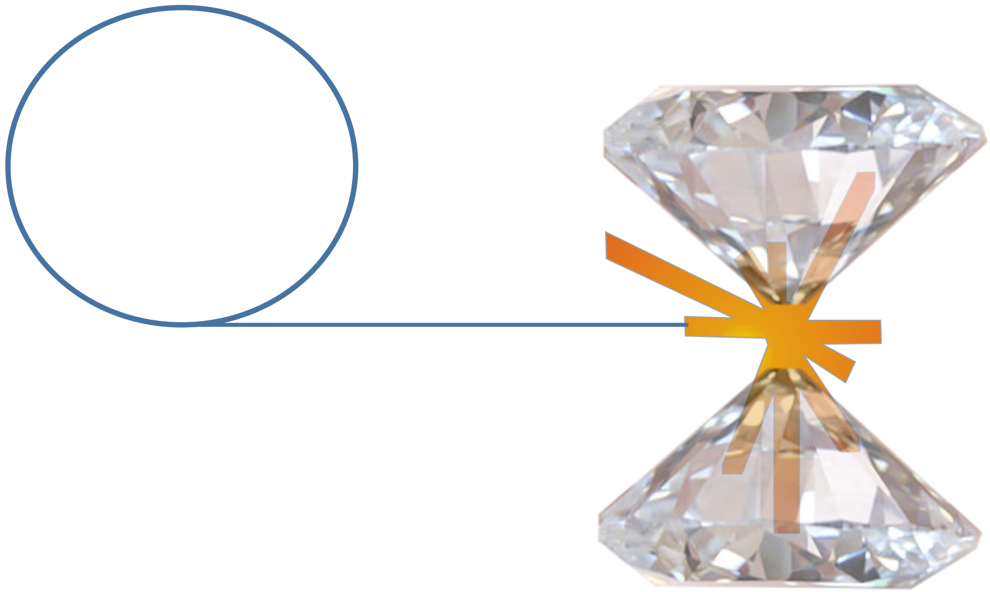
High Pressure Techniques



M. Guthrie, Geophysical Laboratory

- ENERGY FRONTIER RESEARCH IN EXTREME ENVIRONMENTS

Extreme Conditions?

Can mean harsh chemical or radiation environments, ultra high magnetic, electric or strain fields. Here, we'll focus on very high pressures

SI unit for pressure: Pascal, Pa (1 Nm^{-2})
i.e. Force/Area

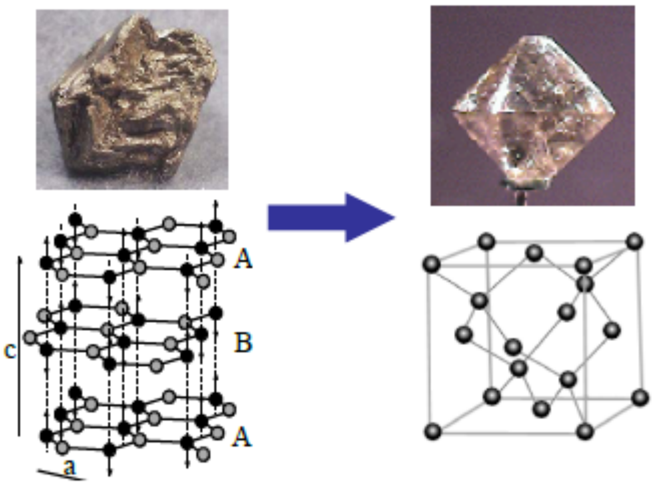
Research at neutron and x-ray facilities is routinely conducted at pressures measured in GigaPascals, GPa*.

Reference
Atmospheric pressure ~ 0.0001 GPa
Deepest point of the ocean ~ 0.1 GPa
Stability field of diamond > 5 GPa
Center of the Earth: ~350 GPa

(*I may slip into kbar = 1000 bar during talk…conversion is easy 1 GPa = 10 kbar)

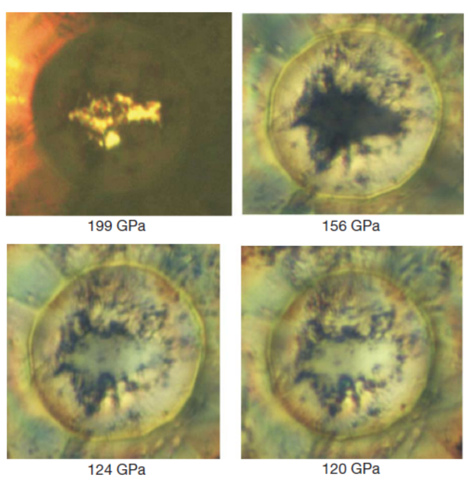
High pressure – a route to new materials

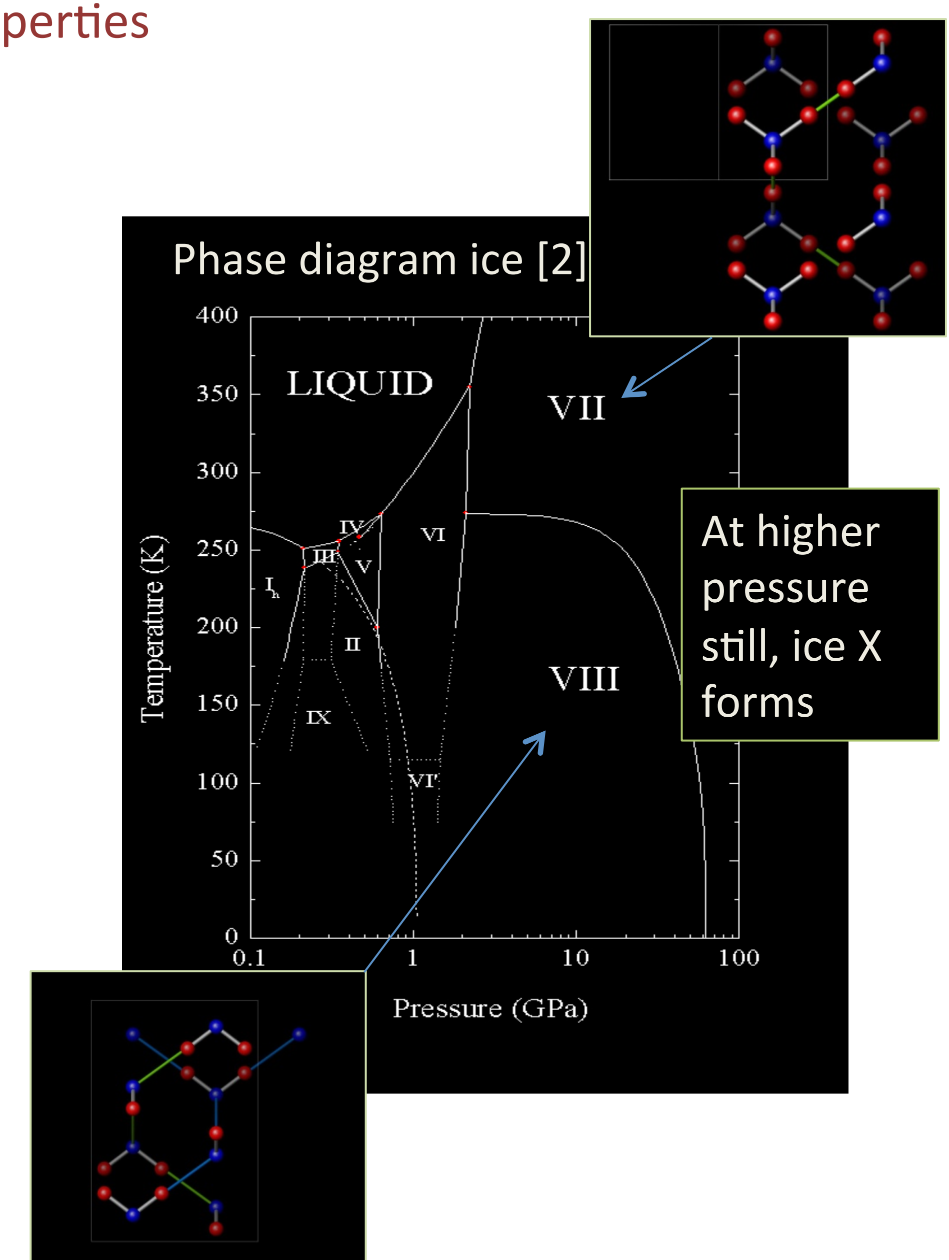
Pressure can radically change ***material*** properties



Polymorphism of Carbon

Transparent sodium [1]





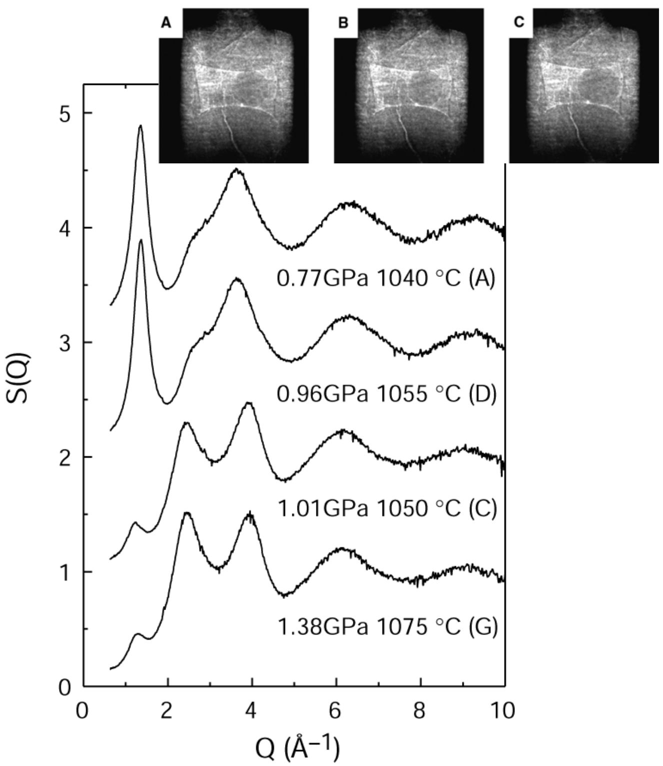
[1] Ma et al Nature 458 182 (2009).

[2] P Pruzan, *Private Comm.*

High pressure – a route to new materials

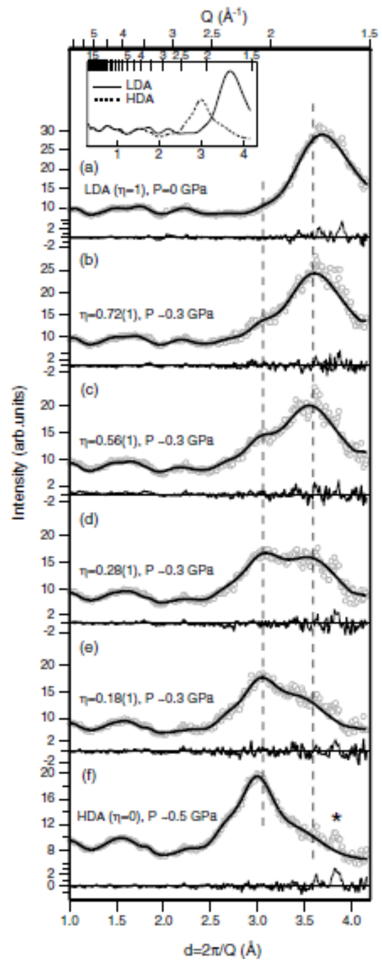
Pressure can radically change ***material*** properties: liquids and glasses too!

In 2000 Katayama *et al* published evidence for reversible 1st order phase transition in liquid phosphorus [1,2]



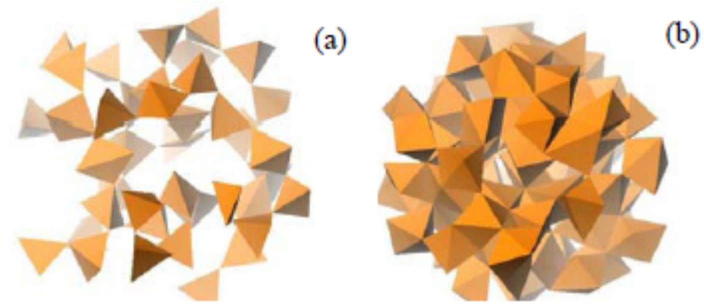
[1] Y Katayama et al, Nature (2000).
[2] Y Katayama et al Science (2004).

Similar transition in water probed using amorphous ice as proxy for high and low density liquids [3,4 & many others…]



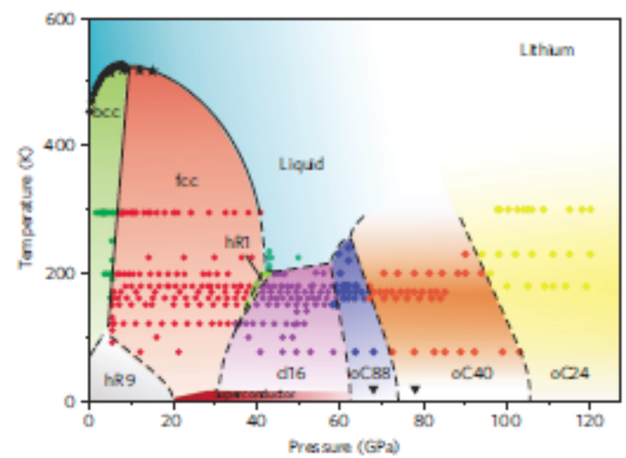
[3] O Mishima et al Nature (1985)
[4] S Klotz et al, PRL (2005)

Local coordination change observed in SiO_2 and GeO_2 (below) [5]



[5]Itie et al PRL 63 (1989); Guthrie et al PRL (2004)

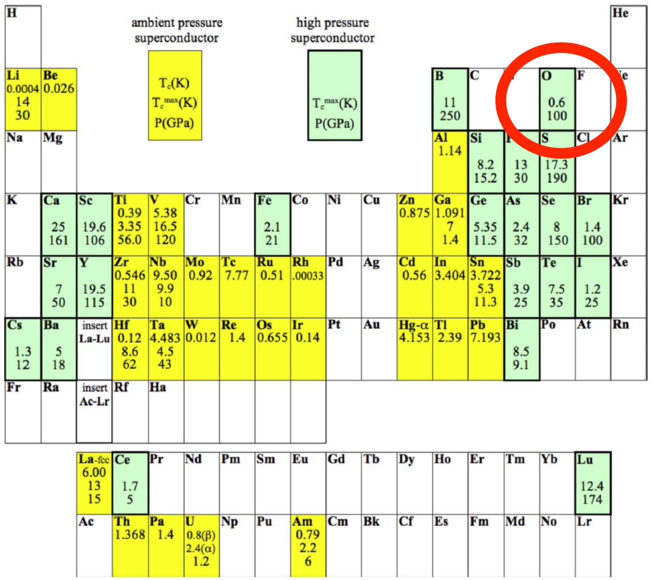
Also exotic behaviour, such as ultra-low temperature melting in lithium [6] and H_2 [7]



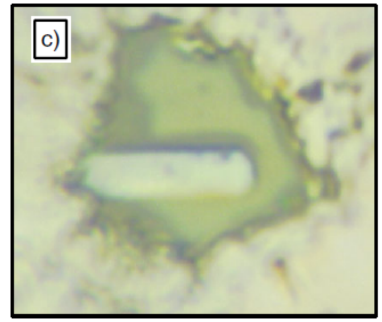
[6] Guillaume et al Nature Phys Online (9 Jan 2011)
[7] Babaev et al PRL (2005).

High pressure – a route to new materials

Pressure can radically change ***electrical and magnetic*** properties

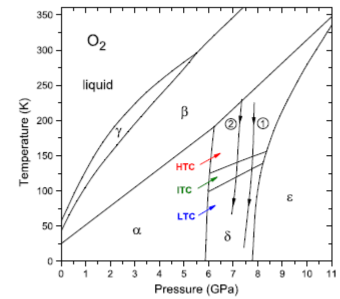


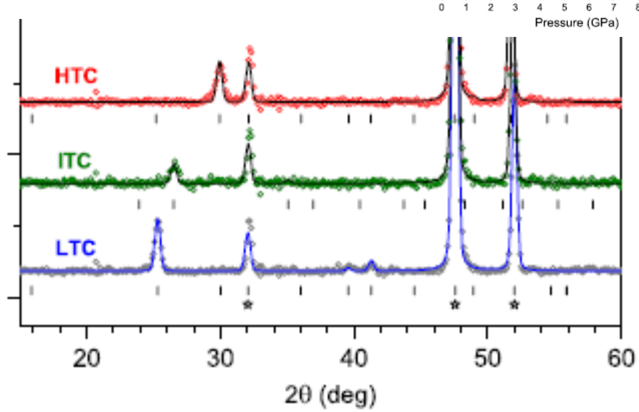
Pressure can induce superconductivity and enhance T_c
[M. Debessai et al PRB 78 064519 (2008).]



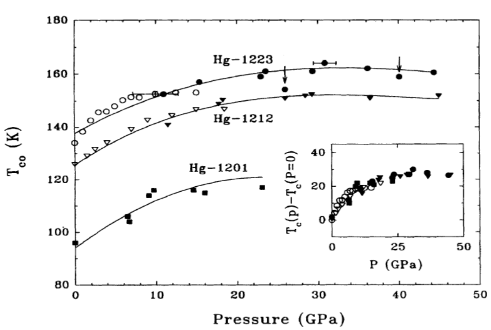
A single crystal of metallic oxygen at 133 GPa
[G. Weck et al PRL 102 255503 (2009).]

O_2 is also simplest *molecular magnet, and* exhibits magnetic transitions under pressure





Klotz et al, PRL 104 11550 (2010).



Highest Tc to date: ~160 K in $HgBa_2Ca_mCu_mO_{2m+2+\delta}$ measured under pressure [Gao et al PRB 50 4260 (1994).

How do you generate high pressures in the lab?

Mechanical compression of gases possible since early in the industrial revolution.
Gas pressures up to ~200 bar (20 MPa) are fairly common.

200-300 kPa (2-3 bar)

1.5 MPa (15 bar)

20 MPa (200 bar)

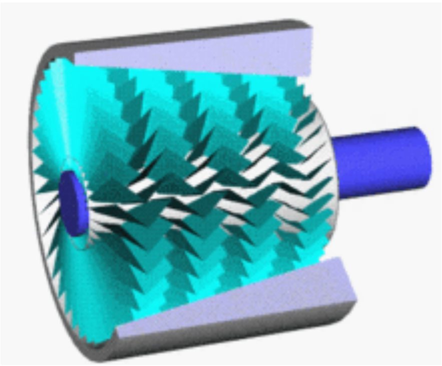
Higher gas pressures of up to 0.2 GPa common in oil & gas industry

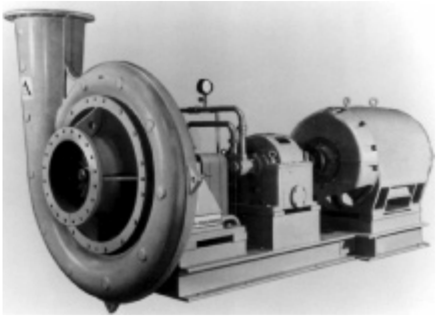
Compressing solids and liquids is much harder, and was considered impossible until early 20th century.

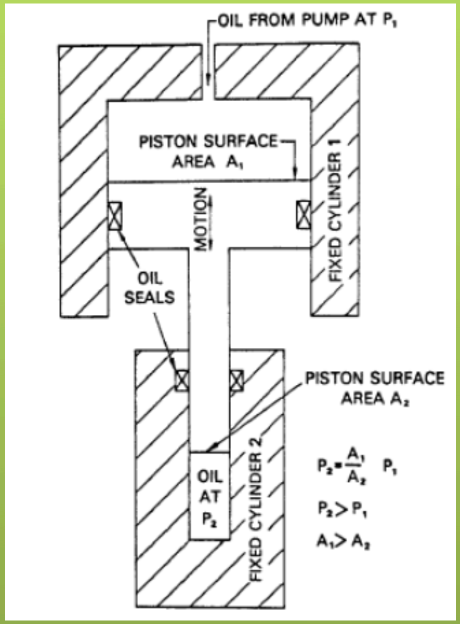
What's the difference between compressing a gas and compressing a solid?

How do you generate high pressures in the lab?

Wide range of gas compressors (see e.g. http://en.wikipedia.org/wiki/Gas_compressor)







For highest gas pressures - one dominant technique: **the piston cylinder.**

P = F/A

- Pressure, P_1 applied to Area, A_1
- This generates force, $F = P_1 * A_1$
- This force is applied to smaller area, A_2
- Generating pressure $P_2 = F/A_2 = P_1 * A_1/A_2$

Generally, the greater the pressure, the simpler the device

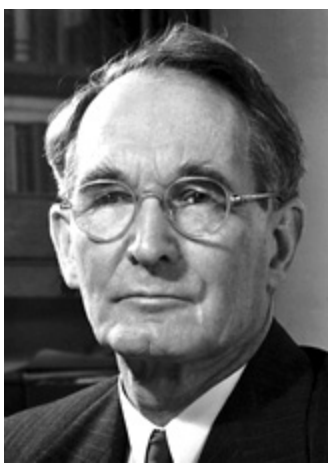
Going beyond the piston-cylinder

How about solids? Can they be compressed using a piston-cylinder?

Yes…Maximum pressures of ~ 2 GPa are relatively routine (max ~ 5 GPa)…this is already enough to compress some solids (consider ice phase diagram – due to rearranging molecules)

But a radically different design was required to go to higher pressure.

This came courtesy of Percy Bridgman in the early 1900's
(and subsequently earned him a Nobel Prize)



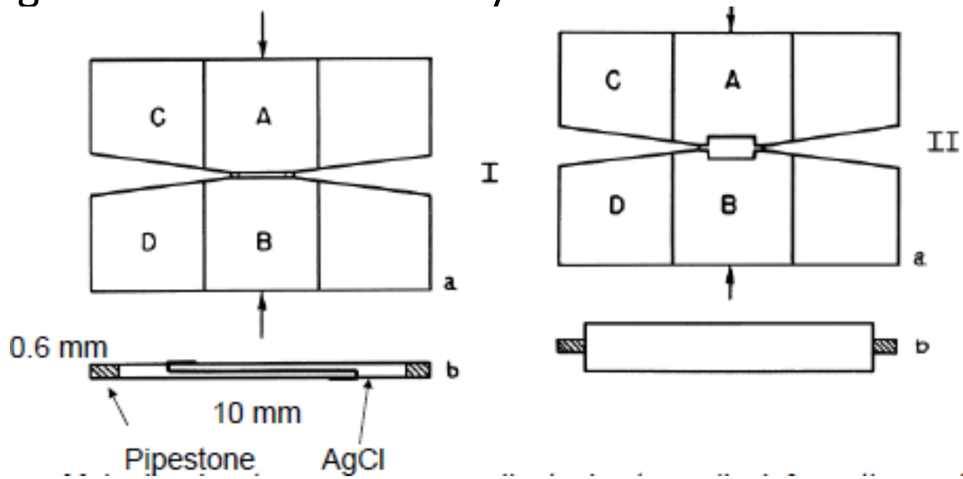
P. W. Bridgman
1882-1961

"You, Mr. Bridgman, have succeeded in doing what was once considered impossible. By the use of new alloys and by other ingenious devices you have been able figuratively speaking, to bring into your laboratory parts of the interior of the earth or of other places where no human being is able to exist, and you have been able there to examine the physical and chemical properties of a quantity of different substances under the enormous pressures you have created. You have thus been able to reveal a number of strange phenomena in the behaviour of matter under other circumstances than those which we consider to be normal."

- Sigurd Curman, President Royal Academy of Sciences,
Prior to presenting Bridgman's Nobel Prize in physics 1946

“Stuck between a hard place and a hard place”

Bridgman’s insight was a technique based around an opposed anvil design – with it he eventually reached ~40 GPa



Three elements of the opposed anvil technique:

1) Two anvils made of a hard material
2) A force to push these anvils together
3) A gasket made of a material that is strong, but able to flow

These same principles apply to the majority of high pressure cells operating today above ~2 GPa at synchrotron and neutron sources.

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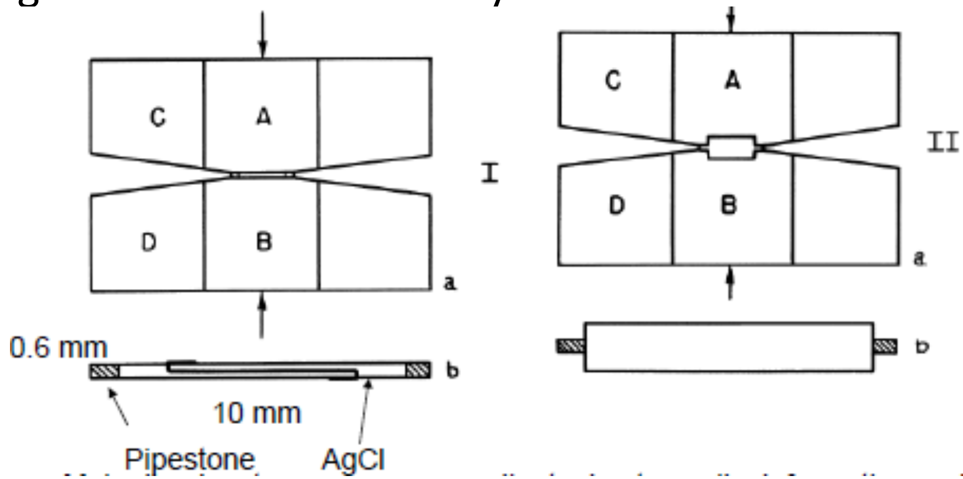

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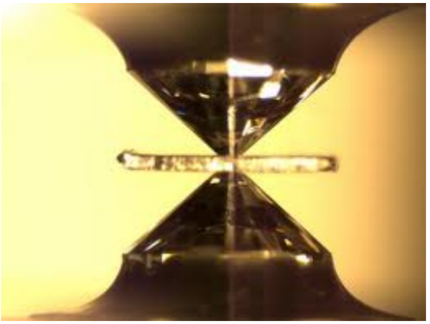
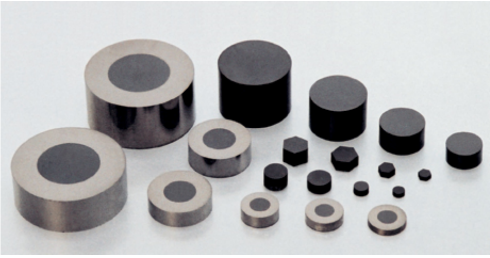
“Stuck between a hard place and a hard place”

What is a hard material? Bridgman used a composite of WC and cobalt). Other materials used are pure WC, sapphire (Al_2O_3), moissanite (SiC), c-BN…



But in almost all cases, the best material is diamond.
Diamond anvils are either single-crystal or poly-crystalline. PCD available (sintered, typically with Co binder). Also in last 10 years ultra-hard nano-PCD (HIME-DIA)



Three elements of the opposed anvil technique:

1) **Two anvils made of a hard material**
2) A force to push these anvils together
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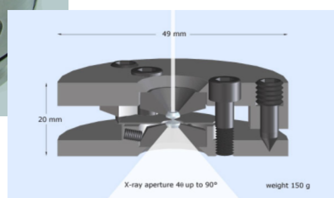
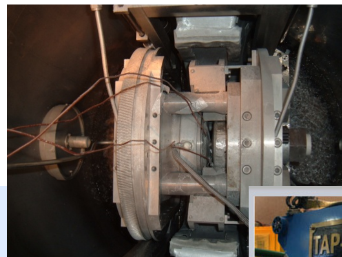
“Stuck between a hard place and a hard place”

The amount of force (and how it’s applied) depends on the area of the sample and the required pressure



X-ray cells (<1 tonne) (screw, membrane, piezo actuator)



“conventional” neutron cells 150-500 tonnes (hydraulic presses)

Multi-anvil 1000-6000 tonnes

Three elements of the opposed anvil technique:

1) Two anvils made of a hard material

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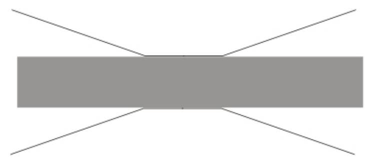
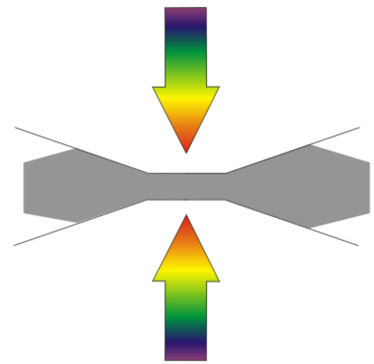
“Stuck between a hard place and a hard place”

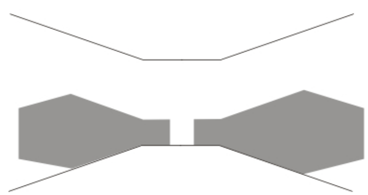
1) Gasket (typically metal, but can also be composite material)

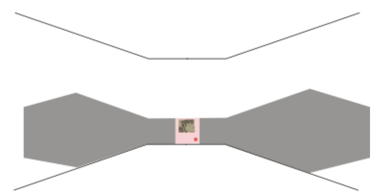




2) Apply force to ‘indent’ gasket:
•Work hardens gasket
•Forms support for diamond tips
•stable geometry (thin)

3) drill hole for sample (for DAC’s need EDM or laser as hole is very small)





4) Load sample, pressure calibrant* and pressure medium*

Three elements of the opposed anvil technique:
1) Two anvils made of a hard material
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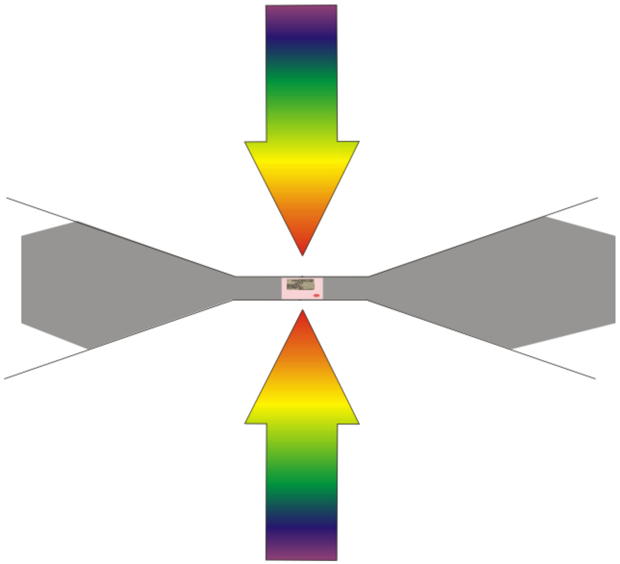
(* discussed soon)

“Stuck between a hard place and a hard place”

Seal cell by applying further force. As gasket can flow, it follows pressure gradient, moving away from sample.

In process, thinning and reducing volume available to sample – increasing pressure.



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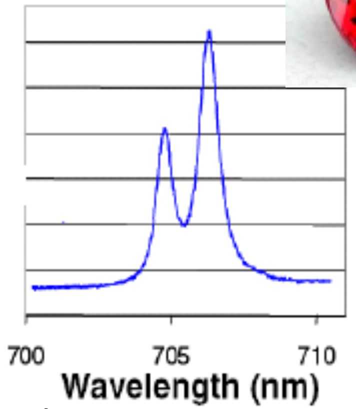
Pressure measurement

As with any experiment, accurate knowledge of the variable you control is very important.

Pressure is measured the same way any other variable is:
calibration of something with a physical response to variable of interest



Example 1) Ruby fluorescence.
•Probably the most ubiquitous pressure sensor above 2 GPa
•Under laser light, ruby fluoresces with particular spectrum
•The wavelength (colour) shifts in a known way with pressure

Example 2) Known equation-of-state of calibrant
•If ruby isn't an option (opaque anvils,high temperature,reactivity)
•Can load a secondary sample with a known pressure-volume relation. Use diffraction to determine volume – and, therefore, pressure.

Others…raman shift of C^{13}, pressure-load curves, ...

How are the calibrants calibrated?

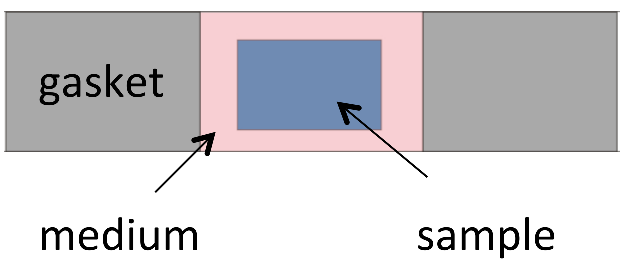
Typically shock wave data (discussed later) can give a direct equation of state.

Pressure media

Imagine hard sample directly squeezed between two diamonds…

Results in enormous strain (often many GPa)

Solution is to surround the sample with a medium that is very soft…



- Because medium is soft, it can't sustain a P gradient
- Sample feels equal pressure on all sides
- Fragile single-crystals, bio-sample can be compressed
- Best media are the inert gases: He, Ne, Ar
- Methanol:ethanol, silicon oil, fluorinert also used

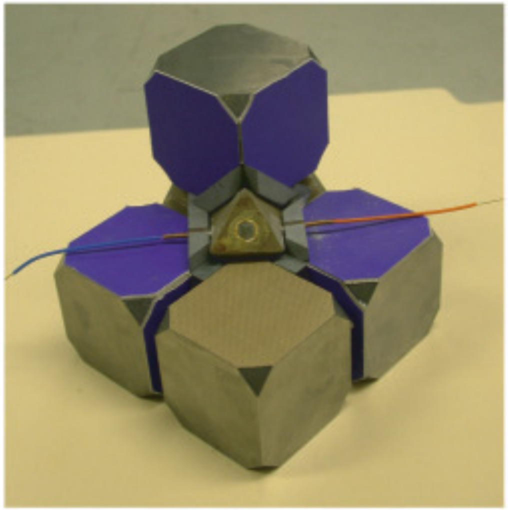
(Need medium that doesn't react with sample)

Beyond two opposed anvils

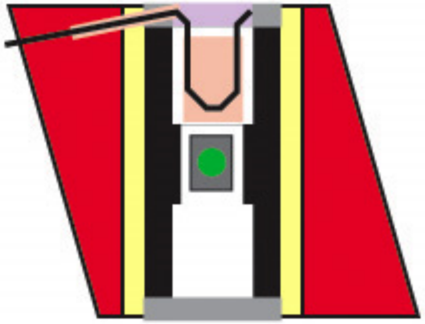
For large volumes, an alternative technique uses multiple (typically 6-8) anvils.
Ideally suited for liquid/glass diffraction studies, tomography, element partitioning studies...

Elements:
•Usually uniaxial force (from very large capacity press (+1000 tonnes) but 6 axis presses exist
•6 anvils with square faces come together to form a cubic sample volume
•8 anvils – cubes with corner cut off - form octahedral sample space. This (square) assembly can be pressed inside 6 regular anvils (double-stage design)

Sample space is typically filled with:
•Gasket
•Thermal insulation
•Graphite Heater
•Contacts for thermocouples/ heater
•Pressure medium/sample encapsulation



8 cubes (5 shown) press on octahedron
Gaskets are made of pyrophyllite



Cross section of octahedron shows:
MgO pressure medium (red)
ZrO2 insulator (yellow)
stepped LaCrO3 heater (black)
Mo rings (grey)
MgO insulating parts (white)
Sample (grey/green)
Thermocouple wire

2-stage design with PCD anvils, can reach ~80 GPa

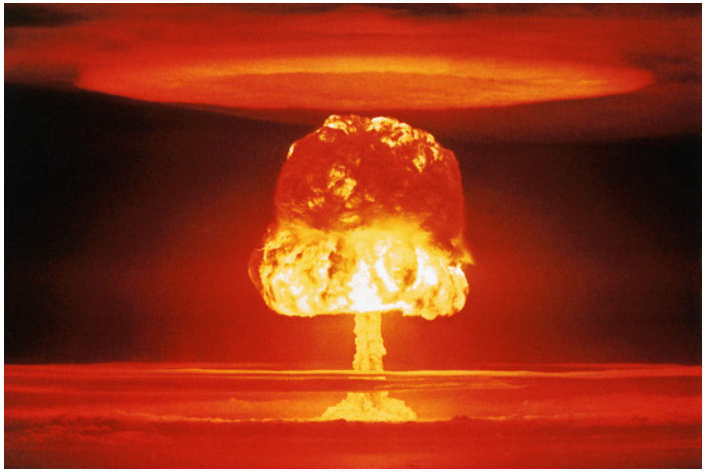
Reference: http://www.gps.caltech.edu/~jed/Multianvilpage.html; http://www.misasa.okayama-u.ac.jp/~hacto/facility_e.html

Dynamic compression

Completely different route to achieve highest pressures is via dynamic techniques:

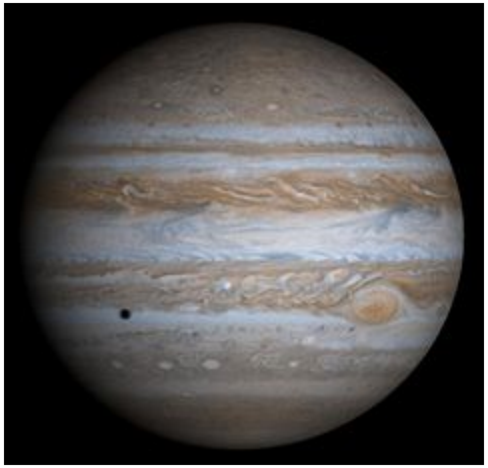
Shockwaves can generate exceptionally high P & T over short time period:

- •Nuclear
- •Gas gun
- •Lasers (NIF)



Under shock, samples experience conditions that lie on a locus in PT space called "Hugoniot"

At NIF expect to reach TPa and 10^4 K regime (Centre of Jupiter)



Alternative techniques using Piezo actuators can look at dynamic phenomena.

DC-CAT is a proposed beamline at APS that will permit synchrotron studies on dynamic compression events

Science at high pressure

Have looked at ways to generate, control and measure extremely high pressures.
In order to conduct *science*, need way to probe effect of pressure on sample material

Great variety of probes:

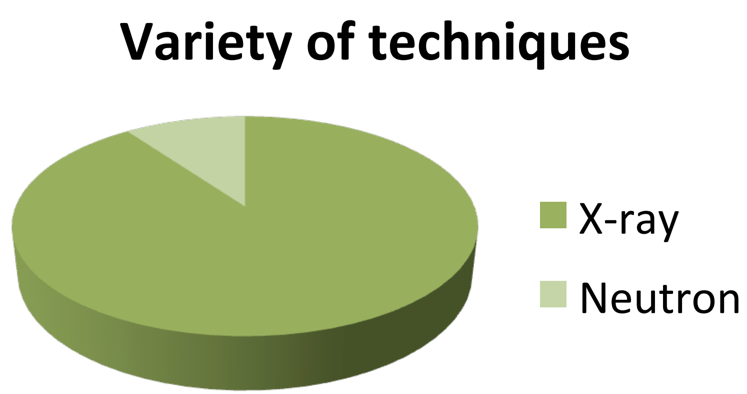
Visual observations
Phase transitions (solid-solid, melting, conductivity), single-crystal growth

Laser-based
Raman, UV & IR spectroscopy
Brillouin

Transport measurements
Electrical conductivity, magnetic suseptibility

Others…
sound velocity, DTA…

Focus here on synchrotron x-ray and neutron based probes



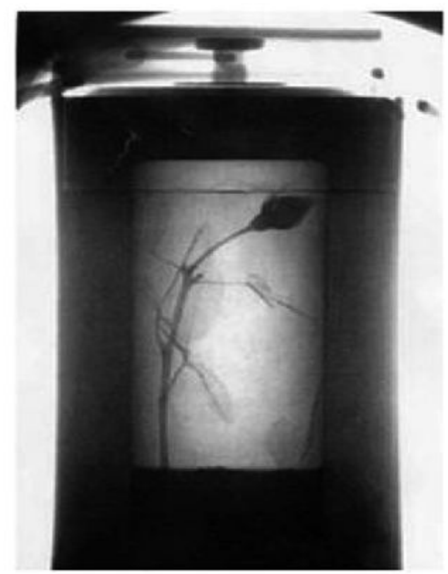
•Above 0.6 GPa, neutrons limited to diffraction, phonon measurements, tomography.
•In contrast, huge (and rapidly expanding) range of synchrotron x-ray techniques: (XRD, XAS, XMCD, XRS, XES, IXS, NRIXS, transmission density, tomography…)

Neutrons have many unique capabilities

1) Scattering length is independent of atomic number and atomic mass
- neutron diffraction is a great tool for studying light atoms. It's the only technique that can precisely locate protons (deuterons), Be, B^{11}, C, N, and O strong scatterers
- isotopic substitution can greatly enhance contrast and can also simplify analysis of non-crystalline matter.
- possibility of negative scattering lengths (e.g. H) means specific pair correlations can be removed.
-same is true for absorption cross-sections: Li^6, H, B^{10} are strong absorbers. Pb is transparent.

2) Neutrons have an intrinsic magnetic moment
- They are scattered by nuclear spins and sensitive to magnetic order.

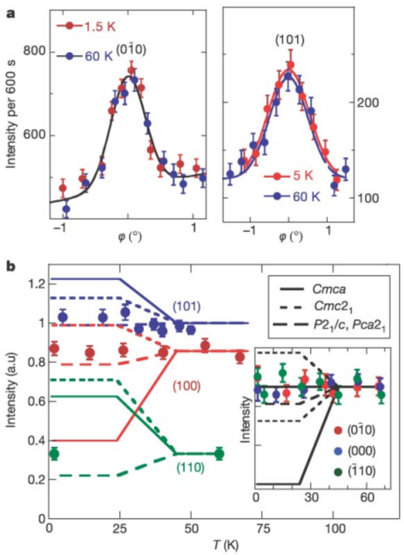
3) Scattering is via inter-nuclear interactions. Pointlike.
- No atomic form factor, so high Q-vectors are accessible. Leading to exceptional real-space resolution.



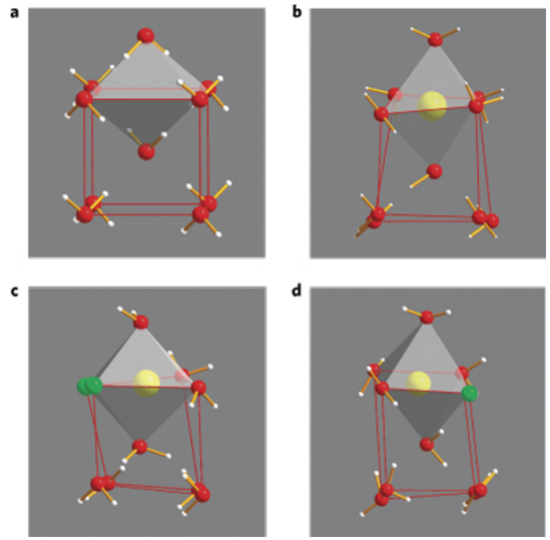
[Neutron imaging and applications, Bilheux et al]

Examples of High-Pressure Neutron science

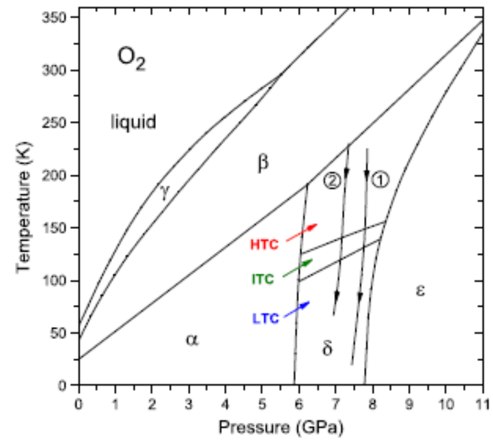
Broken symmetry in hydrogen
Goncharenko & Loubeyre Nature (2005).



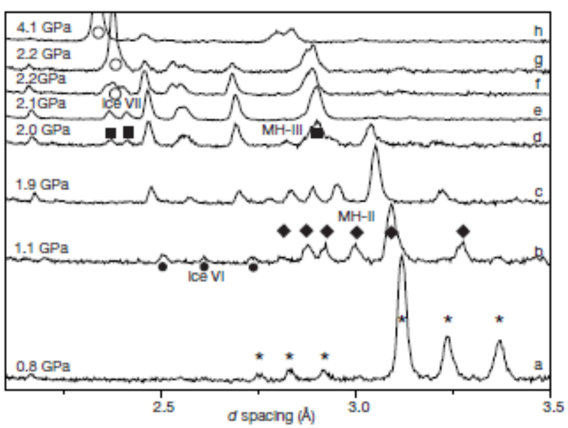
Salty Ice VII
Klotz et al Nature Physics (2009).



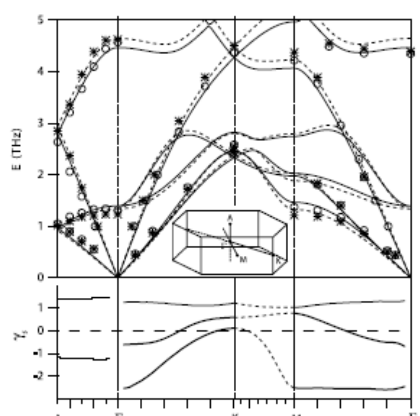
Magnetic ordering in solid O_2
Klotz et al PRL (2010).



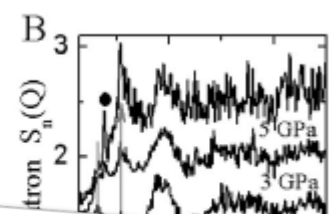
Stability of methane hydrate
Loveday et al Nature (2001).



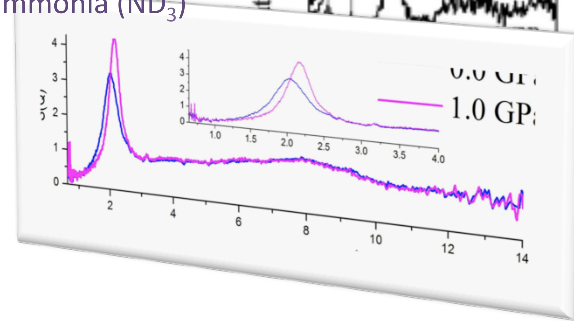
Phonon dispersion in ice Ih
Strassle et al PRL (2004).



IRO collapse in glassy GeO_2
Guthrie et al PRL (2004).

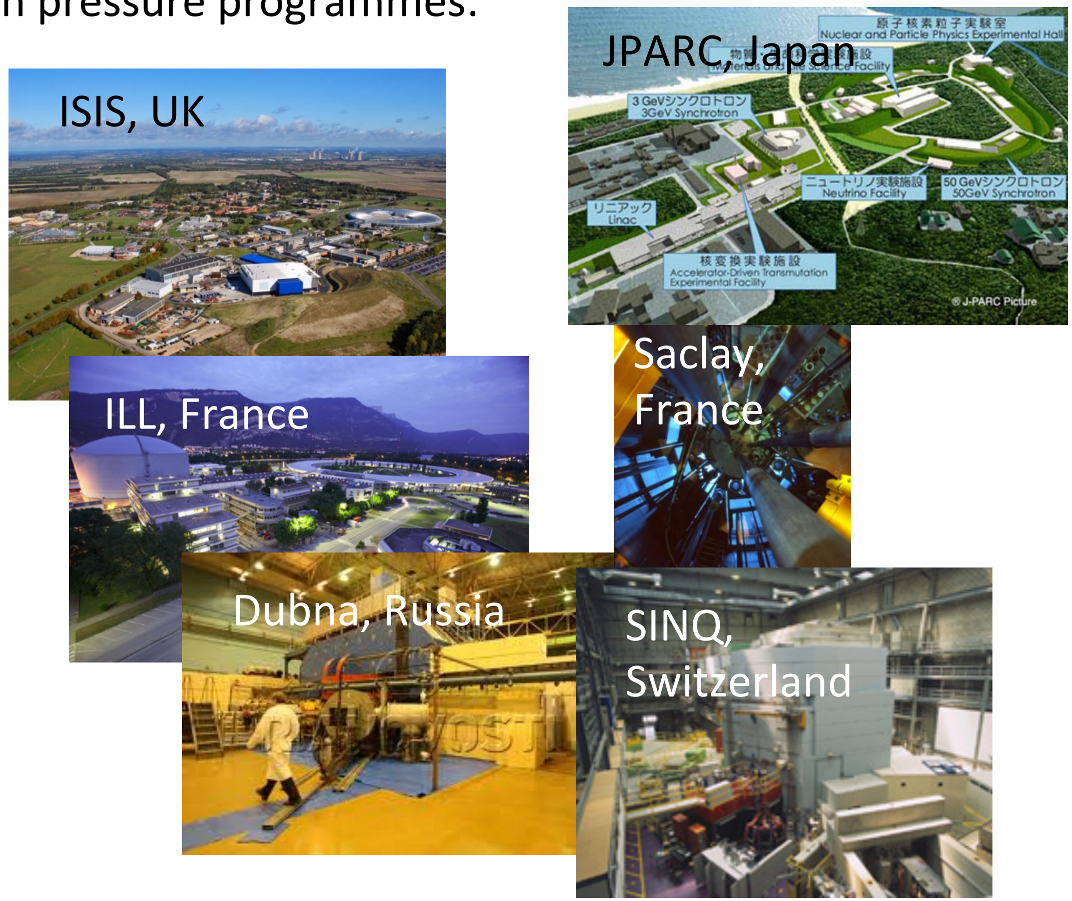


Liquid ammonia (ND_3)

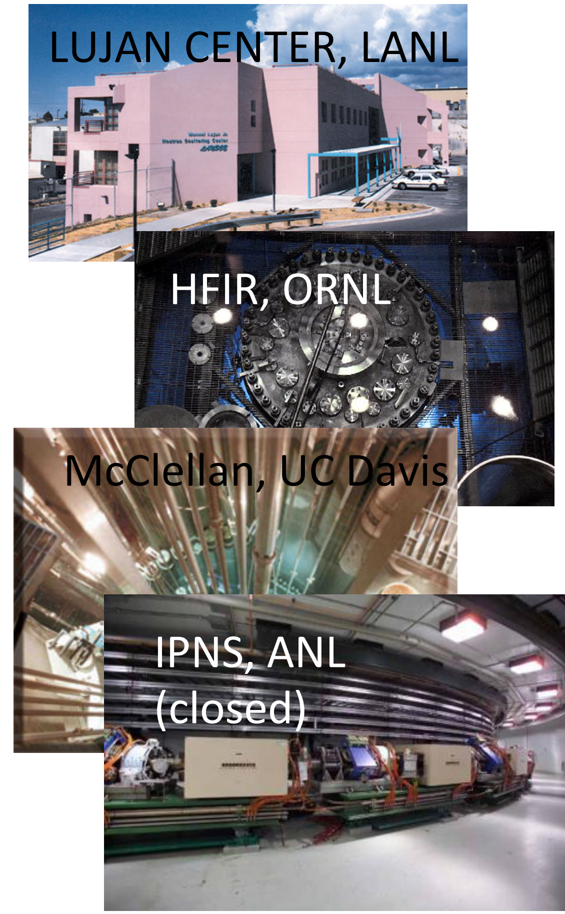


Neutrons science at high pressure

World neutron facilities with
High pressure programmes:



US Facilities:

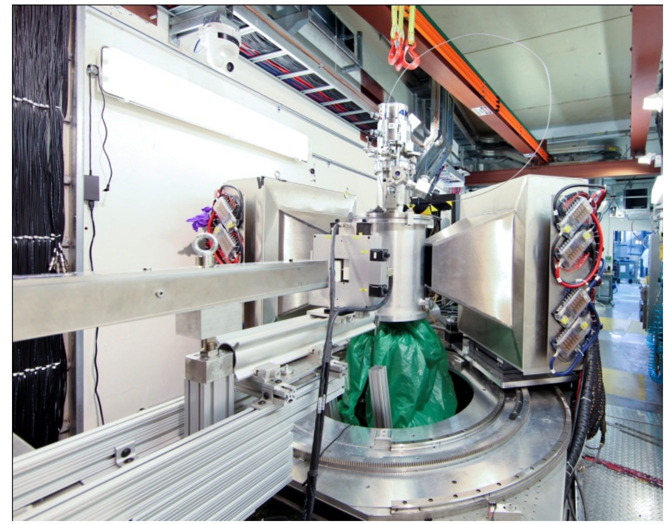


- **Typical max pressure ~ 25 GPa**
- **Max temperature ~ 1500 K**
- **Min temperature ~4 K**

Which facility is missing…

SNAP – high pressure at the SNS

SNAP has enormous potential to revolutionise high pressure neutron science

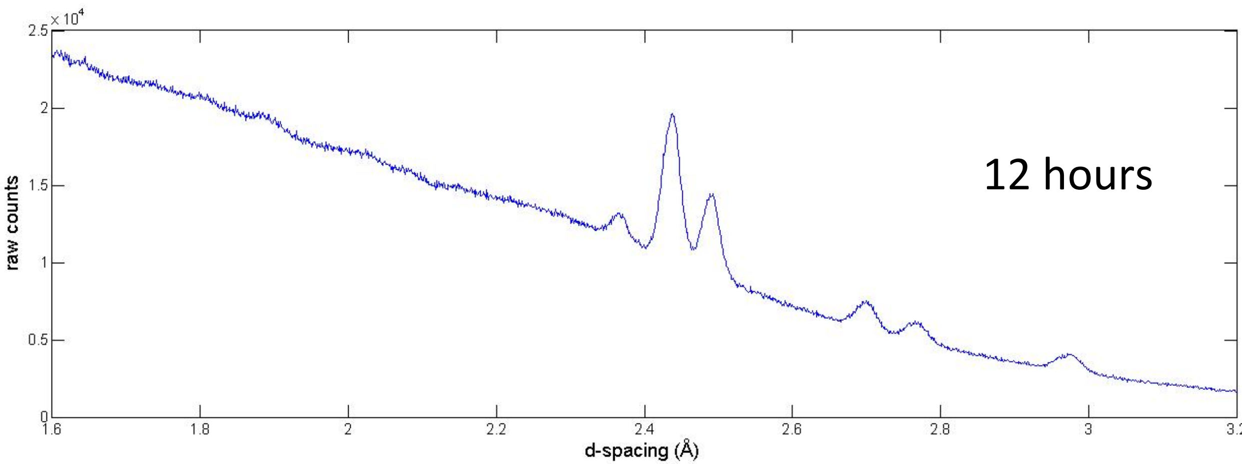


- Highly pixelated area detectors (Anger cameras) give simultaneous access to large volumes of reciprocal space.
- Movable detectors mean wavelength coverage can be swept from low to high Q-vectors (or high to low d-spacing)
- Moveable flight tube can be replaced with different focusing optics (Elliptical or KB).
- Precise (1um) stage permits alignment of very small samples.
- Highly versatile diffractometer: can study single-crystals, powders or even liquid structure

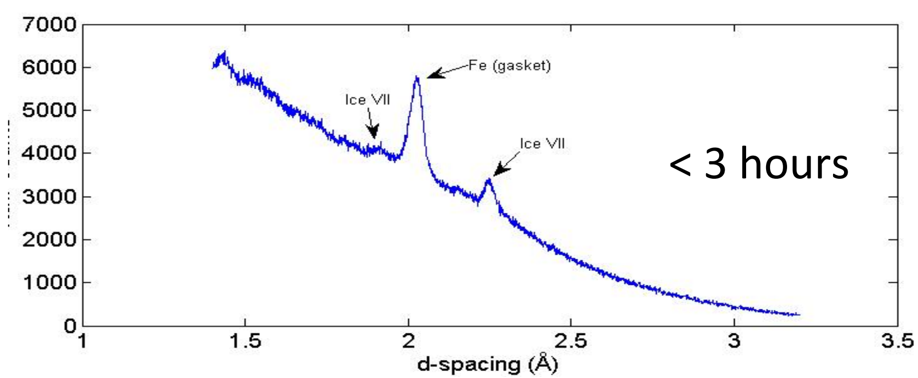
SNAP – high pressure at the SNS

Key is that intense flux means samples can be small

Typical neutron sample volumes are $100 mm^3$.
In last few months high-quality powder data with ~$0.01 mm^3$ (10ug) have been measured on SNAP. **That's a volume reduction of 10,000**



D_2:D_2O hydrate (1 GPa) **$0.08 mm^3$**

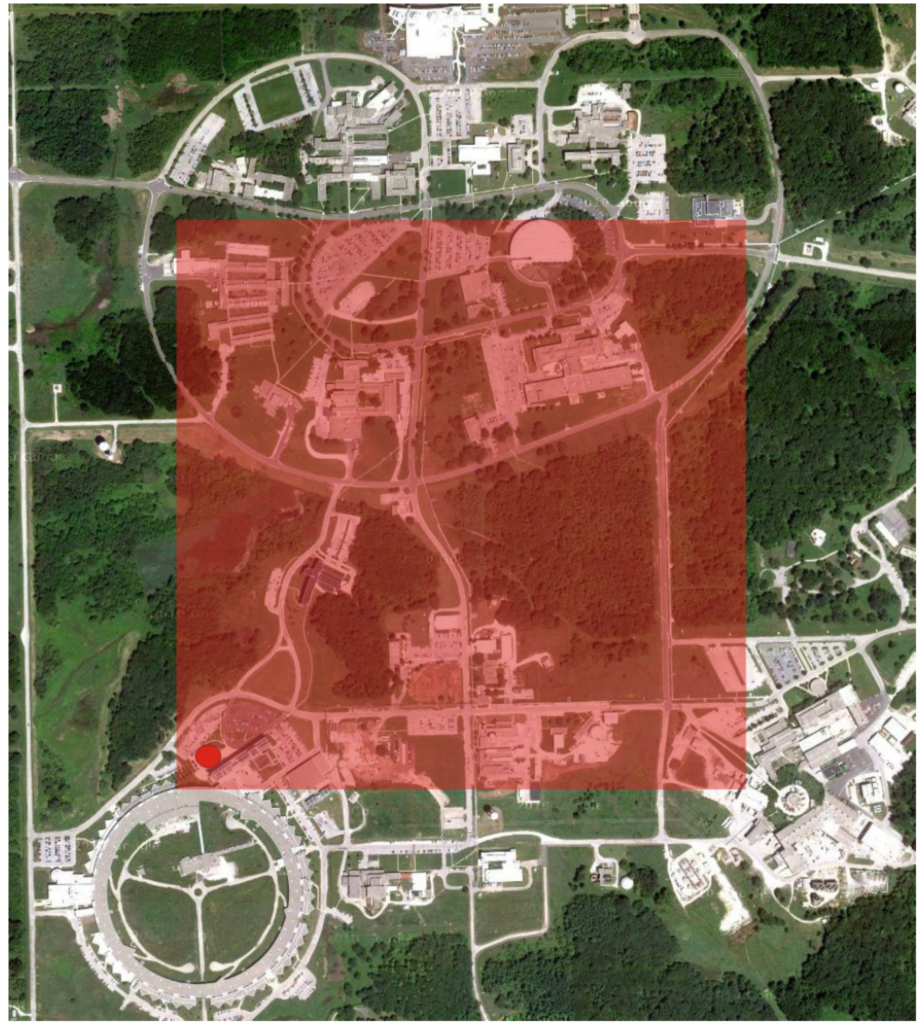


D_2O Ice VII (8 GPa) **$0.01 mm^3$**

SNAP – high pressure at the SNS

Area ratio of > 450

•Means high-quality diffraction data up to 60 GPa with powders in 1-2 years
•100 GPa may be possible with single-crystals.
•Cells built around single-crystal diamond provide optical access:
  •Laser heating to >3000K
  •Simultaneous spectroscopy
  •Gas loading capabilities.



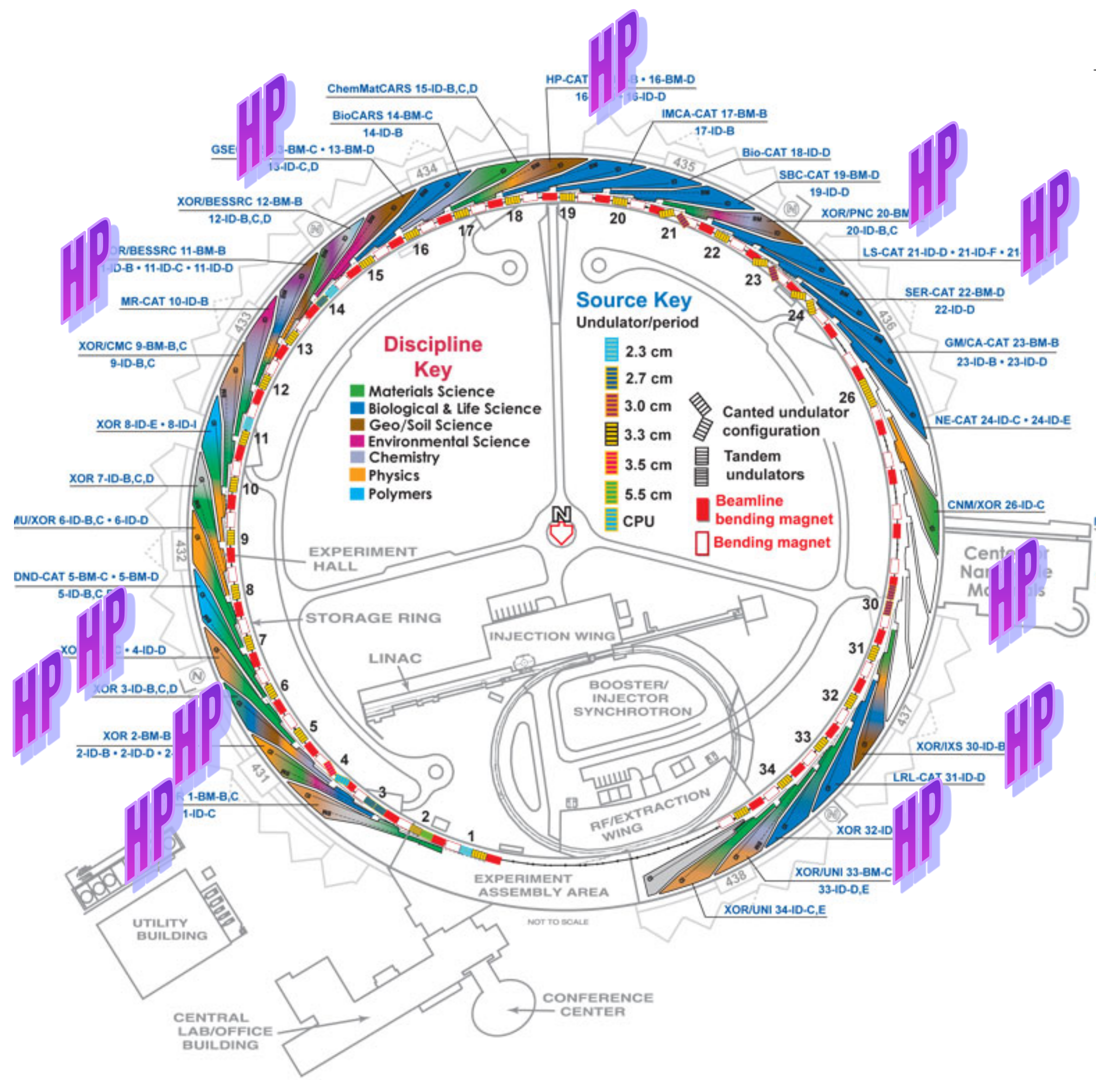
Just entering a new regime for high pressure neutron science

X-ray science at high pressure

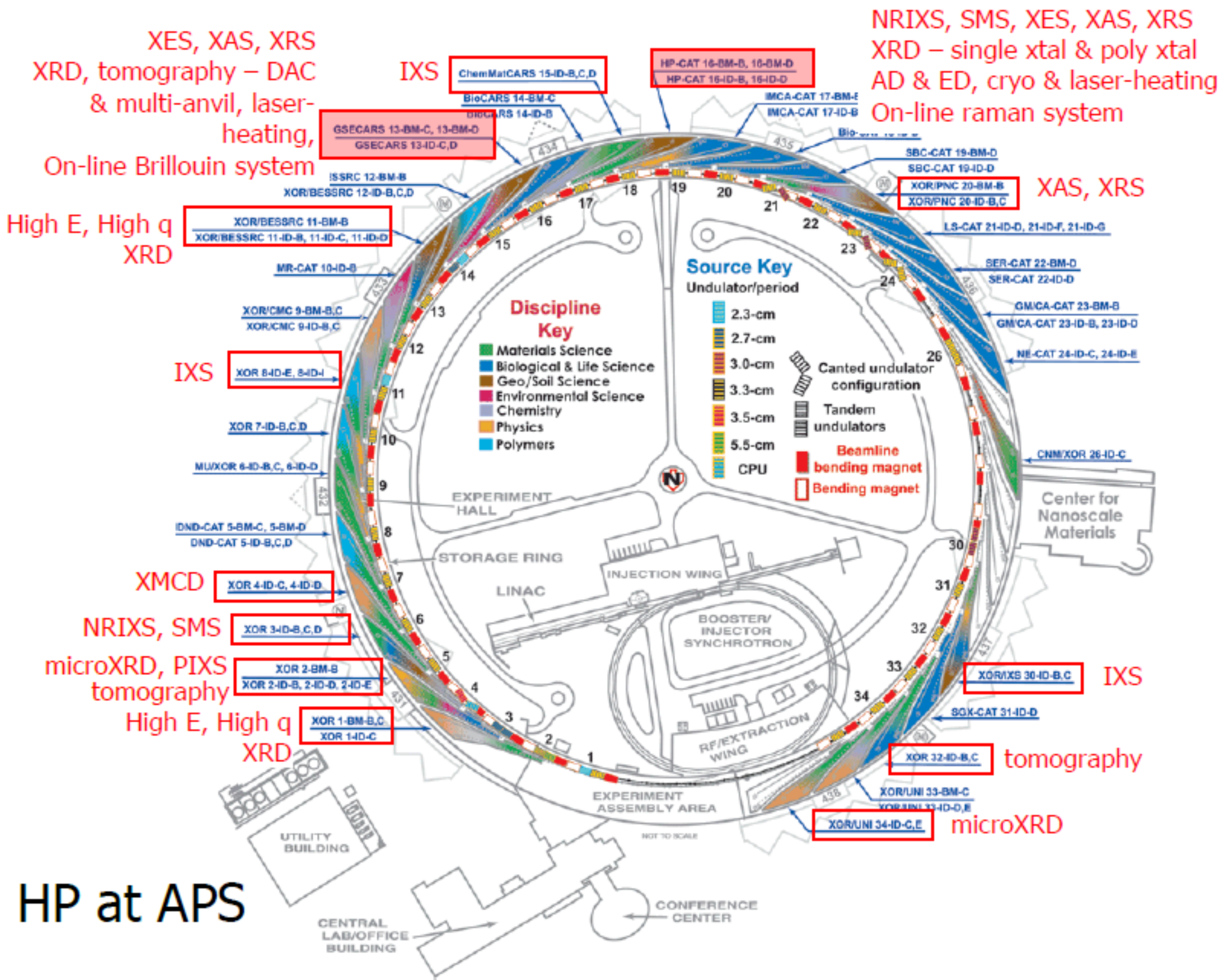
Access to high pressure at synchrotron sources has exploded in last 10 years

All major synchrotrons have dedicated high pressure beamlines (e.g. ESRF, APS, SPring-8, Petra-III,
NSLS, NSLS-II (proposed). Extreme conditions are an integral part of the (ongoing) APS upgrade.

Beyond dedicated beamlines…portable high pressure apparatus are extremely wide-spread.



With few exceptions almost all synchrotron techniques you've heard about this week can be applied at high pressure



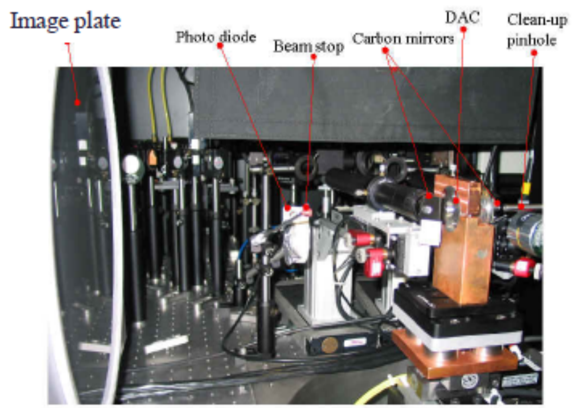
XES, XAS, XRS
XRD, tomography – DAC
& multi-anvil, laser-
heating,
On-line Brillouin system
IXS
ChemMatCARS 15-ID-B,C,D
HP-CAT 16-BM-B, 16-BM-D
HP-CAT 16-ID-B, 16-ID-D
NRIXS, SMS, XES, XAS, XRS
XRD – single xtal & poly xtal
AD & ED, cryo & laser-heating
On-line raman system
BioCARS 14-BM-C
GSECARS 13-BM-C, 13-BM-D
GSECARS 13-ID-C,D
IMCA-CAT 17-BM-B
IMCA-CAT 17-ID-B
SBC-CAT 19-BM-D
SBC-CAT 19-ID-D
XOR/PNC 20-BM-B
XOR/PNC 20-ID-B,C
XAS, XRS
ISSRC 12-BM-B
XOR/BESSRC 12-ID-B,C,D
High E, High q
XRD
XOR/BESSRC 11-BM-B
XOR/BESSRC 11-ID-B, 11-ID-C, 11-ID-D
LS-CAT 21-ID-D, 21-ID-F, 21-ID-G
MR-CAT 10-ID-B
SER-CAT 22-BM-D
SER-CAT 22-ID-D
XOR/CMC 9-BM-B,C
XOR/CMC 9-ID-B,C
GM/CA-CAT 23-BM-B
GM/CA-CAT 23-ID-B, 23-ID-D
NE-CAT 24-ID-C, 24-ID-E
IXS
XOR 8-ID-E, 8-ID-I
Source Key
Undulator/period
2.3-cm
2.7-cm
3.0-cm
3.3-cm
3.5-cm
5.5-cm
CPU
Canted undulator configuration
Tandem undulators
Beamline bending magnet
Bending magnet
Discipline Key
Materials Science
Biological & Life Science
Geo/Soil Science
Environmental Science
Chemistry
Physics
Polymers
XOR 7-ID-B,C,D
MU/XOR 6-ID-B,C, 6-ID-D
CNM/XOR 26-ID-C
EXPERIMENT HALL
Center for Nanoscale Materials
DND-CAT 5-BM-C, 5-BM-D
DND-CAT 5-ID-B,C,D
STORAGE RING
INJECTION WING
LINAC
XMCD
XOR 4-ID-C, 4-ID-D
BOOSTER/ INJECTOR SYNCHROTRON
NRIXS, SMS
XOR 3-ID-B,C,D
microXRD, PIXS
tomography
XOR 2-BM-B
XOR 2-ID-B, 2-ID-D, 2-ID-E
XOR/IXS 30-ID-B,C
IXS
SGX-CAT 31-ID-D
High E, High q
XRD
XOR 1-BM-B,C
XOR 1-ID-C
RF/EXTRACTION WING
XOR 32-ID-B,C
tomography
EXPERIMENT ASSEMBLY AREA
XOR/UNI 33-BM-C
XOR/UNI 34-ID-C,E
microXRD
UTILITY BUILDING
CONFERENCE CENTER
CENTRAL LAB/OFFICE BUILDING

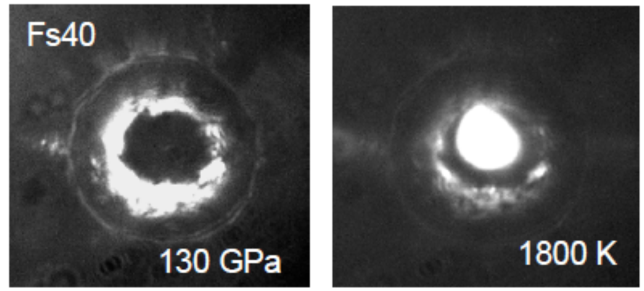
HP at APS

High-pressure diffraction with x-rays

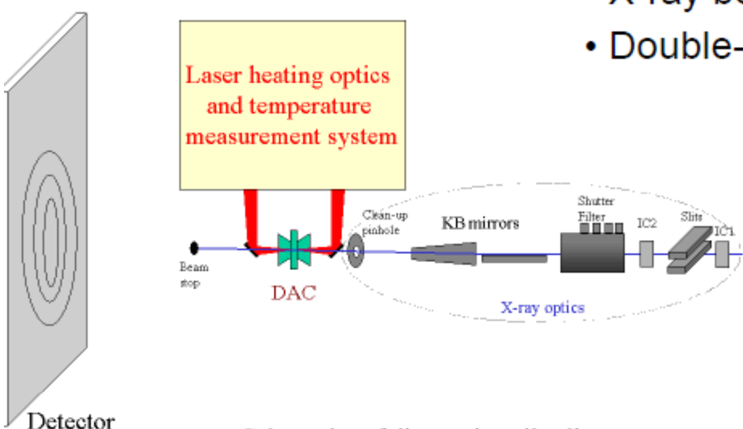
Modern HP beamlines deliver extremely intense, low divergence beams 2-5um

Coupled with laser heating – can reach >300 GPa and >3000 K

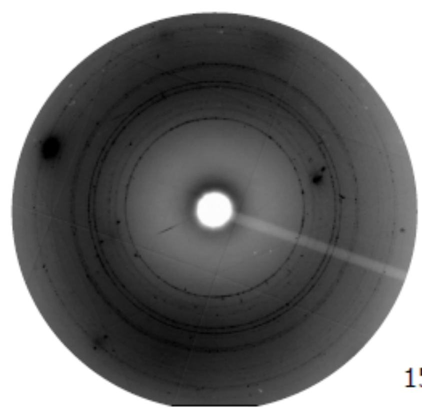




- Gasket hole ~ 60 μm (culet =150 μm, bevel diameter = 300 μm)
- X-ray beam ~ 6 x 7 μm
- Double-sided Nd:YLF laser heating



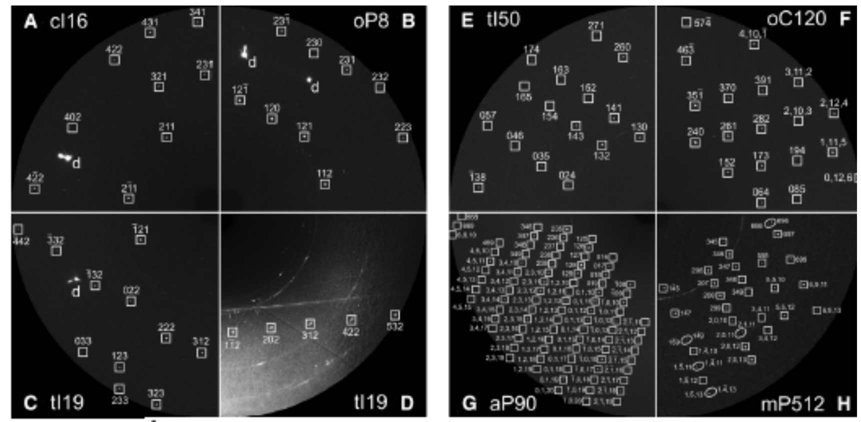
Schematics of diamond anvil cell setup at 13ID-D at the Advanced Photon Source



High-pressure diffraction with x-rays

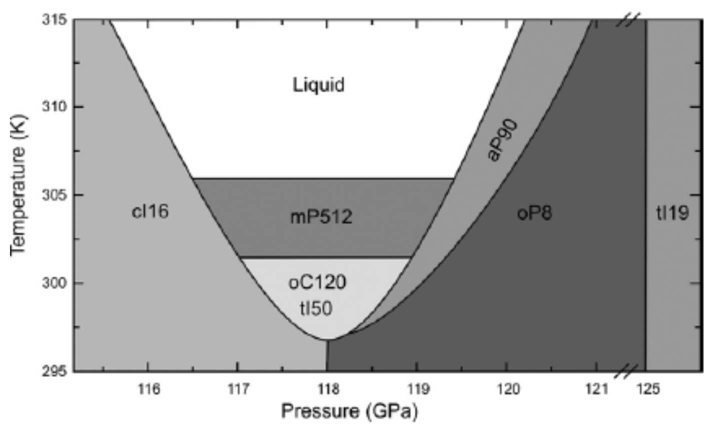
Single-crystal techniques are essential for studying systems that, under pressure, are surprisingly complex (e.g. Na, Li and Rb)

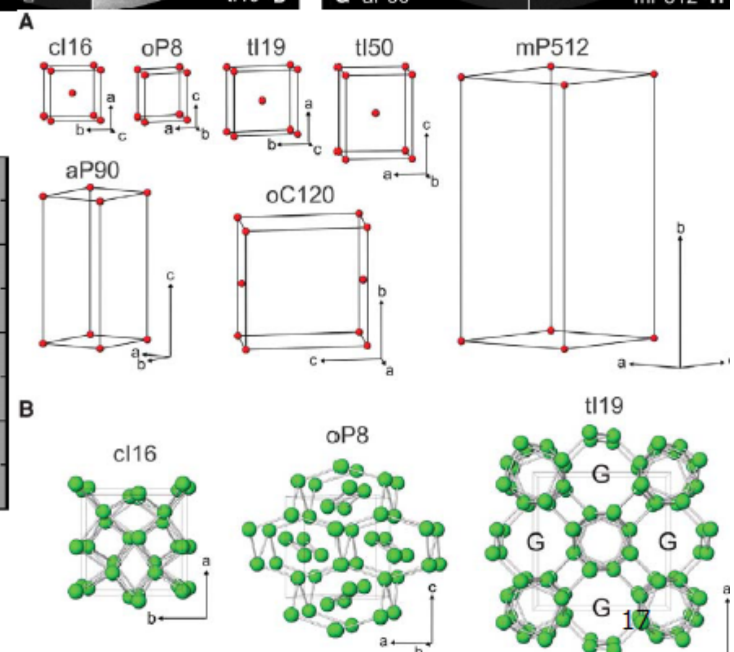
HP Single crystal XRD



Sodium
Phase labeling scheme reflects No. atoms in unit cell.
(at ambient, Na is bcc: 2 atoms in unit cell)

- At minimum in melting curve of Na at ~118 GPa, 7 crystalline phases (many quite complex).





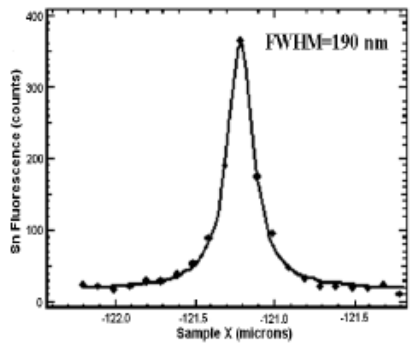
Gregoryanz et al, *Science* 2008

High-pressure diffraction with x-rays

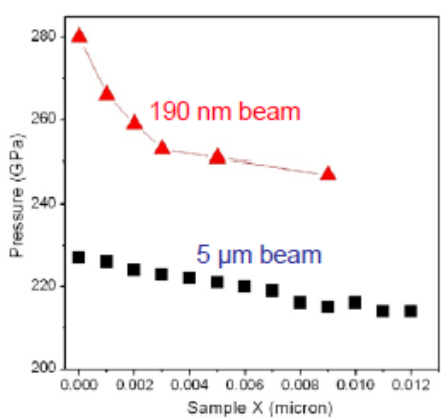
Beams orders of magnitude smaller than neutrons permit sub-micron studies
(could be route to TPa pressures?)

Using 200 nm focused x-ray beam we can...

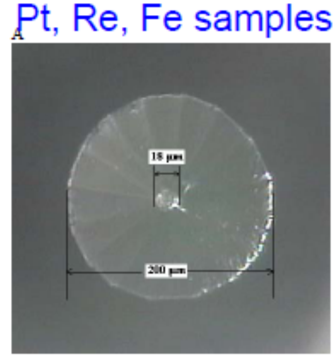
L Wang , PNAS (2010)

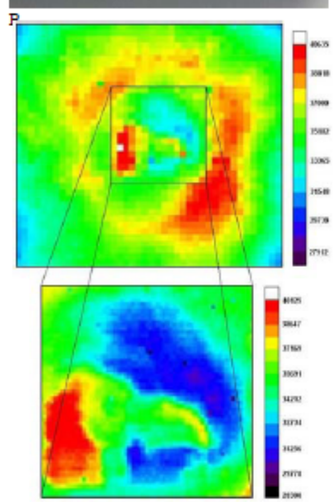


Observe 20 GPa/µm gradiant & peak-pressure in 1-µm area



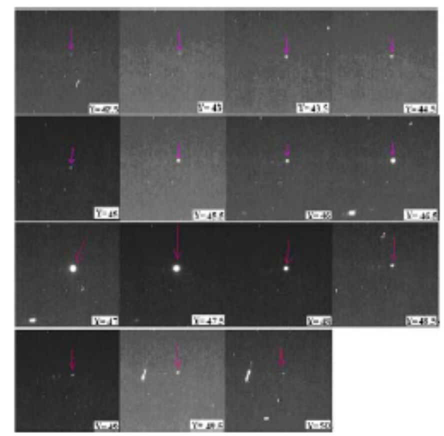
Separate submicron Pt, Re, Fe samples

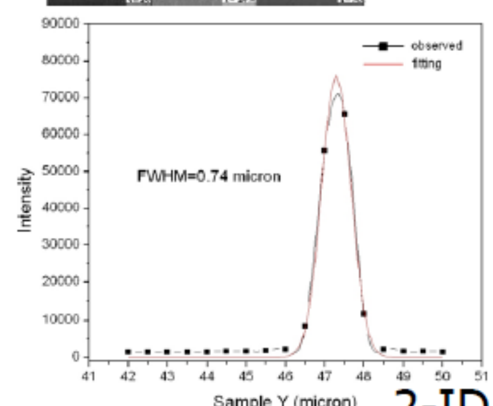




34-ID

Conduct single-crystal XRD on submicron powder



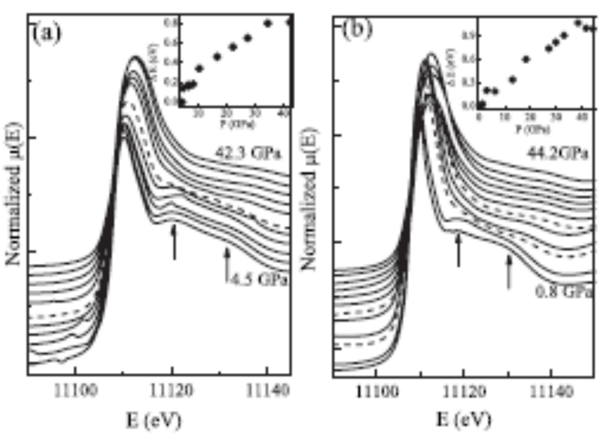


2-ID

X-ray absorption spectroscopy (XAS)

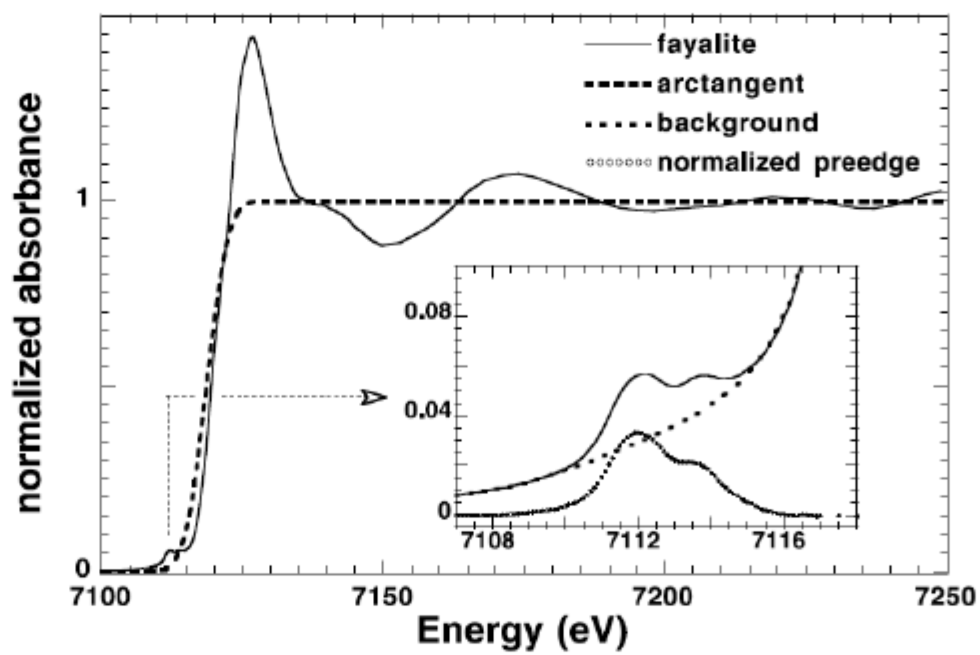
Direct insight into local structure and bonding environment

- Pre-edge position and intensity: oxidation state
- Edge height: concentration
- XAFS: coordination & structure



Coordination change in GeO_2 glass measured with XANES

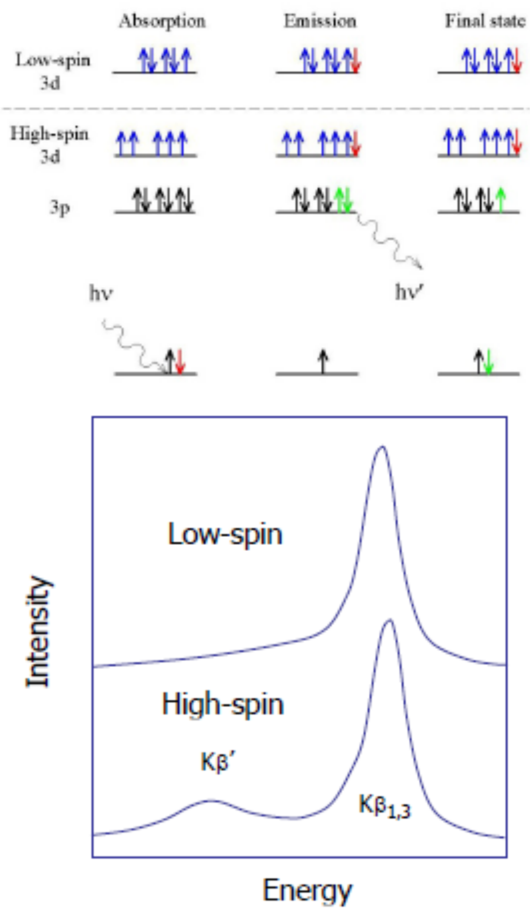
Baldini et al PRB (2010).



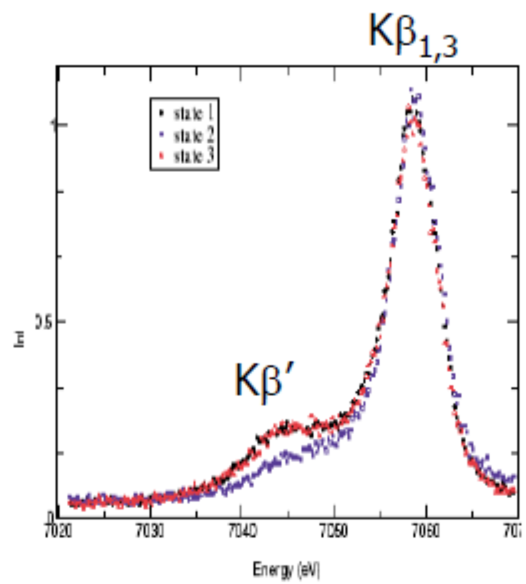
Wilke et al, Amer. Min. 2001

High-pressure x-ray emission spectroscopy (XES)

Observations of high spin-low spin transitions in 3*d* elements



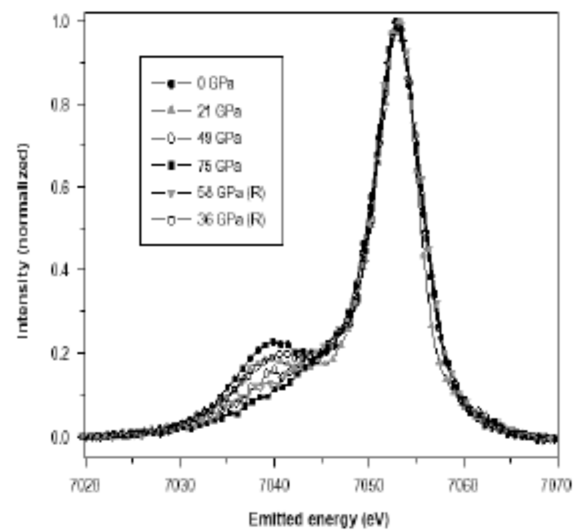
FeO & Fe_2O_3



Badro *et al*, *PRL* 1999

Badro *et al*, *PRL* 2002

(Fe,Mg)O & $(Fe,Mg)SiO_3$



Badro *et al*, *Science* 2003

Badro *et al*, *Science* 2004

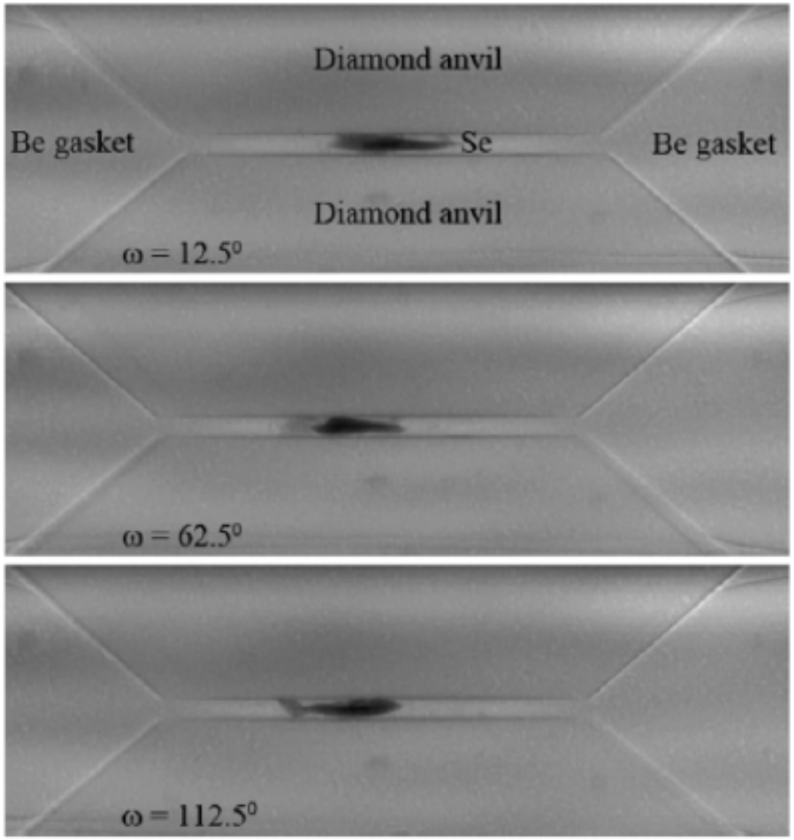
Li *et al*, *PNAS* 2004

Lin *et al*, Science 2007

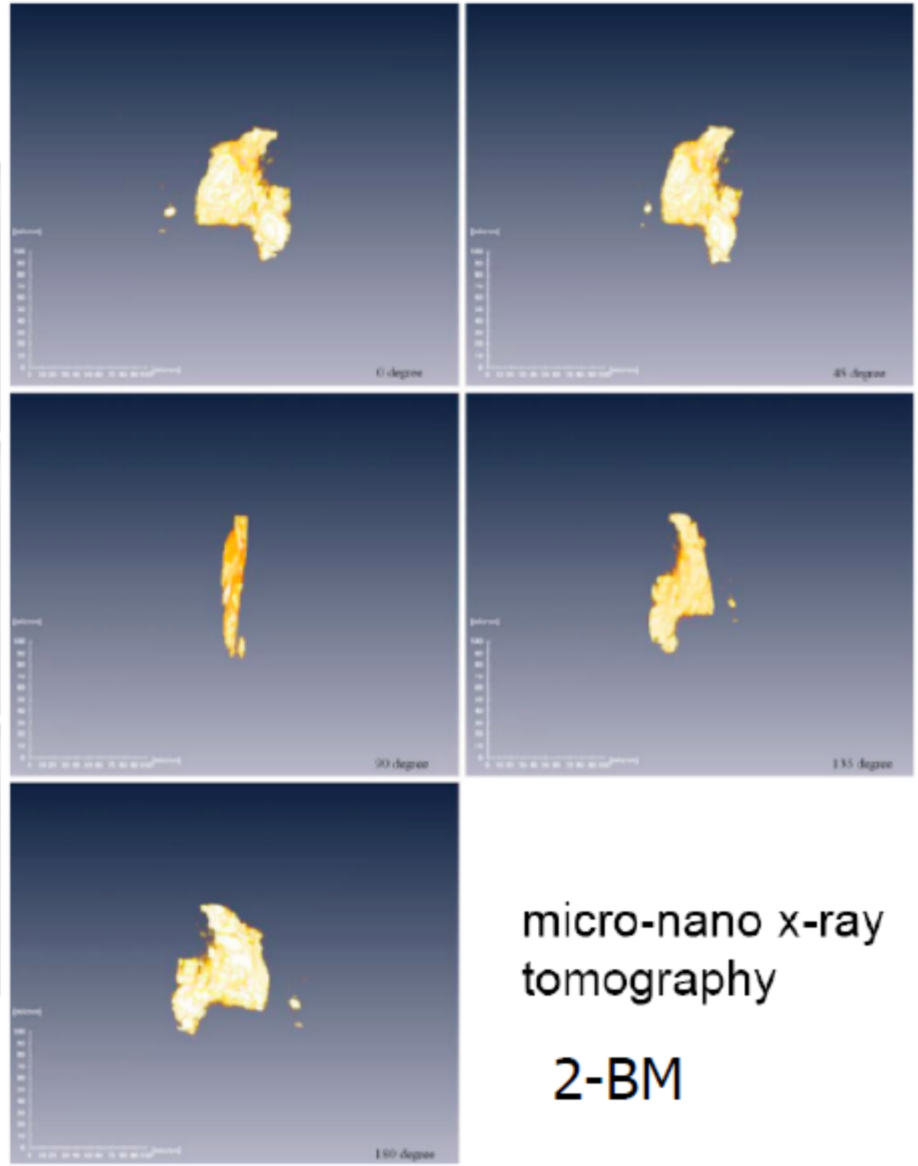
Lin et al, Nature Geo. 2008

Micro-tomography

Accurate volume measurement of amorphous Se at high pressures



Liu *et al*, *Proc. Nat. Acad. Sci.* ***105***, 13229 (2008)



micro-nano x-ray tomography

2-BM

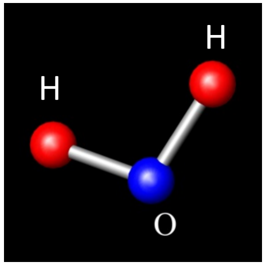
Resolution above is ~ 1um. Using TXM techniques 20nm is possible.
Also, coherent diffraction imaging has been used to image strain dist. In gold nano-particles

Combining X-rays and Neutrons

By performing complementary diffraction studies with both x-rays and neutrons, can gain deep insight into structure of materials.

Example: H_2O*
Oxygen has 8 electrons
Hydrogen only 1

(* for neutron diffraction, use D_2O to avoid incoherent scattering from H nuclei)

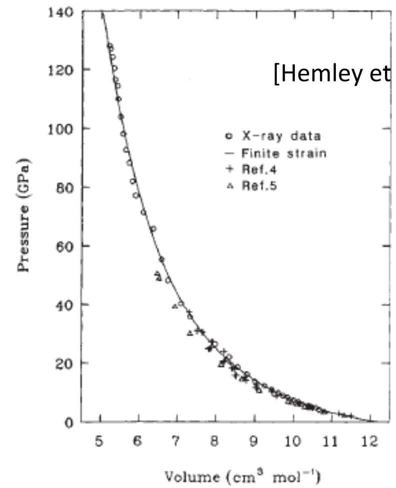


Partial	Neutron	X-ray (Q = 0)
O-O	9%	64%
O-H*	42%	32%
H-H*	49%	4%

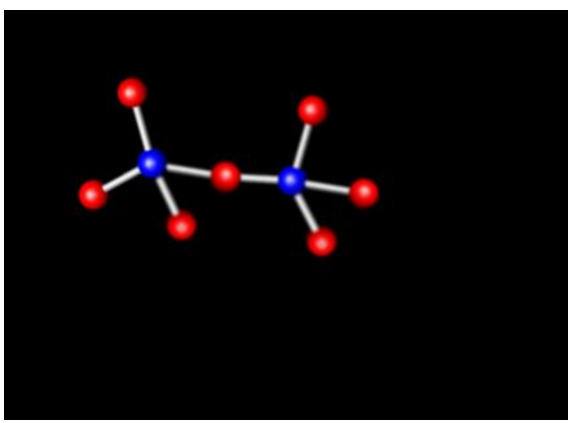
H_2O under high pressure

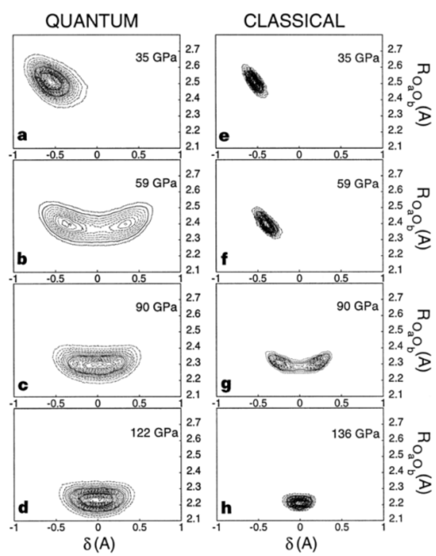
The VII to X transition (where water loses it's molecular character) has been studied with x-rays revealing the O-O separation.

Neutrons are vital to monitor the protons: as the H-bonds shorten and eventually become indistinguishable from the covalent bond –forming a simple (cuprite) H-oxide.
To date, sufficient pressures haven't been achieved for neutron diffraction. But studies of last molecular phase VII has highlighted importance of structural disorder



[Hemley et al Nature (1987)]





Proton highly non-classical on approach to centring [1] (Quantum-tunneling and zero point motion important)

Neutron diffraction vital to experimentally probe proton density distribution

[1] Benoit *et al* Nature (1998).

Summary

•Pressure is a powerful modifier of the physical properties of matter
•In the lab, we are able to achieve static pressures and temperatures approaching the centre-of-the-Earth (and dynamic pressures approaching centre of Jupiter – DC-CAT)
•Scientific capabilities are 'technique-driven', demanding materials with most extreme properties of strength and hardness.
•Synchrotron HP diffraction and XAS techniques are mature, with a huge diversity of x-ray techniques continually being developed.
•Neutrons can make a powerful contribution to HP science, especially in diffraction.
•Now is beginning of new period of growth in neutron capabilities based at new generation of intense sources, such as SNS.
•Combination of x-ray and neutron science will become increasingly important as scope of neutron capabilities improves in next several years