X-rays and high pressure

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Alexandre Magnus

Shockwave experiment
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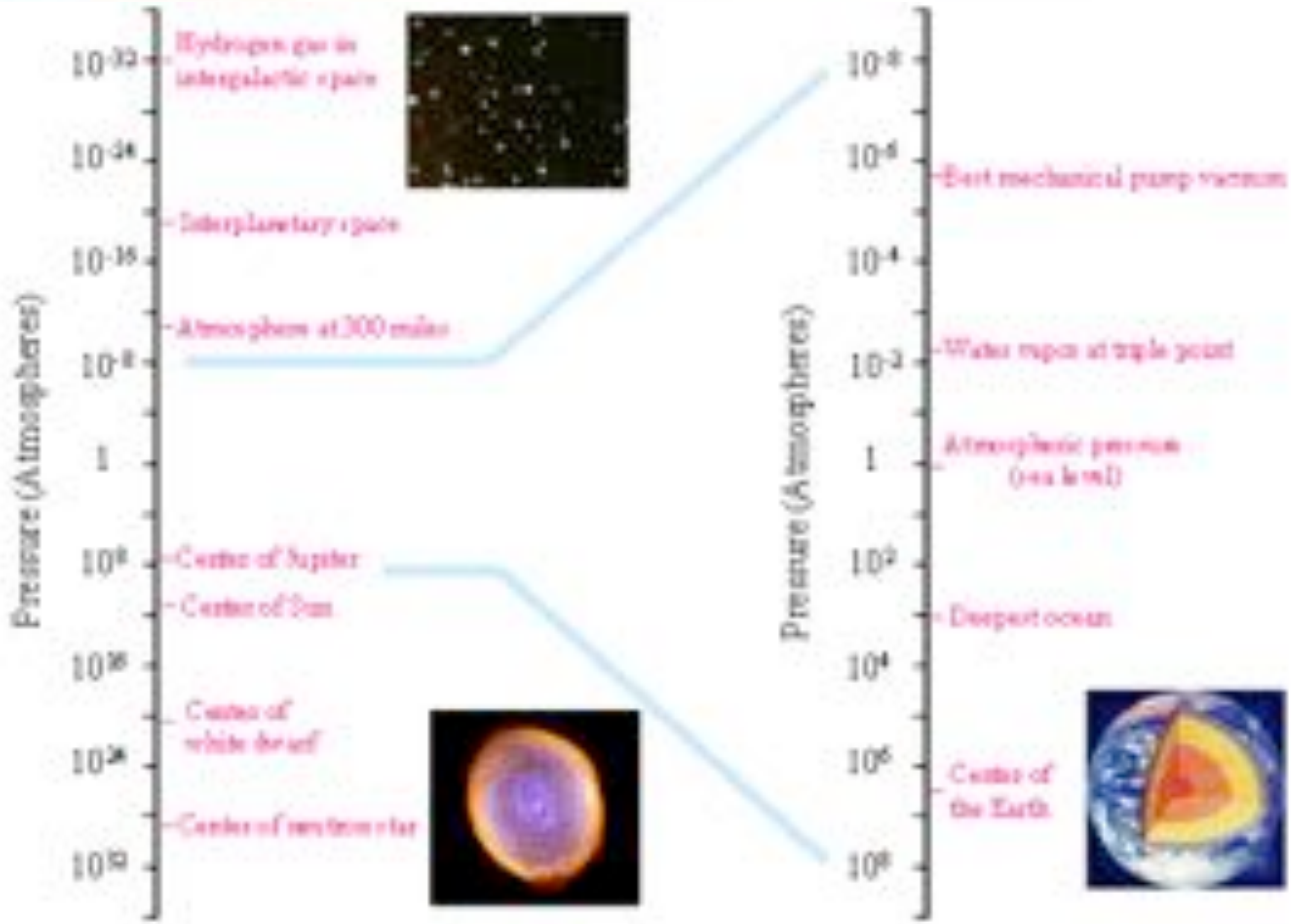
Nilson Dias (IPEN)
Jefferson Bettini (LNNano)
Raul Freitas (LNLS)


X-rays and pressure in the universe:
Stars, supernovas, ...
Neutron star from Nasa

Range of pressure in the universe



From: https://www.gl.ciw.edu/static/users/rhemley/HemleyWilliamson2004.htm

LNLS Laboratório Nacional de Luz Síncrotron

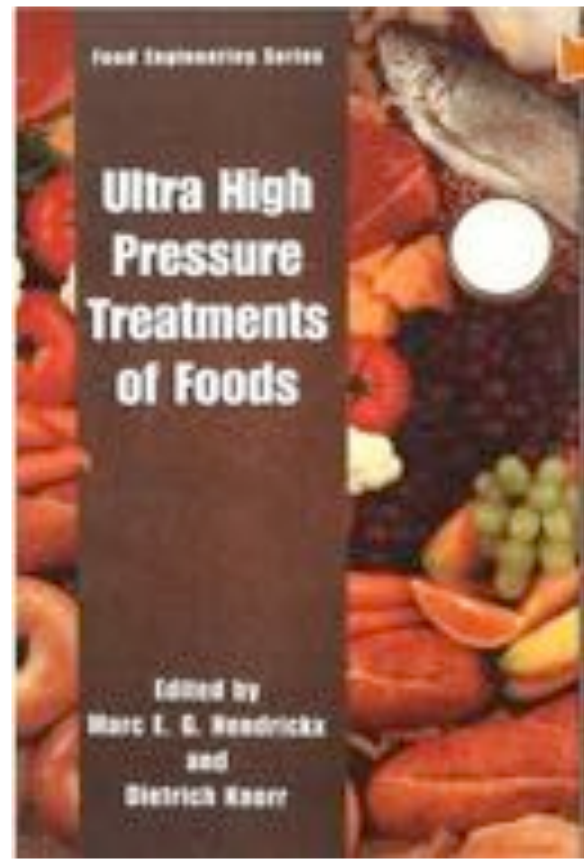
Pressure to make you hungry…

Pressure cooking since 1679 (Wikipedia)

P up to 2 atm

$$PV = nRT$$

A lot of scientific studies on foods under pressure!!!

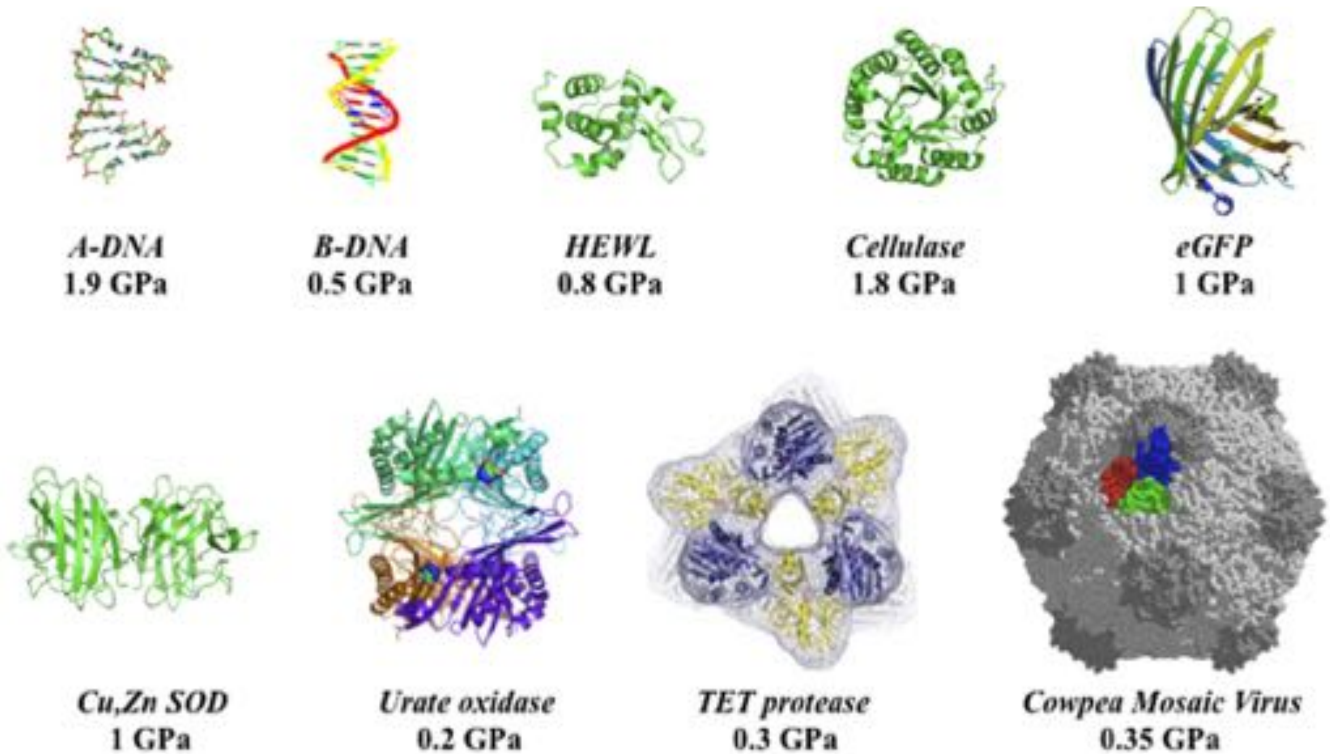


From Amazon.com

Cold press Pasteurization:
Pressed to about
0.5 GPa (5000 atm)

High pressure crystallography

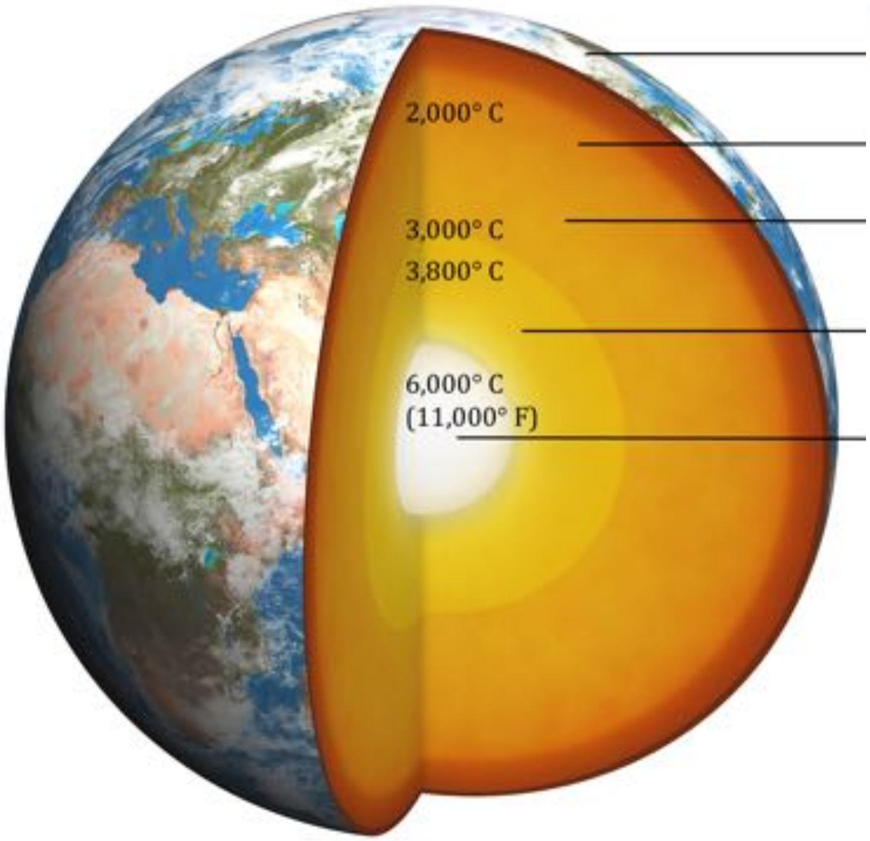
Macromolecular structures investigated under pressure



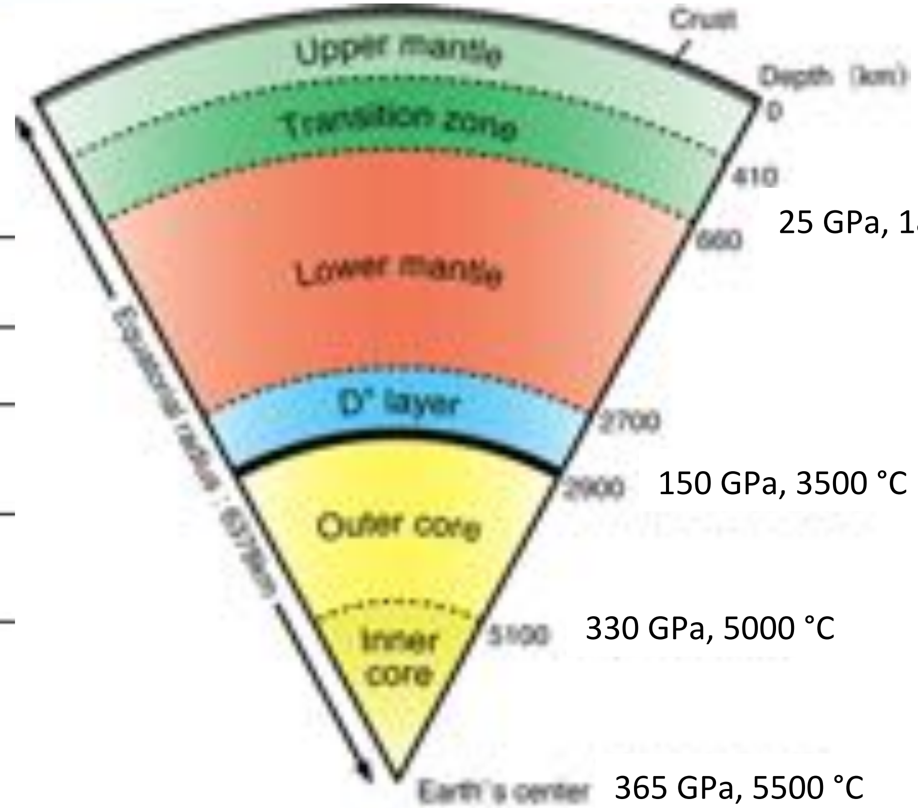
Fourme et al., J. Synchrotron Rad. (2011). 18

Also: high-pressure cryocooling methods for protein crystals to preserve them and to diffract better.

Pressure and temperature inside earth



From: DiscoveryMagazine



25 GPa, 1800 °C

150 GPa, 3500 °C

330 GPa, 5000 °C

365 GPa, 5500 °C

From: Spring8

High pressure crystallography

X-ray diffraction under pressure with the advent of microfocus beamlines

Enormous impact to study earths interior in the last 20 years!!!

Pressure = Force / Area

4 Ton Elephant on one foot:

Pressure =

65 kg woman on 1cm^2 heel:

Pressure =

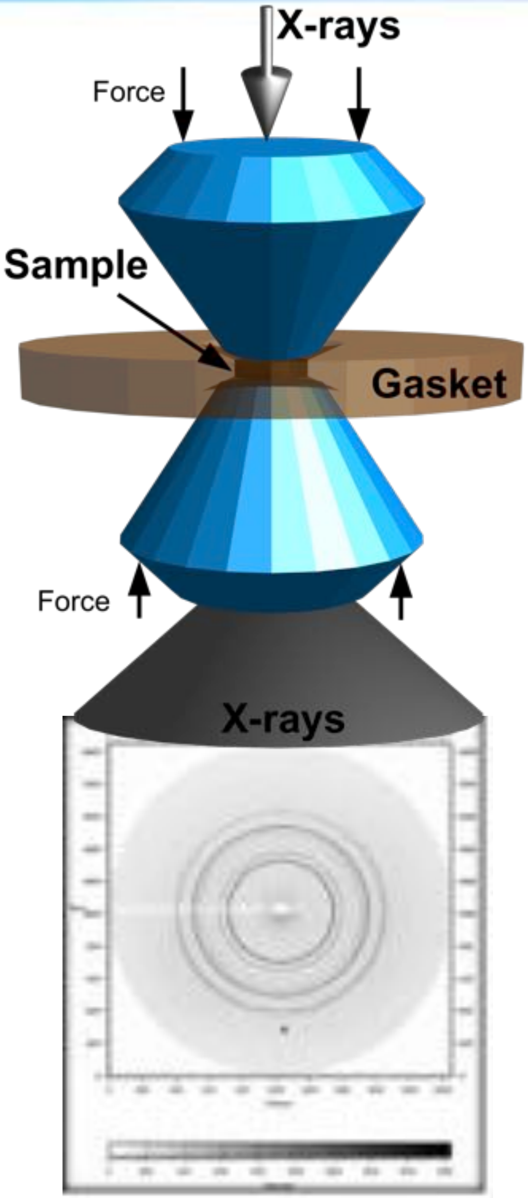
1 Bar = 0.987 Atmosphere

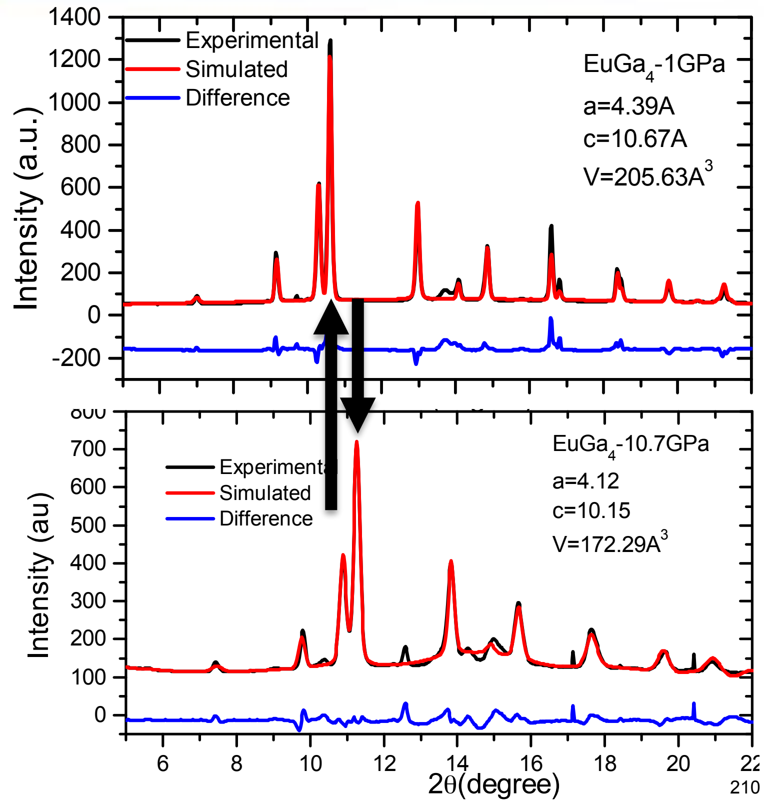
Pressure = Force / Area

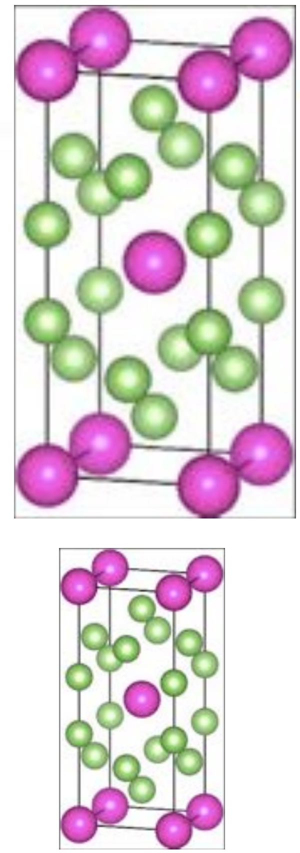
Pressure = 190 Ton / 1 cm^2 **= 19 GPa (1.9x10^5 Bar)**

(Easily achievable today at the XDS beamline downstairs)

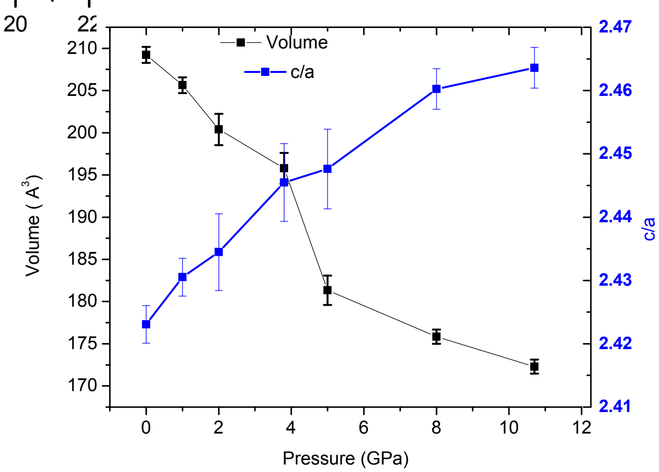
XRD under pressure



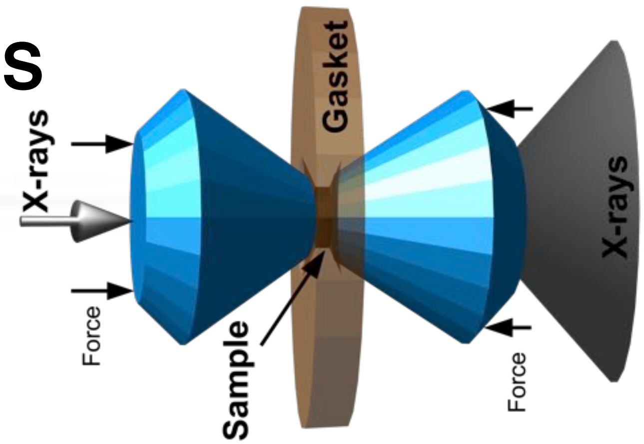




Use of pressure to continuously tune or compress the crystal structure

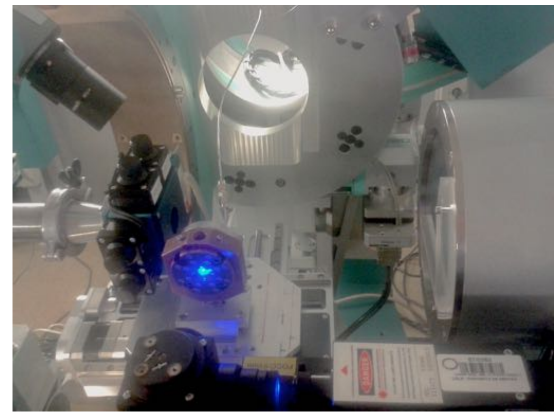


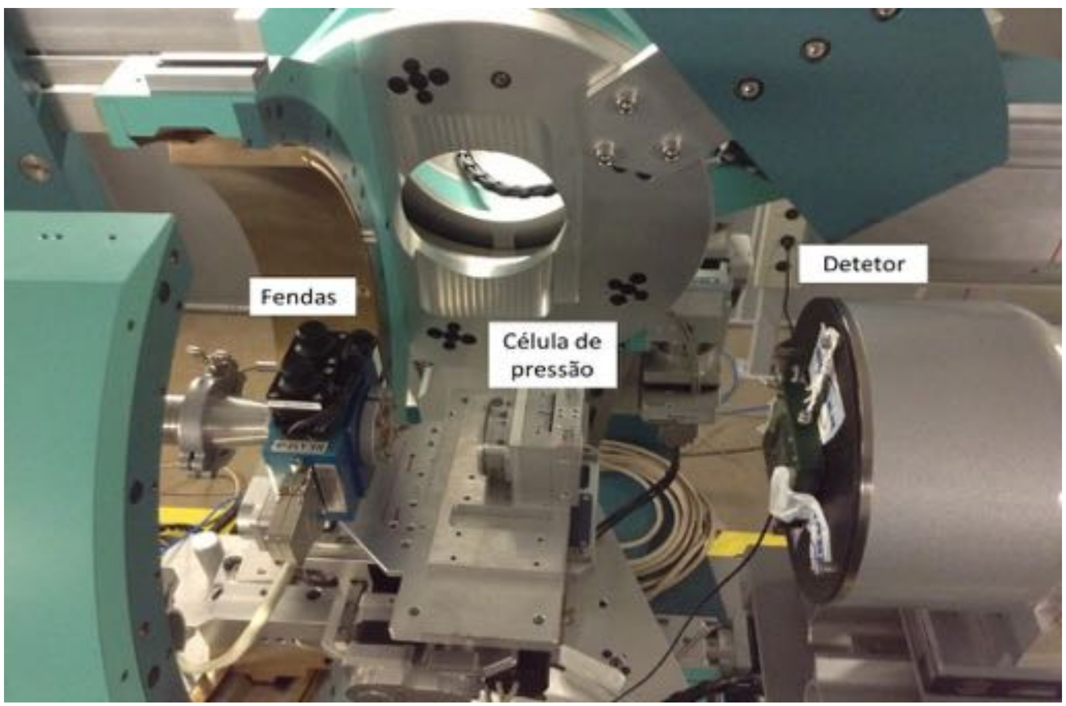
XRD at High Pressures @LNLS

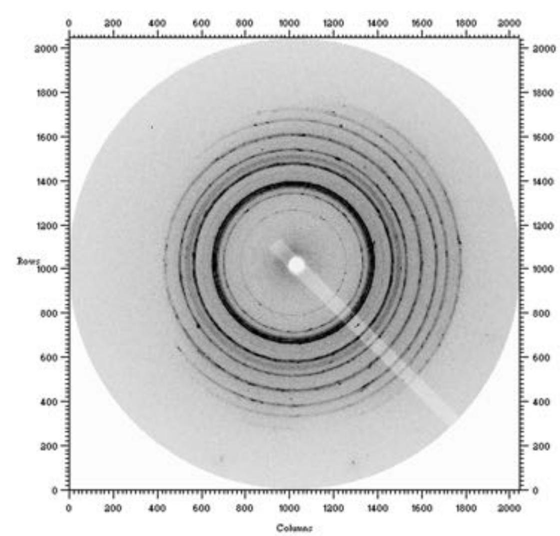


Up to 80 GPa for now

- High energies: > 25 keV
- Small beam sizes: < 0.15 x 0.15 mm^2
- In-situ pressure calibration,
- Temperature control
  - 10 K (cryostat)
  - 3000 K (laser heating, comissioning)

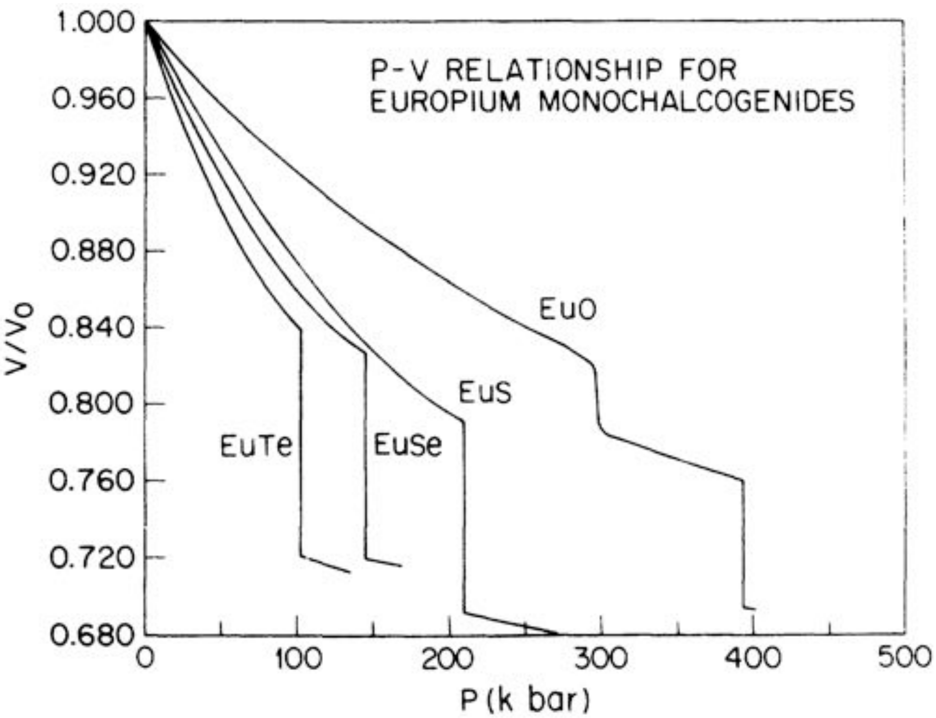






Rare earths under pressure

- Volume collapse with pressure: almost all rare earths
- Mixed valence: half of all rare earths
- **4f electrons:** magnetism, electronic structure



Jayaraman et al., PRB 1974.

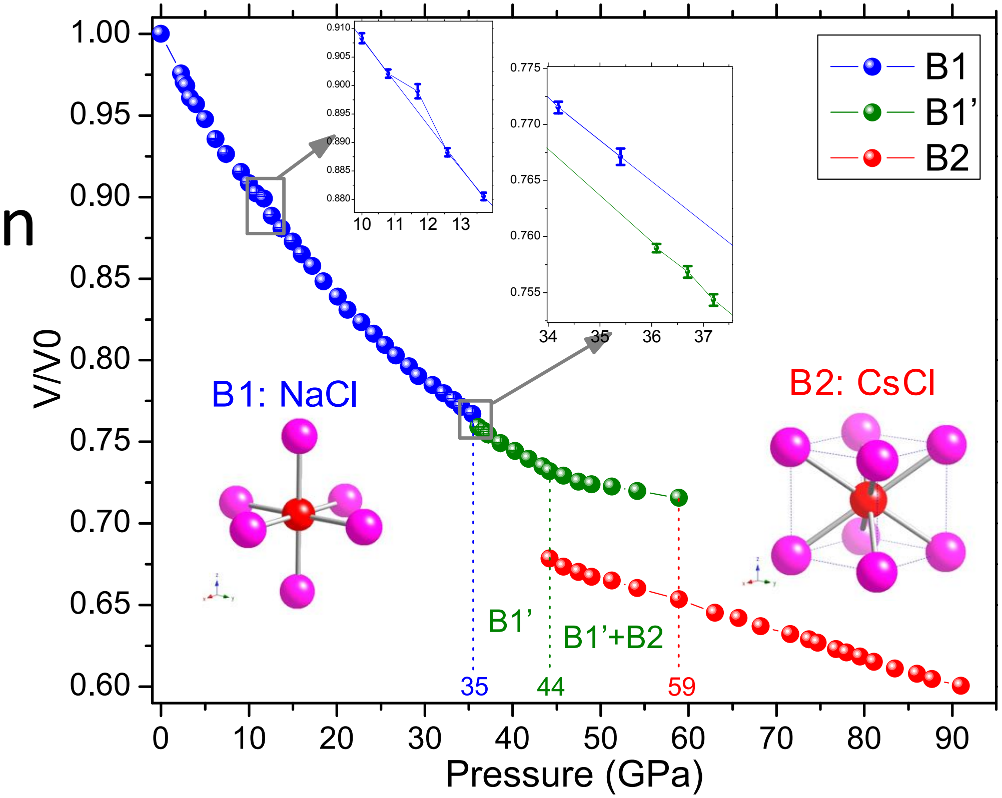
Element	Oxidation states	Electronic configuration 2^+	3^+	4^+
La	3		$4f^0$	
Ce	3, 4		$4f^1$	$4f^0$
Pr	3, 4		$4f^2$	$4f^1$
Nd	3		$4f^3$	
Pm	3		$4f^4$	
Sm	2, 3	$4f^6$	$4f^5$	
Eu	2, 3	$4f^7$	$4f^6$	
Gd	3		$4f^7$	
Tb	3, 4		$4f^8$	$4f^7$
Dy	3		$4f^9$	
Ho	3		$4f^{10}$	
Er	3		$4f^{11}$	
Tm	2, 3	$4f^{13}$	$4f^{12}$	
Yb	2, 3	$4f^{14}$	$4f^{13}$	
Lu	3		$4f^{14}$	

C. M. Varma , Rev. Mod. Phys. 1976

EuO volume under pressure

XRD at Sector 16/HPCAT/APS: structure

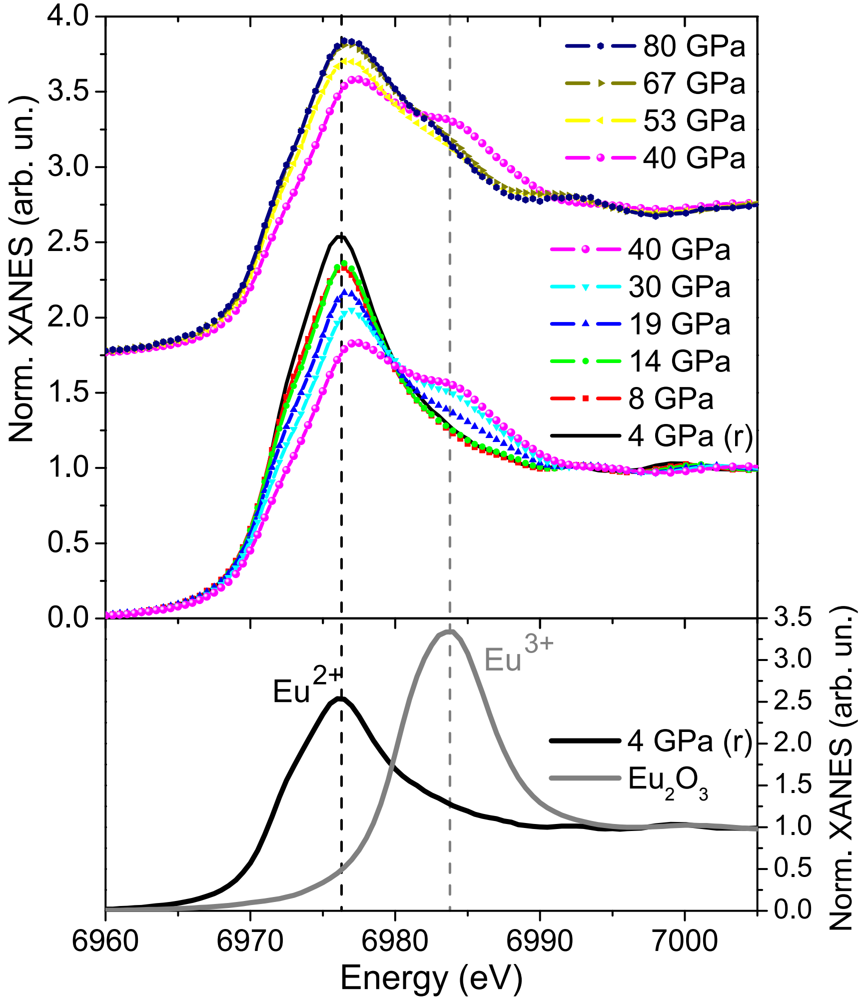
- Lattice contraction as a function of pressure
- Electronic instabilities at low pressure
- **B1 -> B2 transition**
  - Local volume expansion
  - Coordination change
  - Predicted valence transition to Eu^{3+}

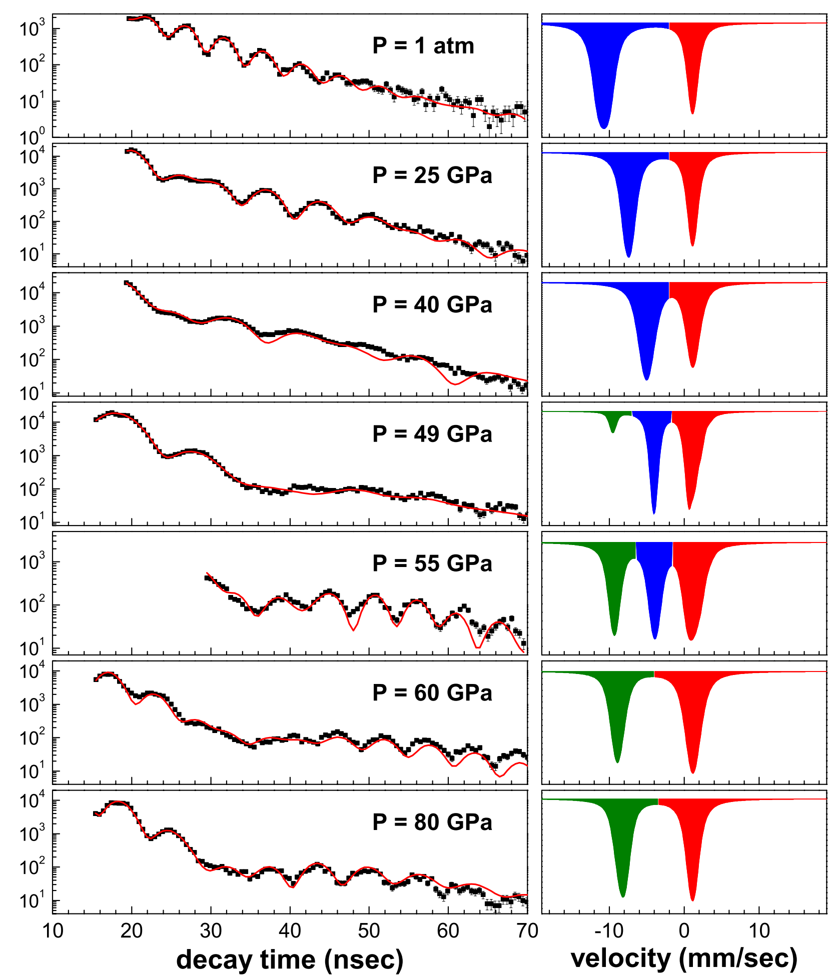


EuO: Valence change w/ pressure

Valence change towards 3+ ($4f^6,5d^1$) Up to 40 GPa, as expected.

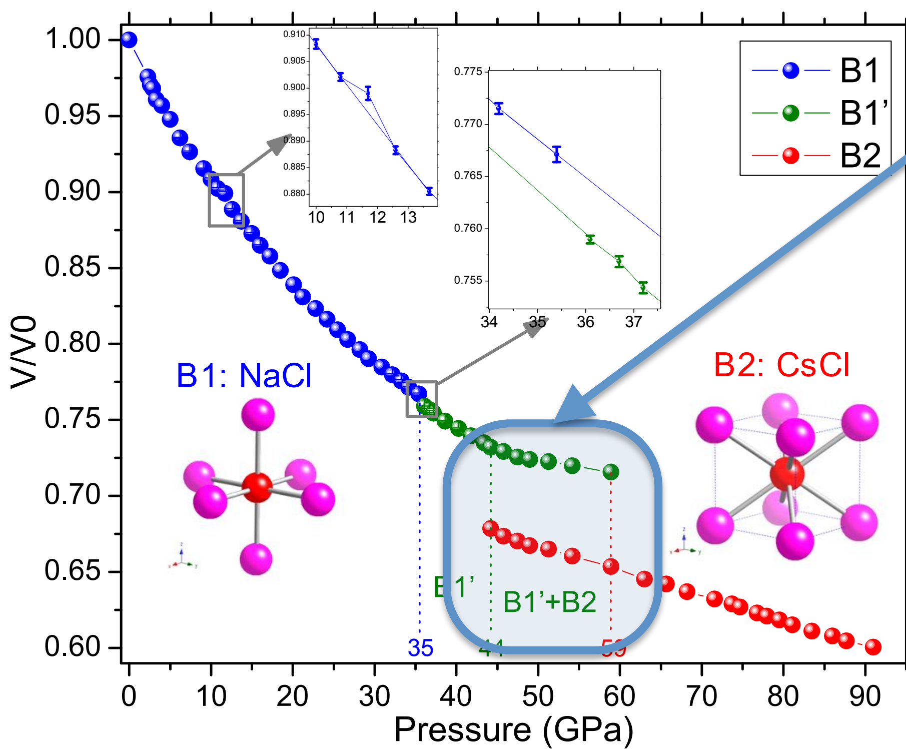
Contrary to the expected valence goes **from 2.3+ back to 2+**

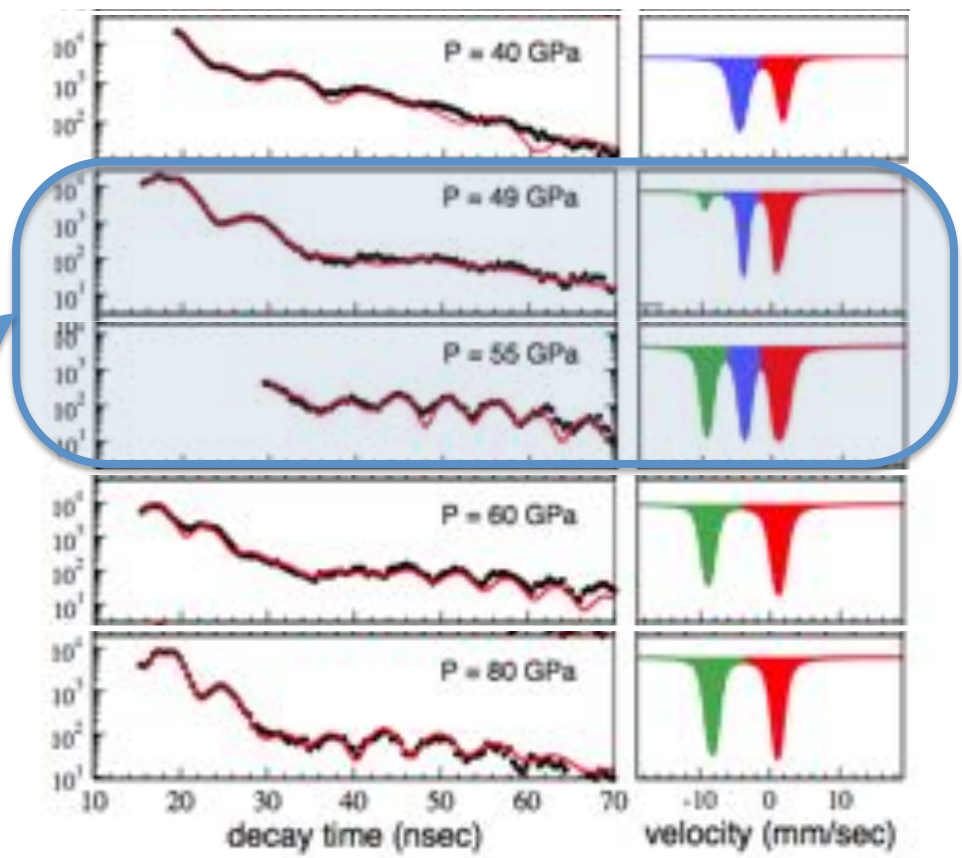




Homogeneous VS inhomogeneous

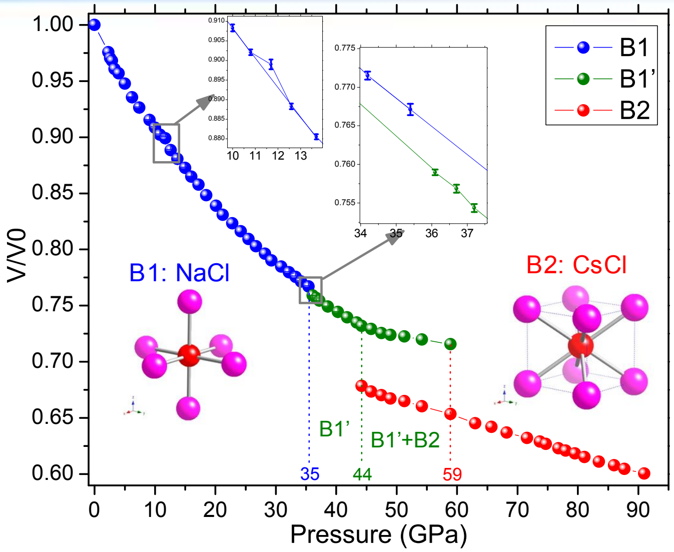
- Homogeneous valence at each crystal phase
- Inhomogeneous valence in the coexisting phase region



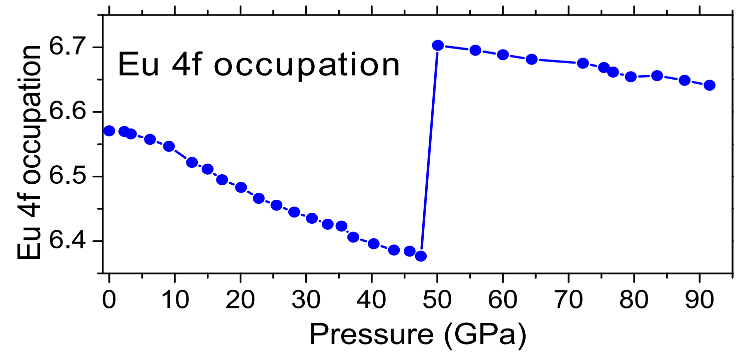


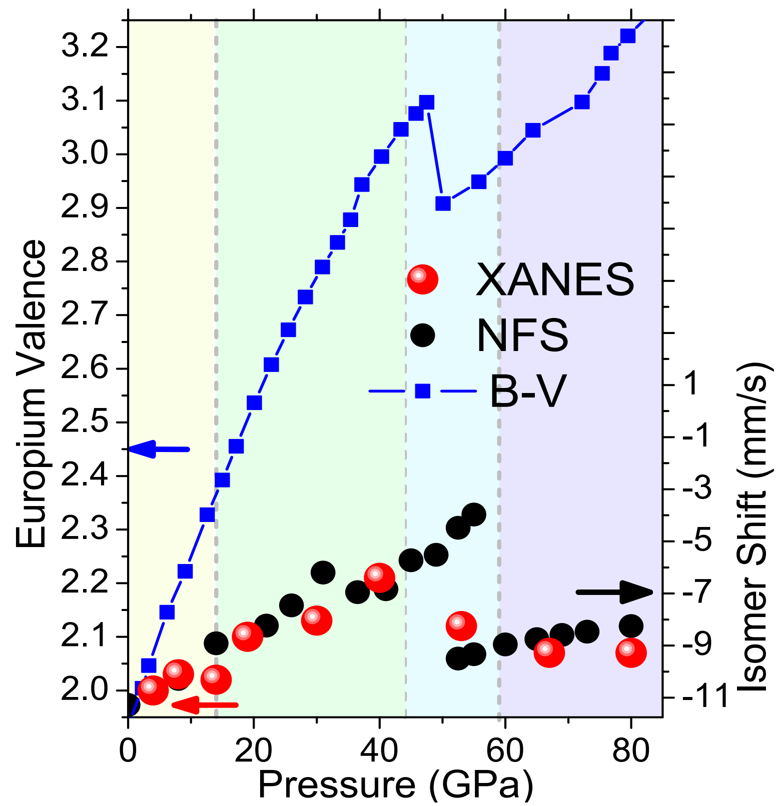
(Dis)Agreement with theory

Bond distances: **XRD**



LDA+U simulations (Wien2k):





Bond-valence parameterization:

Brese & O'Keeffe, ACTA Cryst. B 47, 192 (1991).

"bond length is a unique function of bond valence"

$$v_{ij} = \exp[(R_{ij} - d_{ij})/b]. \qquad \sum_j v_{ij} = V_i.$$

Constants:

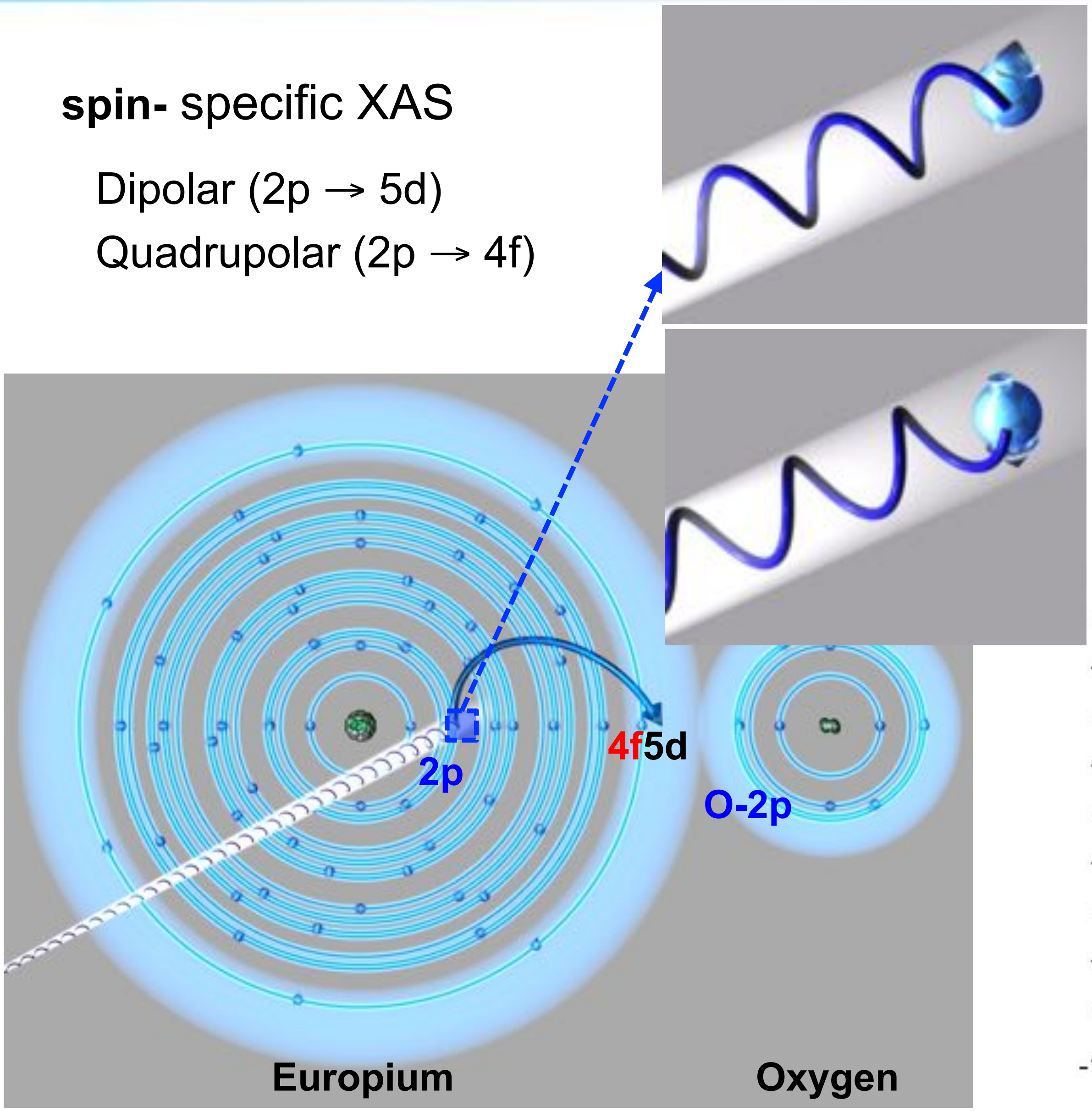
b = 0.37 Å ; $\boldsymbol{R_{ij}}$ **(Eu²⁺)** = 2.147 Å ; $\boldsymbol{R_{ij}}$ **(Eu³⁺)** = 2.076 Å

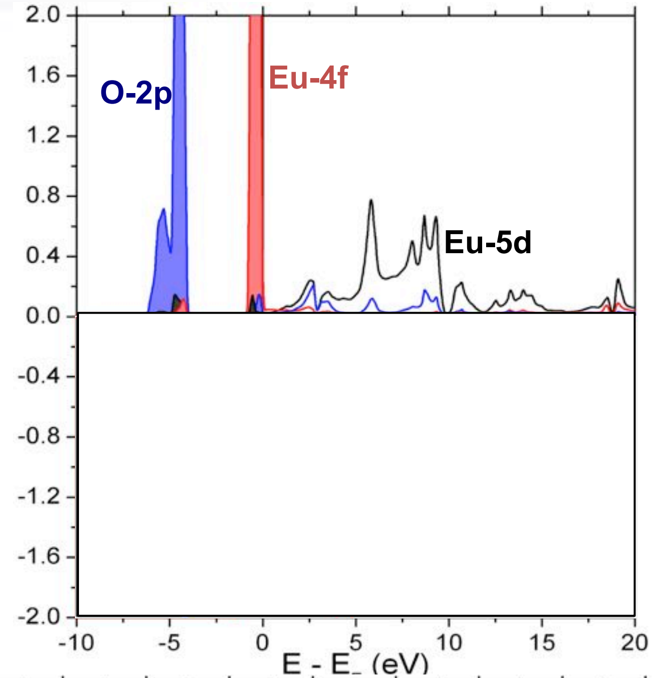
X-ray Magnetic Circular Dichroism

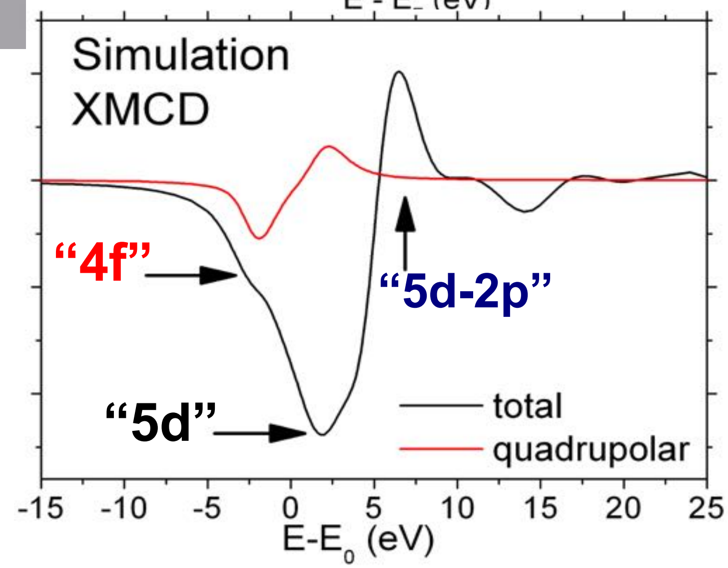
spin- specific XAS

Dipolar (2p → 5d)

Quadrupolar (2p → 4f)



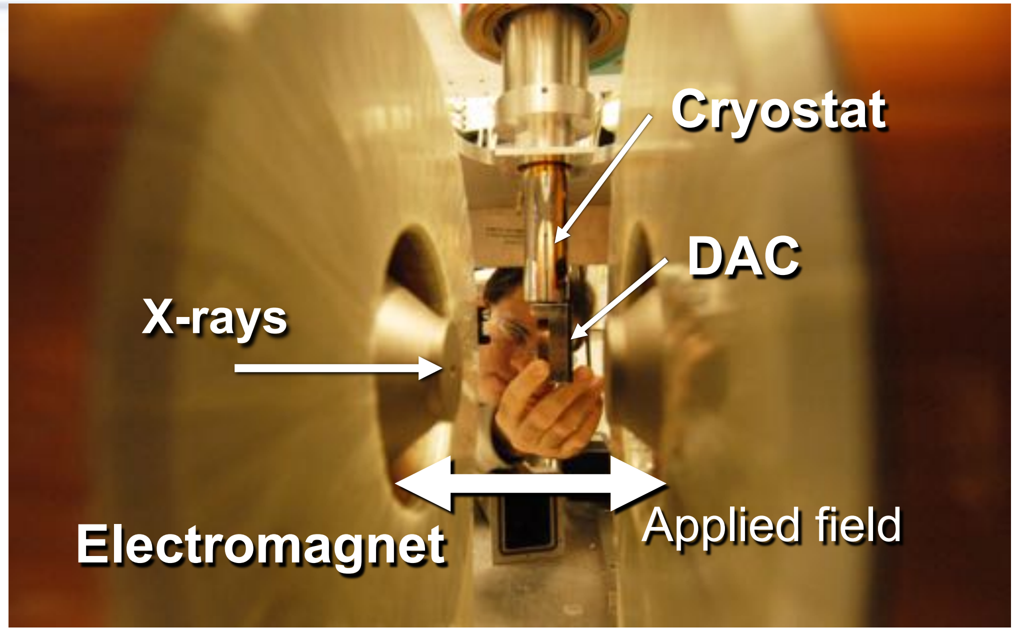




High pressure XAS/XMCD

4-ID-D beamline

Advanced Photon Source



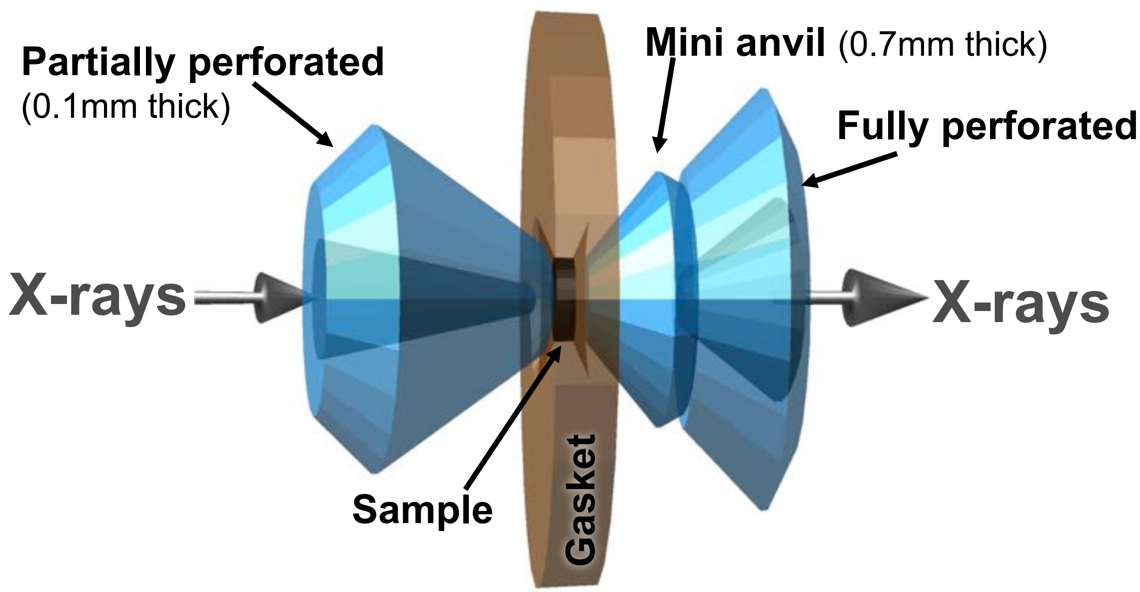
In-situ pressure calibration:

DAC translated to a

Ruby fluorescence station

Performed experiments up to **90 GPa**, so far.

P > 150 GPa are possible

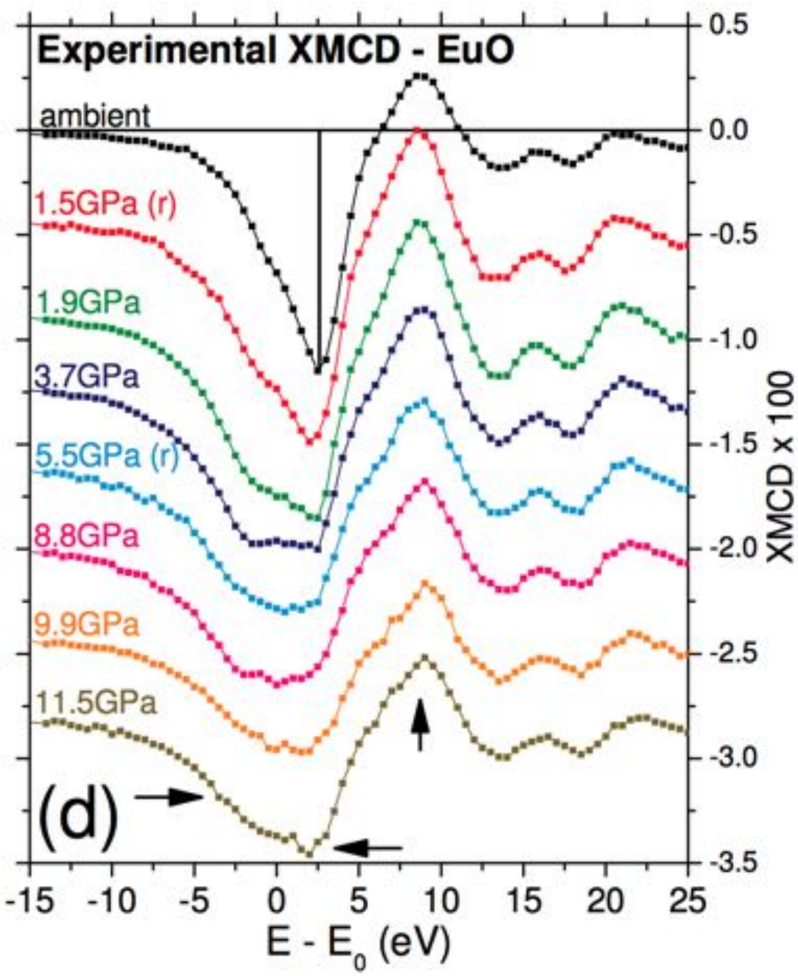


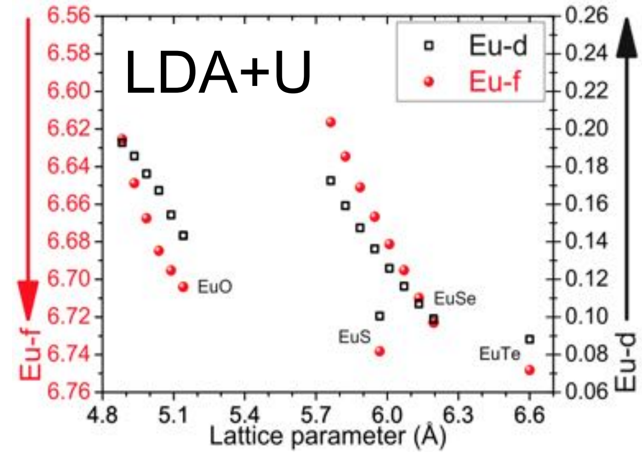
High Pressure Research 28, 185 (2008)

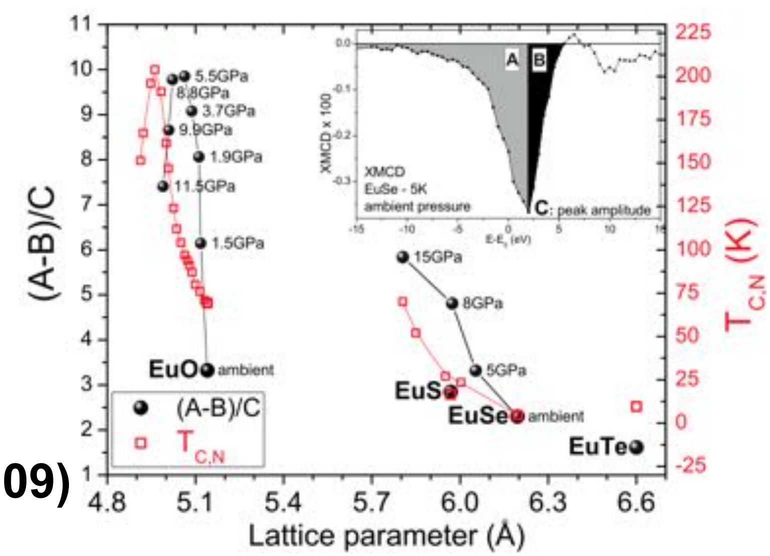
Rev. Sci. Instrum., 78, 083904 (2007)

at APS: Europium monochalcogenides

T_C increases with lattice contraction: **4f – 5d mixing (indirect exchange)**







Souza-Neto et al., Phys. Rev. Lett., 102, 057206 (2009)

EuO under pressure

P < 14 GPa: quantum state of fractional 4f/5d occupations

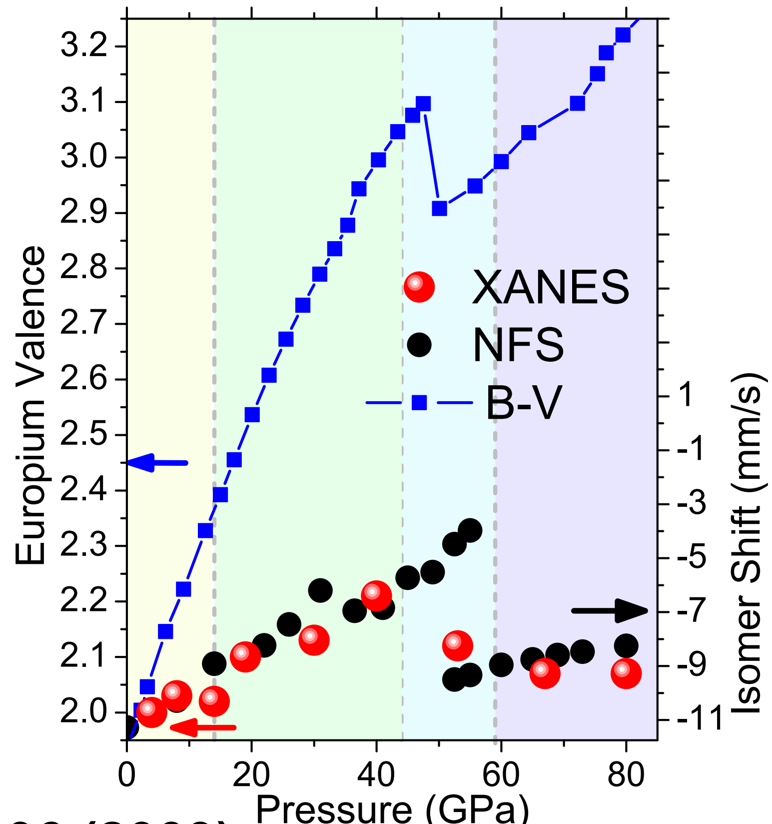
14 < P < 44 GPa: fluctuating valence between Eu^{2+} and Eu^{3+}; homogenously distributed; with characteristic frequency determined by the 4f bandwidth.

44 < P < 59 GPa: inhomogeneous valences concomitant with the mixture of NaCl and CsCl phases

P > 59 GPa: reentrant Eu^{2+} valence ground state is unexpectedly recovered!

Bond-valence parameterization does not work universally

Strong implications to the physics of 4f systems



Science editors' choice v337 p504, (2012).

Souza-Neto et al., Phys. Rev. Lett., 102, 057206 (2009)

Souza-Neto et al., Phys. Rev. Lett. 109, 026403 (2012)

How to apply extreme pressures?

Titanic: 53000 Ton

1 cm^2

Pressure = 50000 Ton / 1 cm^2 **= 5 TPa (5×10^8 Atm)**

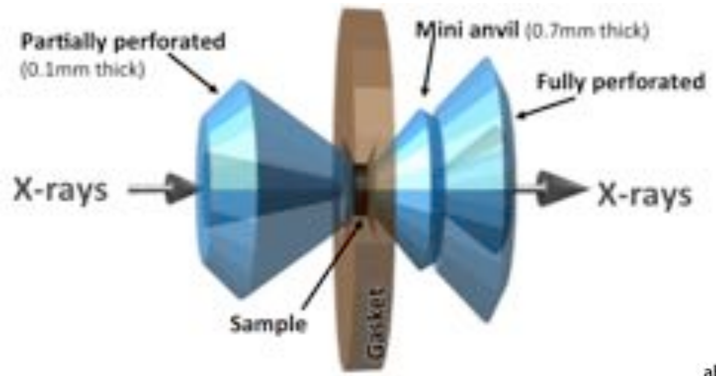
(That's more challenging and motivating)

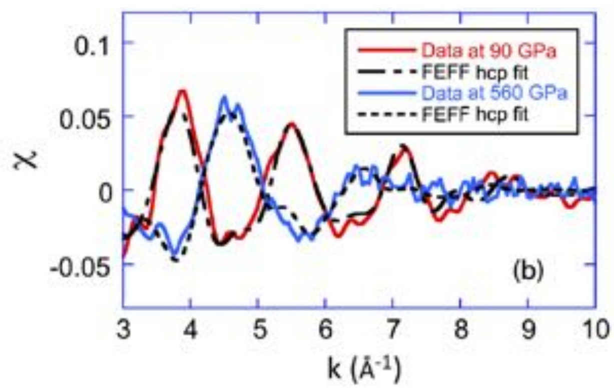
Synchrotron techniques under extreme

- Must go for extreme pressure, temperature and field

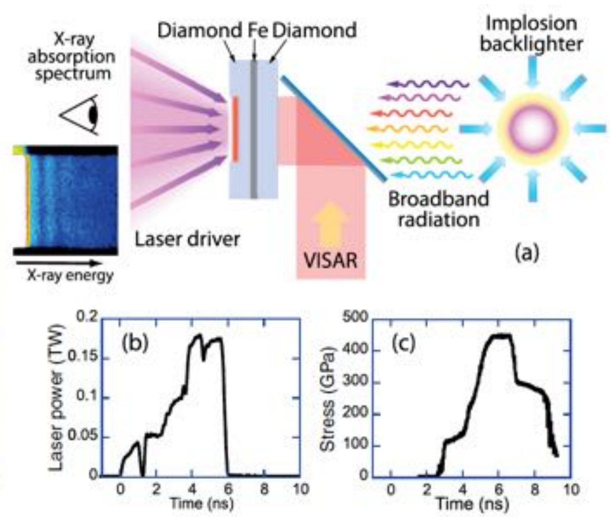
Small volume: DAC + Laser heating:
400 GPa, 6000 K, 1μm^3

Large volume (LVP):
30 GPa, 3000 K, 1 cm^3





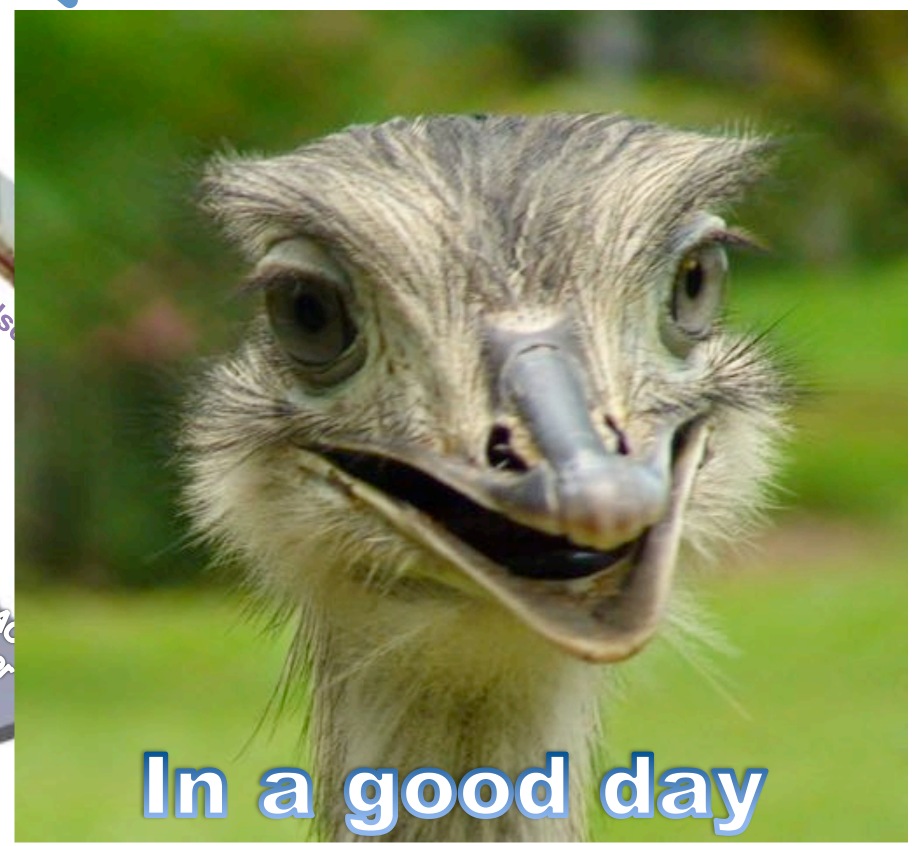
Extreme: Shock wave:
100 TPa, 10^8 K, 1μm^3



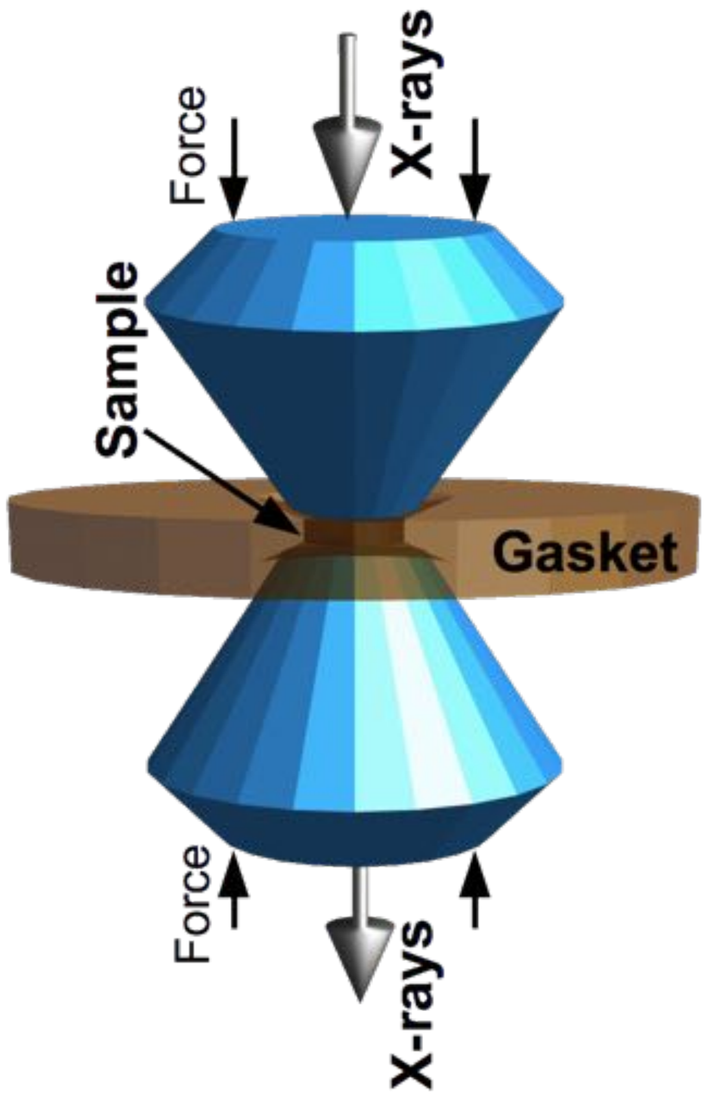
EMA beamline at SIRIUS

Extreme condition XRD/XMCD/XES/XRS

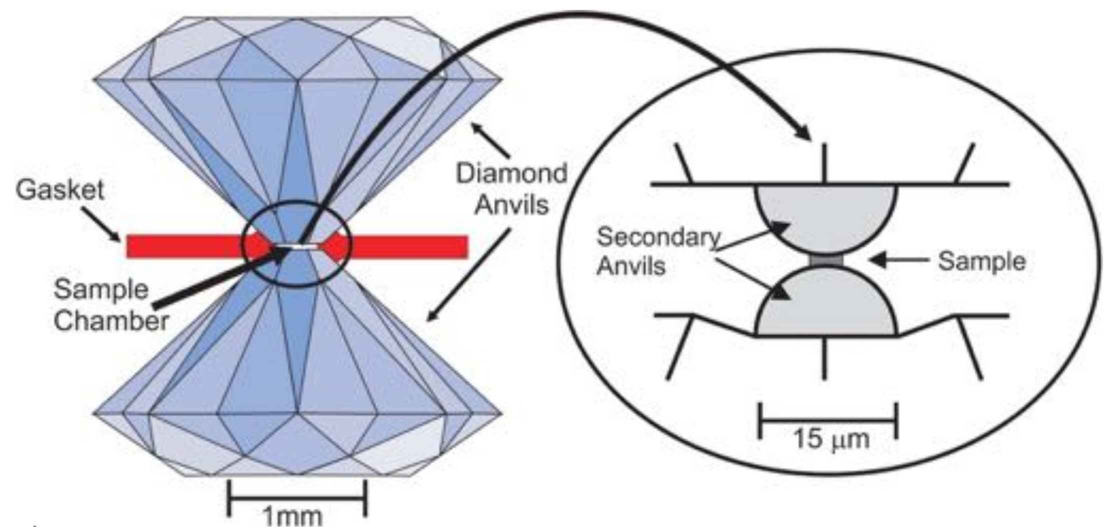
With very small x-ray beamsize



High pressure with DAC



"High-pressure X-ray science on the ultimate storage ring"
Malcolm I. McMahon
J. Synch. Rad. (2014). 21, 1077-1083

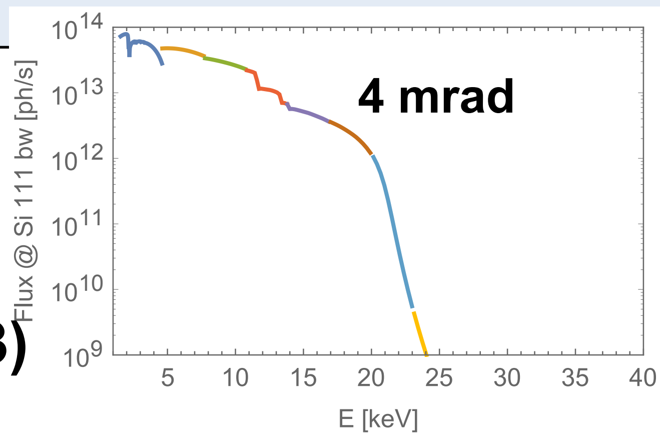


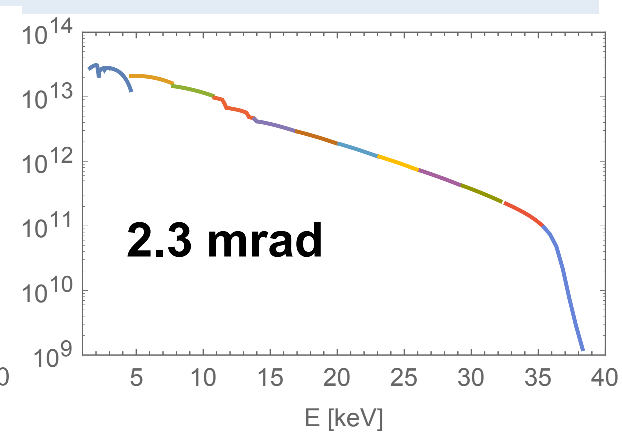
Two-stage DAC to reach pressures as high as 800 GPa.

General specifications

Source		**SCU16.5** or IVU19 @ low β-straight
Energy range		**2.7 keV to 35 keV**
Monochromator		Vertical bounce DCM, Si (111) & Si (220)
Polarization control		Circular/Linear using ¼ wave plate
Photon Flux hutch: **10 keV**	@ Magnet	**1×10^{14} photons/s** (direct focusing, DF)
		$4\text{x}10^{13}$ photons/s (direct focusing, DF)
	@ Laser hutch:	**$2\text{x}10^{12}$** photons/s (secondary source, SS)
Beamsize hutch: (divergence) 10 keV	@ Magnet	**2x1 μm^2** (1x0.2 $mrad^2$) (DF)
		0.5x0.5 μm^2 (4x0.4 $mrad^2$) (DF)
	@ Laser hutch:	**0.3x0.5 μm^2** (0.7x0.4 $mrad^2$) (SS)

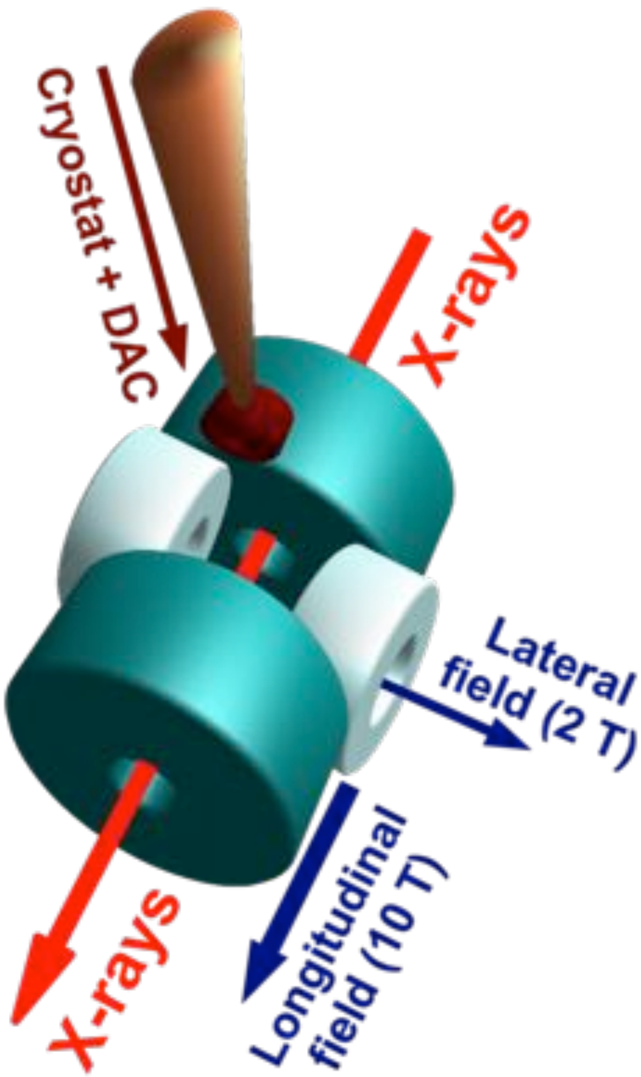
Flux at sample w/
Direct focusing at
Laser hutch
(for magnet hutch, x3)





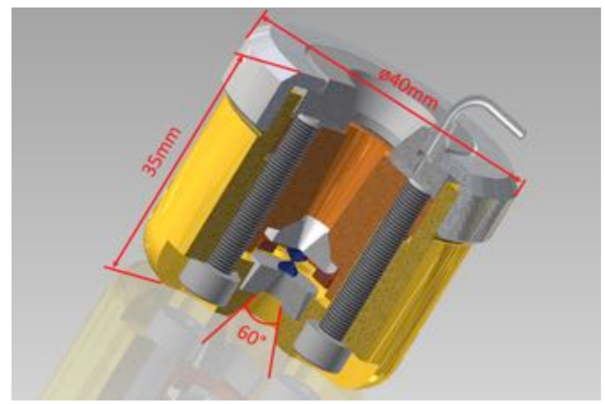
XMCD/XMLD under pressure

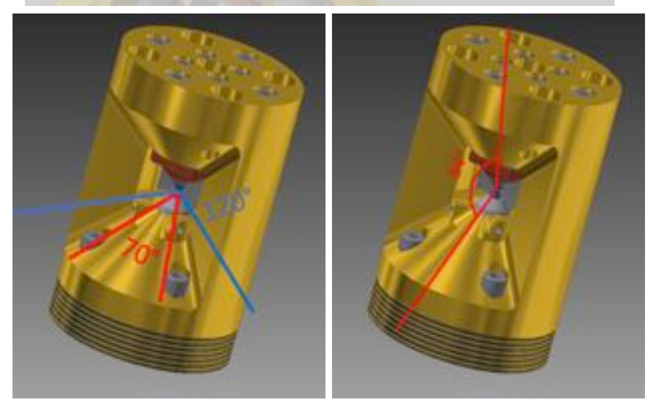
Large bore SC magnet



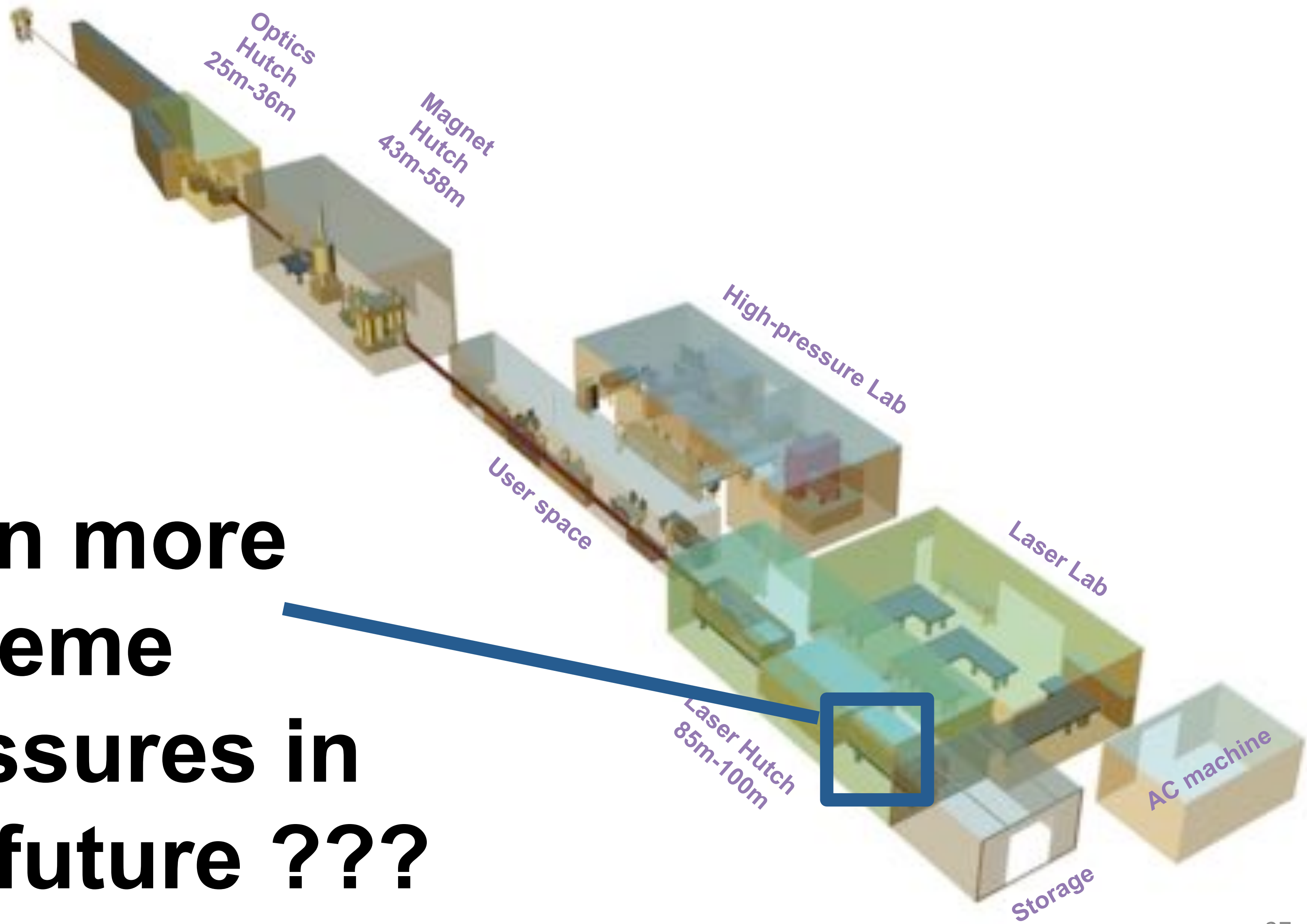
< 2μm² focused beamsize
With long working distance

Custom anvil cells





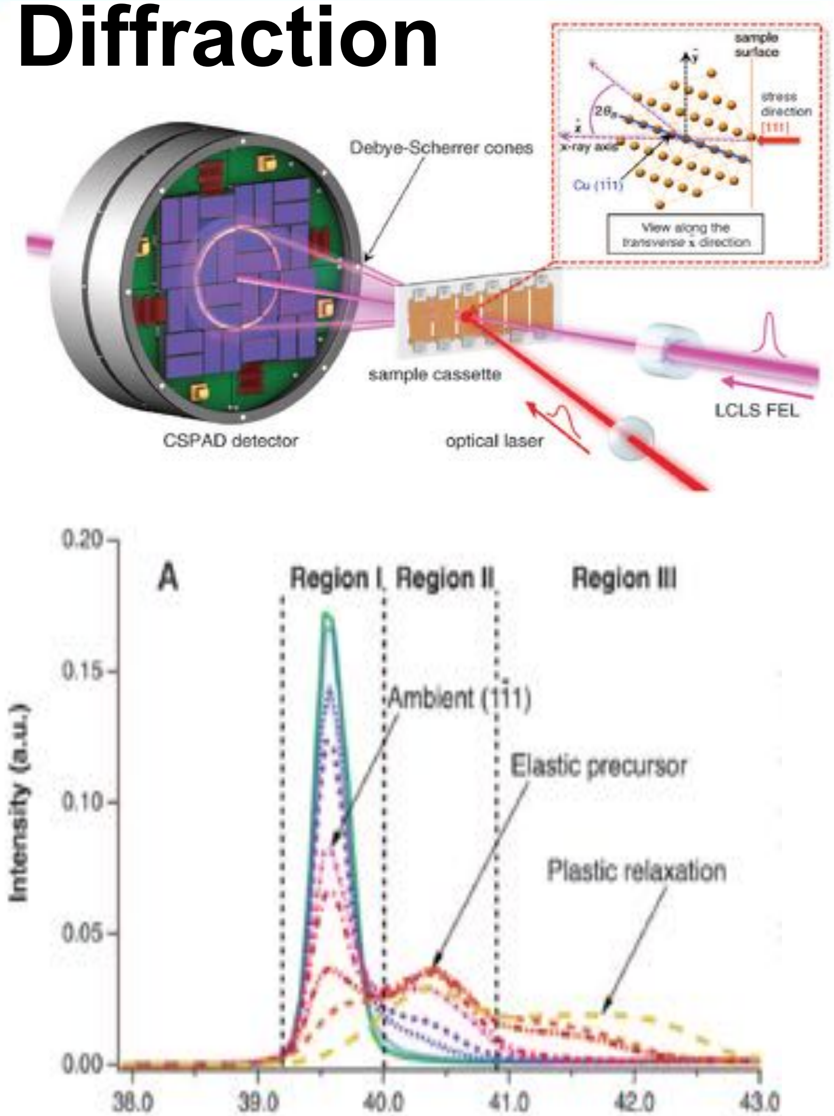
EMA beamline at SIRIUS



Even more extreme pressures in the future ???

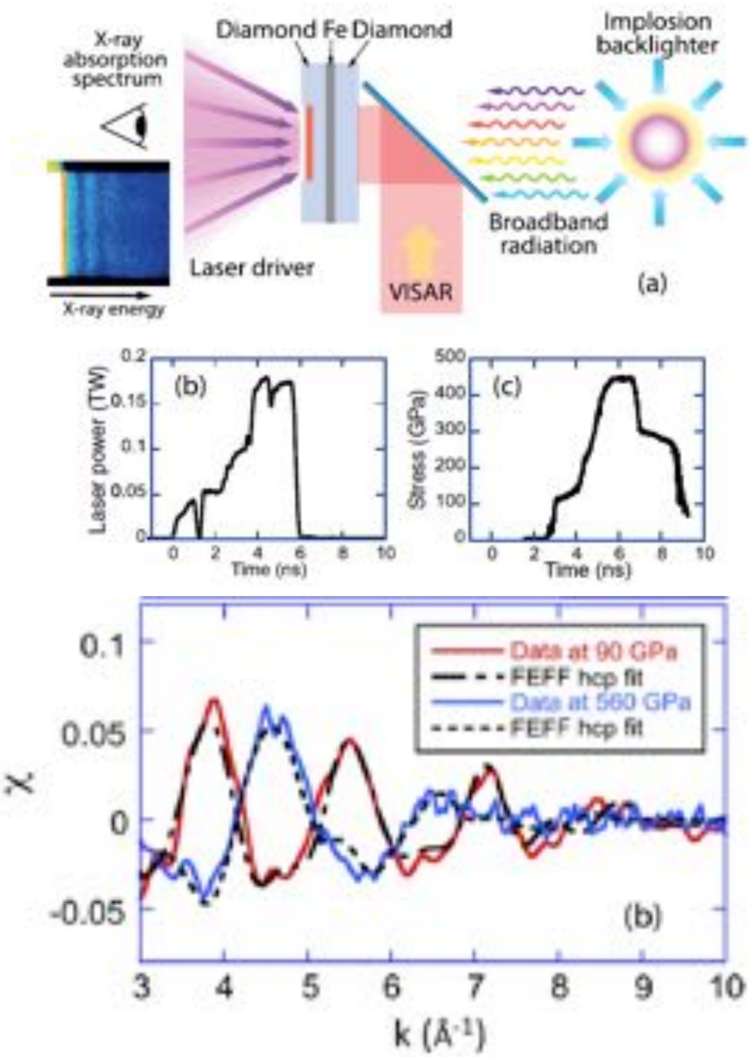
Shockwaves + X-rays

Diffraction



11 OCTOBER 2013 VOL 342 **SCIENCE**

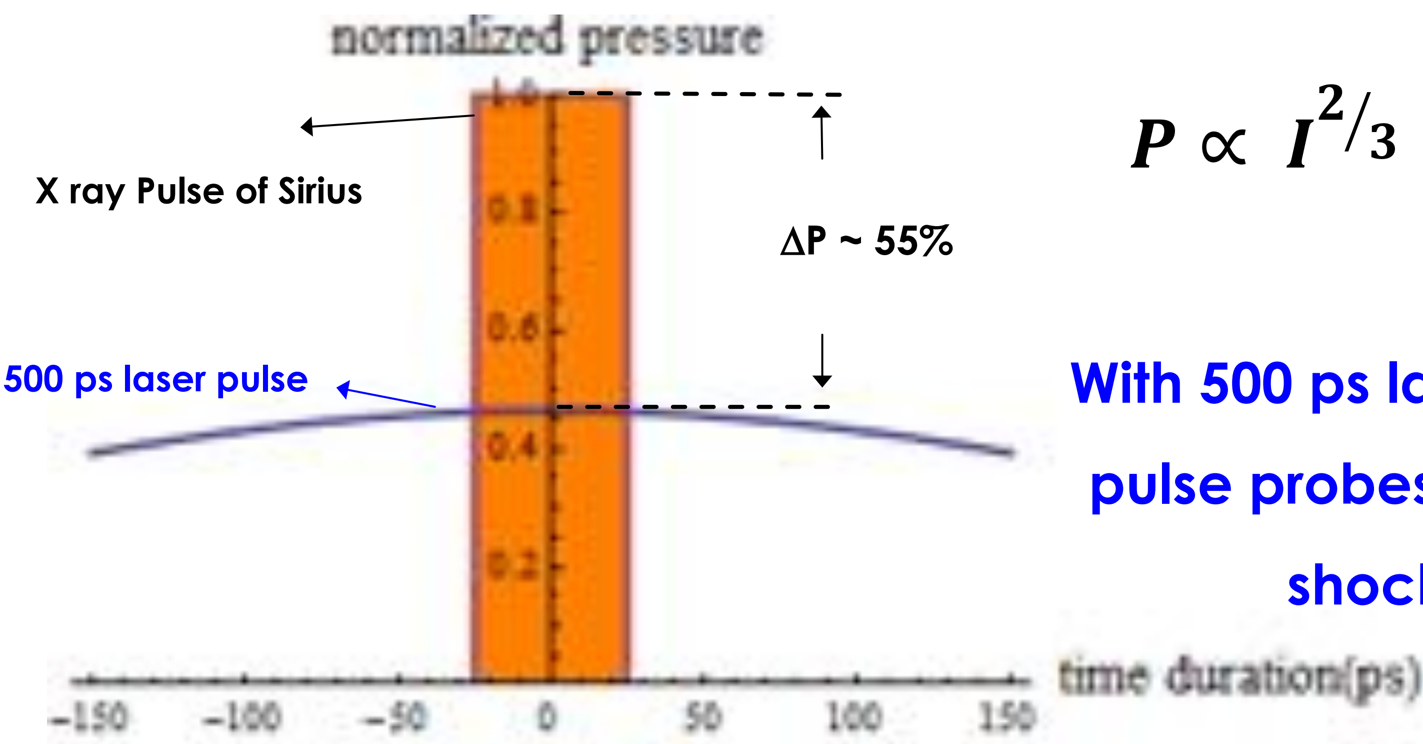
EXAFS



PRL 111, 065501 (2013)

Shockwave + Sirius ?

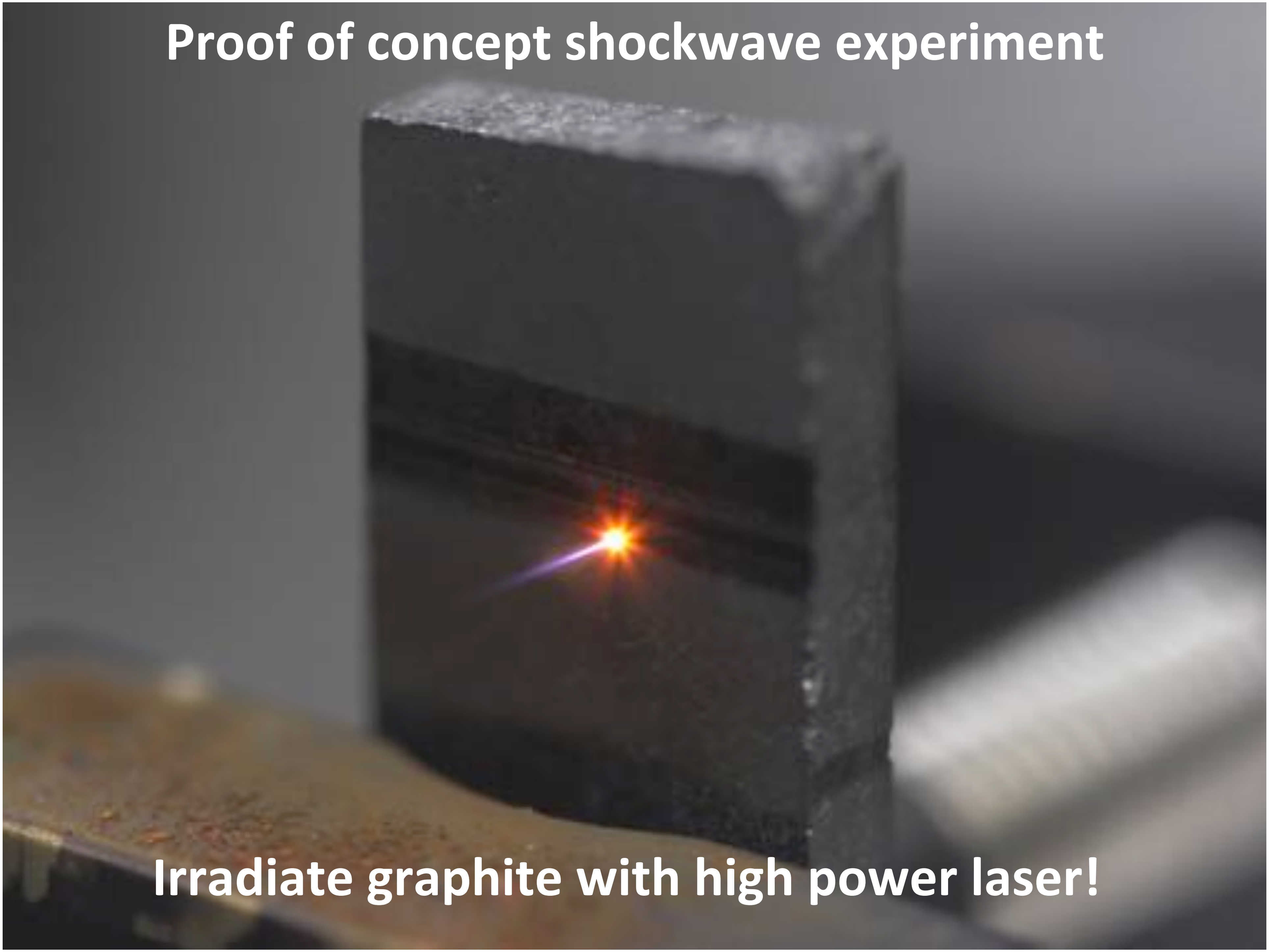
Laser induced extreme conditions experiments at Sirius



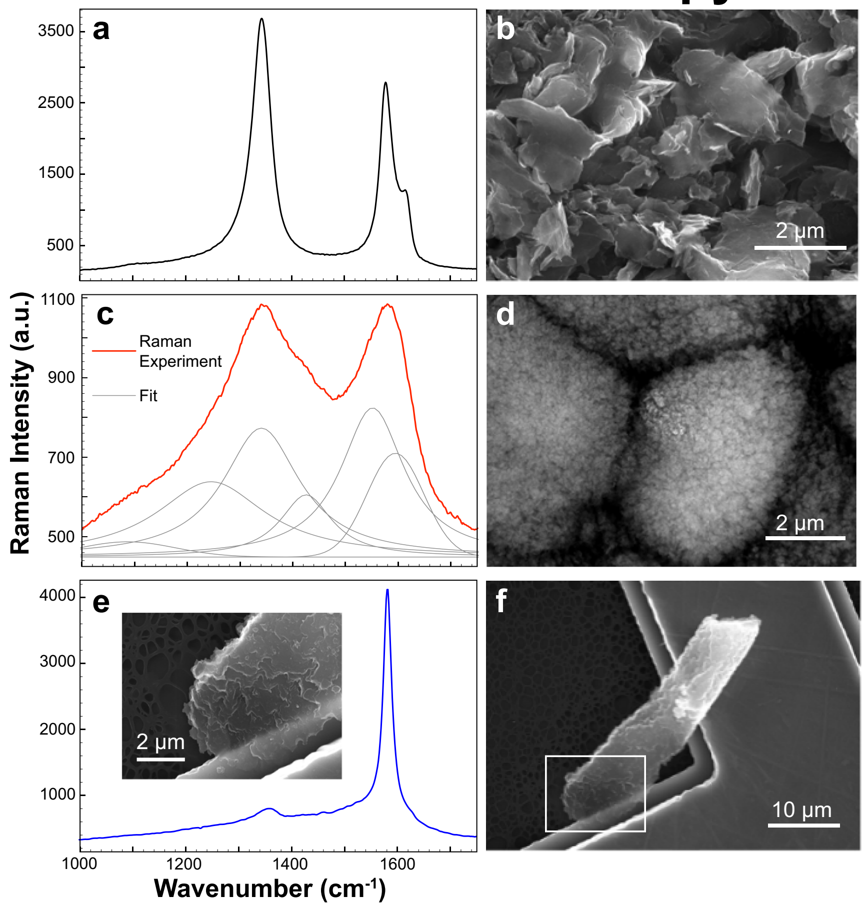
$$P \propto I^{2/3} = \left(\frac{\varepsilon}{\Delta t . \Delta A}\right)^{2/3}$$

With 500 ps laser pulse, X-ray pulse probes a steady state shock waves

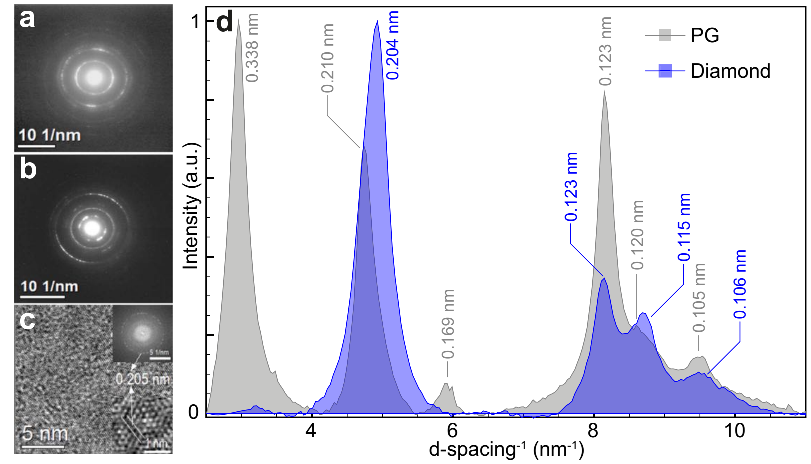
By Francisco Maia et al.


Proof of concept shockwave experiment
Irradiate graphite with high power laser!

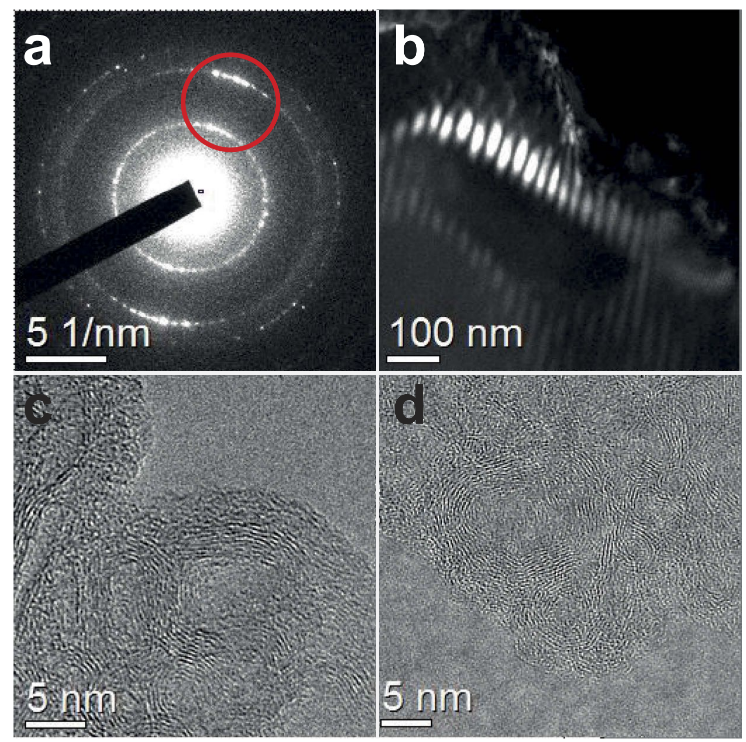
Raman and Microscopy:



Electron diffraction of nanocrystals



“Nano onion rings”:



SCIENTIFIC REPORTS

OPEN

Synthesis of diamond-like phase from graphite by ultrafast laser driven dynamical compression

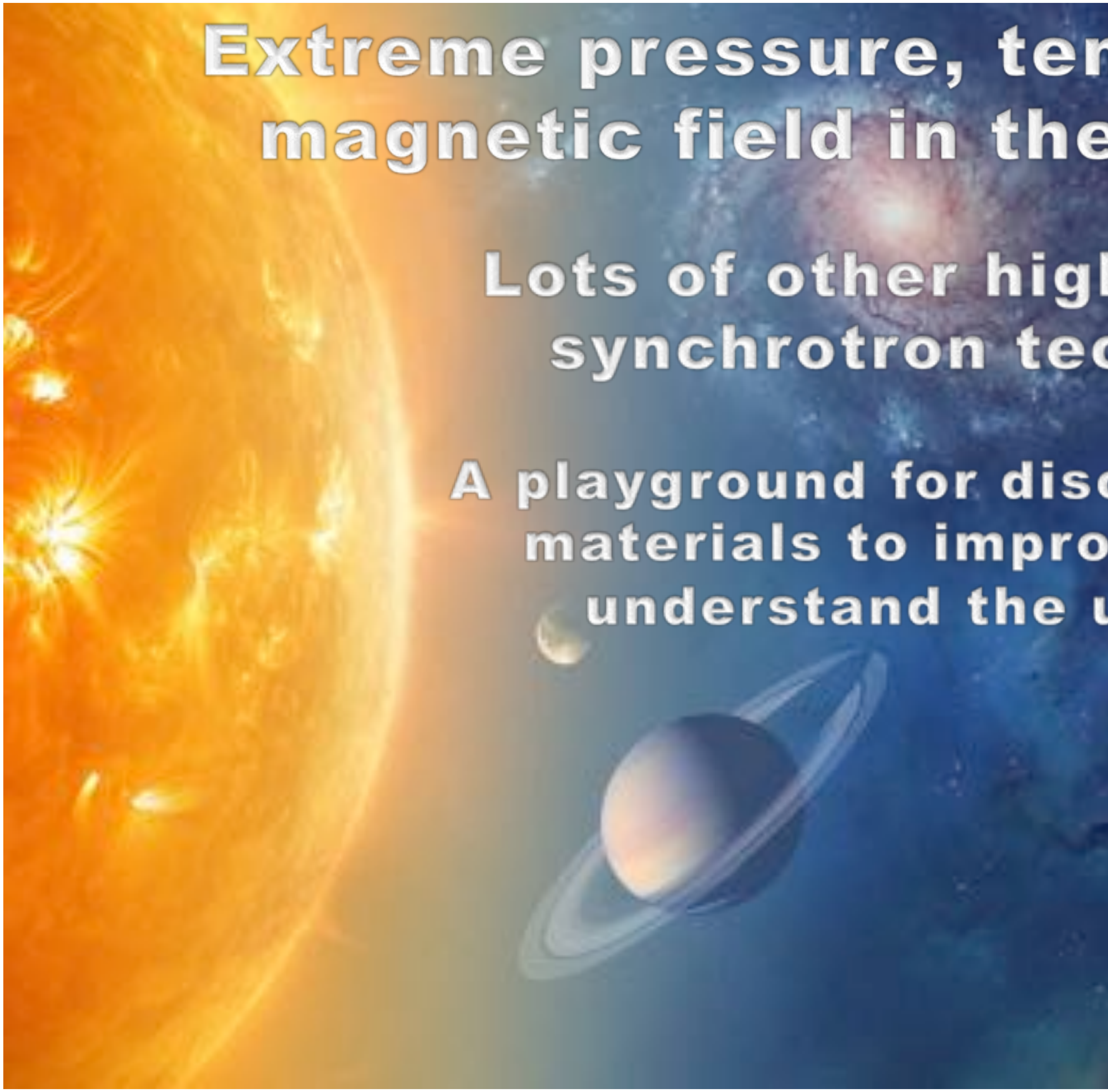
Received: 06 January 2015
Accepted: 08 June 2015
Published: 07 July 2015

Francisco C. B. Maia[1], Ricardo E. Samad[2], Jefferson Bettini[3], Raul O. Freitas[1], Nilson D. Vieira Junior[2] & Narcizo M. Souza-Neto[1]

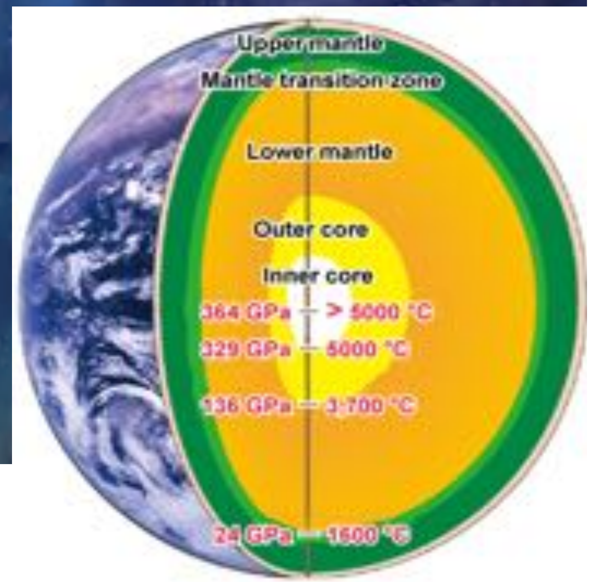
Extreme pressure, temperature, magnetic field in the universe

Lots of other high pressure synchrotron techniques

A playground for discovering new materials to improve life and understand the universe.



From: www.nasa.gov



From: Spring8:

Questions?