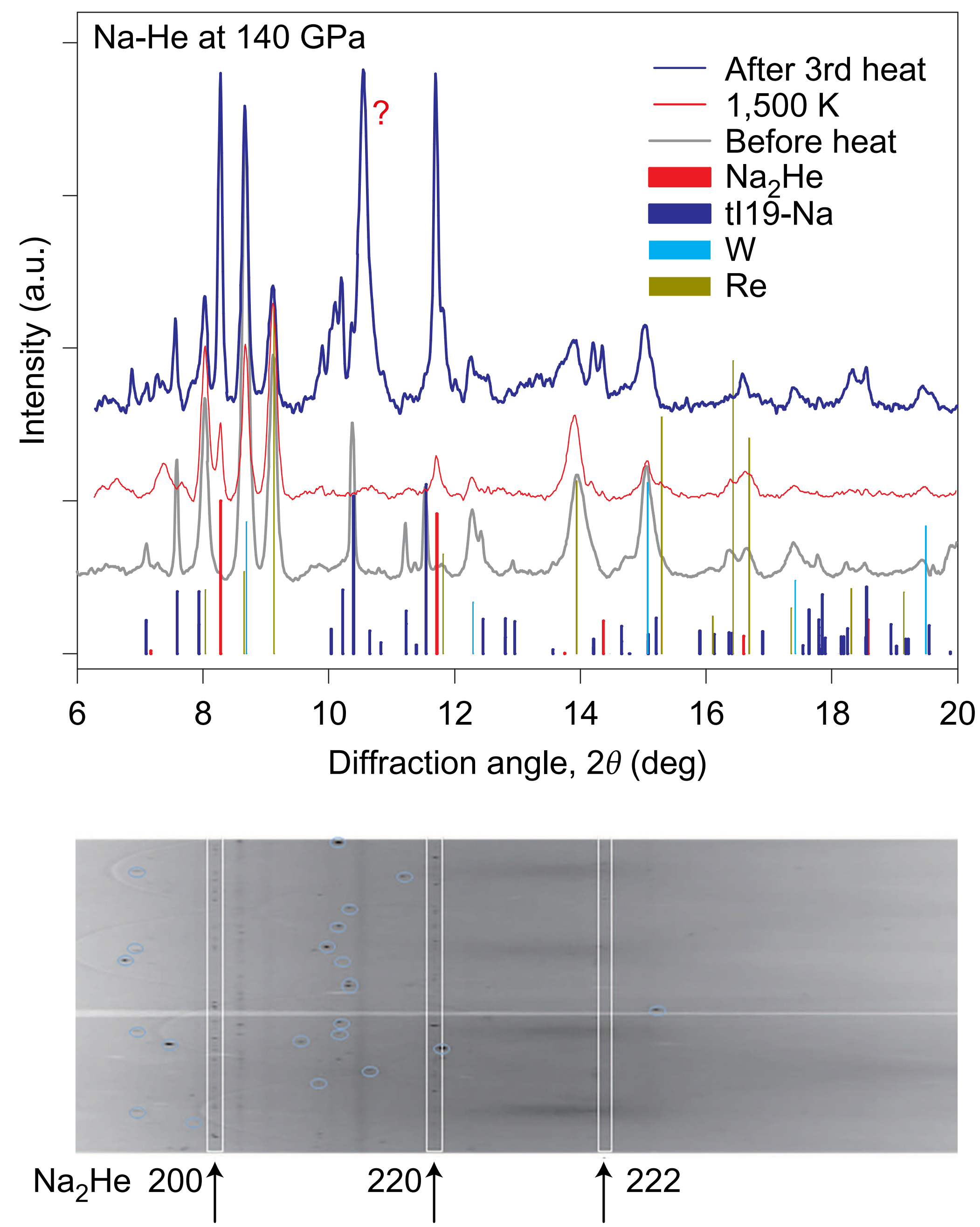
The finding was later further confirmed via nuclear resonant scattering

Trojan et al., Science, 2016

Noble chemistry & electride

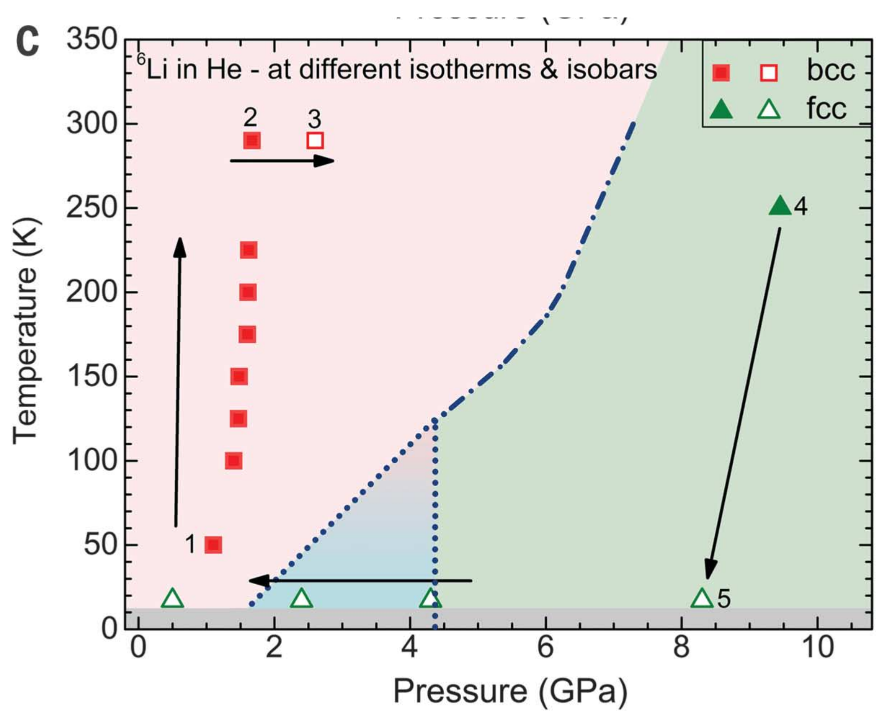
powder x-ray diffraction



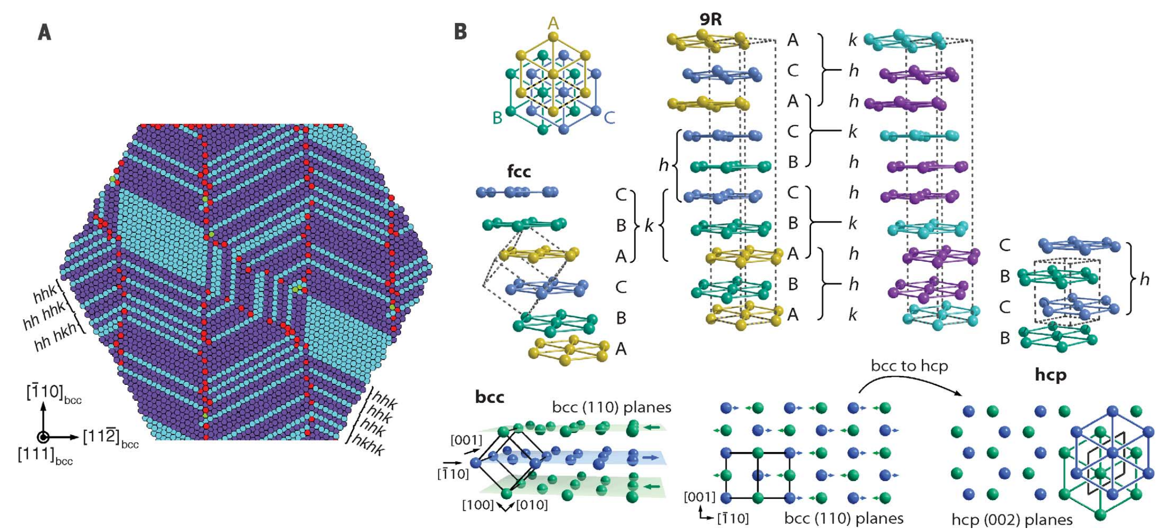


Prediction and synthesis of a stable compound of helium and sodium at high pressure.
Dong et al., Nature Chemistry, 2017

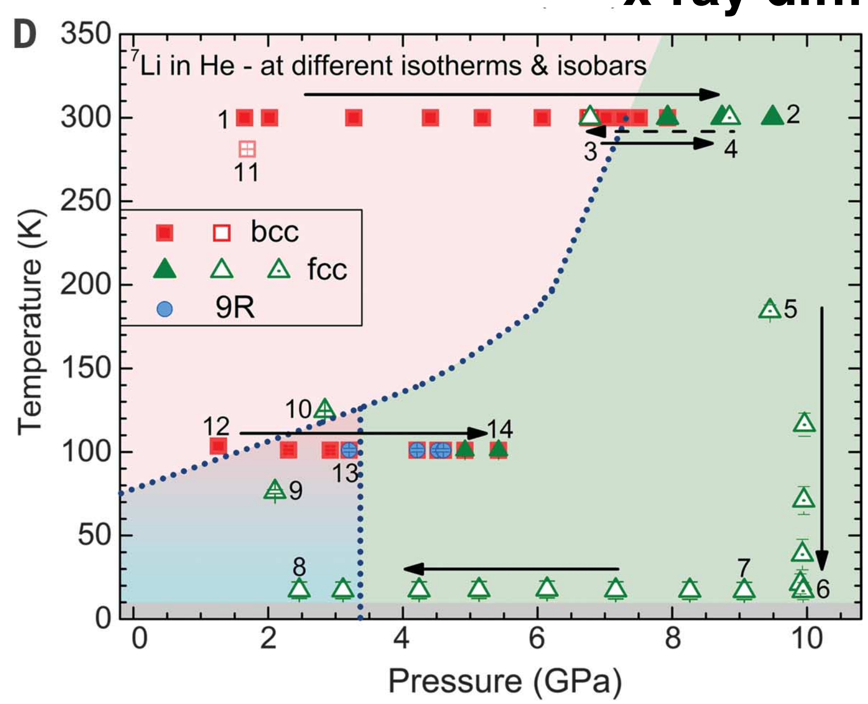
Lithium isotope effect



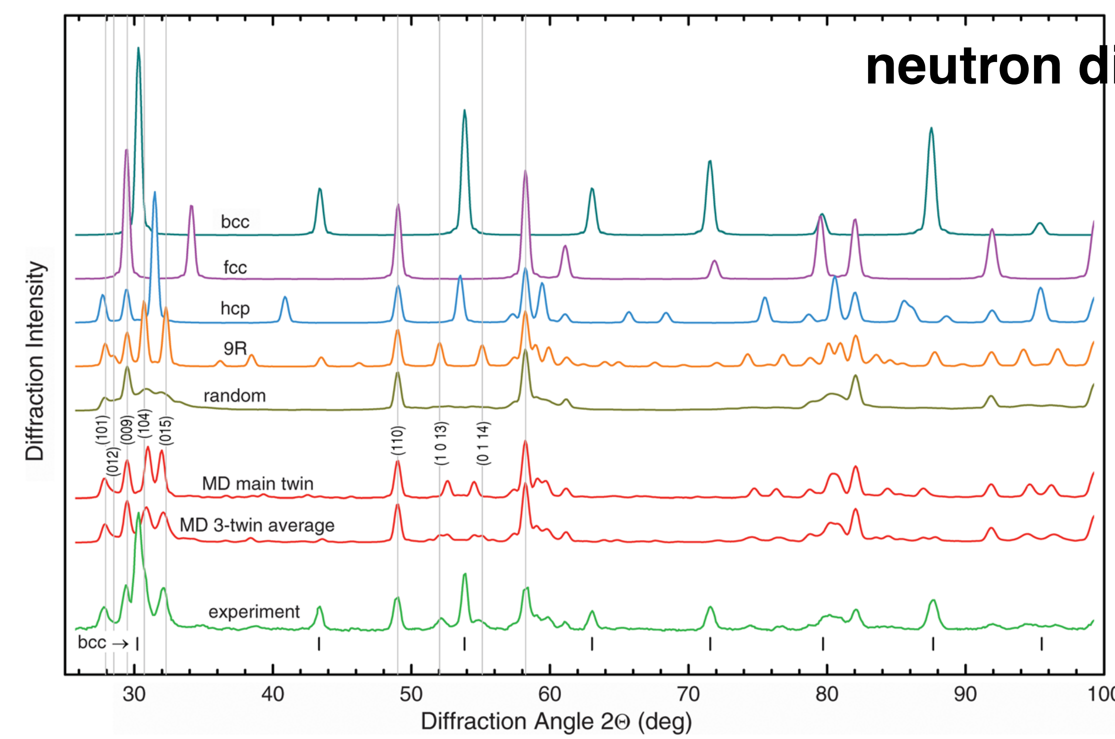
MD calculations



x-ray diffraction



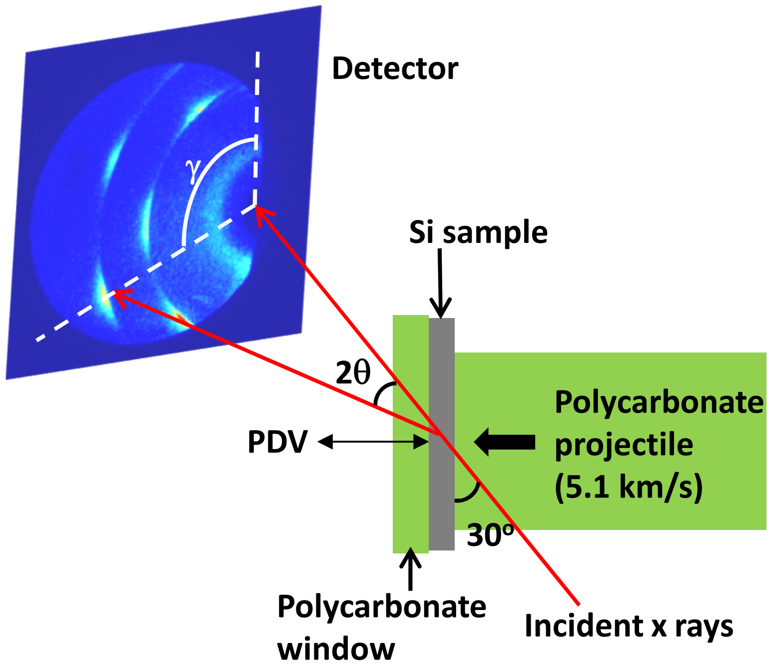
neutron diffraction



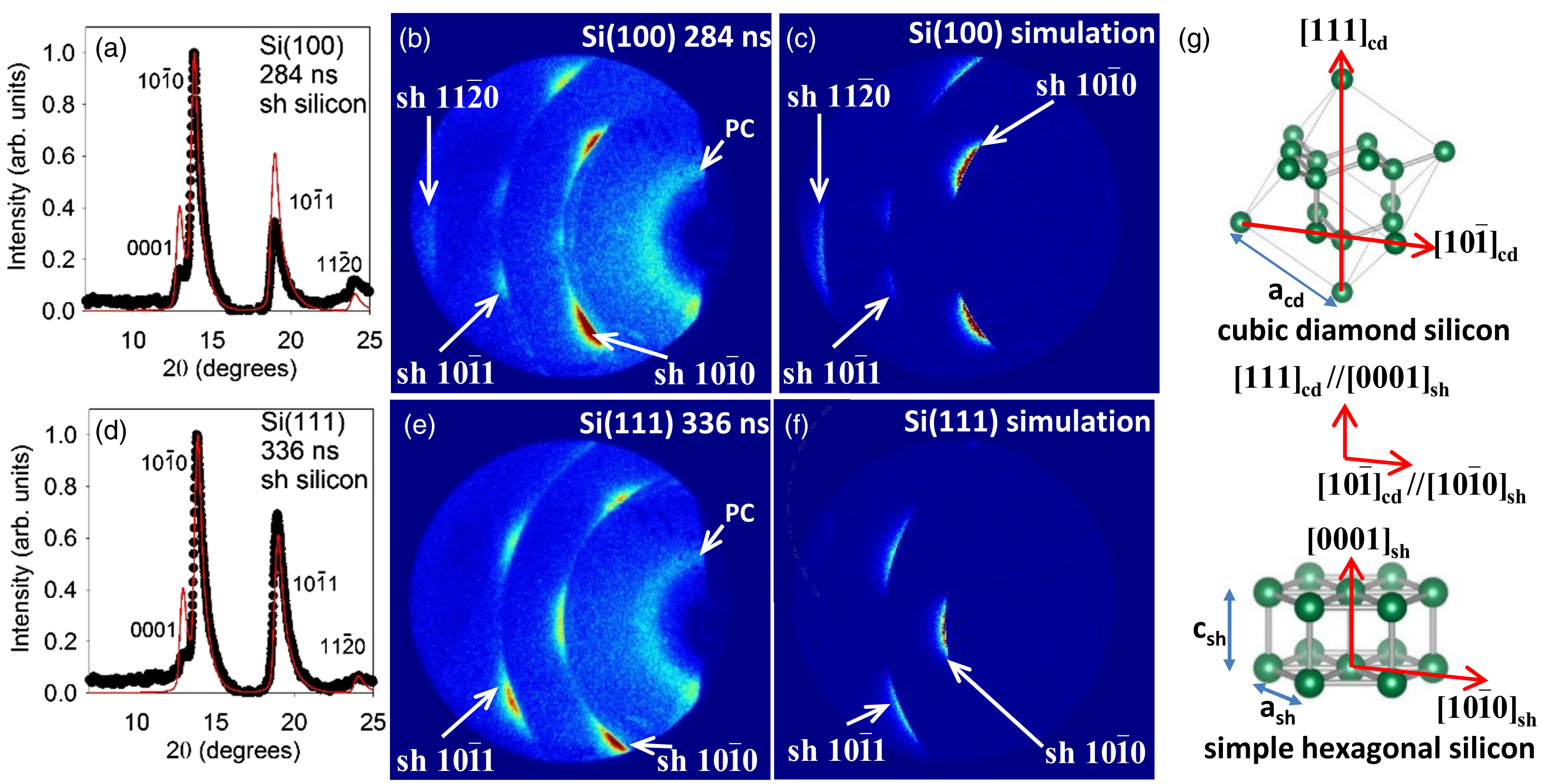
The lightest metal still holds many surprises, even at modest P-T

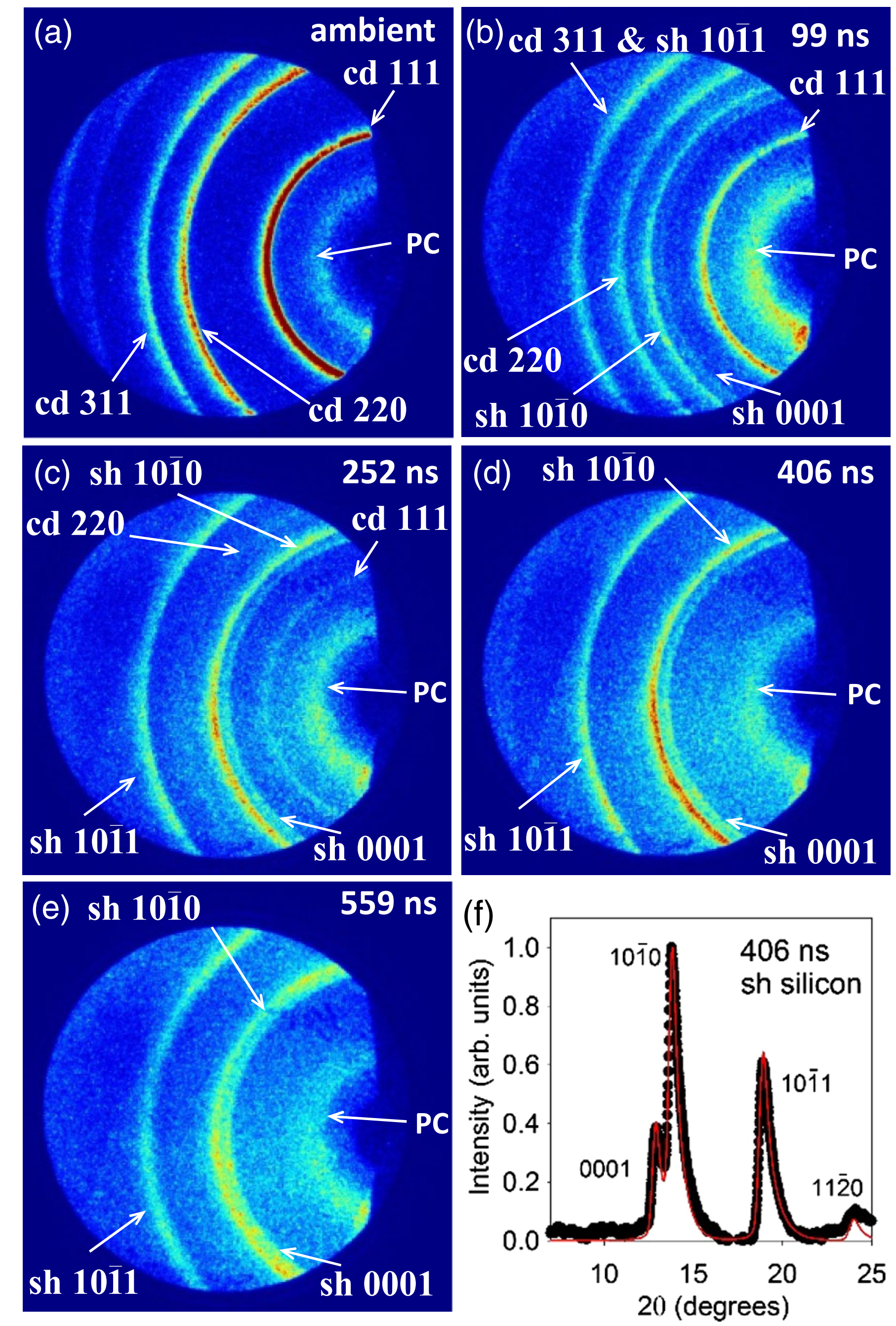
Auckland et al. Science, 2017

Shocked silicon powder and crystals



pink beam diffraction
DCS Sector 35

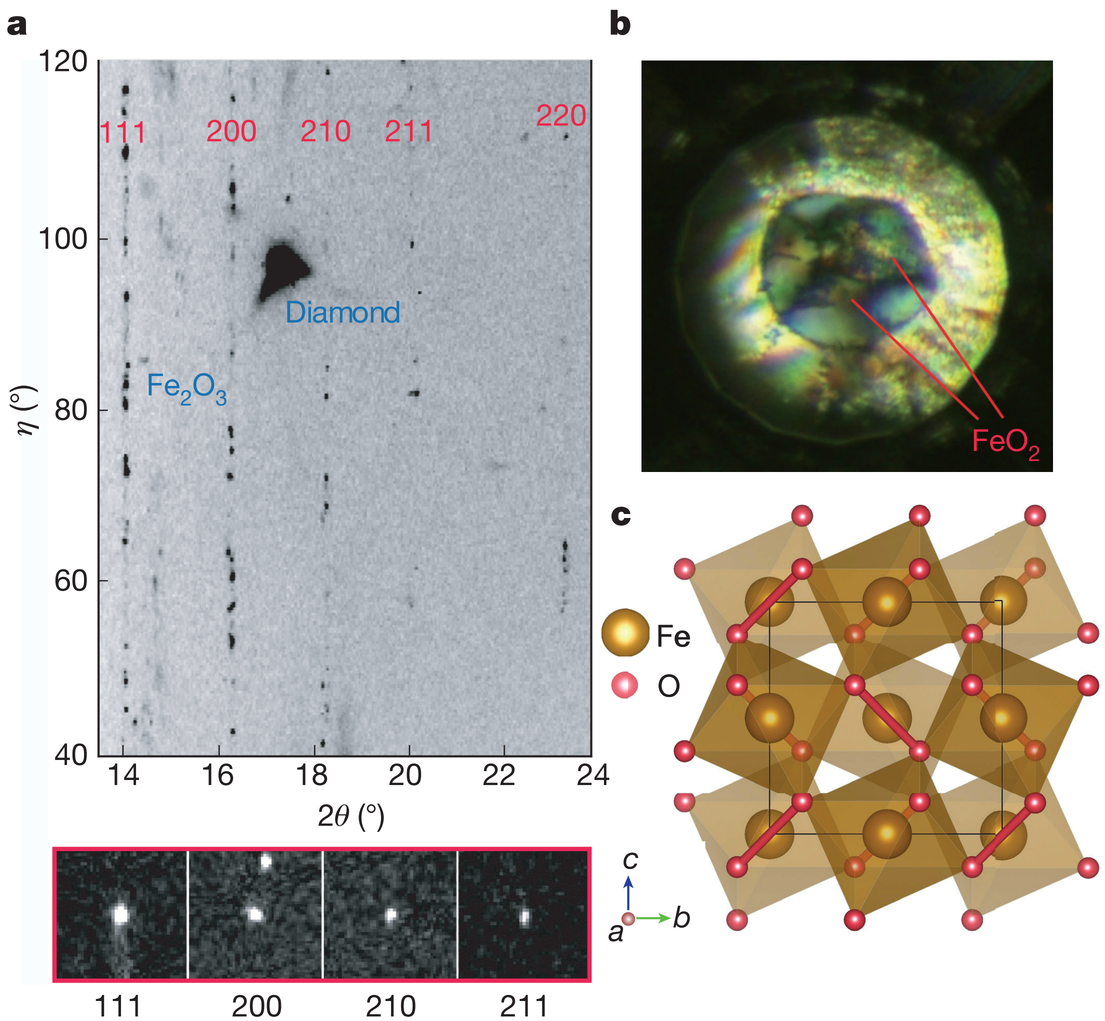




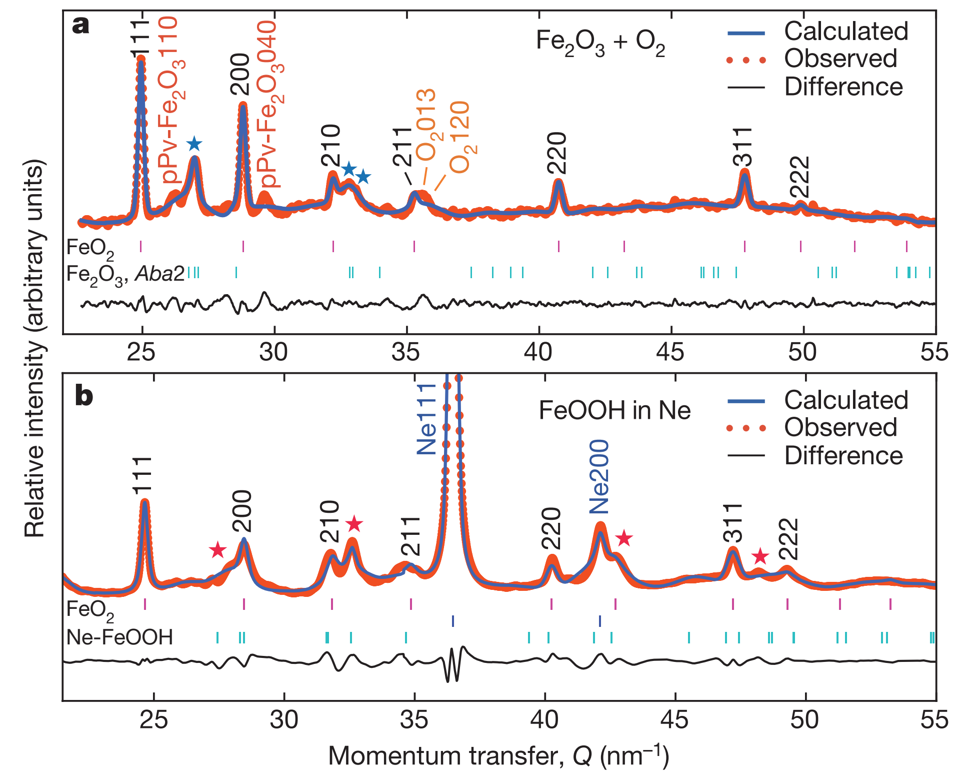
Turneaure et al., PRL 117, 045502, 2016

Time resolved shock compression of silicon allows observing the high-pressure phase at these conditions for the first time and study the reciprocal orientation of the crystals before and during the shock.

Iron oxide, the latest



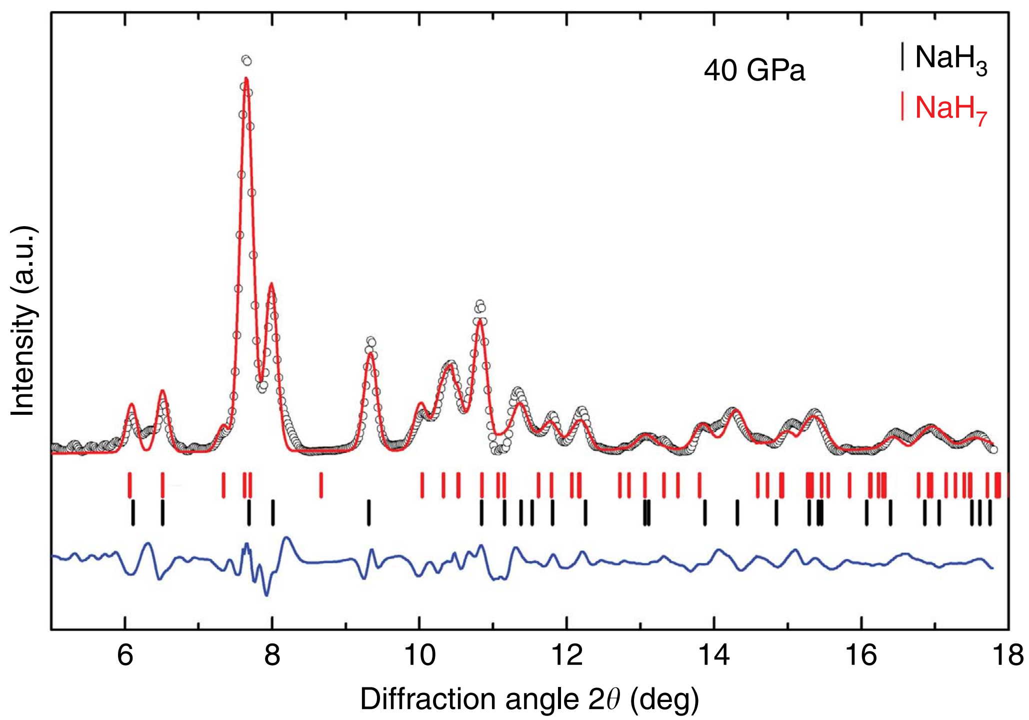
Hu et al., Nature, 2016

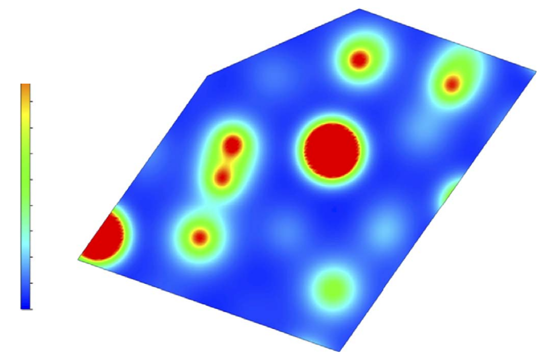


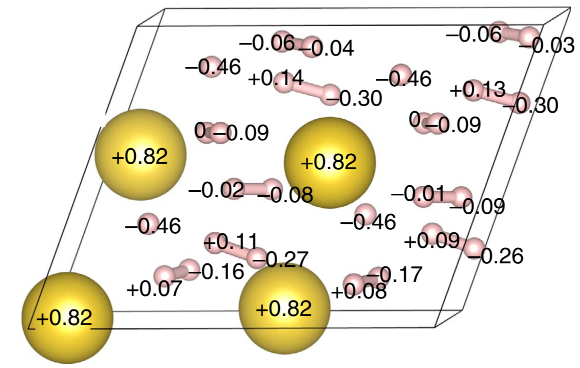
FeO_2 a compound first predicted from first principles calculations to be a plausible deep-Earth phase was obtained experimentally from the breakdown of FeOOH

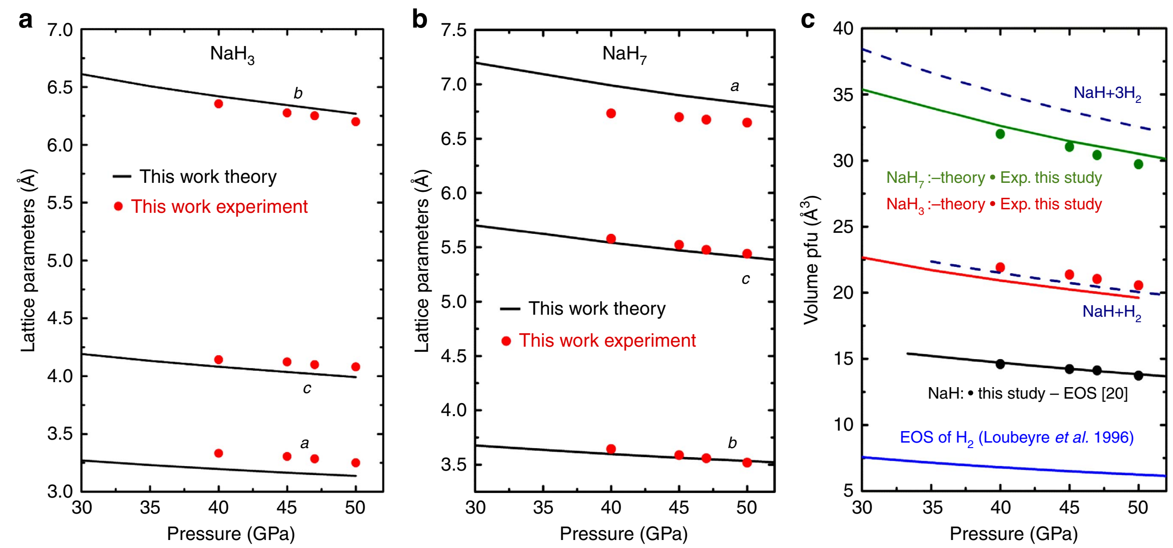
Synthesis of Na-H compounds

x-ray powder diffraction









Struzhkin et al. Nature Communications, 2016

Two hydrogen-rich compounds, NaH_3 and NaH_7 were synthesized at high P-T. The characterization was performed via XRD and Raman analysis in combination with theoretical calculations.

Peculiarities of high-pressure data

Most synchrotron and neutron techniques can be applied to high pressure studies, but in most cases the data quality is decreased and the analysis is not straightforward.

Data are affected by limited access, absorption and scattering of the windows.

Samples might be non ideal in thickness and size, show severe strain range, coexistence of polymorphs and reacted and unreacted material.

- data analysis might require corrections and tailored manipulation,
- often the data interpretation is not unique, hence multiple techniques and theoretical calculations are necessary to solve a problem.

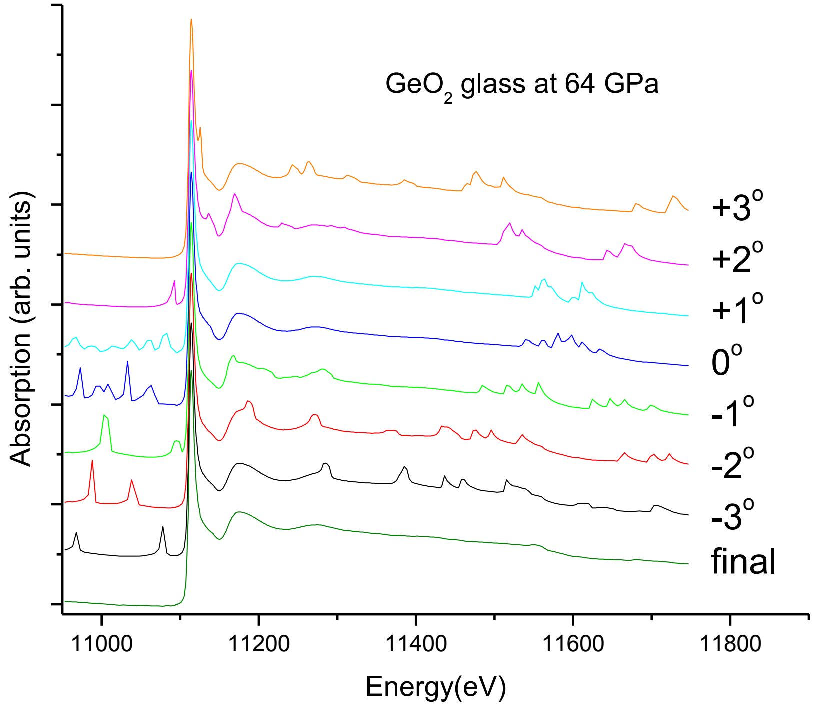
Synchrotron and neutron high-pressure techniques are very rapidly evolving allowing for new and better science to be performed.

This is indeed a very good time for high-pressure science as new experimental opportunities are becoming available!

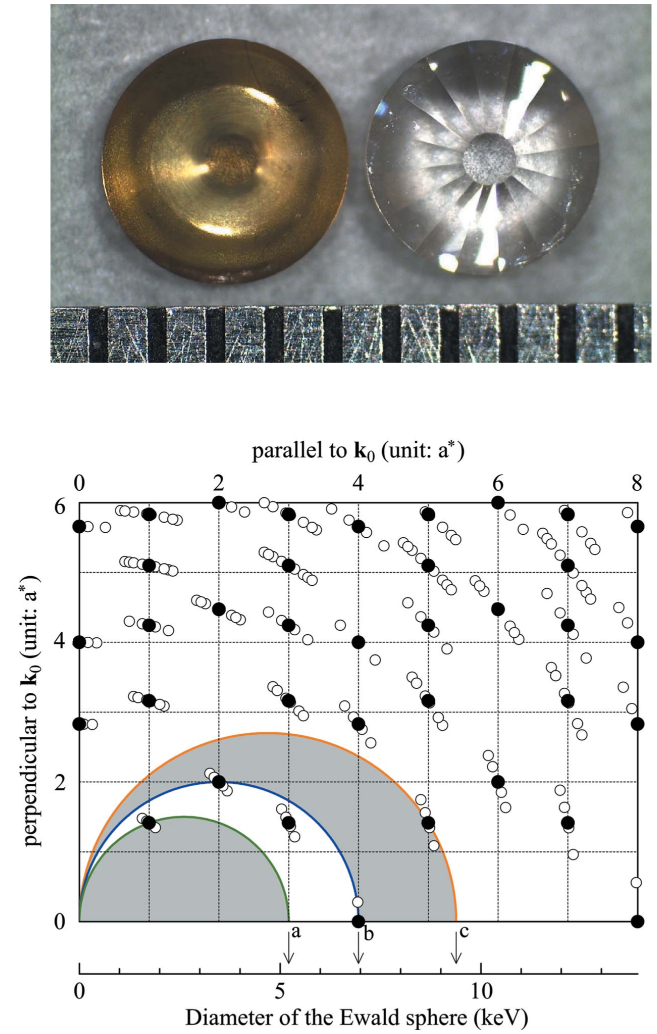
XAFS, challenges of DAC measurements

DAC experiments are performed in different geometries:

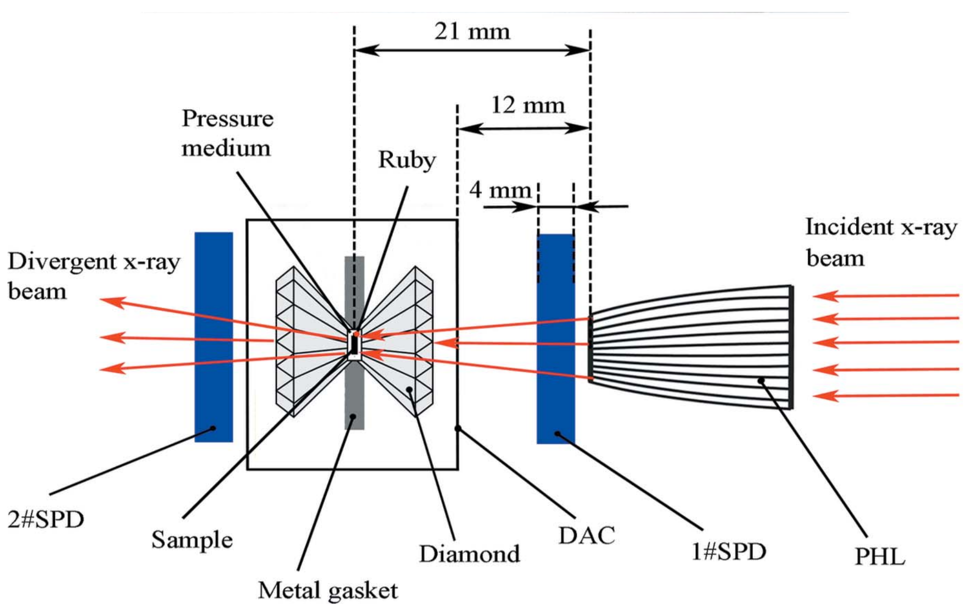
- radial, sample thickness and uniformity are hardly ideal
- axial, glitches appear in the spectra due to diamond diffraction



Glitch removal algorithm
Hong et al., J.Phys.: Conf. Series, 2013

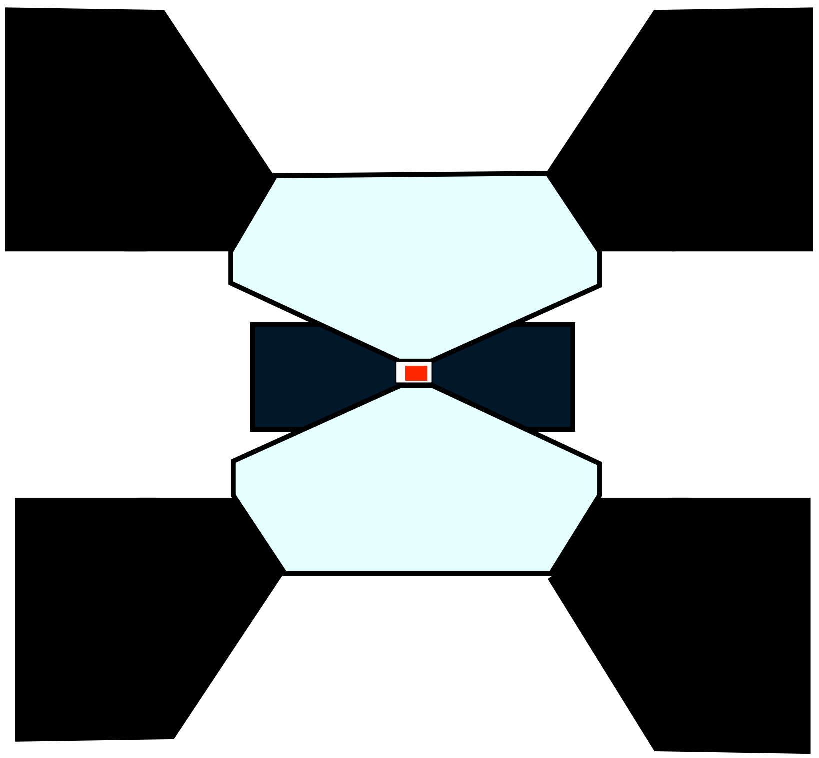


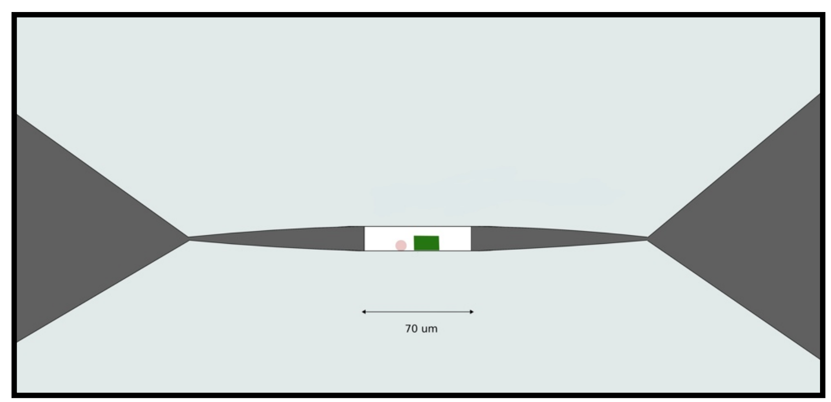
Nano crystalline anvils
Ishimatsu et al., J Synchr. Rad., 2012



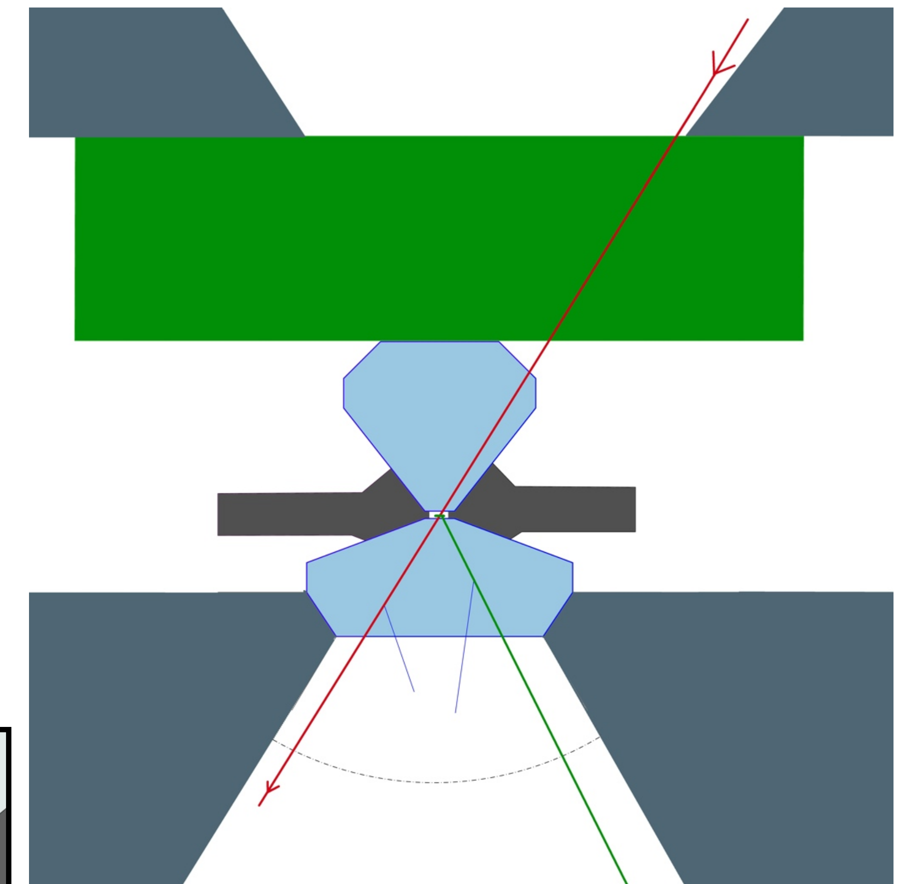
Use of polycapillary half-lens
Chen et al., J. Synchrotron Radiation, 2013

Monochromatic single-crystal micro diffraction in the DAC





WIDE ACCESS DAC & diamonds

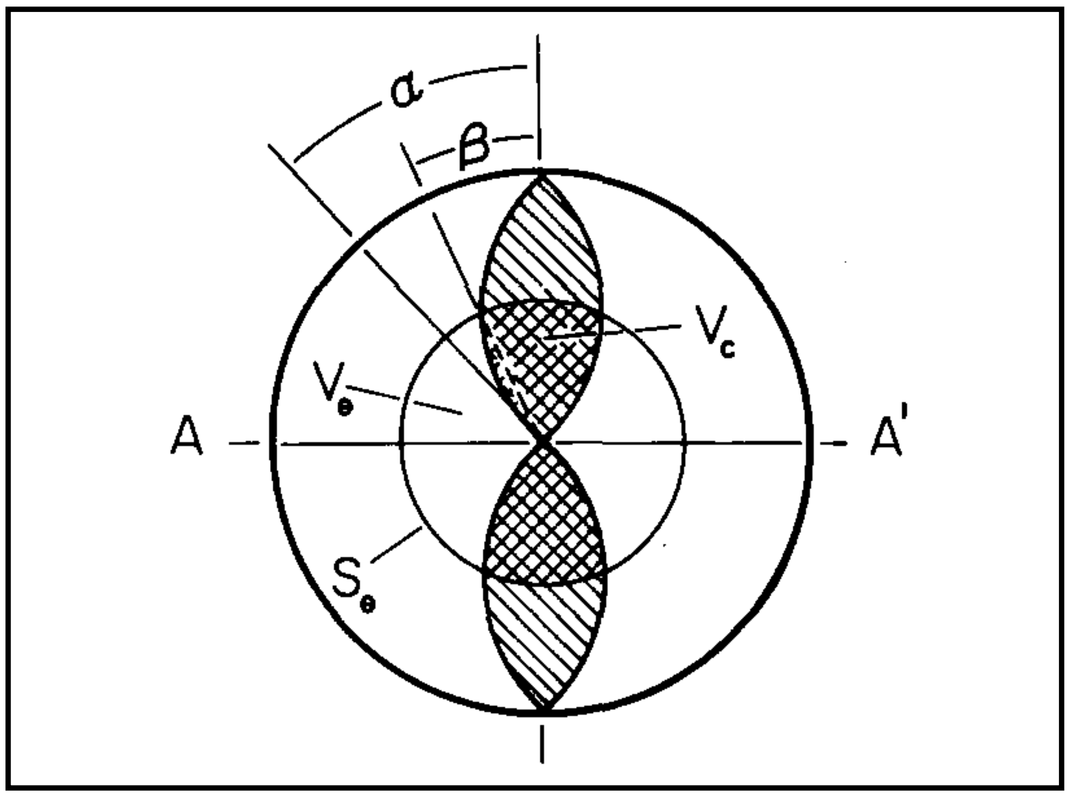


- Great efforts are made to obtain relatively high quality crystals, these include use of soft pressure-transmitting media and/or annealing.
- Wide access conical anvils (Boehler & De Hansetters 2004) and/or semitransparent seats are critical for high-pressure crystallography.

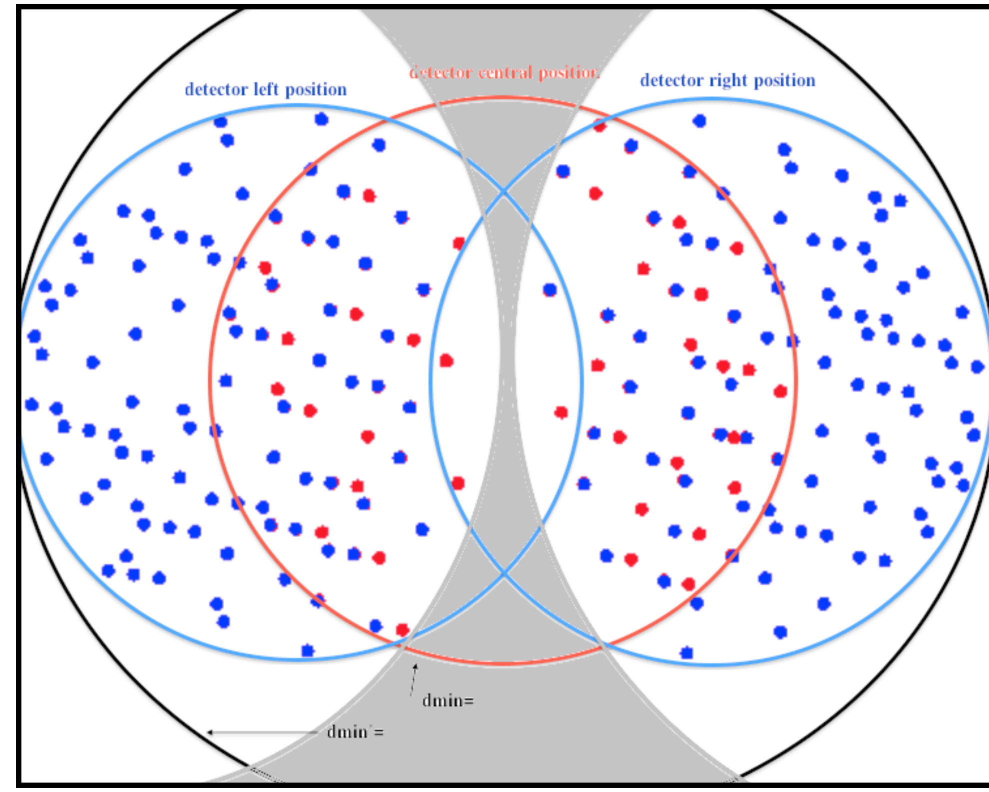
Reciprocal space access

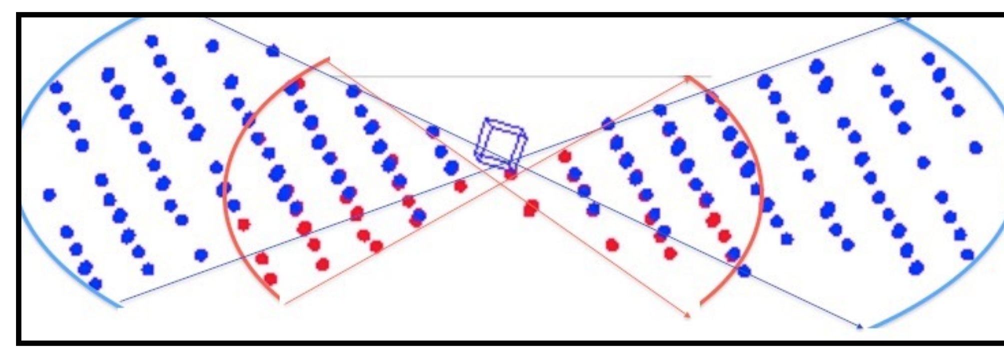
The DAC body determine large blind regions

- rotation range bounded by upstream cell opening
- diffracted beams are confined to a cone defined by the downstream opening



Merrill and Bassett, Rev Sci Inst, 1974

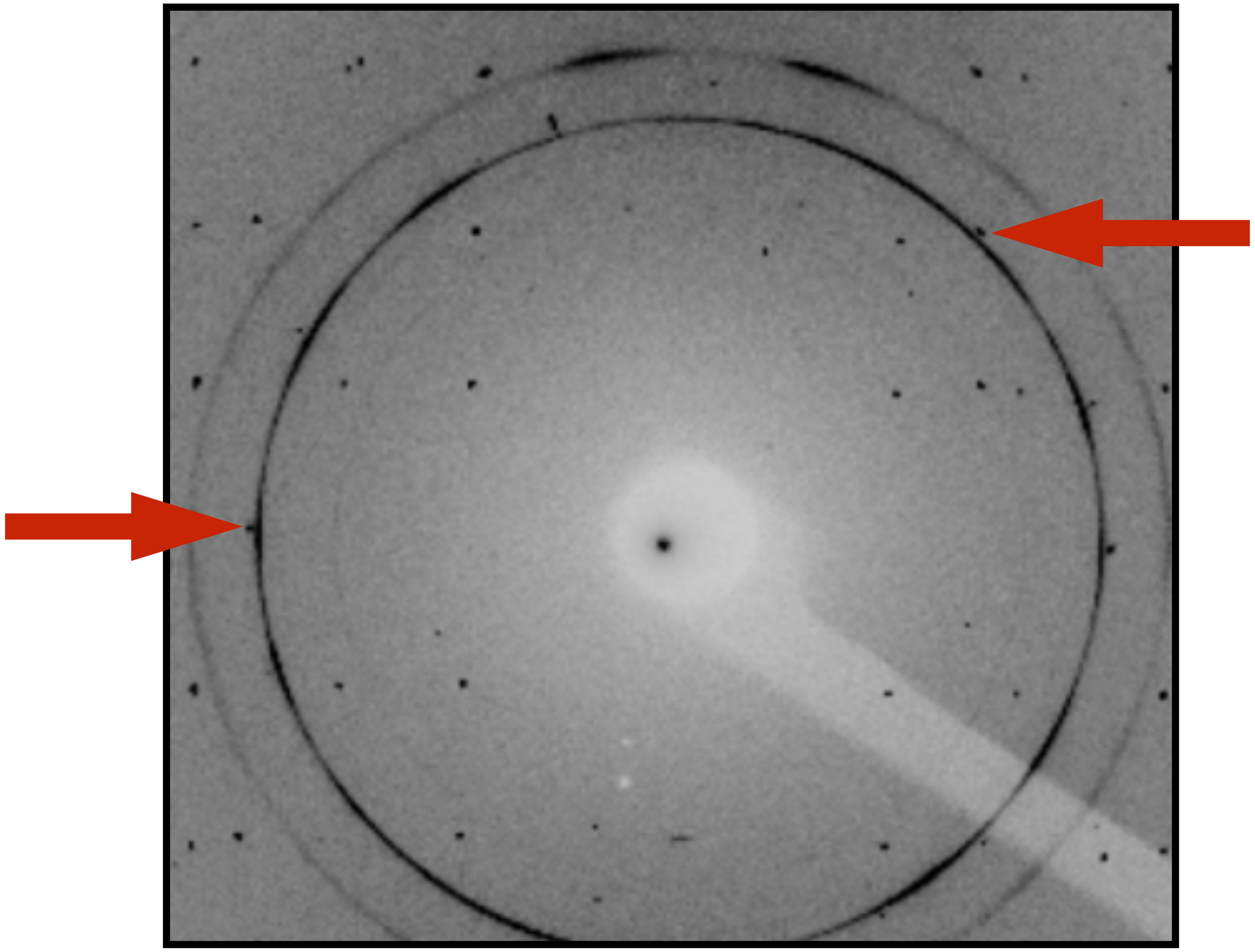




example of diffraction peaks distribution in the reciprocal space

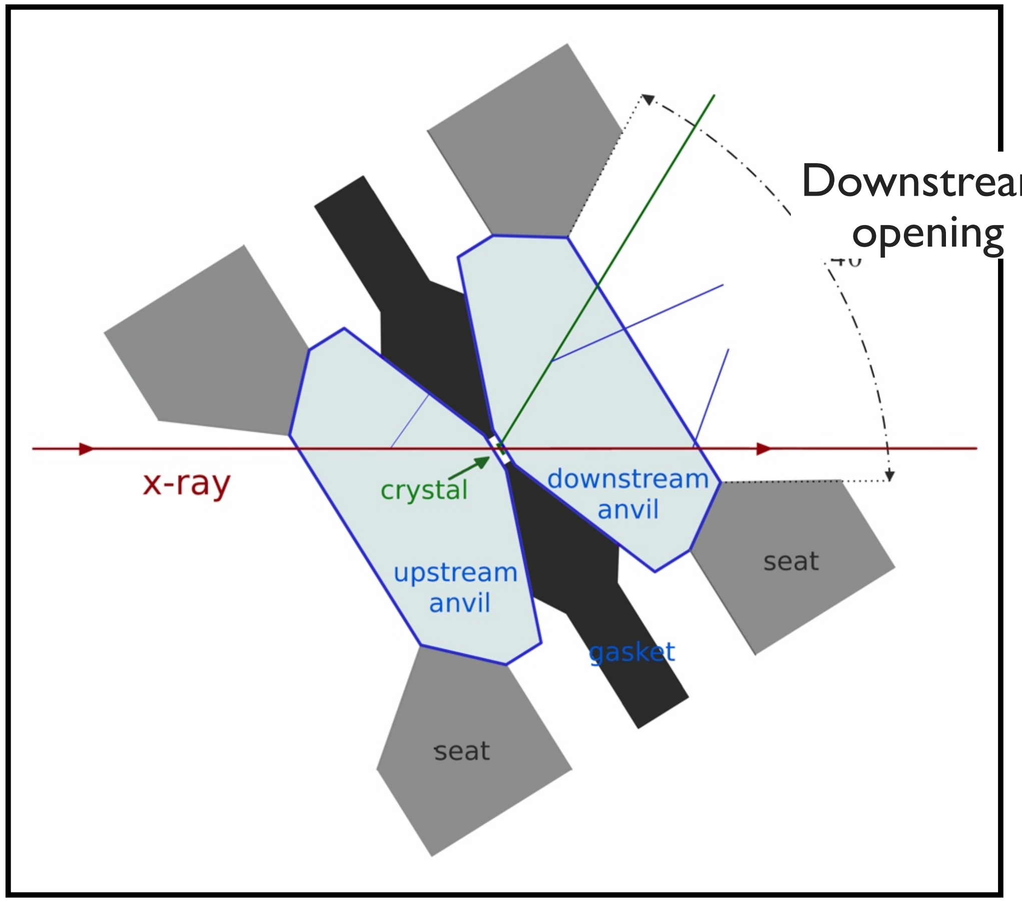
Partial and overlapping peaks

Some peaks are discarded due to overlapping with parasitic scattering

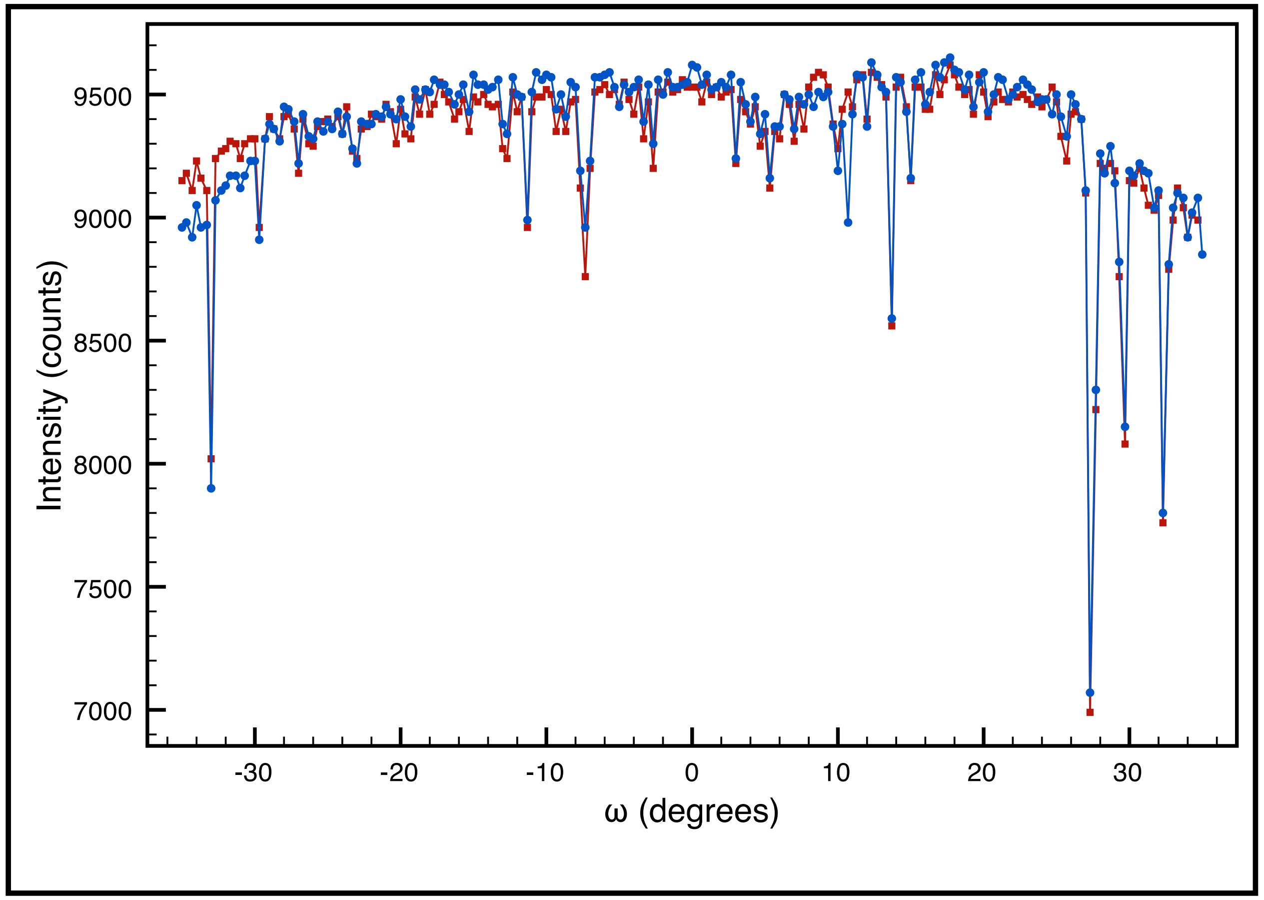


Glitches caused by diamond diffraction

- the incident beam as well as the beam diffracted by the sample are attenuated by diamond diffraction events
- the intensity reduction is significant
- sample peaks are randomly affected by this problem
- it is possible but not practical to correct for diamond diffraction glitches
- the effect is minimized by collecting highly redundant datasets

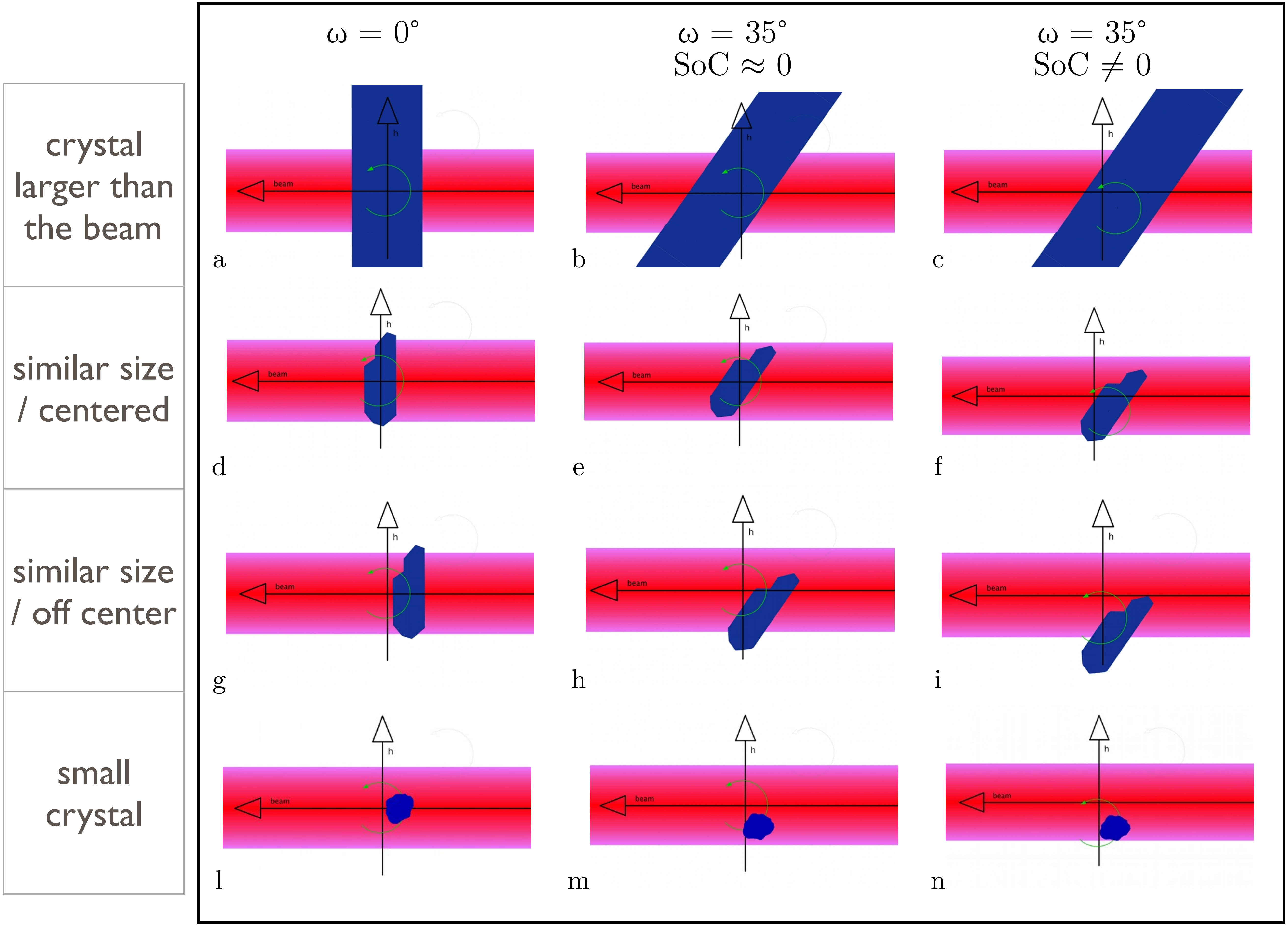


Sketch down the vertical axis of a diamond anvil cell



Intensity of the beam transmitted through the DAC as a function of the rotation angle

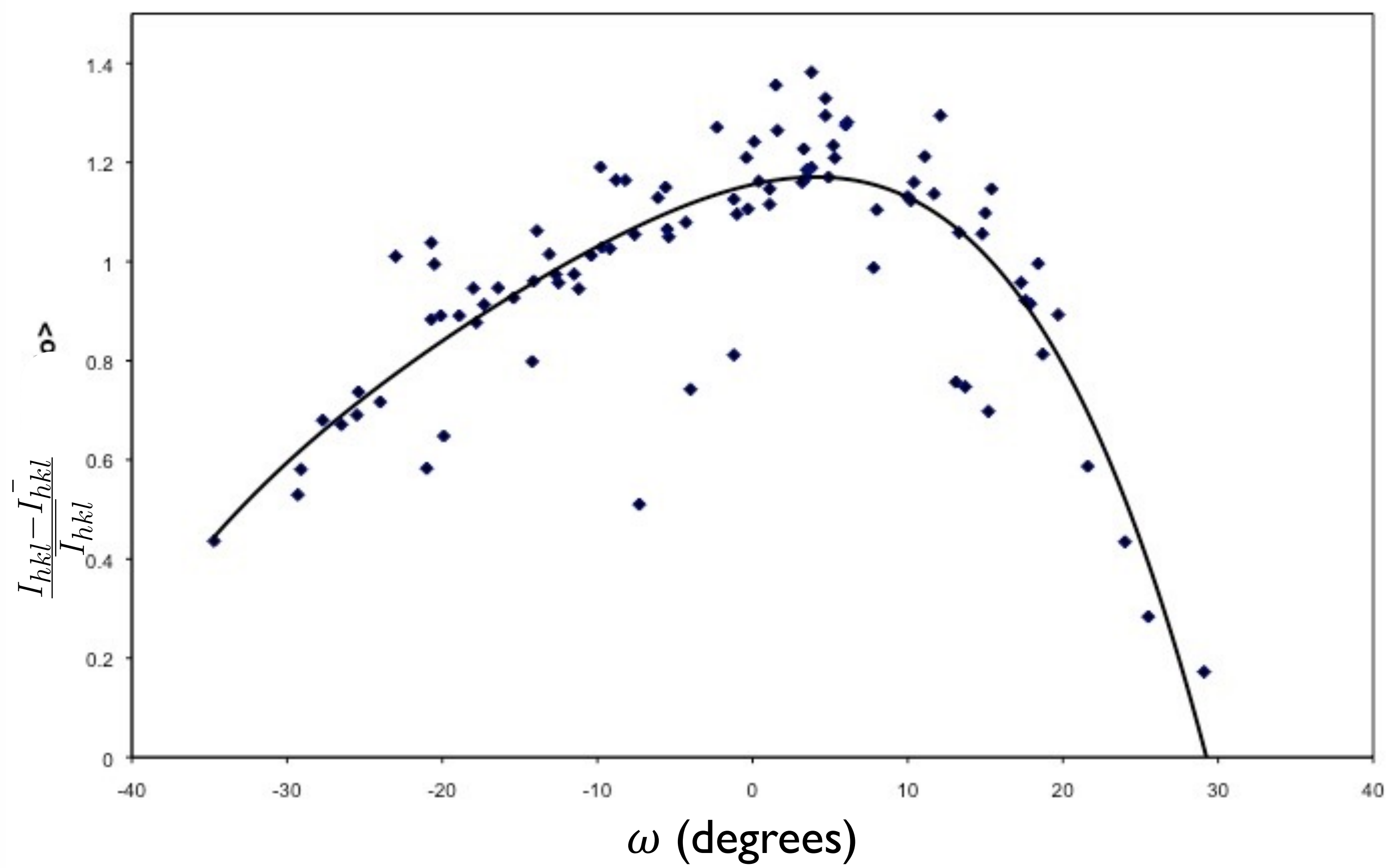
Variable illuminated crystal volume



Variations of I*Vcr: Empirical correction

- In case of crystals much larger than the beam, the volume of crystal in the beam shows a simple variation (cosω)
- An empirical correction can be obtained for high symmetry structures
- After eventual corrections for DAC absorption, we can study the ω-dependence of the relative difference between the intensity of a reflection with respect to the average of the set of equivalents: $(I_{hkl} - \langle I_{hkl} \rangle)/\langle I_{hkl} \rangle$
- We can express such changes as an ω-dependent correction to be applied to the incident flux and the initial volume of crystal intercepting the beam

Correction for a poorly aligned magnetite crystal



Comparison of refined parameters from raw and corrected data with the literature

	Rint %	R1 %	Rall %	wR2 %	Goof	u	U_O (Å^2)	U_T (Å^2)	U_M (Å^2)
Sasaki (1997)			1.6	1.0		0.2555(2)	0.0084(4)	0.0065(2)	0.0067(2)
raw data	31	5.3	5.3	12.3	0.95	0.253(1)	0.001(3)	0.003(2)	0.001(2)
corrected	7.3	1.8	1.8	3.6	1.41	0.2552(4)	0.008(1)	0.0078(5)	0.0062(5)

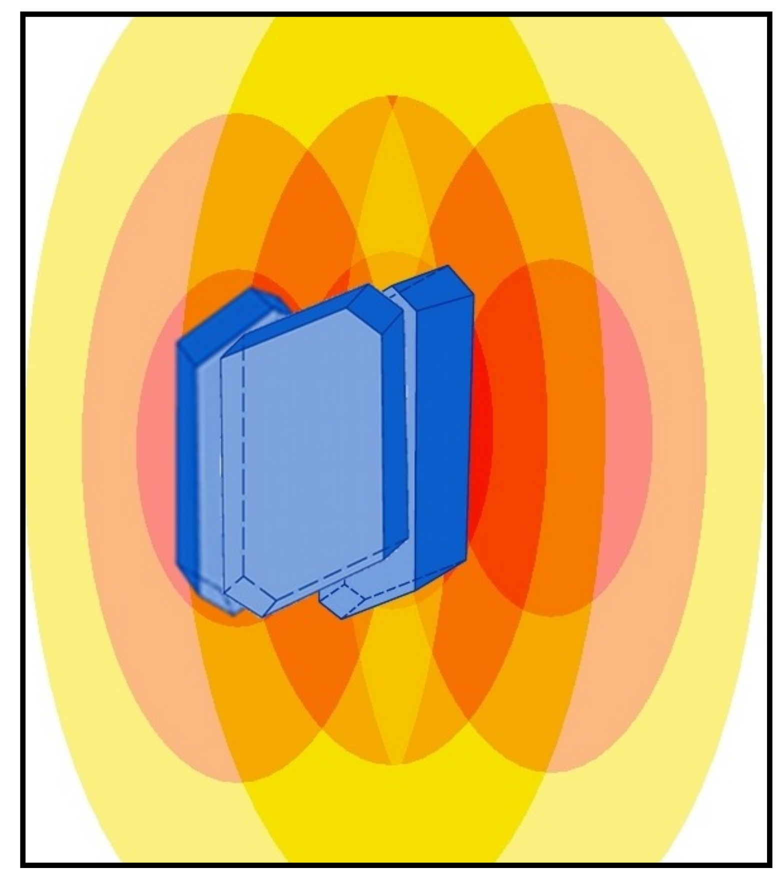
- The comparison suggests that the empirical correction can be very effective for high-symmetry crystals
- Although model-dependent, such correction may be derived, with caution, from F_O-Fc values

Rastering oscillation images

- In some cases the instrument and sample alignment are hardly controllable. This is for instance the case of cryostat measurements requiring bulky equipment with external pipes that apply a torque on the sample stage, increasing the instrument sphere of confusion
- A possible solution consists in the collection of multiple diffraction images at different positions at ω_0

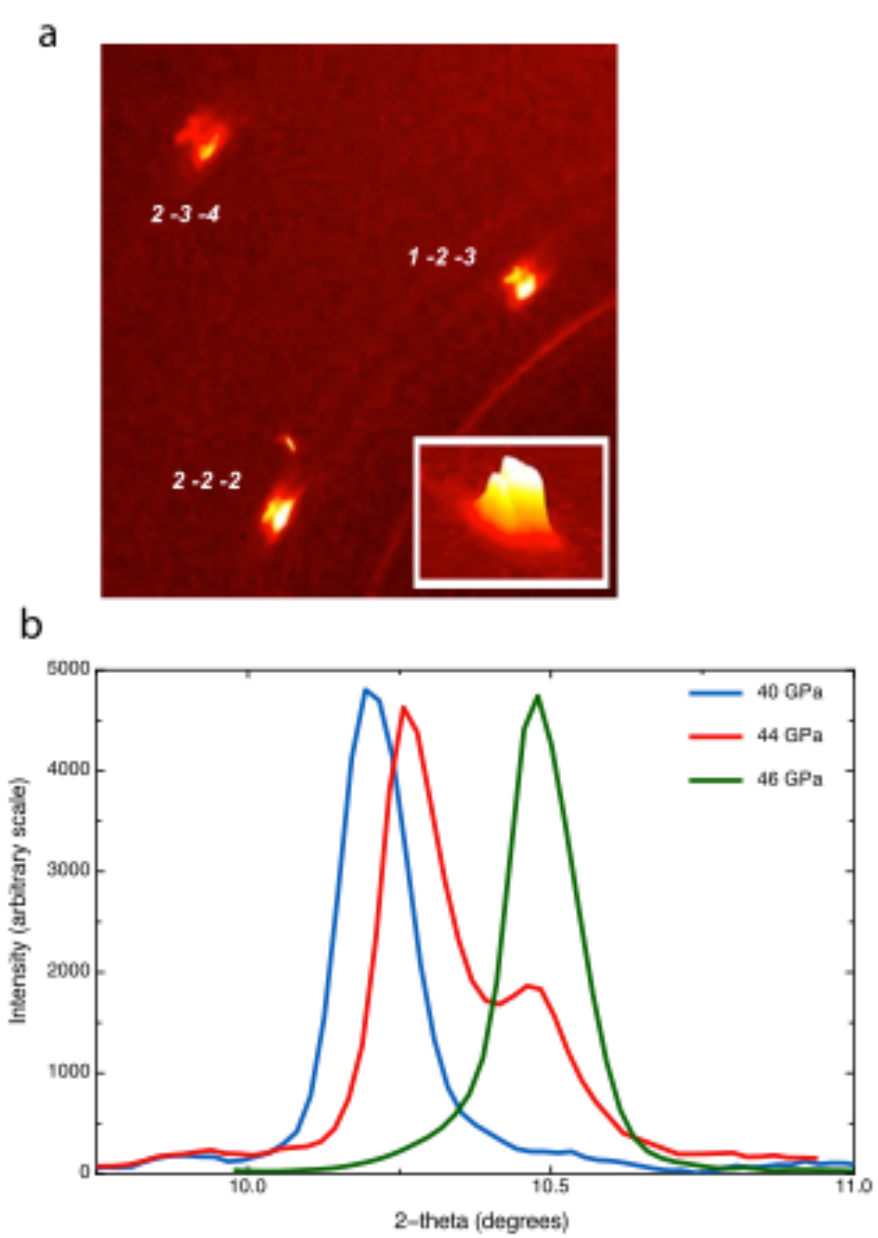
~4 μm Re sphere

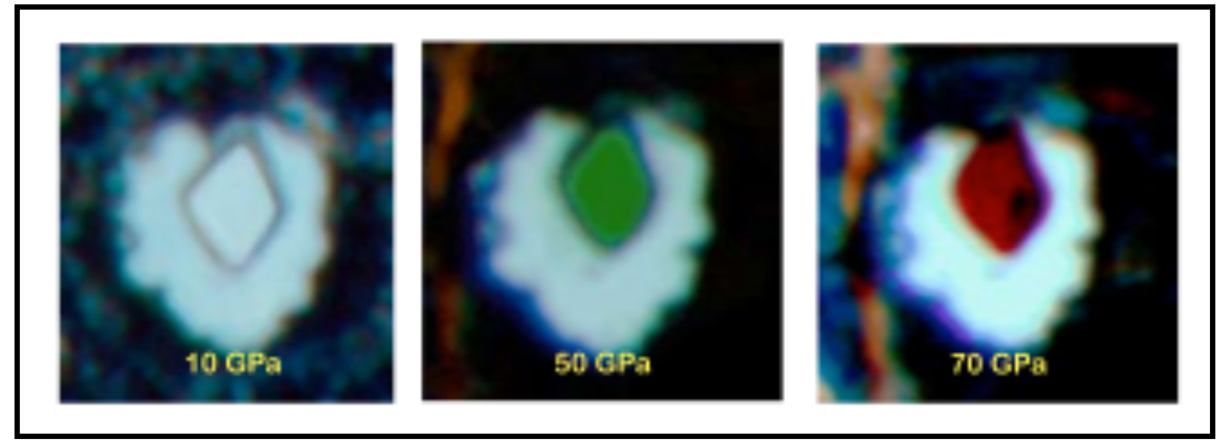
the use of a microsphere allows excellent focusing and reproducible positioning

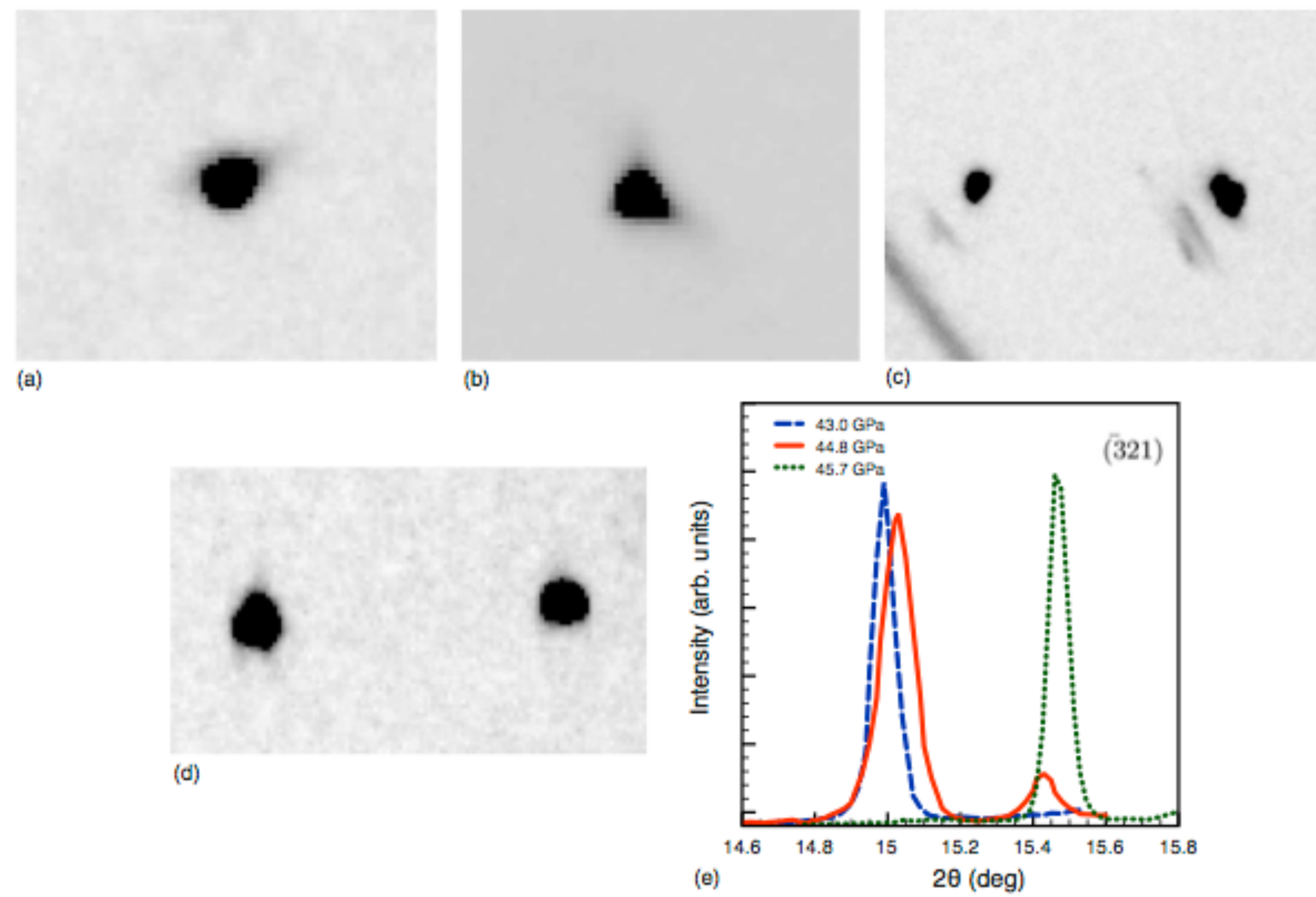


Schematic view perpendicular to the beam of a rotating crystal and "three beams"

Application: Single crystal diffraction of $FeCO_3$ to 90 GPa







GEOPHYSICAL RESEARCH LETTERS, VOL. 36, L23306, doi:10.1029/2009GL039652, 2009

Siderite at lower mantle conditions and the effects of the pressure-induced spin-pairing transition

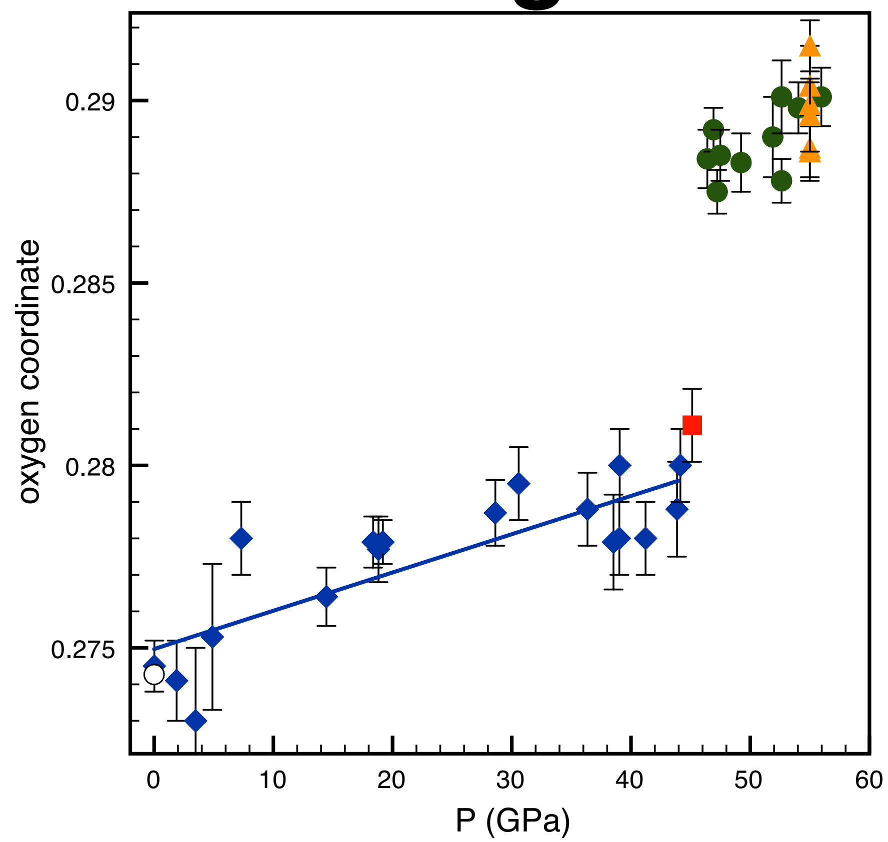
B. Lavina,[1] P. Dera,[2] R. T. Downs,[3] V. Prakapenka,[2] M. Rivers,[2] S. Sutton,[2] and M. Nicol[1]

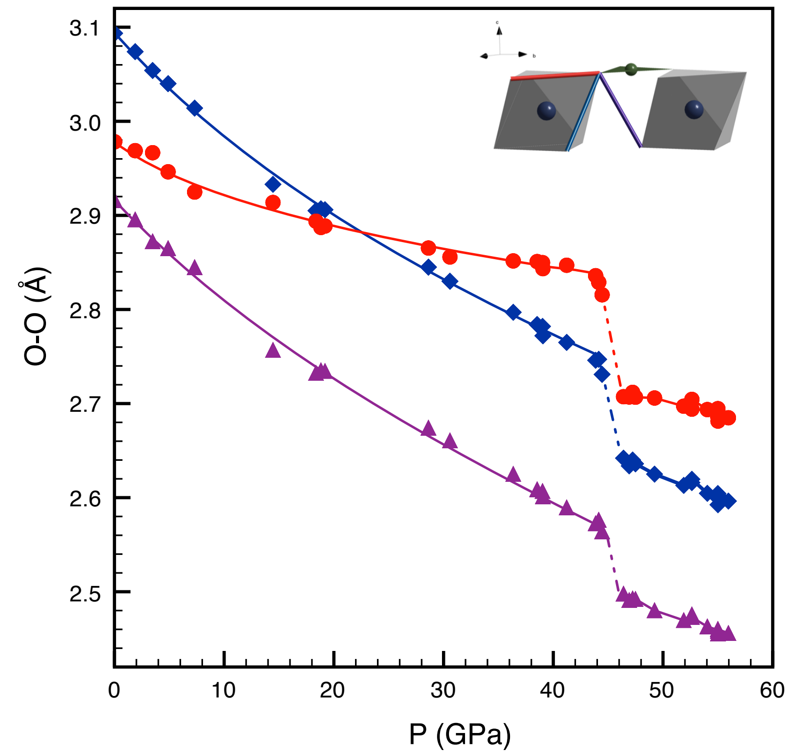
PHYSICAL REVIEW B **82**, 064110 (2010)

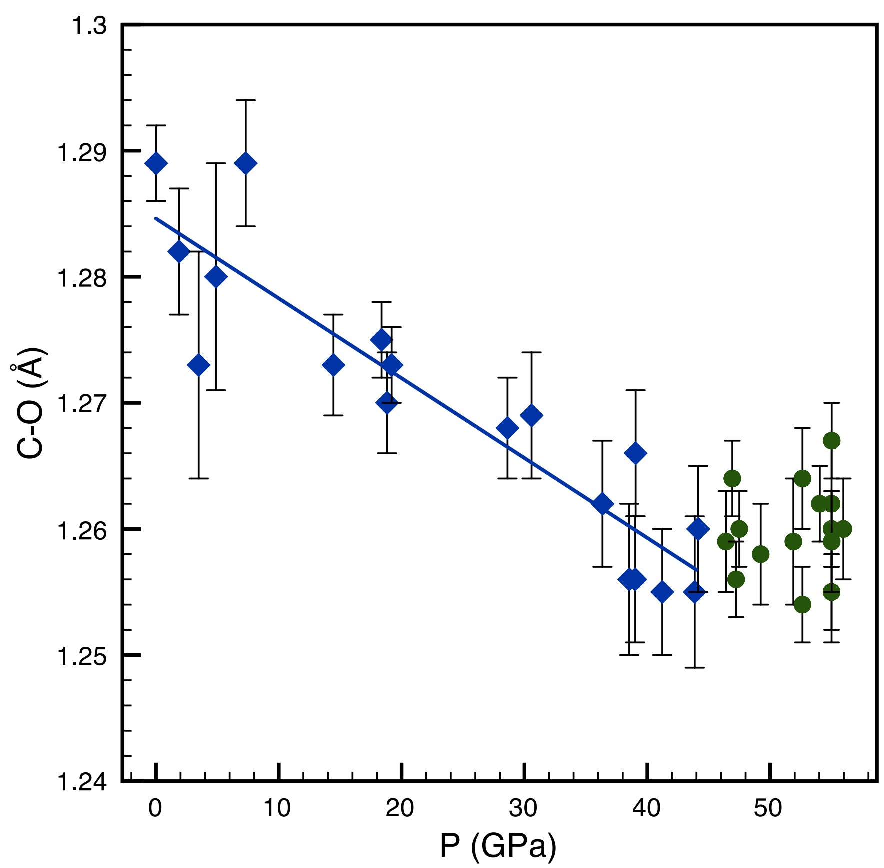
Structure of siderite $FeCO_3$ to 56 GPa and hysteresis of its spin-pairing transition

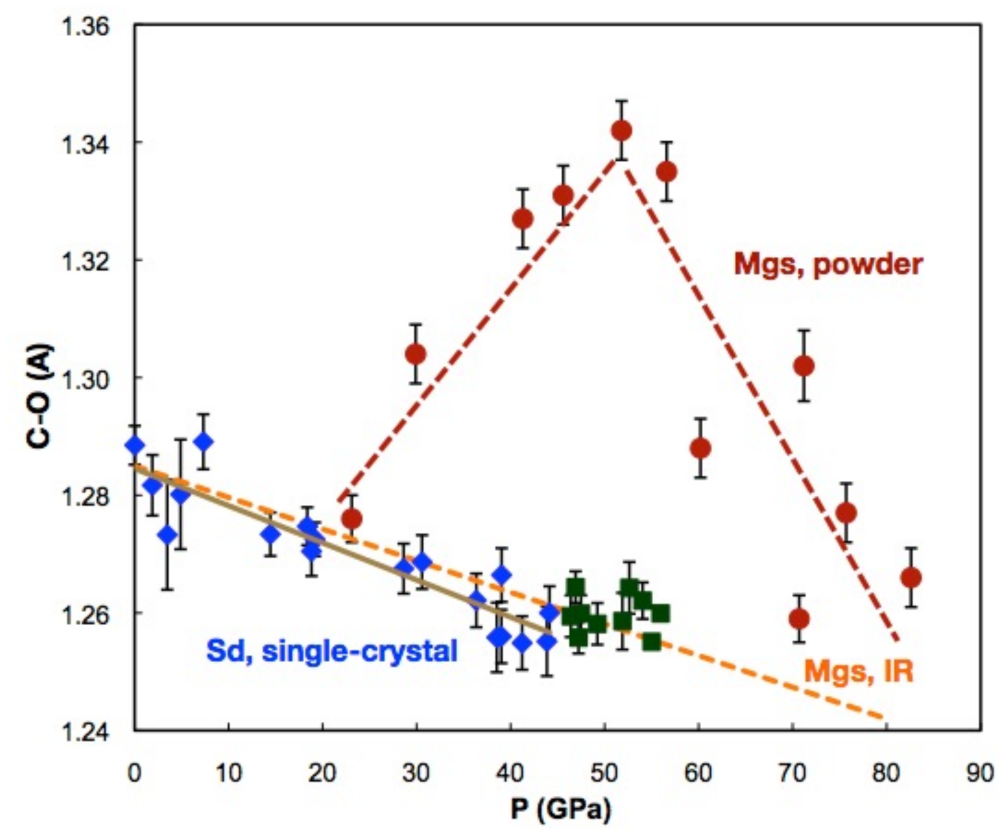
Barbara Lavina,[1] Przemyslaw Dera,[2] Robert T. Downs,[3] Wenge Yang,[4,5] Stanislav Sinogeikin,[4] Yue Meng,[4] Guoyin Shen,[4] and David Schiferl[1]

Accurate bond lengths measurements

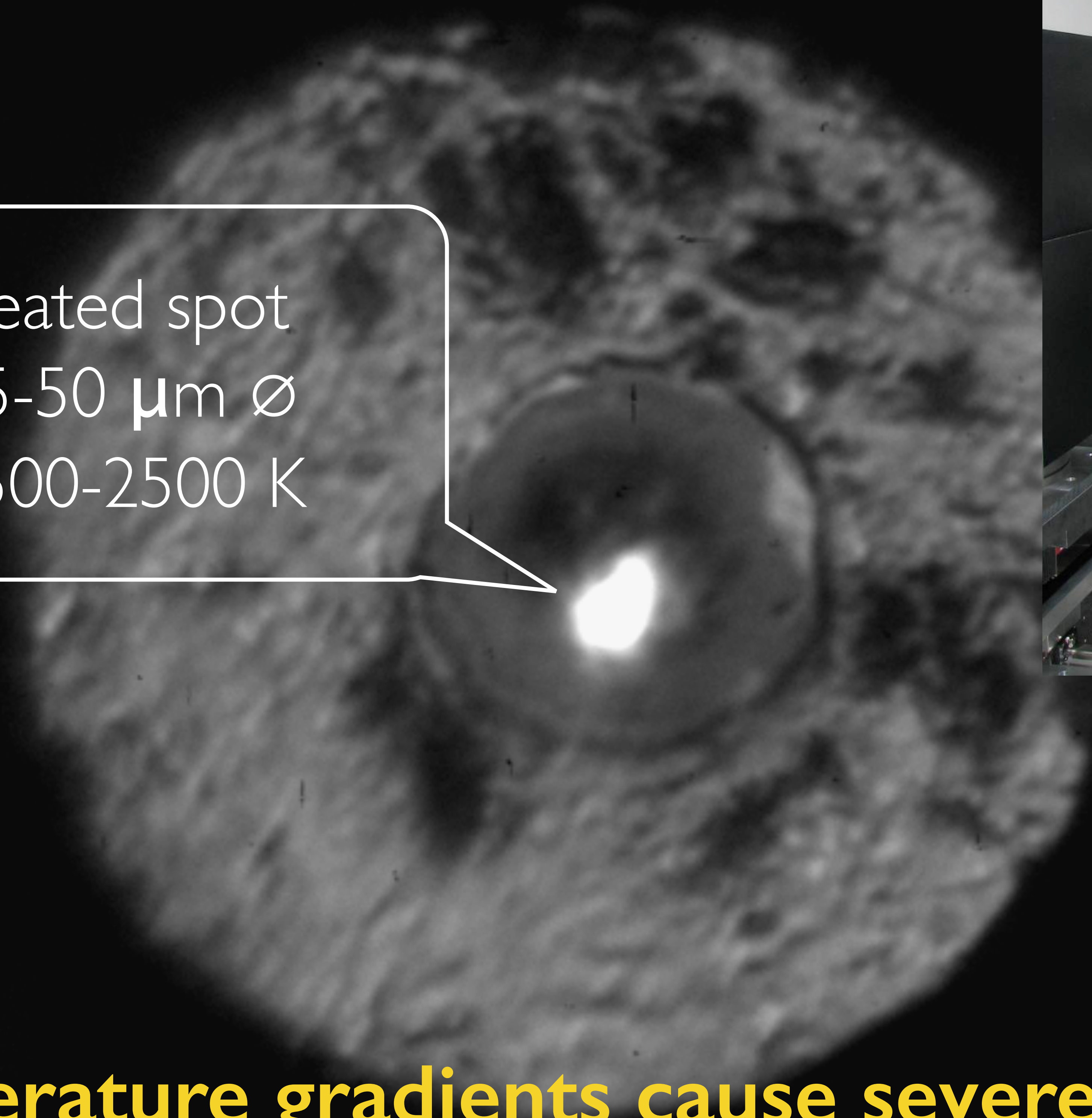


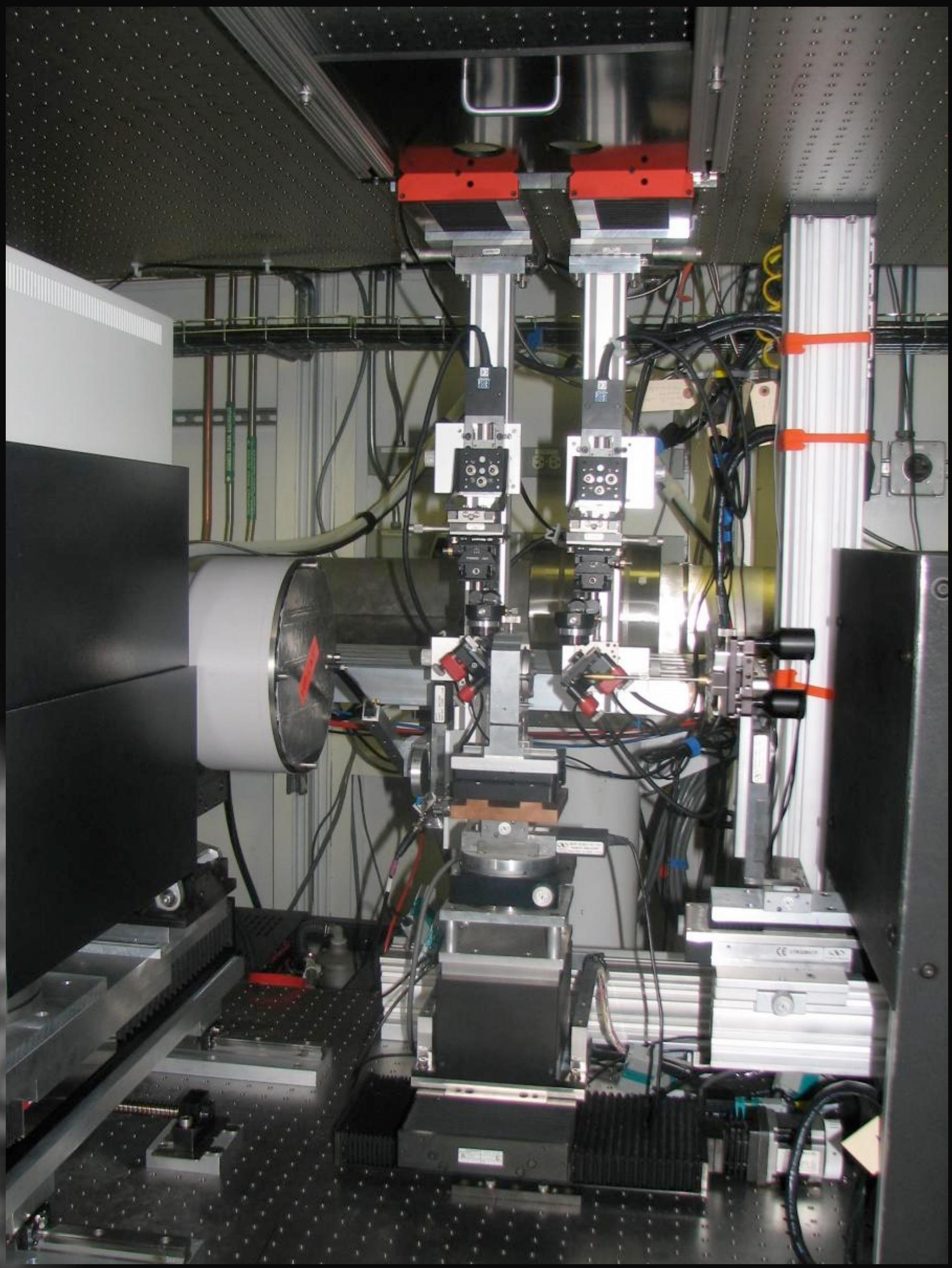






High P-T Synthesis: New Iron Oxides

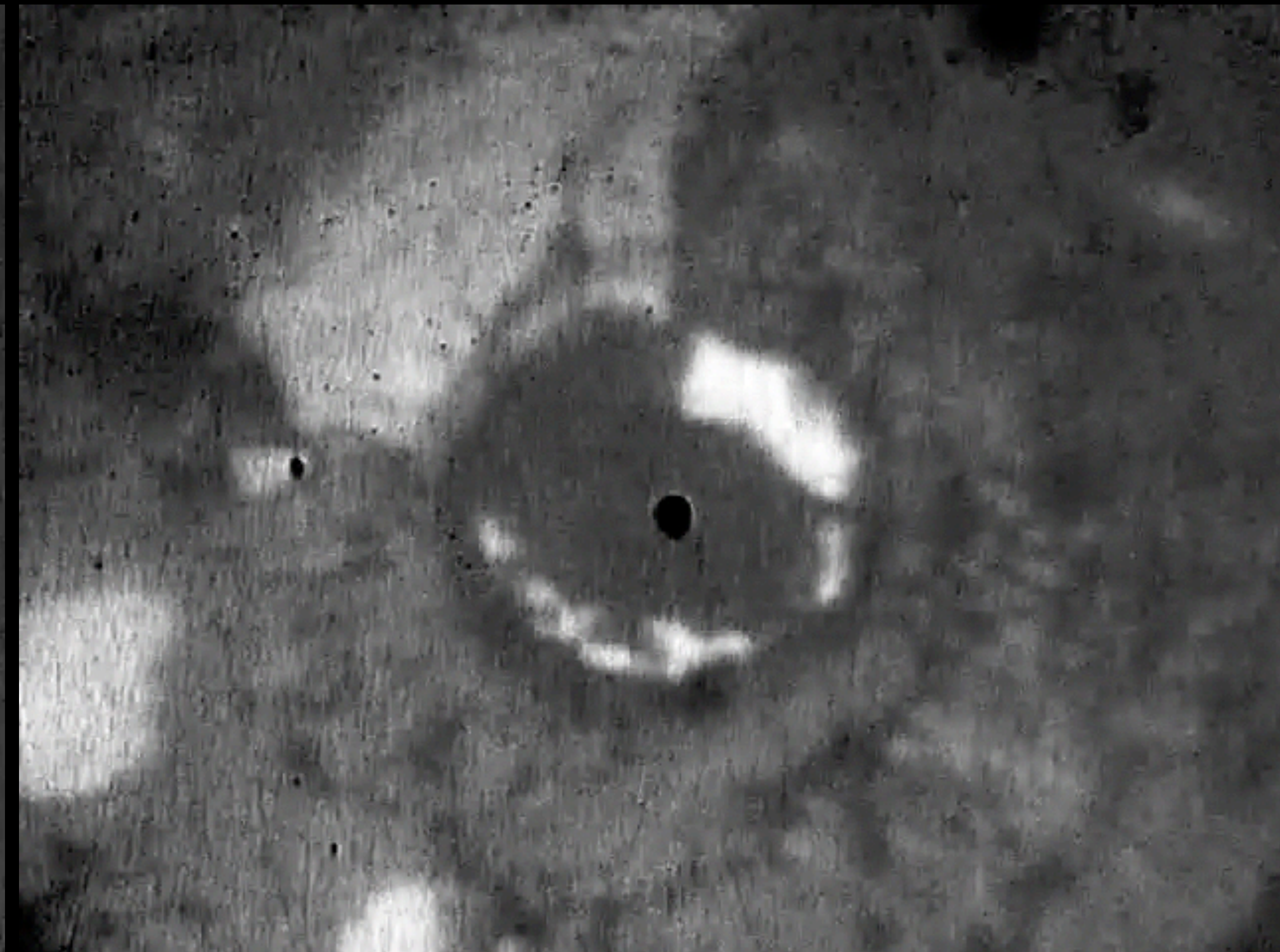


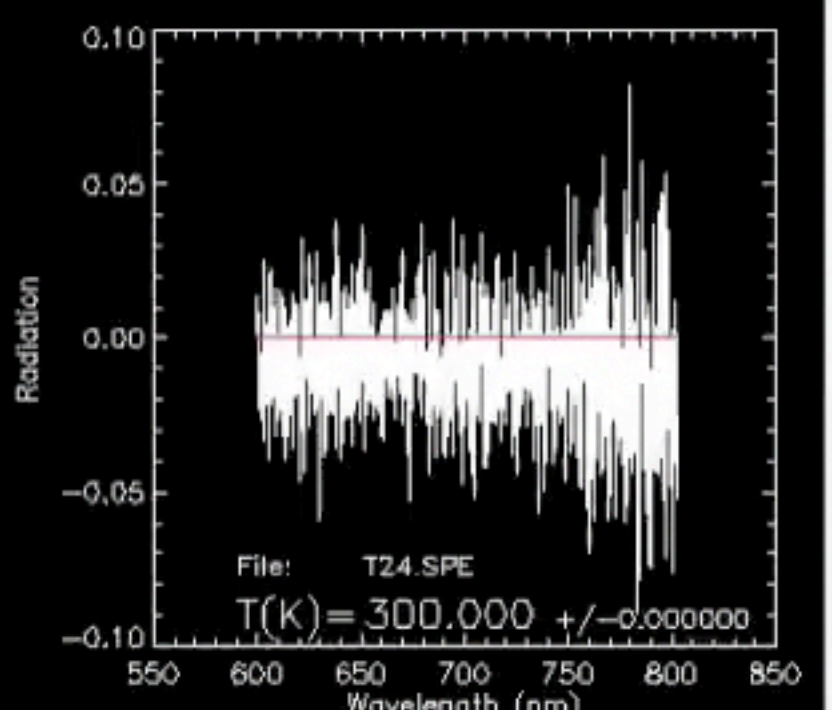


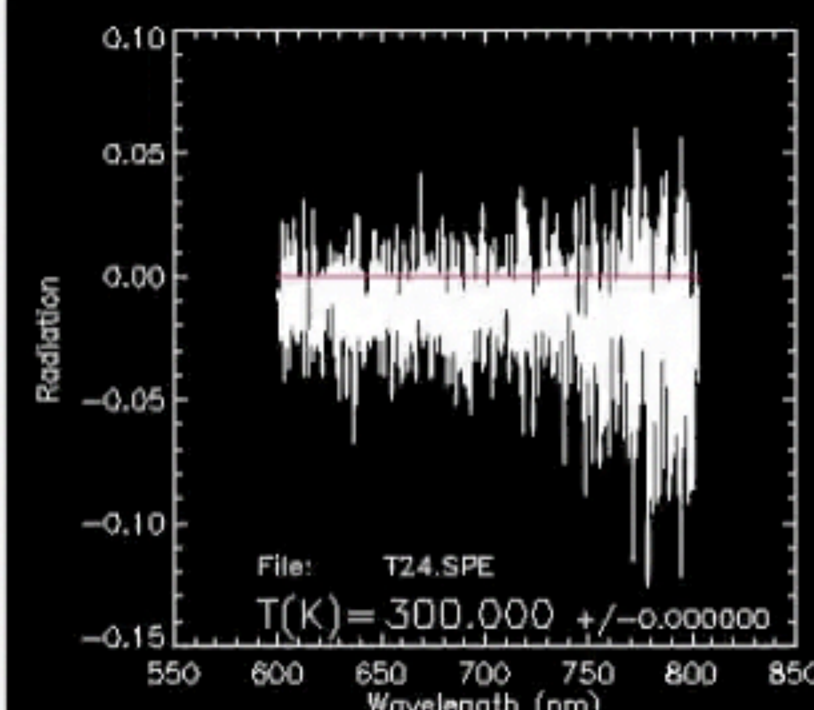
HPCAT-16IDB

laser heating system
Meng et al. RSI 2015

temperature gradients cause severe heterogeneities




0.10
0.05
0.00
−0.05
−0.10
Radiation
File: T24.SPE
T(K)= 300.000 +/−0.000000
550 600 650 700 750 800 850
Wavelength (nm)

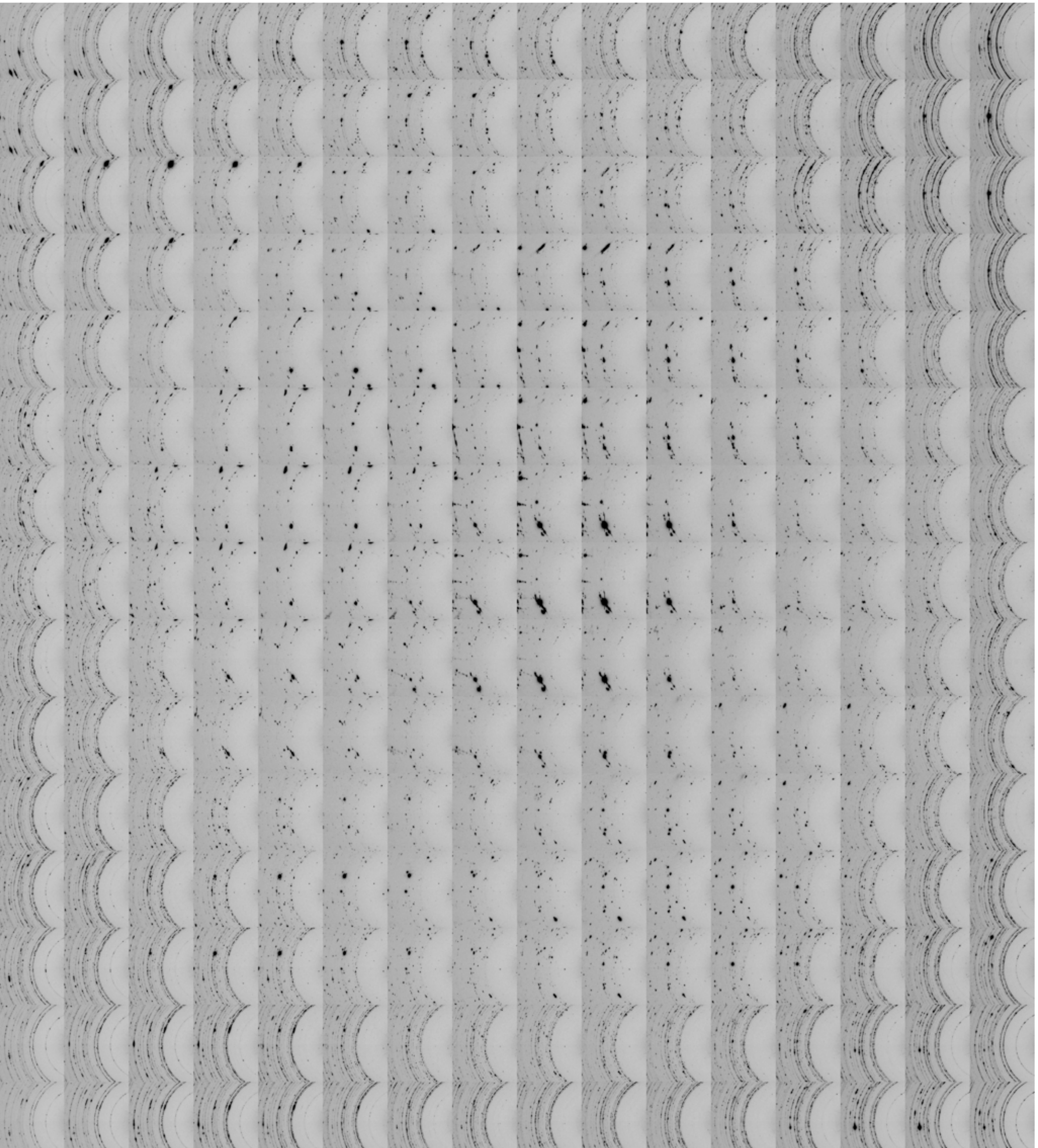

0.10
0.05
0.00
−0.05
−0.10
−0.15
Radiation
File: T24.SPE
T(K)= 300.000 +/−0.000000
550 600 650 700 750 800 850
Wavelength (nm)

Challenges In Synthesis And Characterization

- minimal samples strain are important to characterize structures with relatively large unit cells, in a soft medium grain growth exacerbates thermal gradients
- large thermal gradients may cause chemical gradients in addition to grain size and phase heterogeneity
- non stoichiometry and defect structures are to be expected in Fe-O compounds
- such problems are much greater in systems with complex phase diagram

Most syntheses result in highly heterogeneous samples with respect to phase and grain size

Grain Size Variability

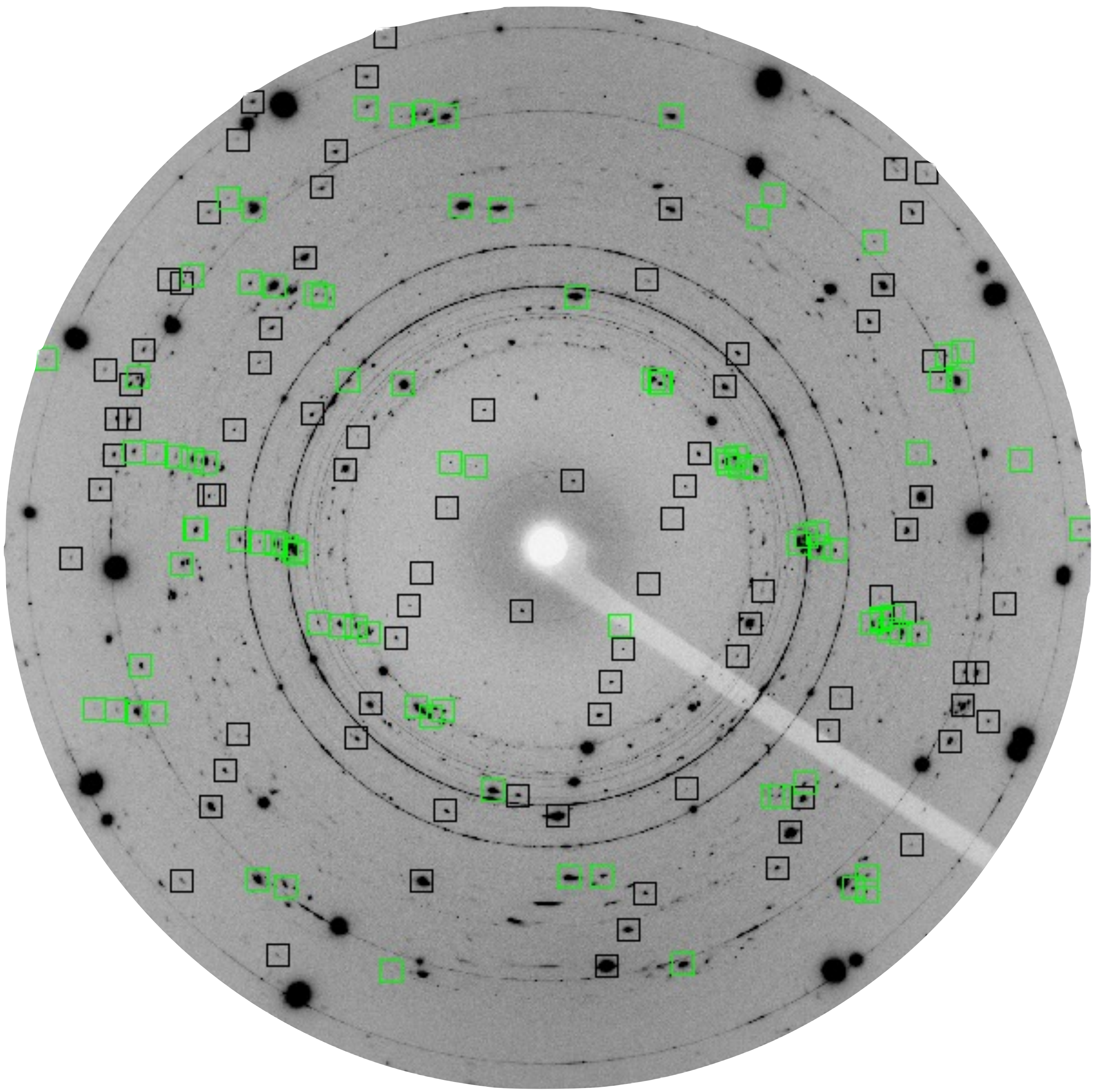


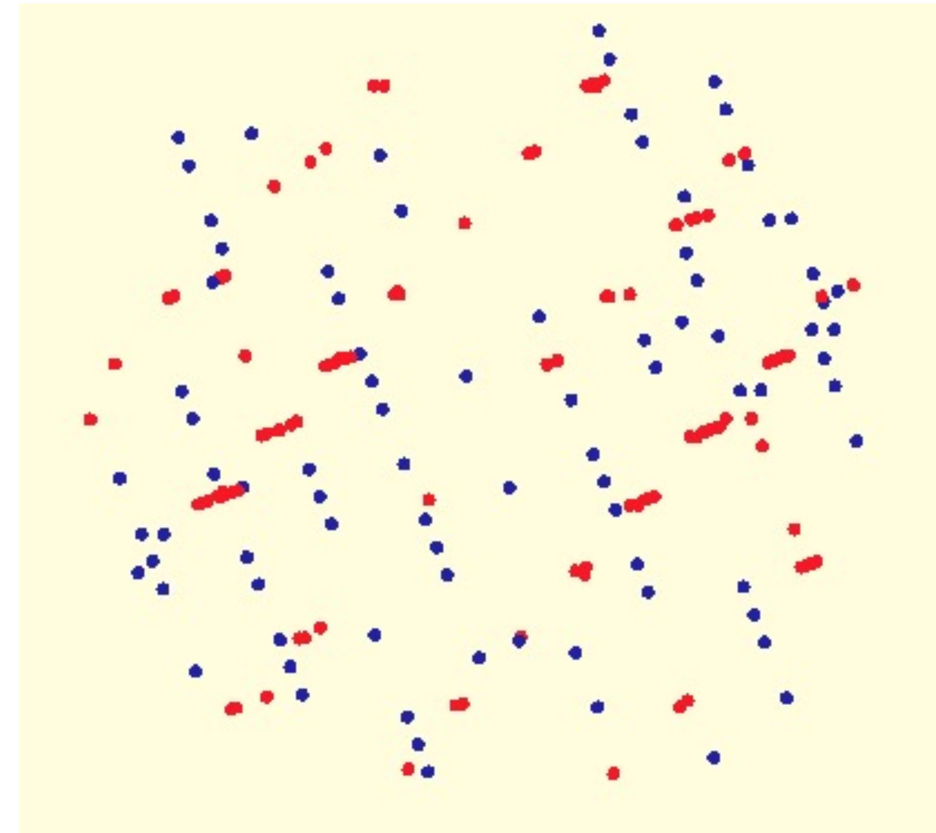
As a result of thermal gradients, laser-heated samples might develop a range of grain sizes.

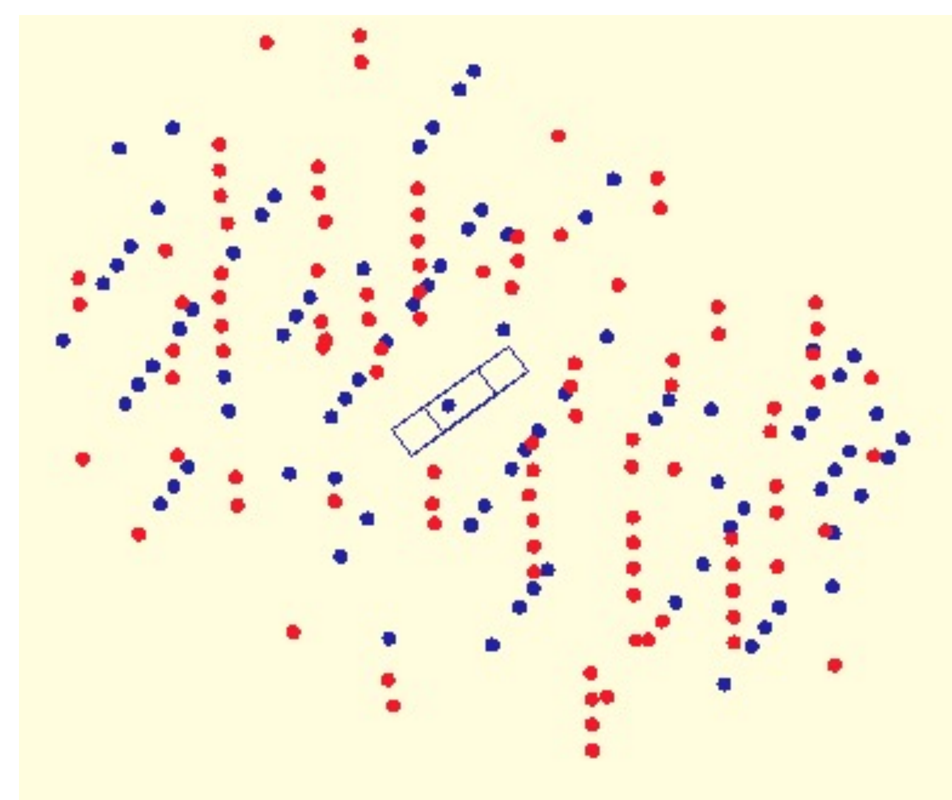
Often, no ideal powder or single crystal patterns can be collected.

It is apparent that data collection, reduction and analysis strategies needs to be tailored to the grain size.

Fe_5O_6 Large Grains Patterns From Selected Locations







Procedure Video Publication

Synthesis and Microdiffraction at Extreme Pressures and Temperatures

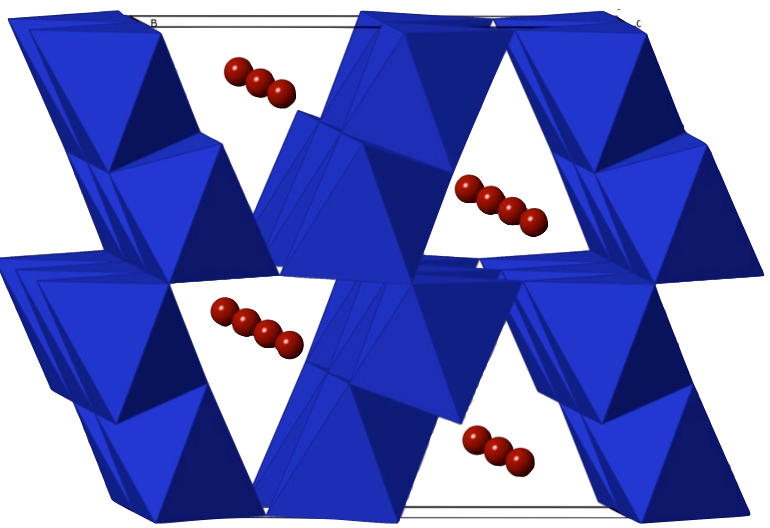
Barbara Lavina[1], Przemyslaw Dera[2], Yue Meng[3]

[1]High Pressure Science and Engineering Center, Department of Physics and Astronomy, **University of Nevada, Las Vegas**, [2]GeoSoilEnviroCARS, **University of Chicago**, [3]High Pressure Collaborative Access Team, **Carnegie Institution of Washington**

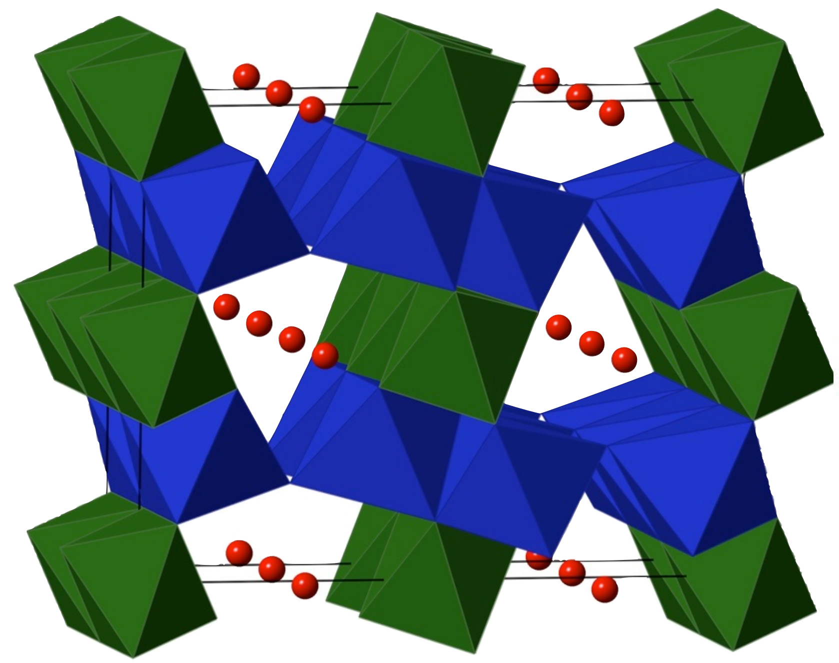
http://www.jove.com/video/50613
https://barbaralavina.wordpress.com/

Two New High-P Iron Oxides

h-Fe_3O_4



Fe_4O_5

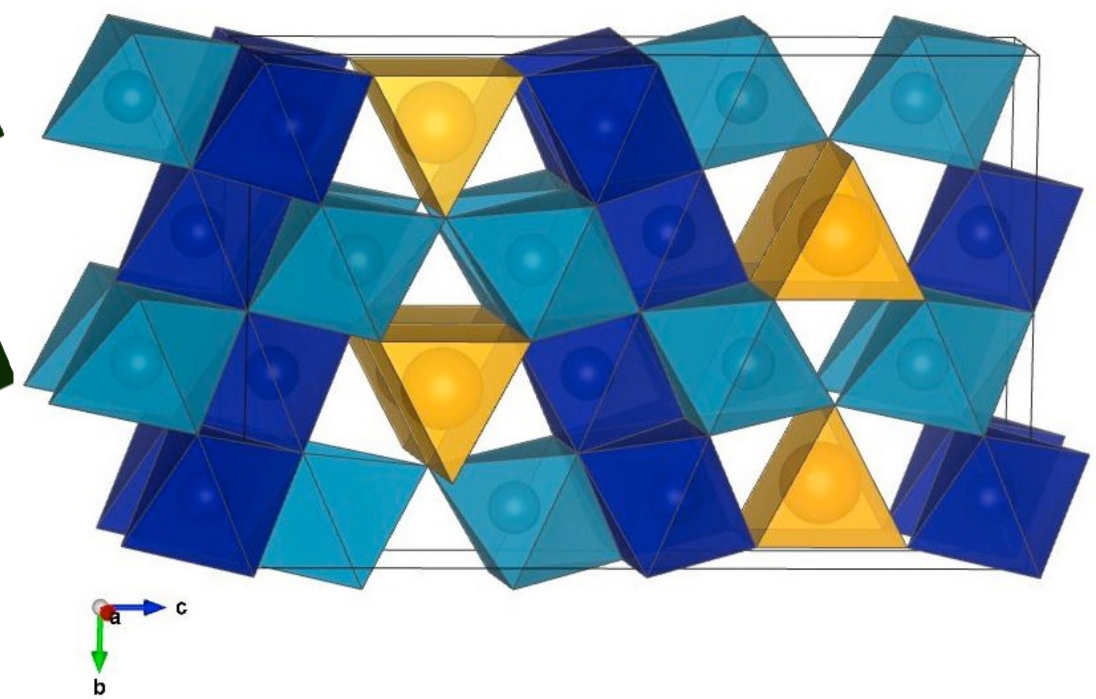


Discovery of the recoverable high-pressure iron oxide Fe_4O_5

Barbara Lavina[a,b,1], Przemyslaw Dera[c], Eunja Kim[b], Yue Meng[d], Robert T. Downs[e], Philippe F. Weck[f], Stephen R. Sutton[c], and Yusheng Zhao[a,b]

PNAS | **October 18, 2011** | vol. 108 | no. 42 | **17281–17285**

Fe_5O_6

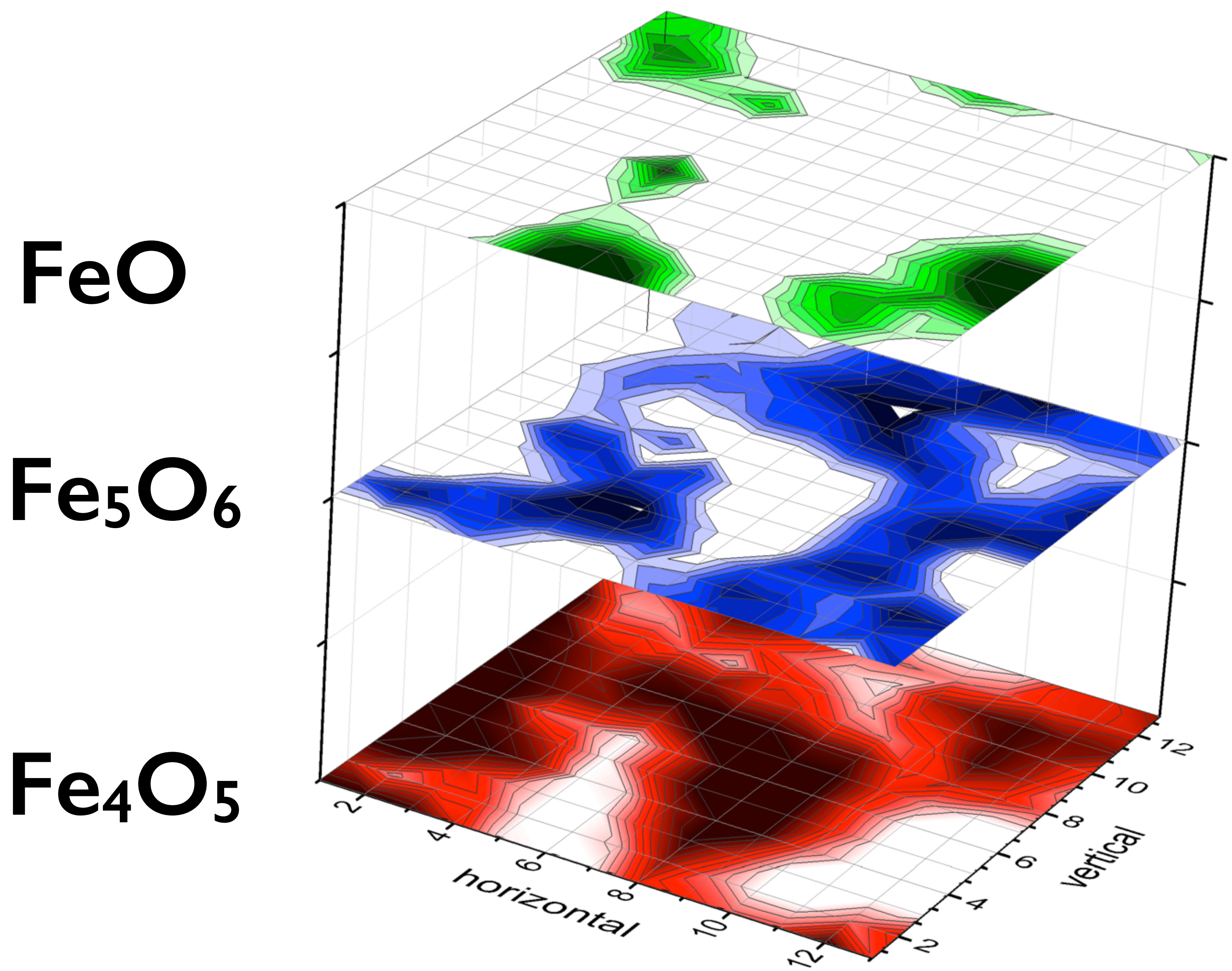


Unraveling the complexity of iron oxides at high pressure and temperature: Synthesis of Fe_5O_6

Barbara Lavina[1]* and Yue Meng[2]

Sci. Adv. 2015;1:e1400260 26 June 2015

Phase heterogeneities



- Interesting phase mapping can be obtained reasonably fast
- The distribution of synthesized iron oxides (red: Fe_4O_5, blue: Fe_5O_6, green: wüstite) supports the inferred composition of Fe_5O_6, the new phase is chemically intermediate between wüstite and Fe_4O_5 and is in fact more abundant in between the two known oxides.
- There are no evidences in the P-T range investigated of a “continuum” of Fe_3O_4+FeO compounds!

Summary

- The high-pressure world is extremely fascinating and exotic, far from being fully understood and explored, even for elements.
- High-pressure experiments are uniquely challenging, including achieving desired conditions, probing samples, processing and interpreting data.
- Large scale user facilities such as the APS and the SNS but many others in the USA and around the world provide unique and constantly improving research opportunities.
- Probing matter and processes as they occur in controlled environments is exciting and certainly will have an even greater role in the future.

Suggested readings