Eglantine Boulard
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Institut de minéralogie,
de physique des matériaux
et de cosmochimie (IMPMC)

Mantle Mineralogy

- Experimental Petrology and Mineral Physics
- Mineralogy of the mantle and subducting slabs
- Case Study: Deep Carbon Cycle

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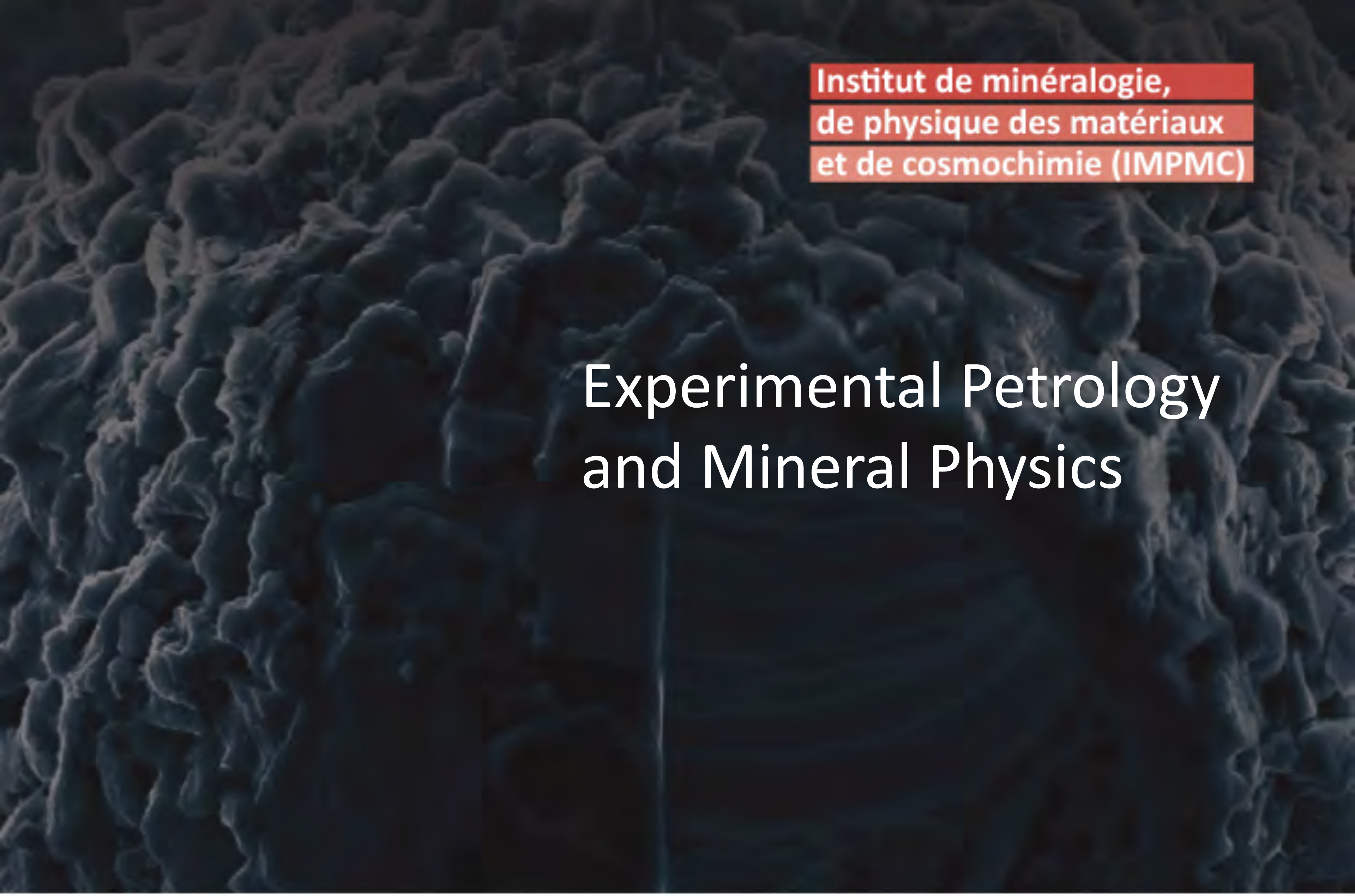
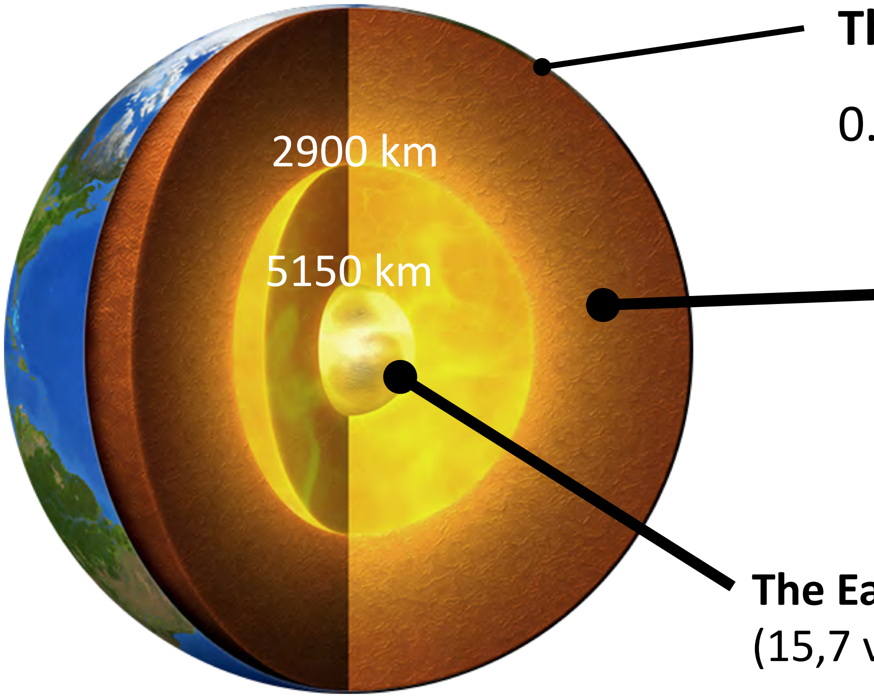


Experimental Petrology and Mineral Physics

Earth's Mantle Natural Samples



The continental crust:

0.4 mass % (0.8 vol. %) the Earth.

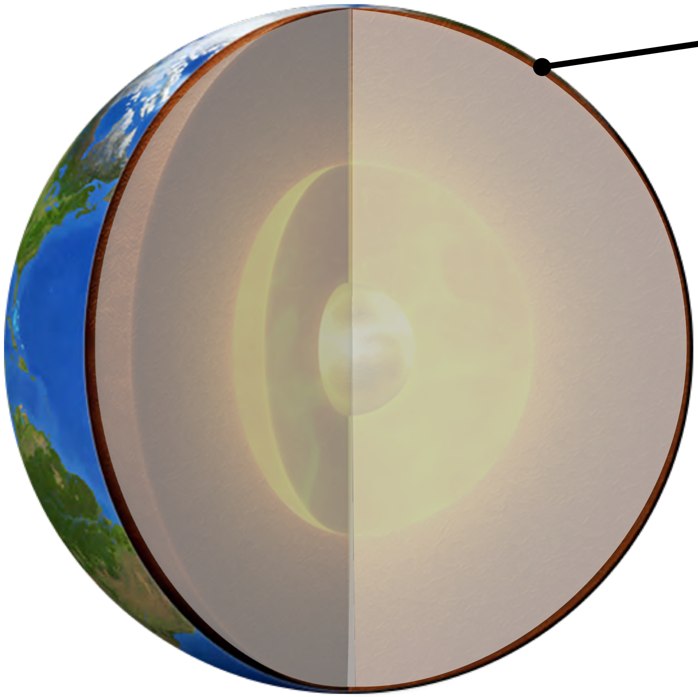
The Earth's mantle:

67% of Earth's mass (83 vol.%)

The Earth's core: outer core : 30.8 mass % (15,7 vol.%) ; inner core 1.7 mass % (0.7 vol.%)

Credits: C. Duflot (IMPMC)

Earth's Mantle Natural Samples

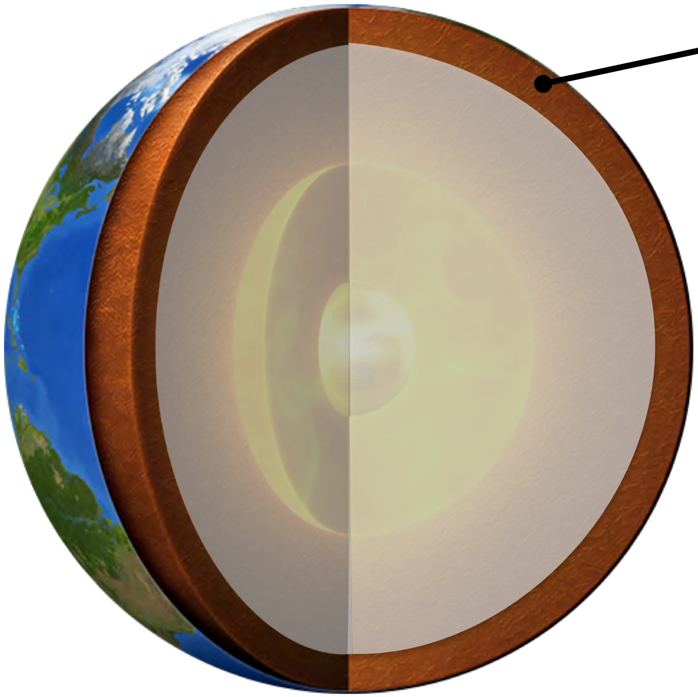


Moho discontinuity: Ophiolite

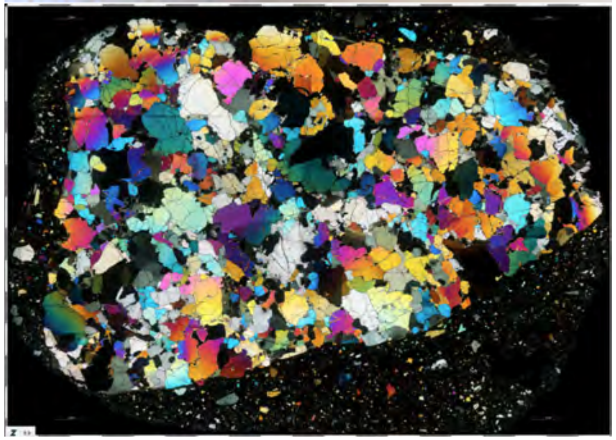
Oman Ophiolite
Credits: Pierre Thomas (ENS Lyon)

Credits: C. Duflot (IMPMC)

Earth's Mantle Natural Samples



Upper Mantle :
Peridotite enclaves in lava



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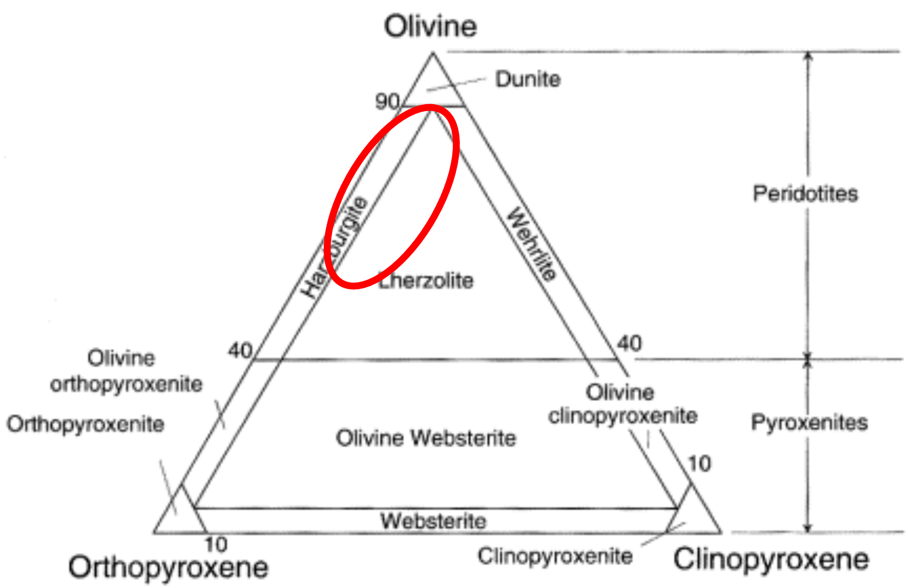
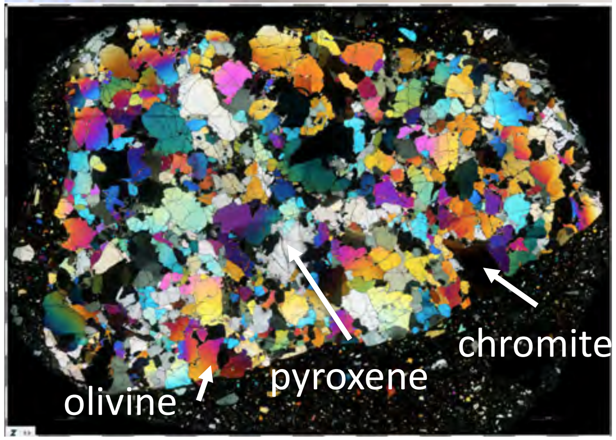
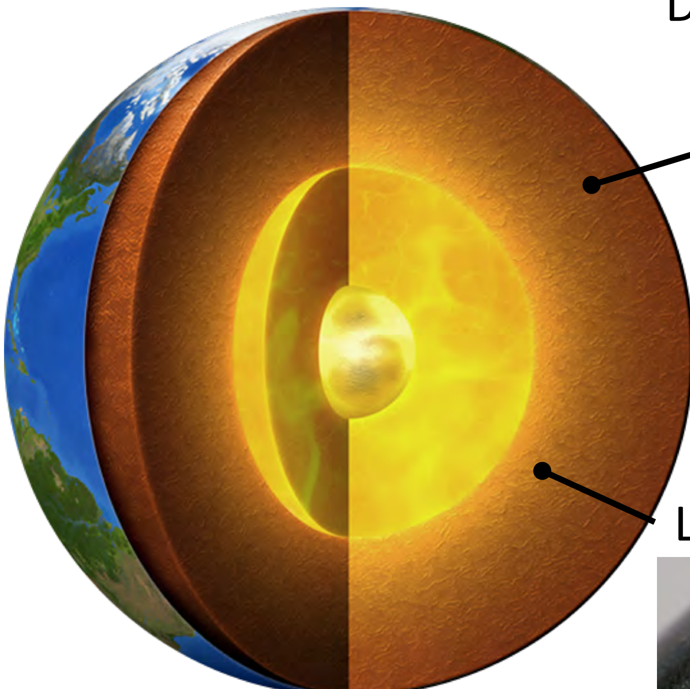
Earth’s Mantle Natural Samples



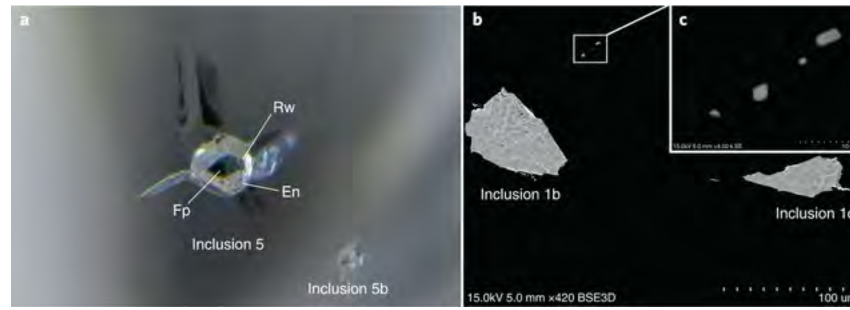


Earth’s Mantle Natural Samples



Deep Mantle : Diamond Inclusions

Transition Zone



Gu et al., Nat. Geoscience, 2022

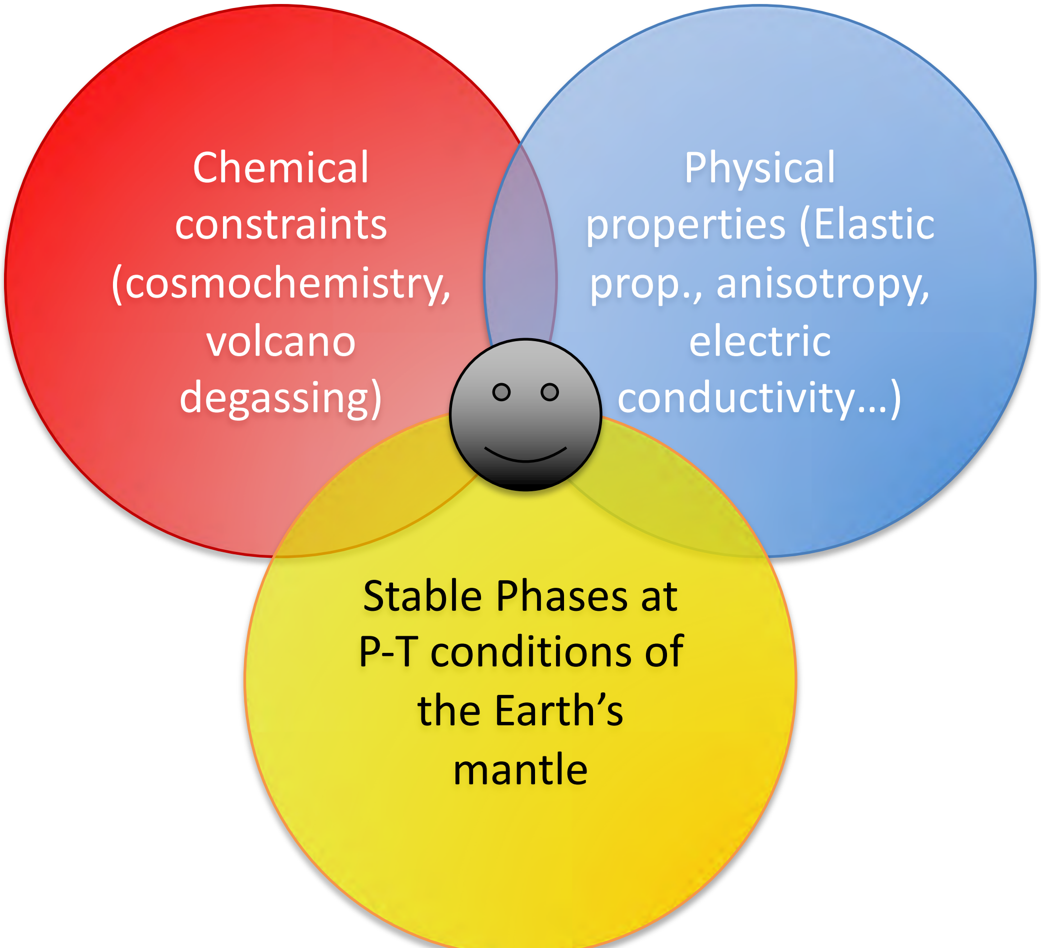
Lower Mantle

Smith et al., Science, 2018

Tschauner et al., Science, 2021

Credits: C. Duflot (IMPMC)

Needs From Mineral Physics



Needs From Mineral Physics

- Phase diagrams
- Physical properties of minerals
- Description of the crystalline structures

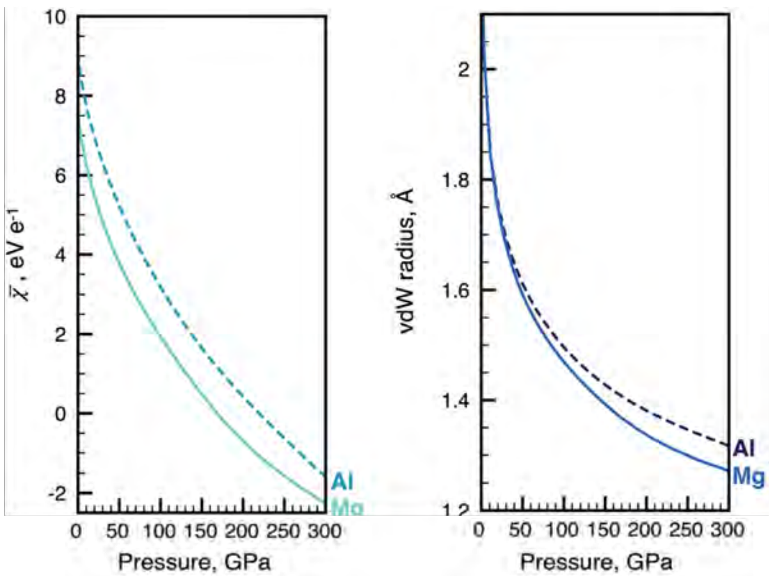
@ mantle conditions

=

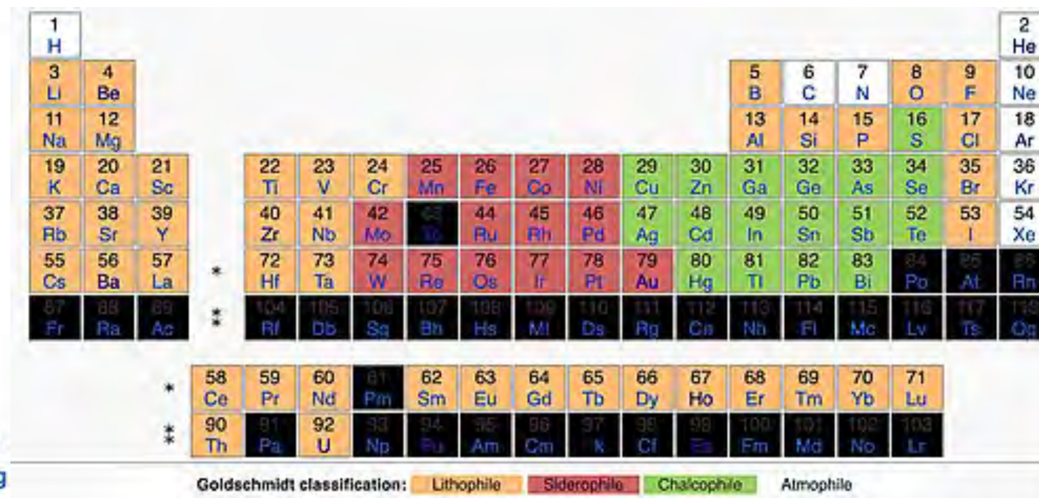
@ high pressure and temperature

Pressure Modifies Everything

- Atomic scale



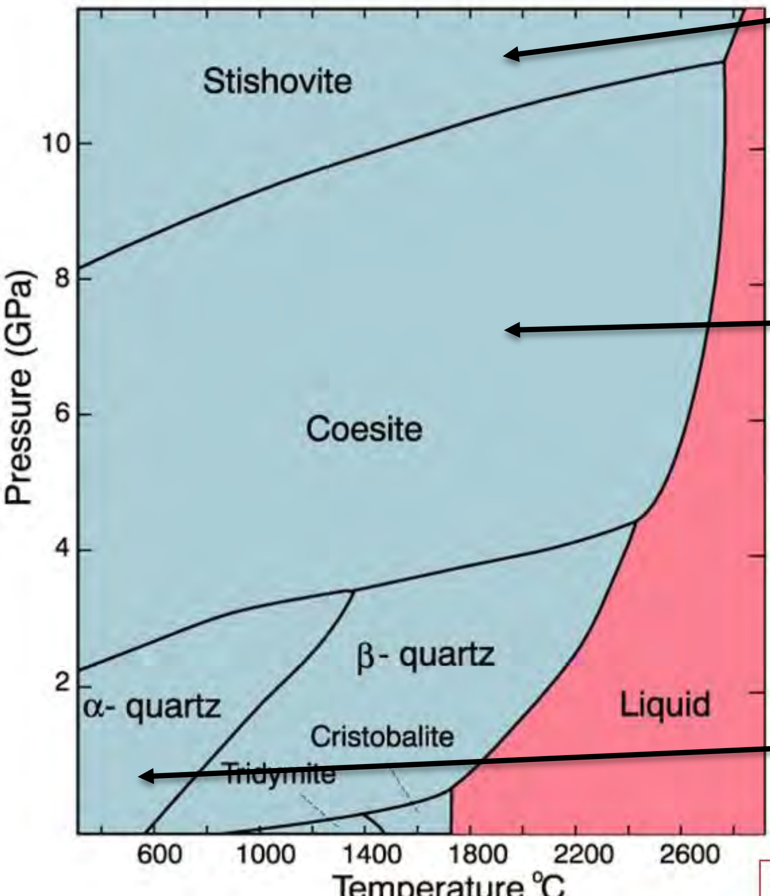
electronegativity radius

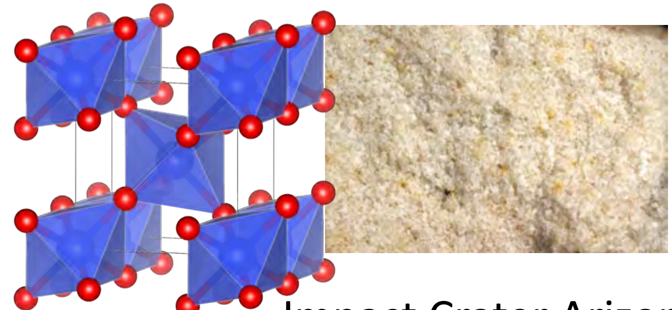


Rahm et al., Chemical Science, 2021

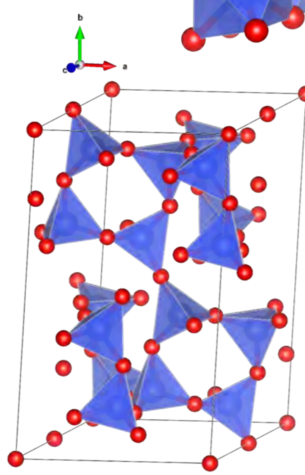
Pressure Modifies Everything

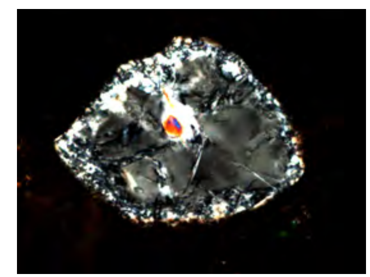
- Coordinations numbers



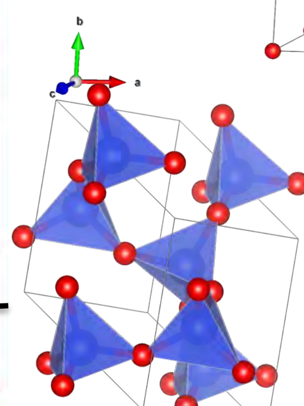


Impact Crater Arizona



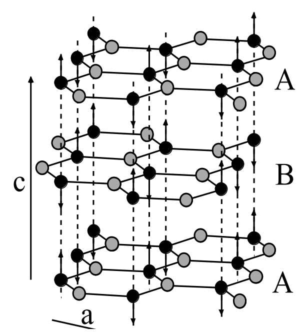


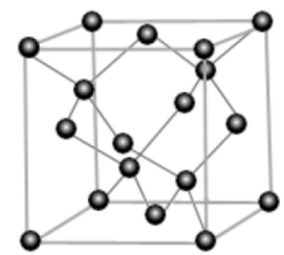
Eclogite South Africa



Pressure Modifies Everything

- Type of bondings

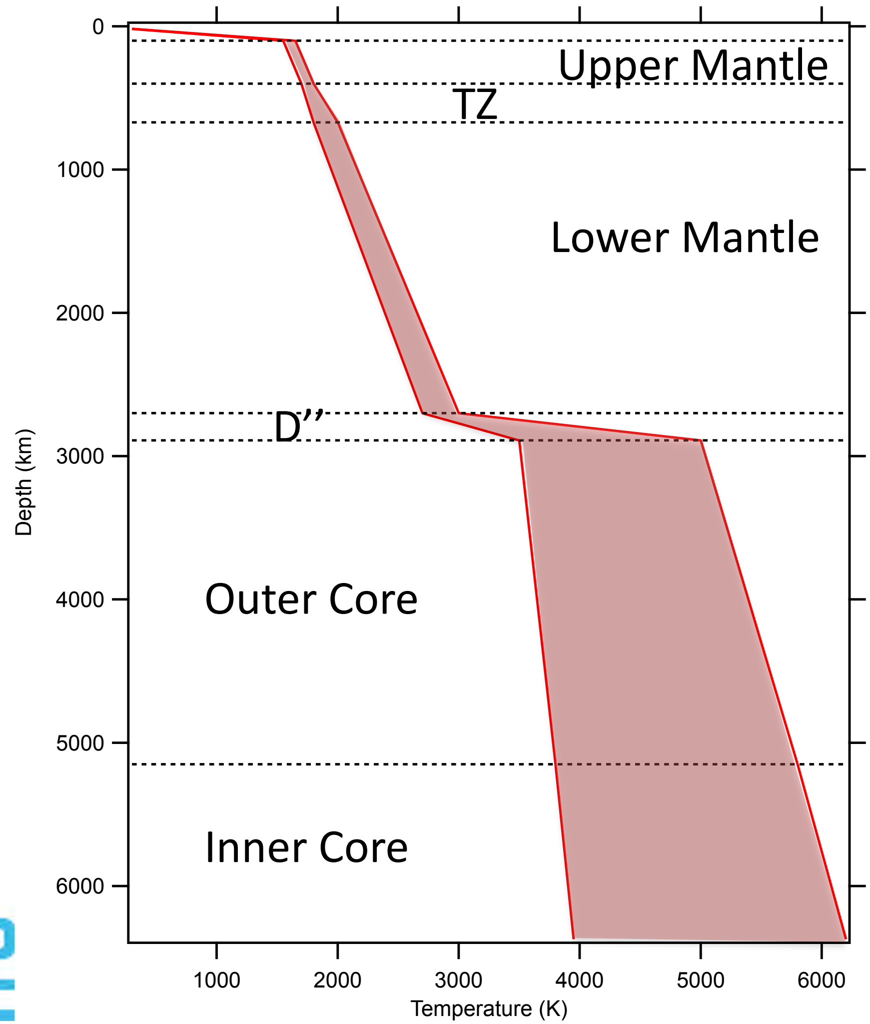




Strength	Soft	Hard
Thermal conductivity	Good	Good
Electric Conduction	Good	Poor

Reaching High Pressure

- P-T Conditions in the Mantle



3 GPa : lithosphere/asthenosphere
13 GPa : Forsterite => Wadsleyite
24 GPa : Ringwoodite => Bridgmanite

125 GPa
135 GPa

329 GPa : Solid/Liquid Fe

Reaching High Pressure

Basic principle:

$$\boldsymbol{Pressure = \frac{Force}{Surface}}$$

$1\ \mathrm{kg}\frac{m}{s^2}$

1 Pa = 1 Newton/m^2

P $_{atm}$: 1 bar = 10^5 Pa

high pressure can be generated by:

- **Large force**
- **Small surface**

Static Compression = Duration of the experiment is indefinite ≠ **Dynamic Compression**

Reaching High Pressure

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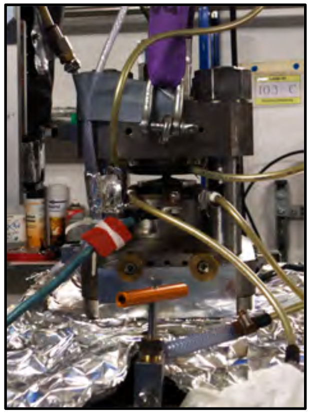
Reaching High Pressure

Paris-Edinburgh



200 tons

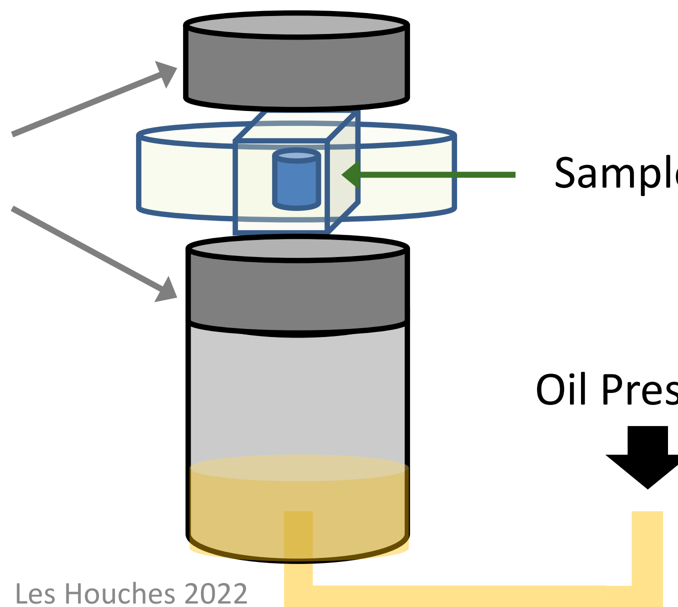
Piston Cylinder

250 tons

Multi Anvils

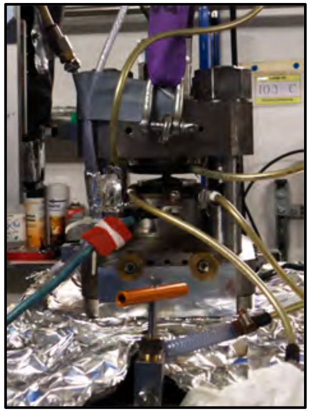
>1000 tons

Pressure Measurement :
Calibration P(oil)/ P (GPa)



Reaching High Pressure

Paris-Edinburgh



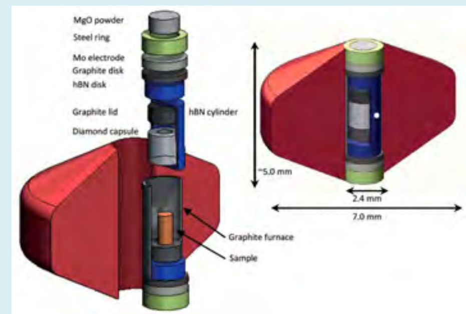
Piston Cylinder

Multi Anvils

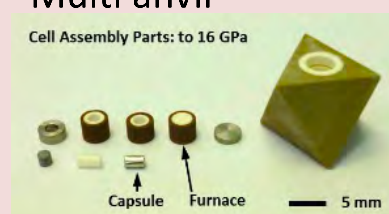
High Temperature

Resistive Furnace : Graphite, Re, $LaCrO_3$

Paris-Edinburgh



Multi anvil



Temperature measured by thermocouple or estimated from calibration : P(watt)/T(°C)

Reaching High Pressure

Basic principle:

$$\boldsymbol{Pressure = \frac{Force}{Surface}}$$

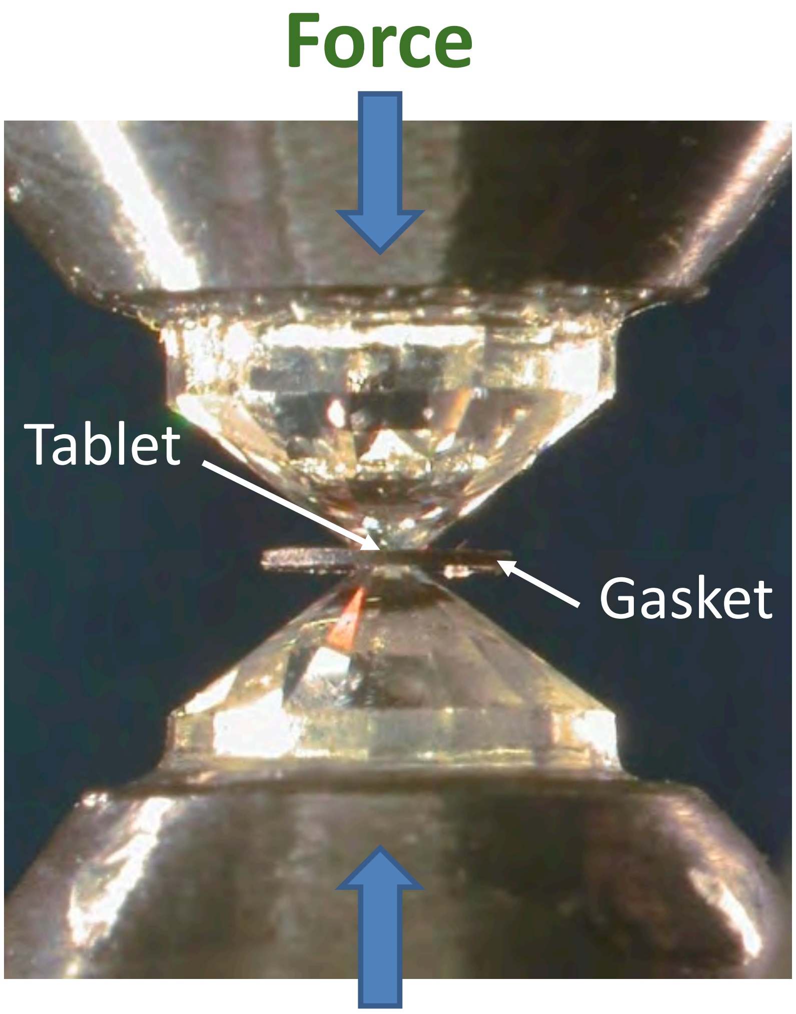
high pressure can be generated by:

- **Large force**
- **Small surface**

Static Compression = Duration of the experiment is infefinite ≠ **Dynamic Compression**

Reaching High Pressure

- Diamond Anvil Cell (DAC)



Choosing the Right Tool

	Piston Cylinder	Multi Anvils Paris-Edinburgh	Diamond Anvil cell
P-T range	4 GPa – 1800 K (120 km)	25 GPa – 3000 K (750 km)	>350 GPa – X000 K (6300 km)
Sample Size	Ø5 mm ↕ 10 mm	Ø1-3 mm ↕ ~5 mm	Ø20-100 μm ↕ 20-40 μm
Length of the Exp.	Days	Days	Minutes
In situ/ex situ	Only Ex Situ	In situ sometimes possible	In situ

In Situ Versus Ex Situ

- **In Situ**

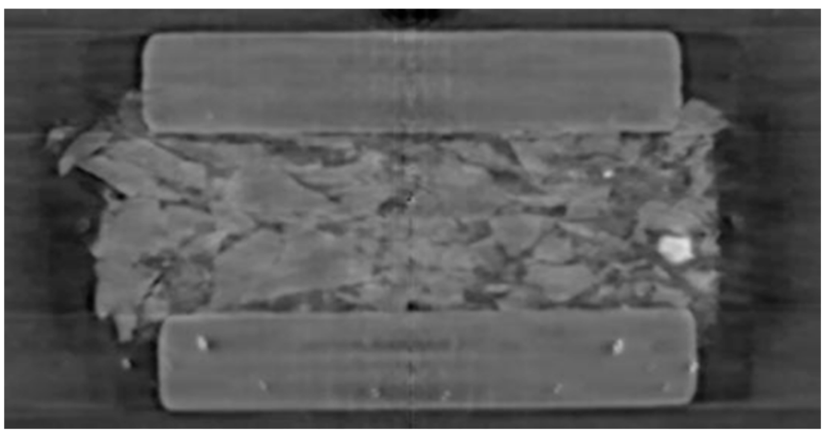
Within the press

at HP-HT conditions

- **Ex Situ**

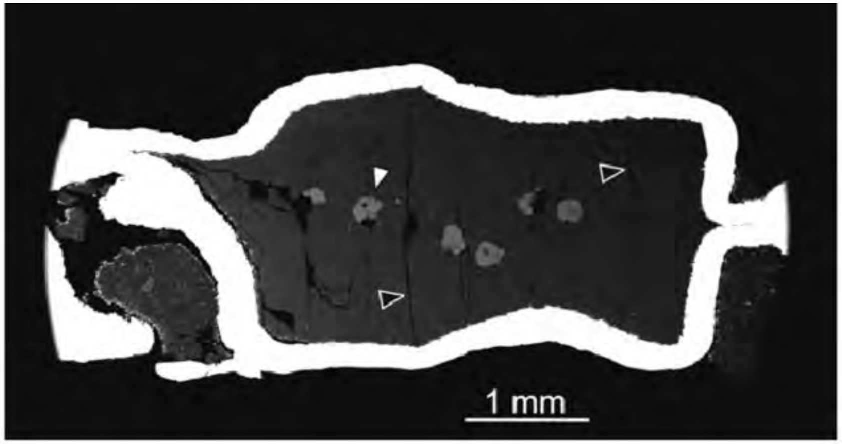
On recovered Sample

« Cook and Look »



Boulard et al., JSR, 2018

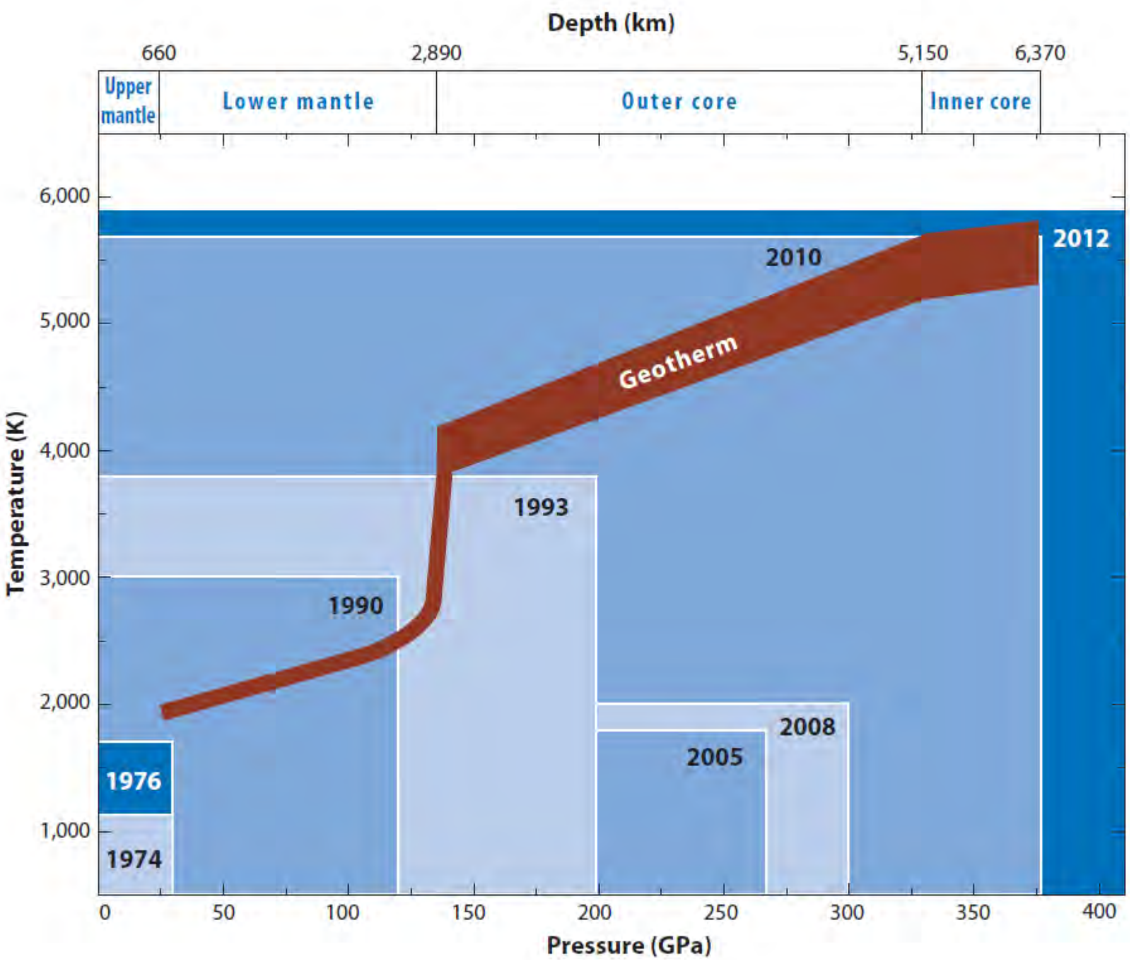
Rhyolite and forsterite at 3 GPa- 1200 K



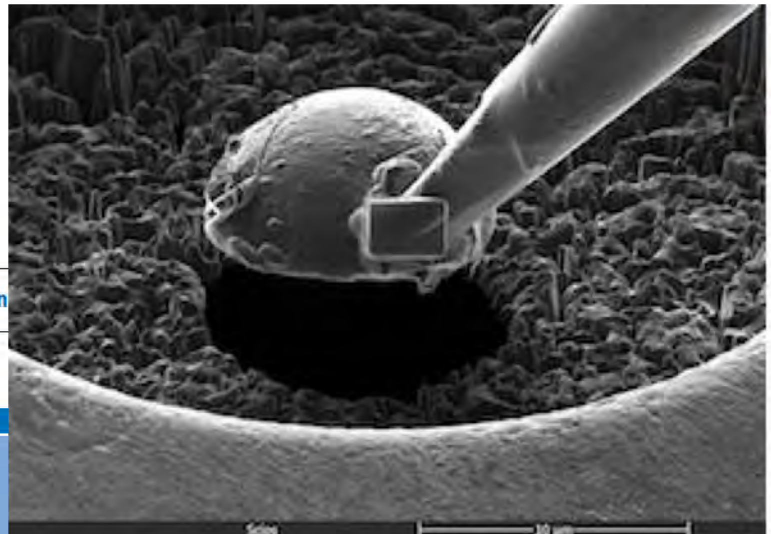
Cesare et al., Geofluids, 2013

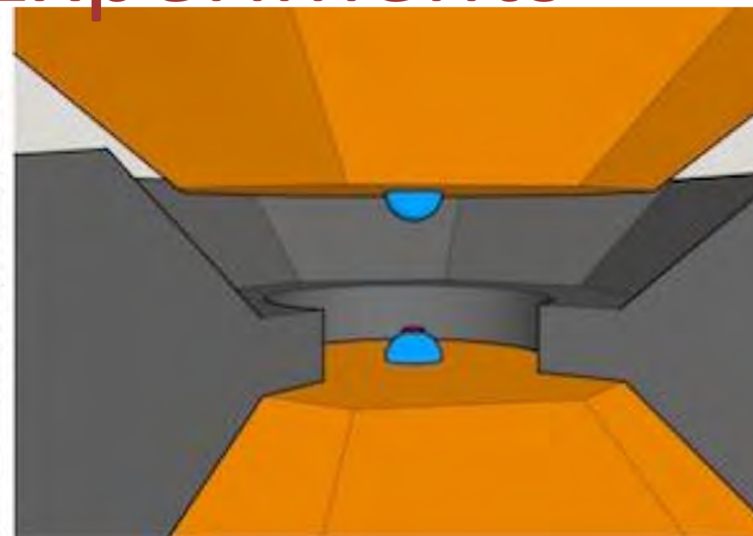
Migmatite at 0.5 GPa- 750 °C

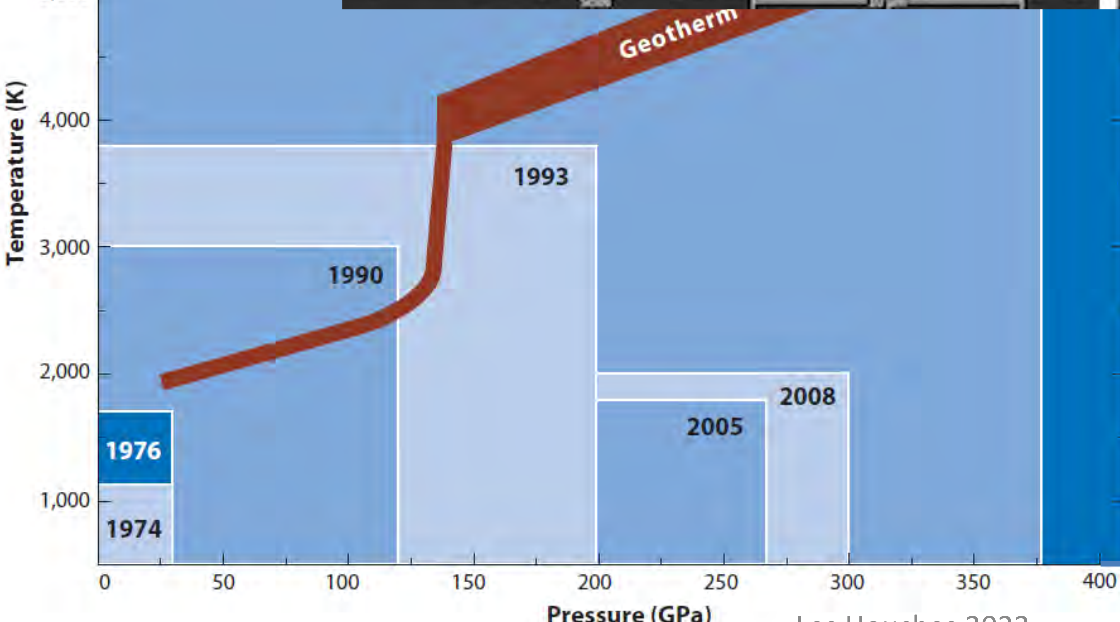
Diamond Anvil Cell Experiments

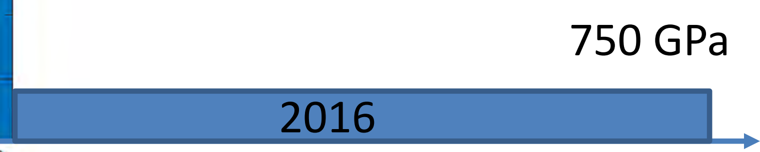


Diamond Anvil Cell Experiments



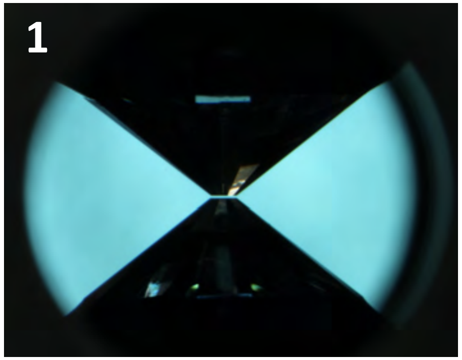




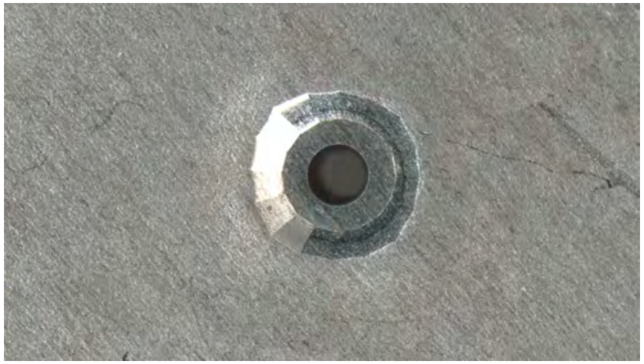


Natalia Dubrovinskaia *et al.*, *Science Advances* (2016)

Diamond Anvil Cell Experiments

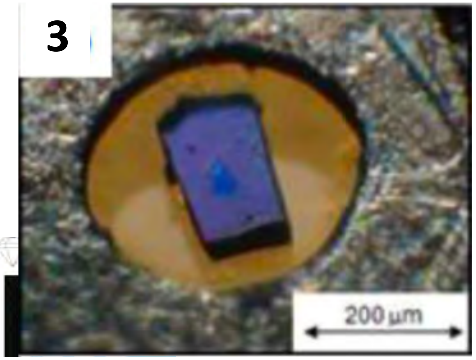


Alignements



Gasket Preparation

http://www.crystal.chem.ed.ac.uk/

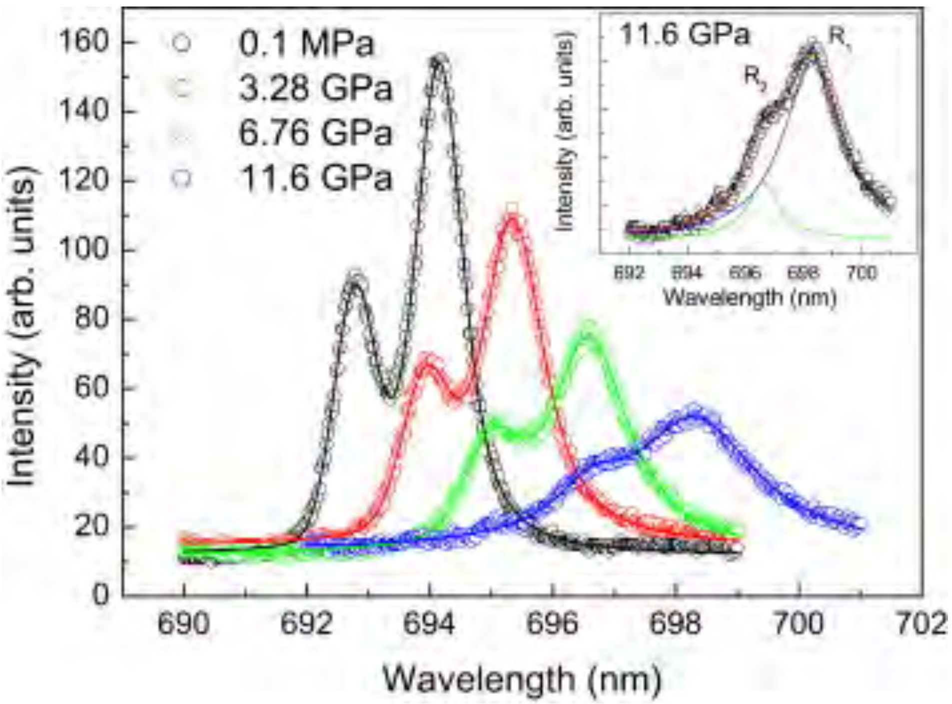


Sample Loading together with a ruby ball (<5 µm

Machon et al., 2018

Diamond Anvil Cell Experiments

- Pressure Measurements

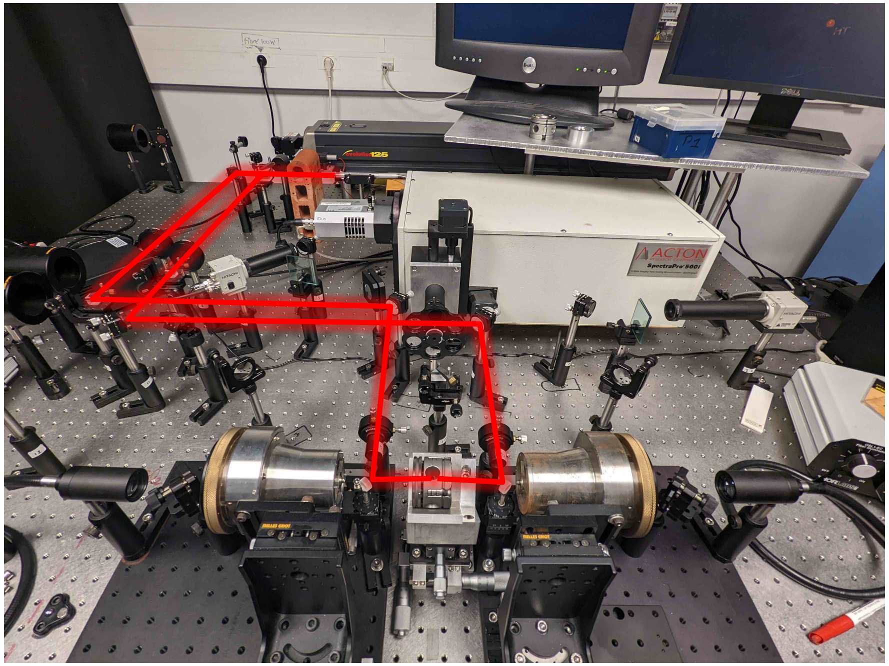


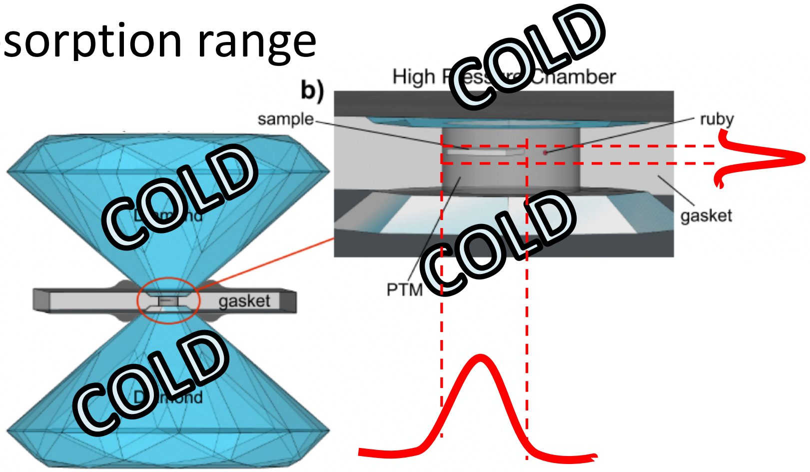
Jeong et al., Current Applied Physics, 2013

Diamond Anvil Cell Experiments

- Reaching HighTemperatures

YAG or CO_2 LASER : Depending on the sample absorption range



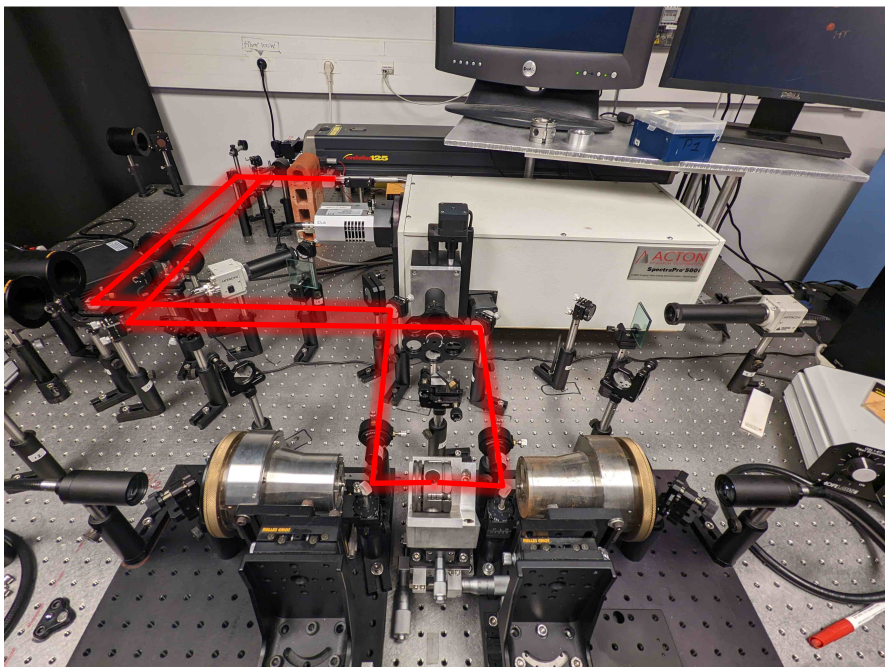


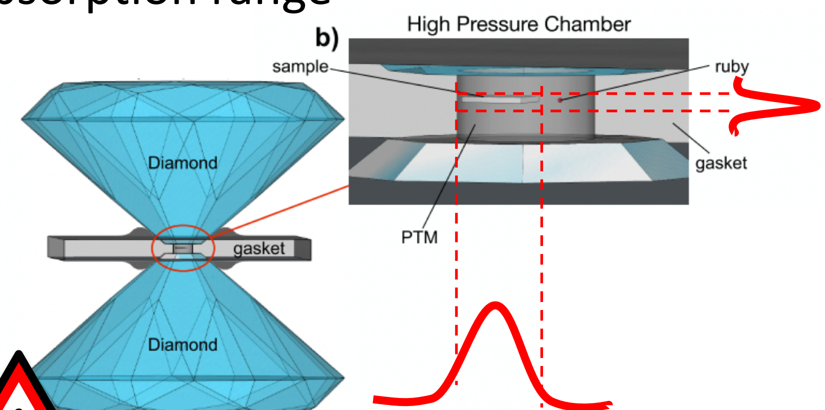
Need to isolate the sample from the diamonds
-> Use of thermal insulator (KCl or NaCl) or pressure transmitting medium (He, Ar, Ne)
->Thermal Gradient, that depends on the thermal conductivity of the pressure medium

Diamond Anvil Cell Experiments

- Reaching HighTemperatures

YAG or CO_2 LASER : Depending on the sample absorption range





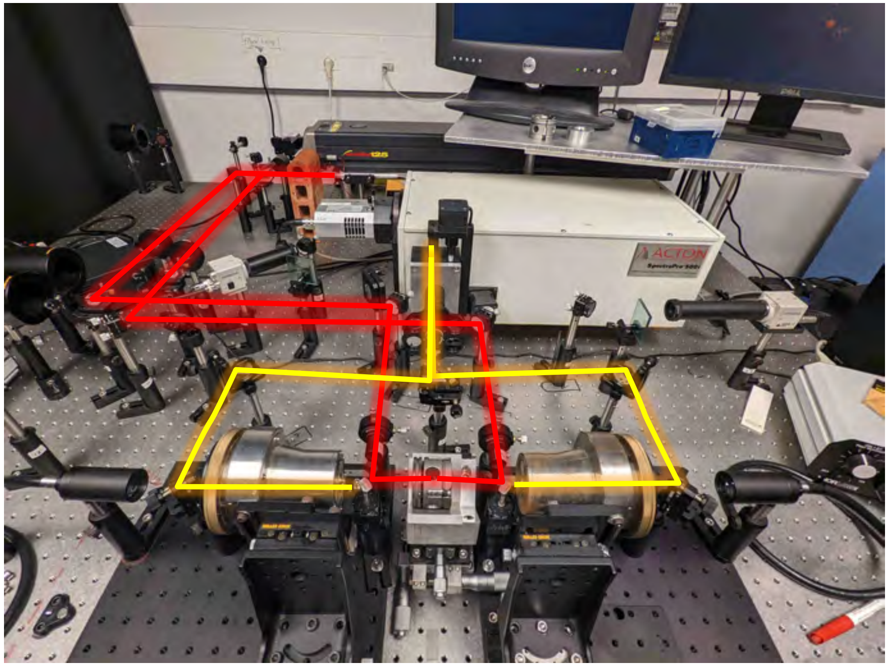
- Chemical Migration : Soret diffusion (Fe, Al, Mg, K)
- Chemical Pollution of the Sample (i.e. hydration)
- Carbon Diffusion from the diamond anvils

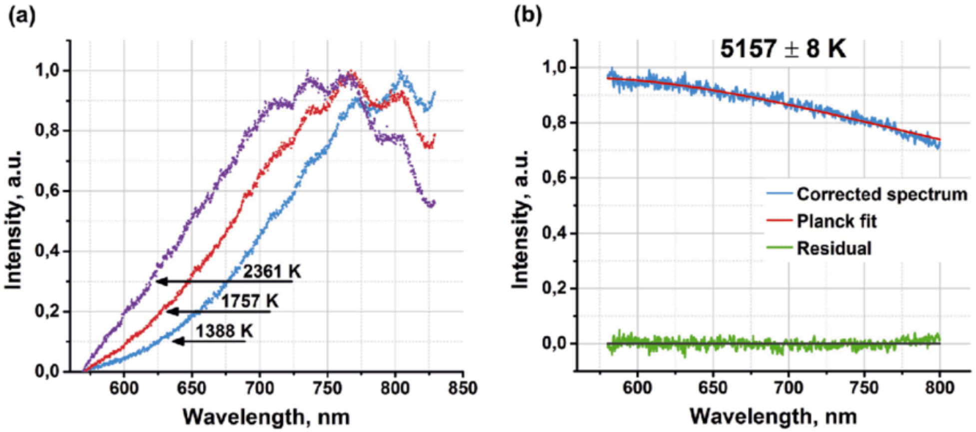
Diamond Anvil Cell Experiments

- Temperature Measurements

spectral radiometry by fitting the radiated thermal signal from the sample surface with the Planck's law:

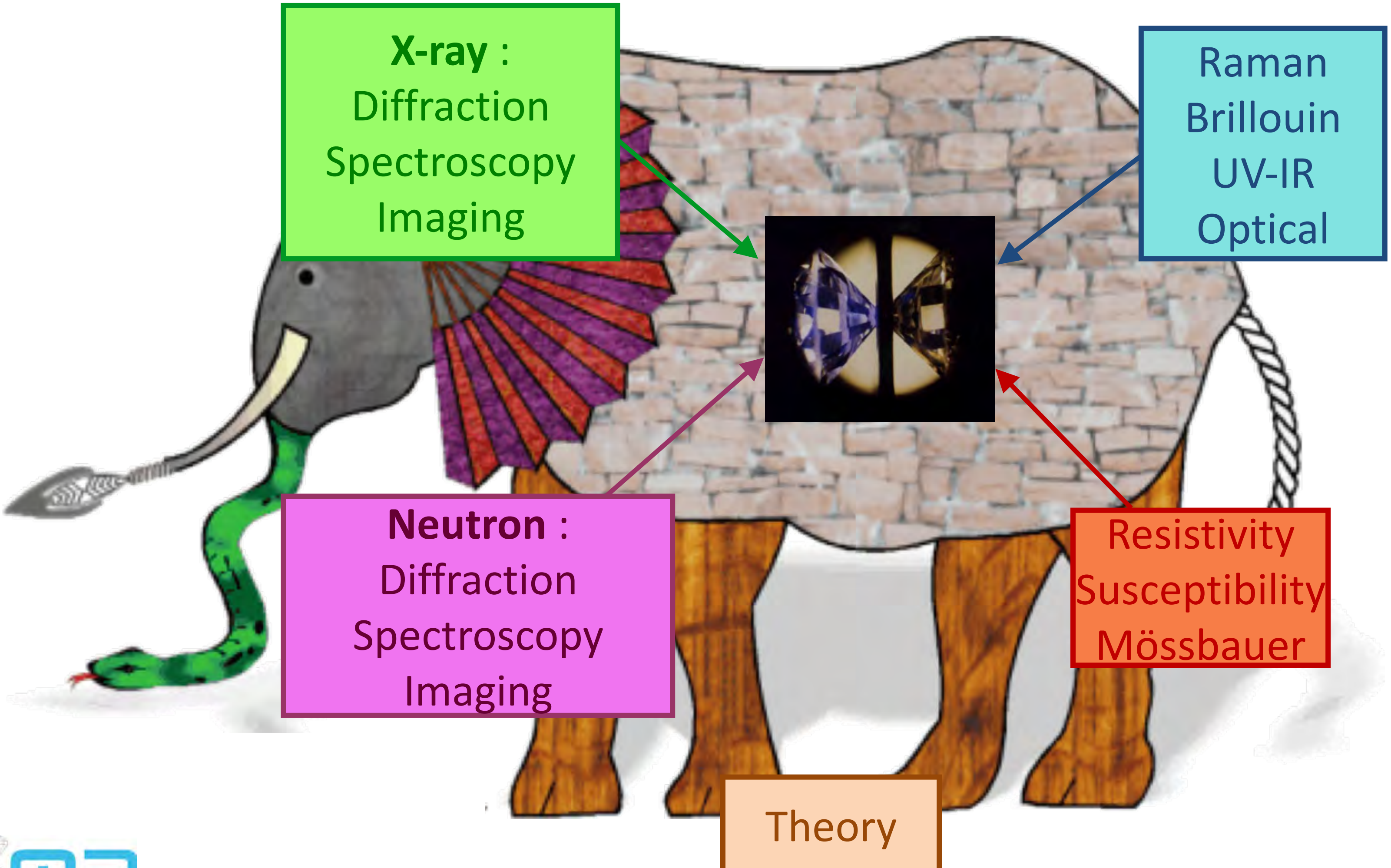
$$I(\lambda,\epsilon,T) = \epsilon\frac{2\pi hc^2}{\lambda^5}\frac{1}{exp(hc/\lambda K_B T)-1}$$





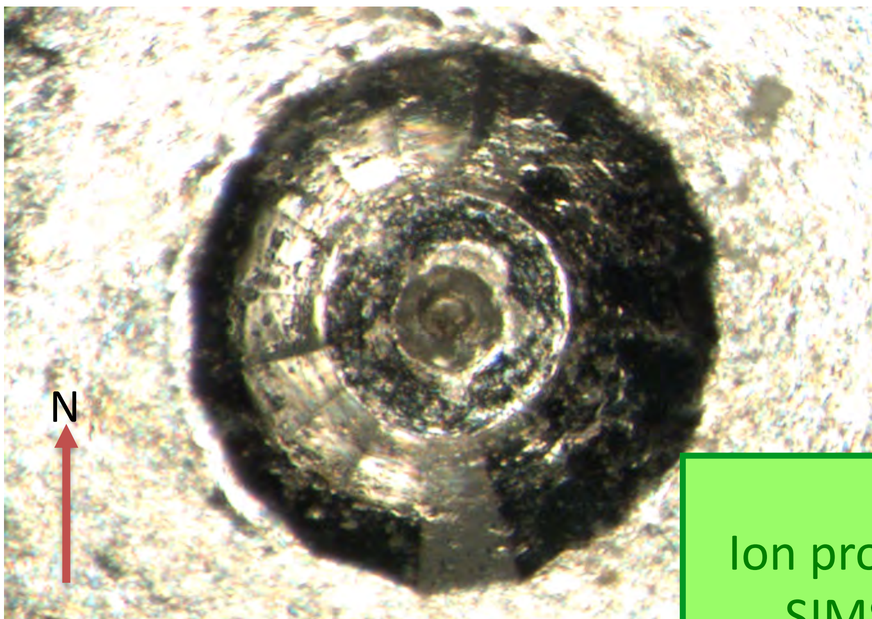
Fedotenko et al., Rev. Sci. Inst., 2019

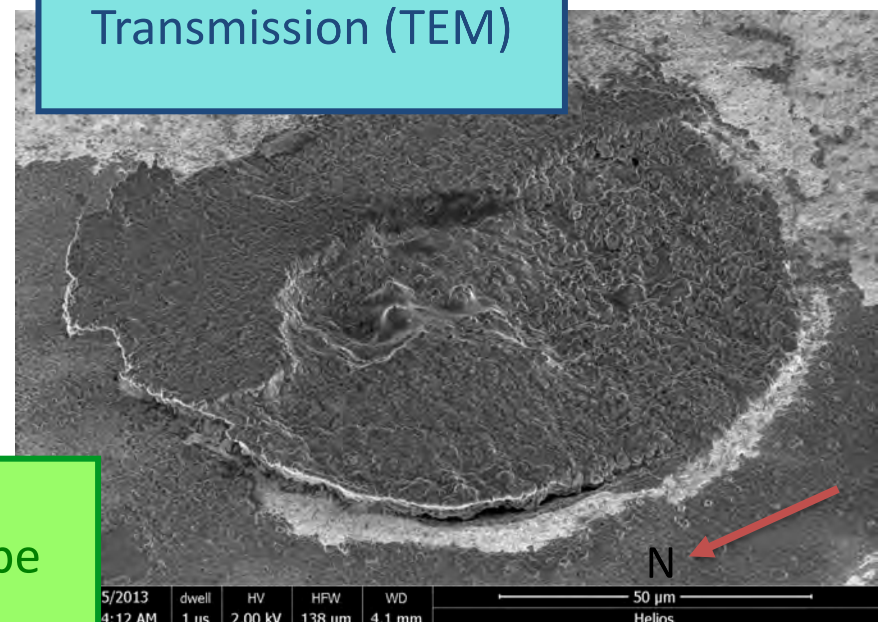
Integration of Multiple in situ Probes



Integration of Multiple ex situ Probes

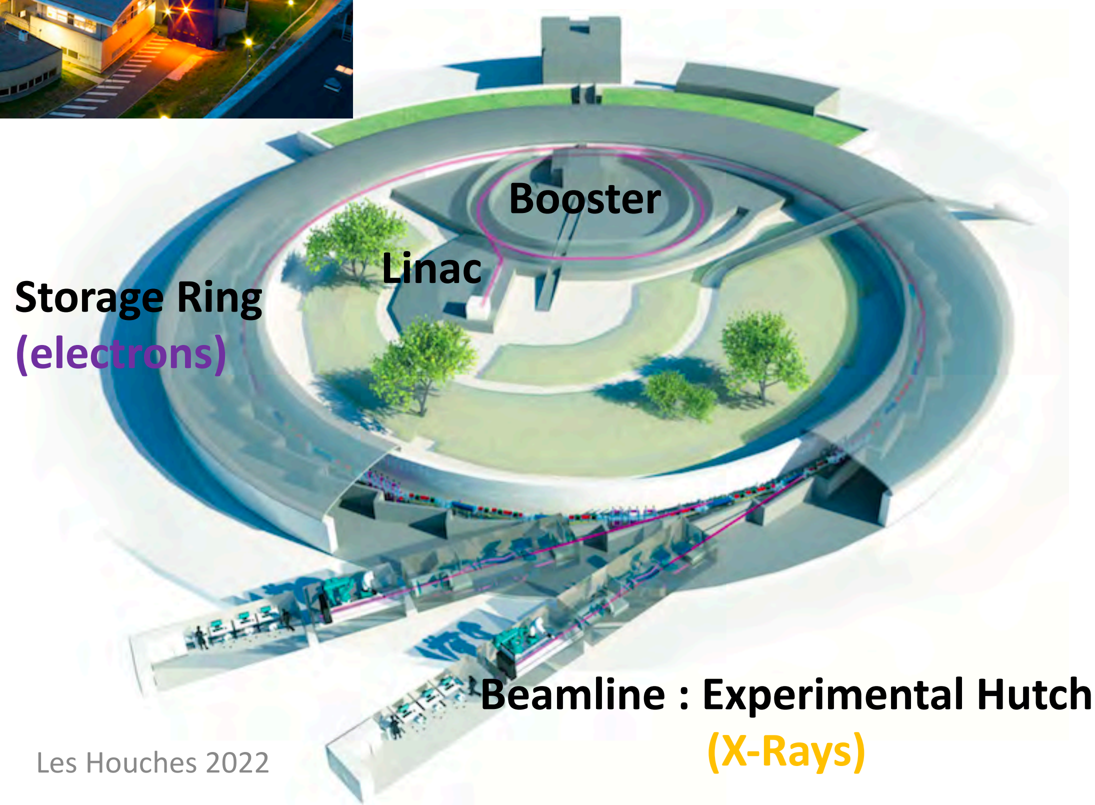
Electron Microscopies :
Scanning (SEM)
Transmission (TEM)





Ion probe
SIMS

Synchrotron as X-Ray Sources



Analytical Techniques Examples

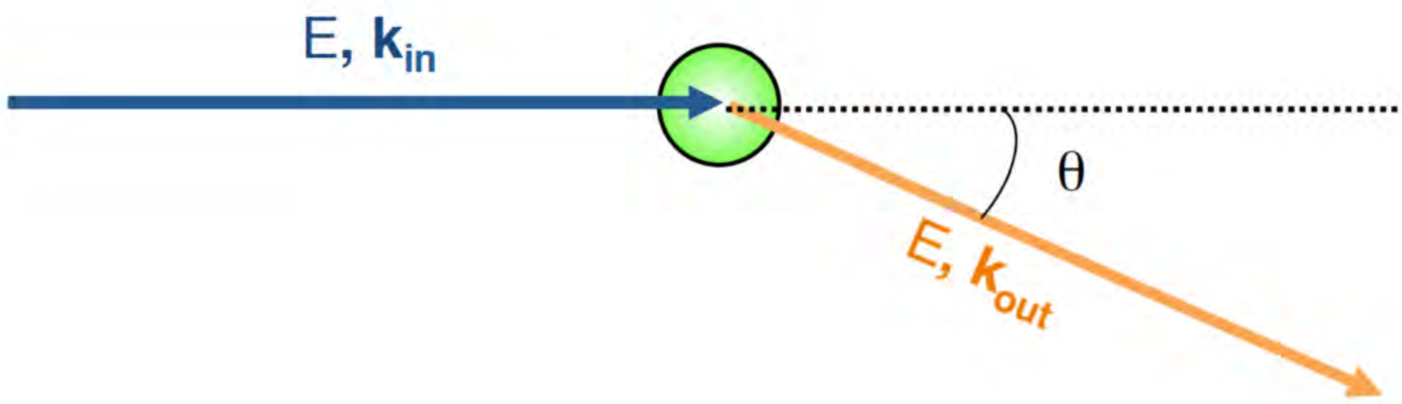
In Situ Analyses:

- **The routine technique : what can we do with X-Ray Diffraction (XRD) ?**
- Crystallo-chemistry description techniques
- How do we measure V_P V_S at HP-HT ?

Ex Situ Analyses:

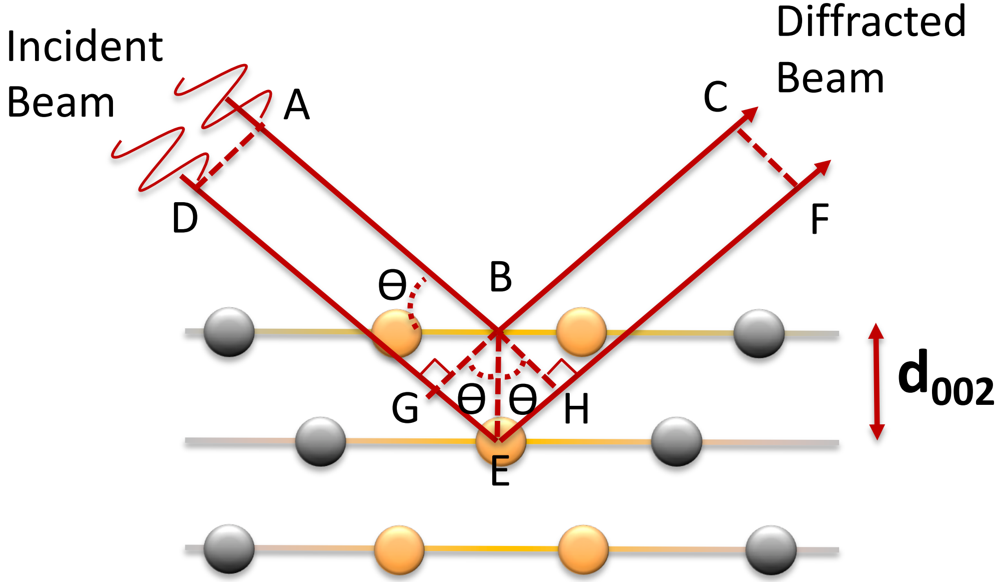
- Transmission Electron Microscopy (TEM)

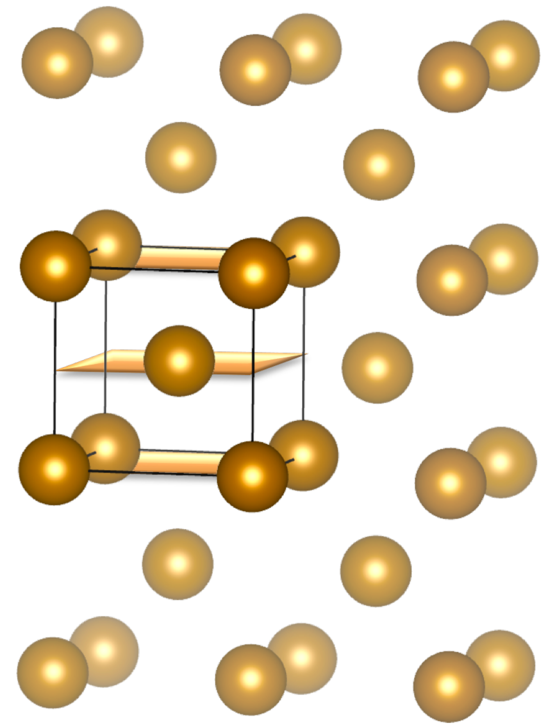
Elastic Scattering : X-Ray Diffraction



No energy transfer
Spatial deviation : $\boldsymbol{\theta} \neq 0$

Elastic Scattering : X-Ray Diffraction





Constructive interference if the difference between optic paths is nλ :

GE + EH = nλ => Bragg's Law : 2d sinθ=nλ

X-Ray Diffraction

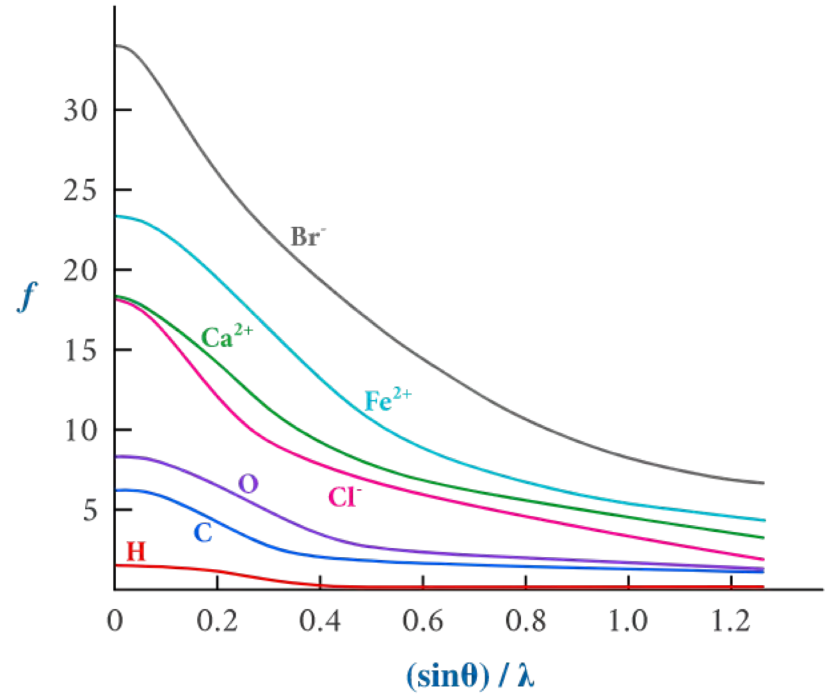
Atomic Scattering Factor f :

$$f = 4\pi \int_0^{\infty} \rho(r) \frac{\sin\ kr}{kr} r^2\, dr$$

r = atomic radius

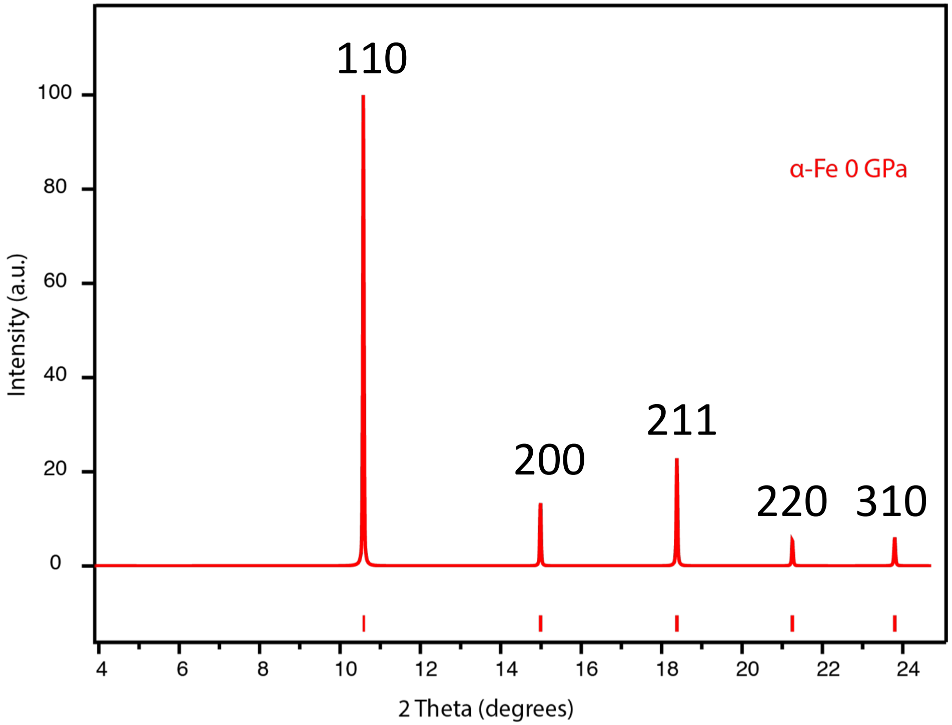
$\boldsymbol{\rho}$(r) = electron density

$$k = \frac{4\pi sin\theta}{\lambda}$$

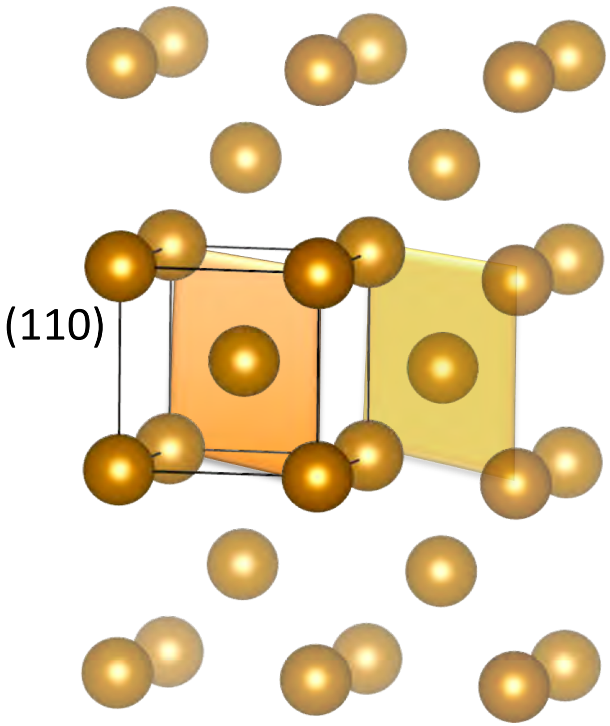


- Scattered Intensity is proportionnal to Z (light elements scattered slightly : hard to localised)
- Scattered intensity decreased at high angles

X-Ray Diffraction

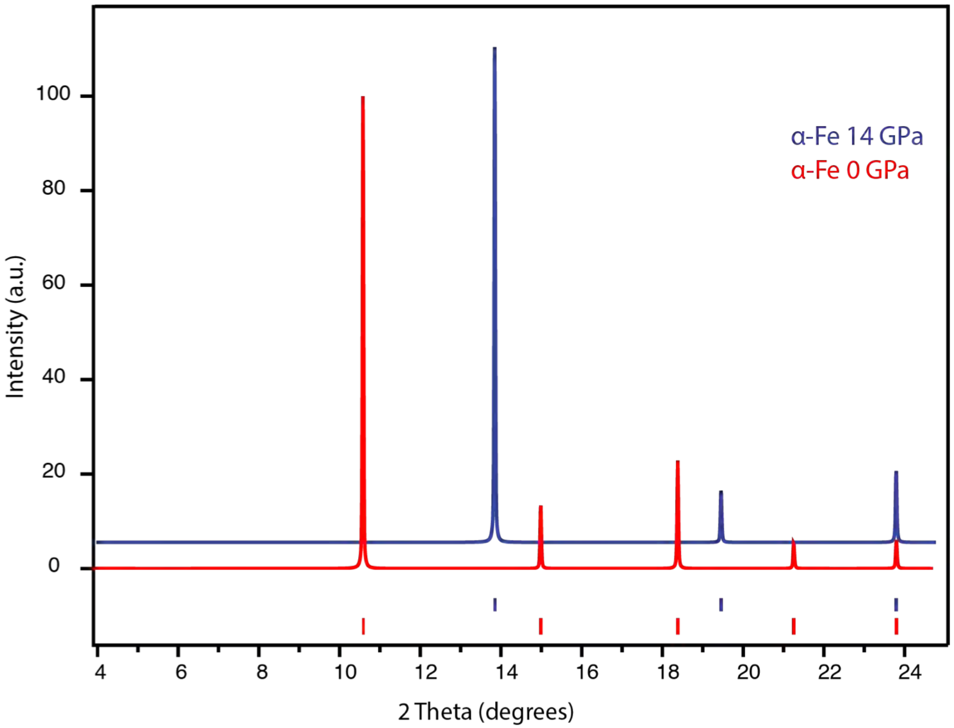


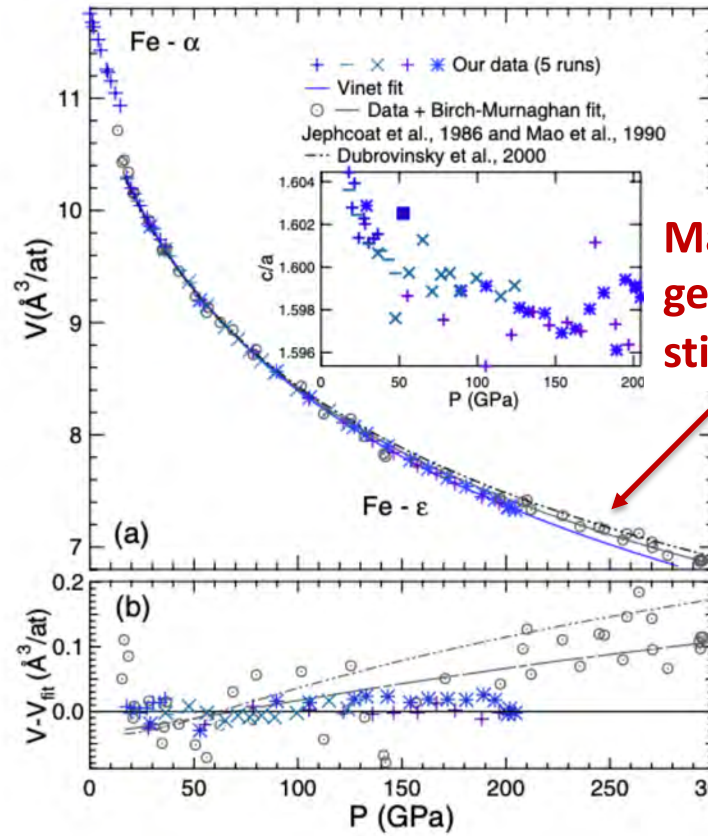
α-Fe : Im-3m



Refine unit cell parameters => unit cell volume => density

X-Ray Diffraction : Elastic Behavior





Material gets stiffer

Dewaele et al., PRL, 2006

X-Ray Diffraction : Elastic Behavior

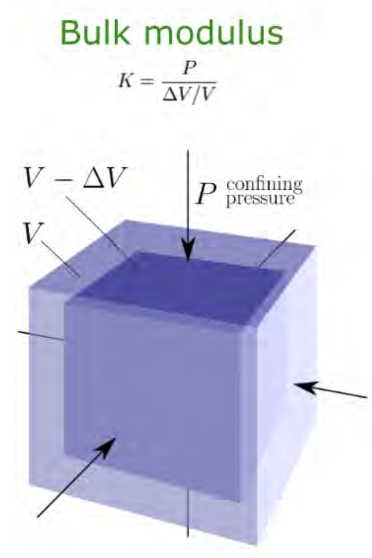
Determine the **bulk modulus K :**

$$\boldsymbol{K} = -V\frac{dP}{dV} = \rho\frac{dP}{d\rho}$$

describes how much pressure is required to cause a unit volume change

Compressional wave velocity :

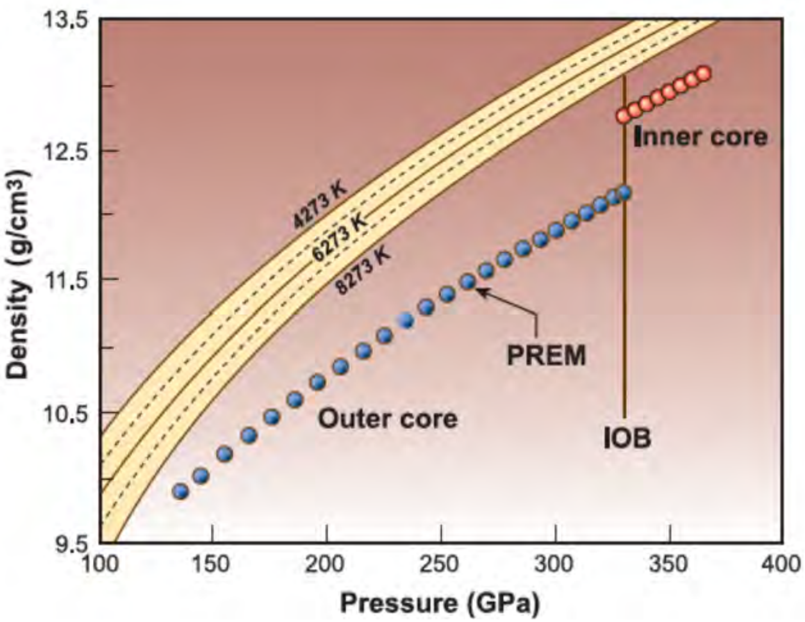
$$V_P = \sqrt{(\boldsymbol{K} + \frac{4}{3}G)/\rho}$$



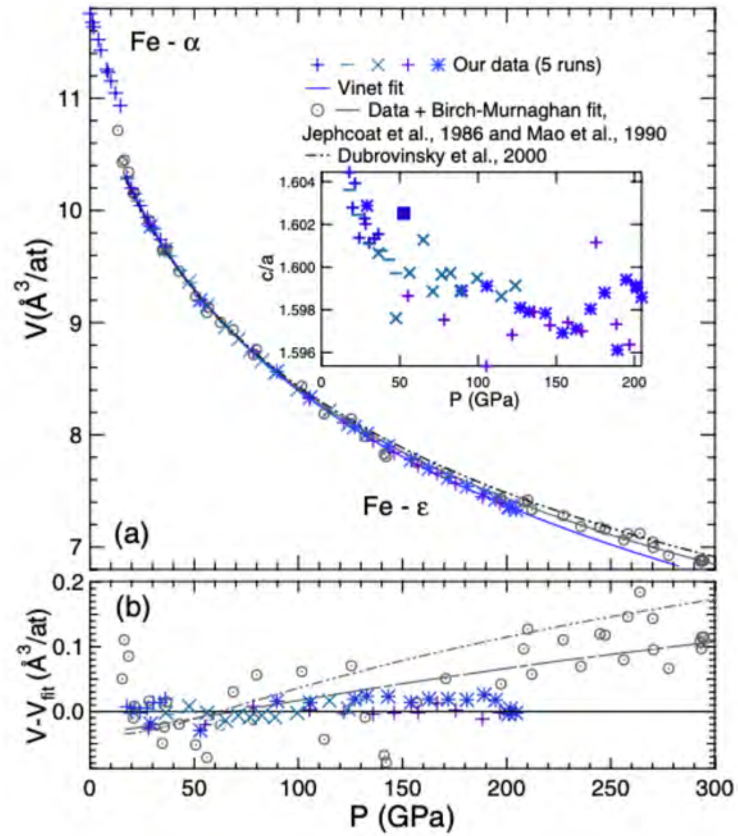
Different EOS :

- Birch-Murnaghan
- Vinet
- Mie-Gruneisen

X-Ray Diffraction : Elastic Behavior



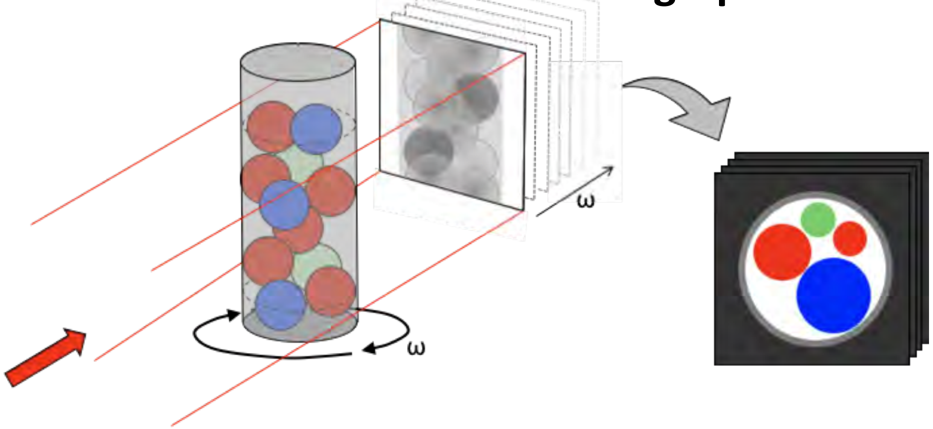
Fiquet et al., Elements (2008)



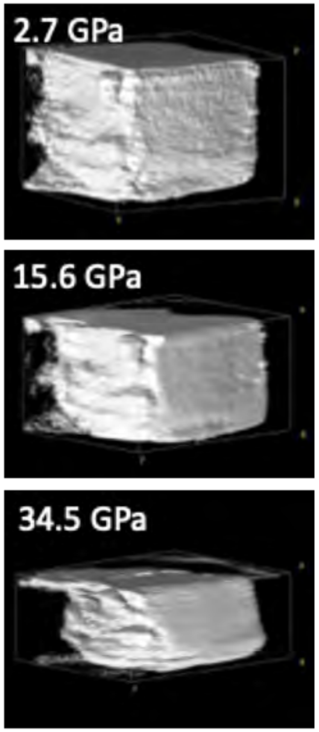
Dewaele et al., PRL, 2006

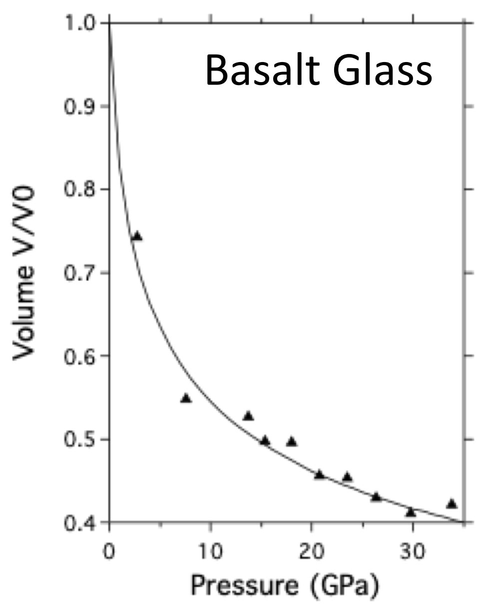
Other Method for EOS Measurements : X-Ray Tomography

Collect 2D Radiographies

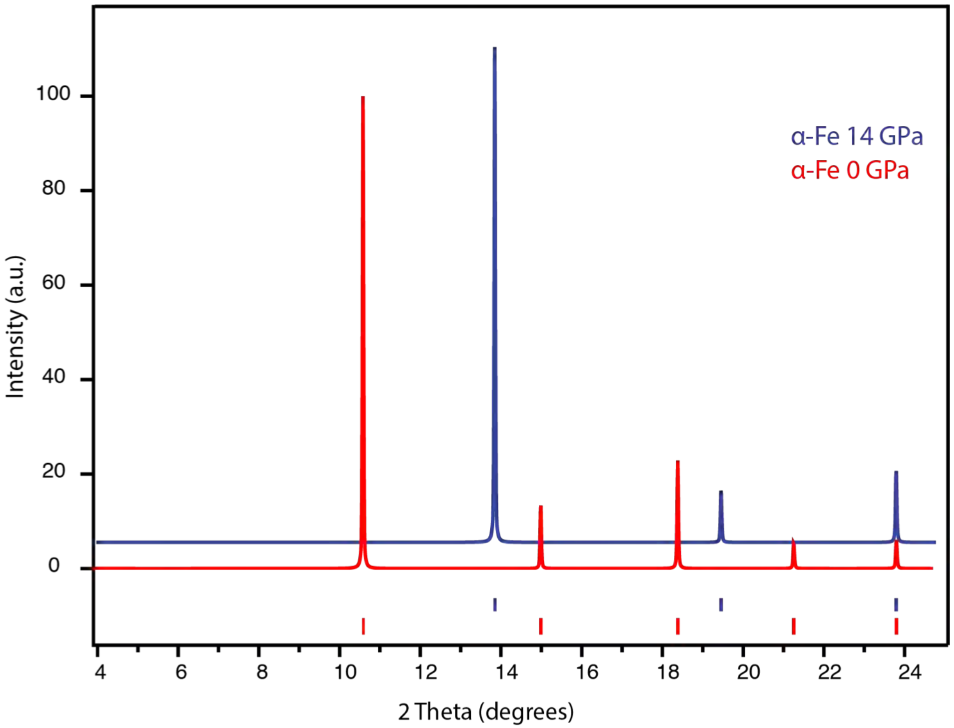


Compute Reconstructed Volume and Slices

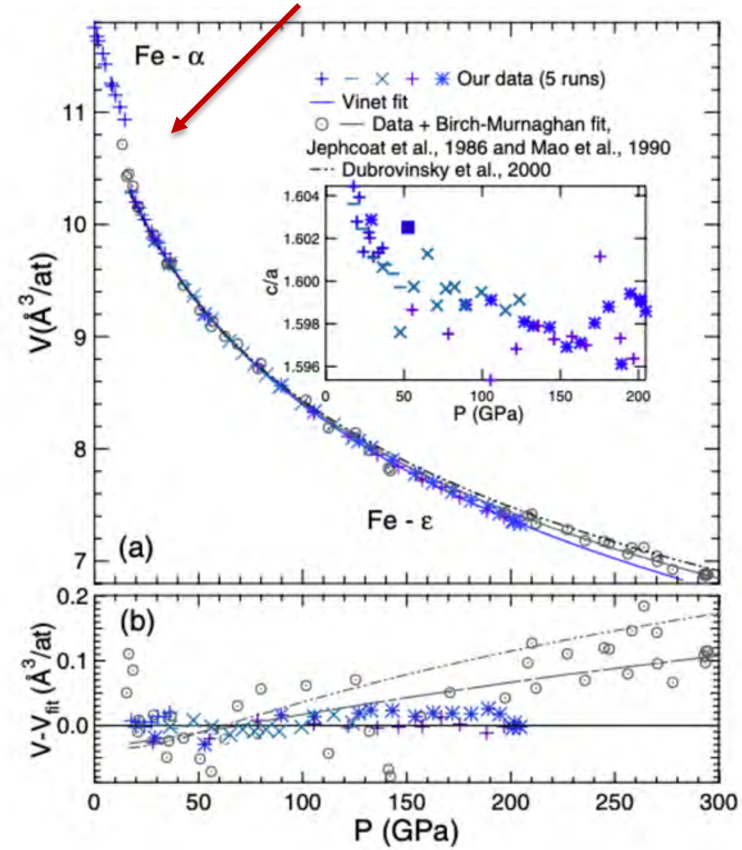




X-Ray Diffraction : Elastic Behavior

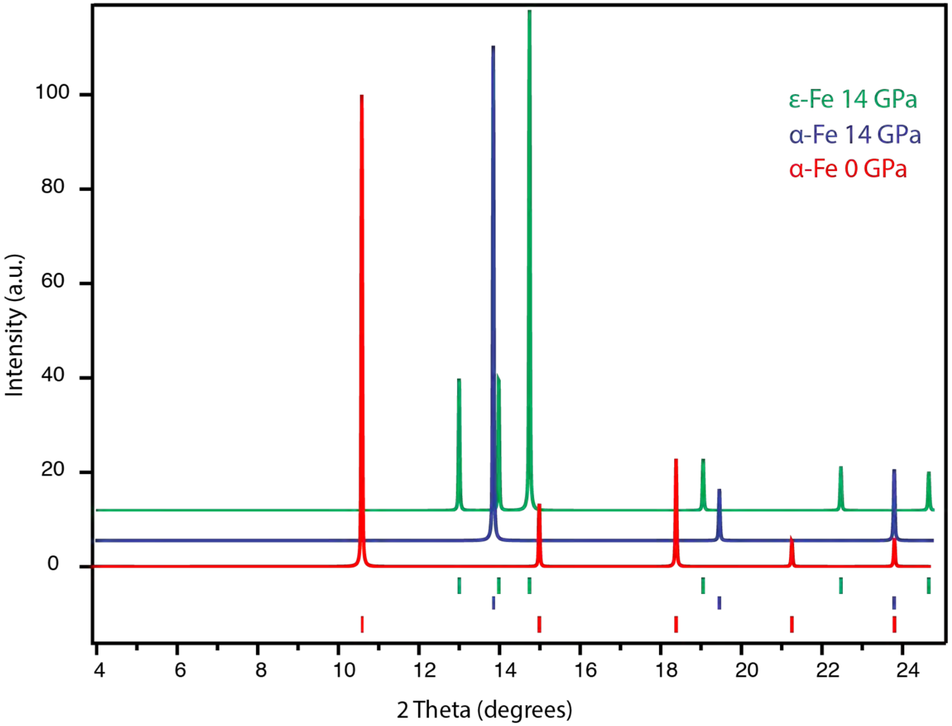


V drop = phase transition

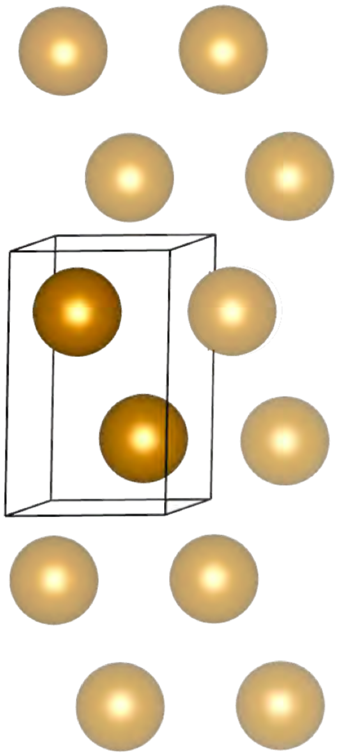


Dewaele et al., PRL, 2006

X-Ray Diffraction: Phase Transition

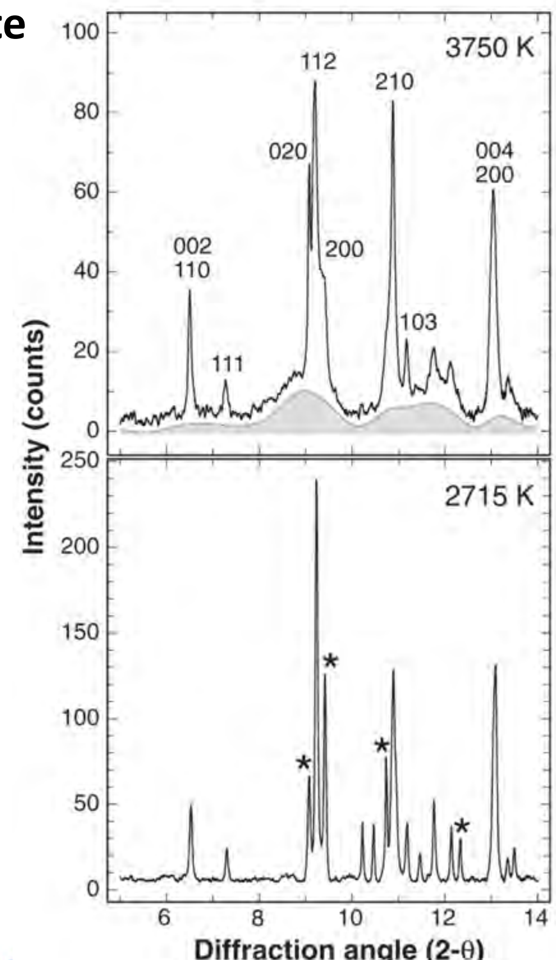


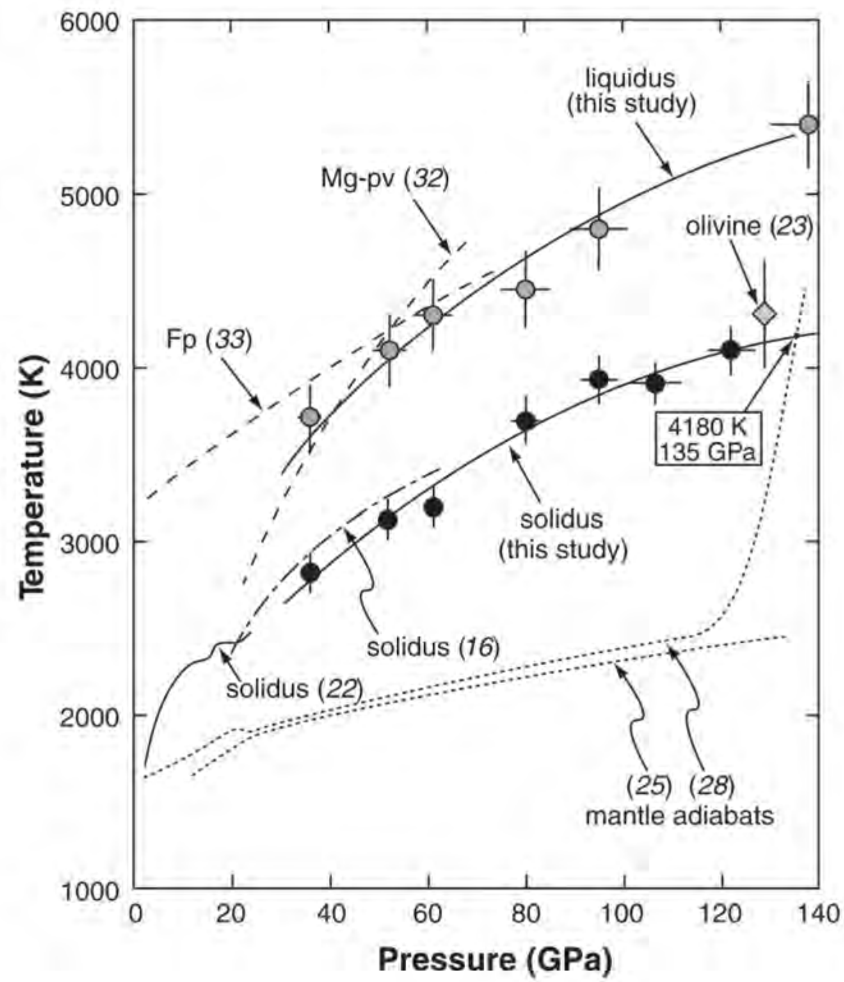
Ɛ-Fe : Im-3m



X-Ray Diffraction: Solidus/Liquidus Determination

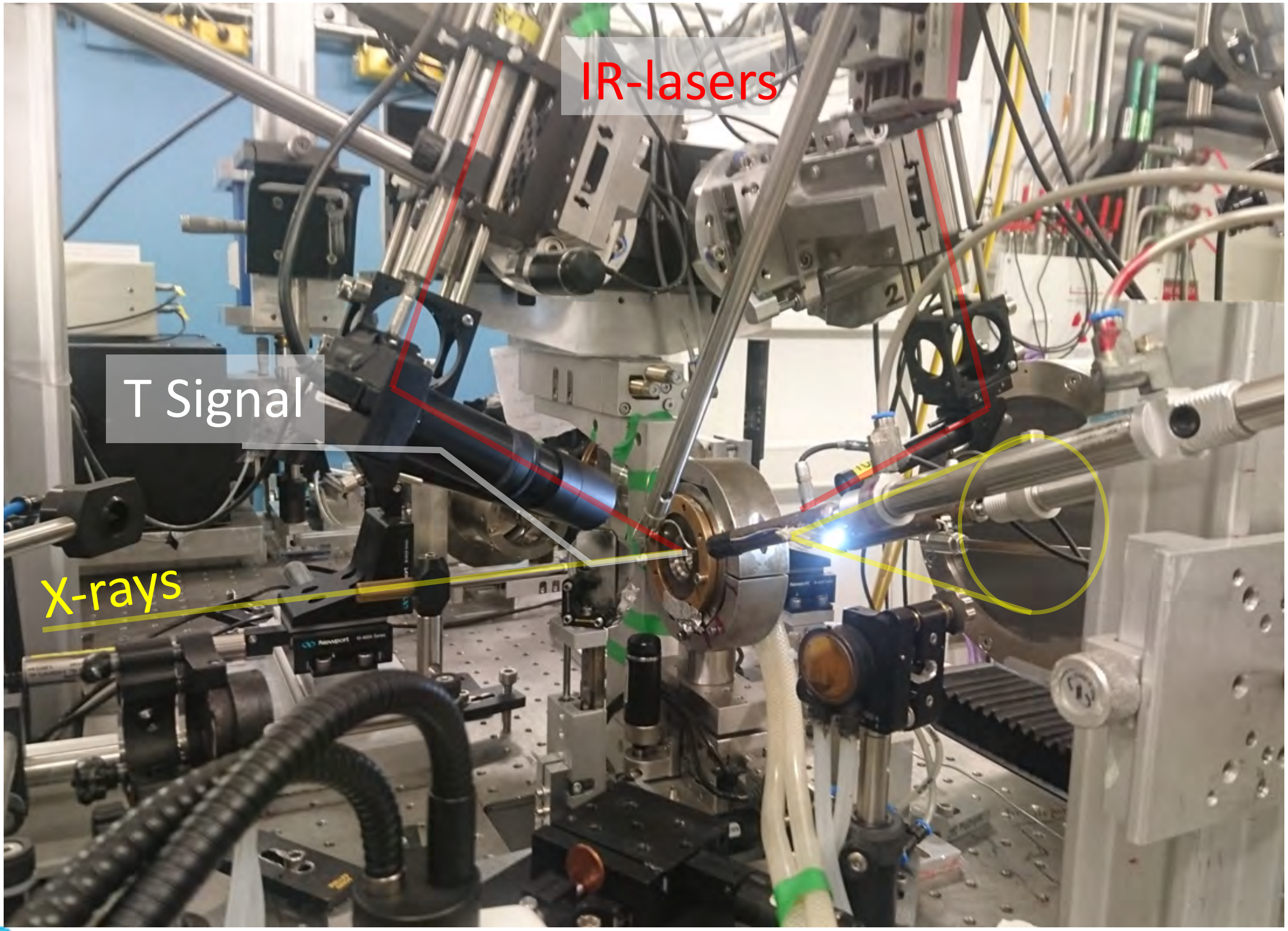
Peridotite



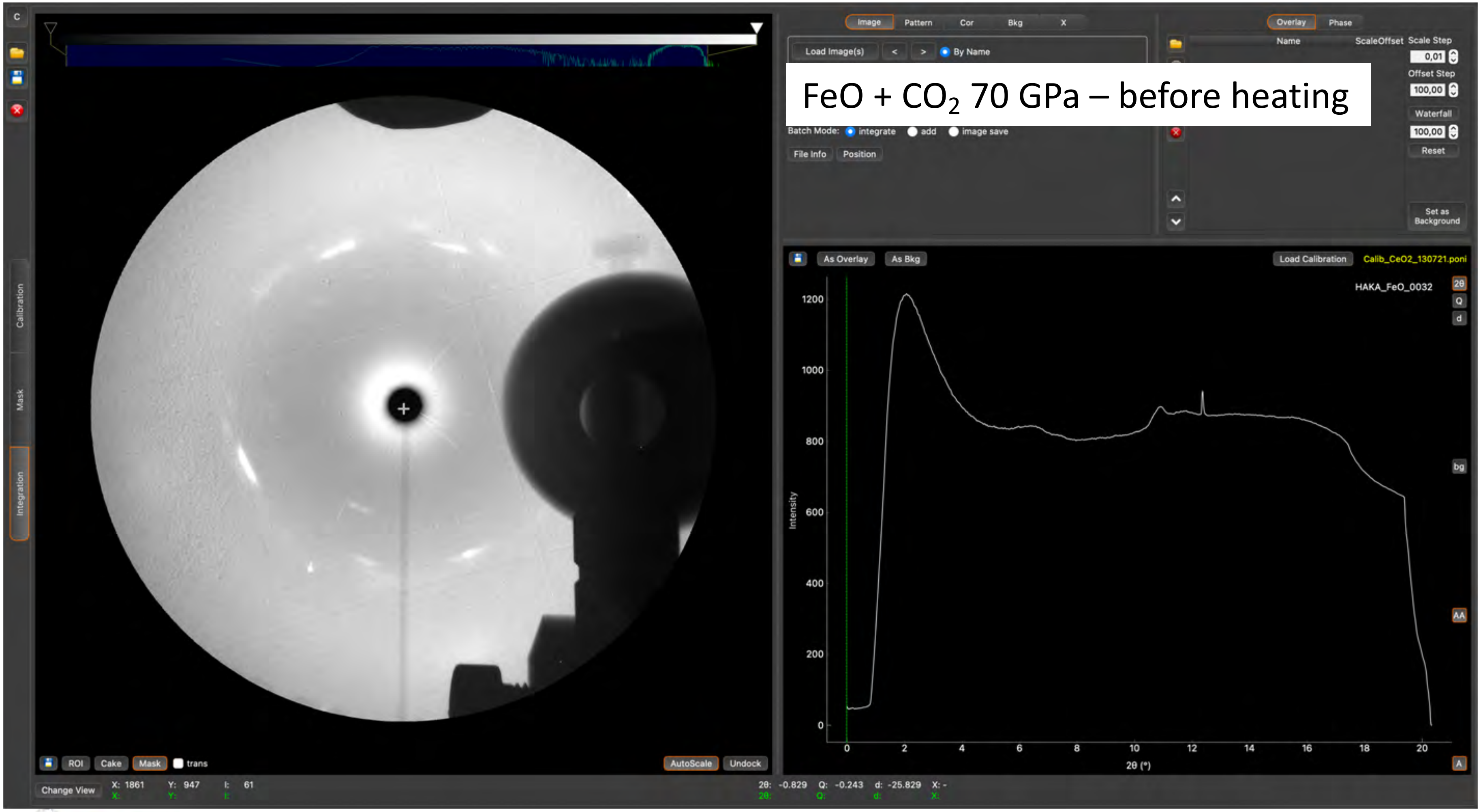


Fiquet et al., Science (2010)

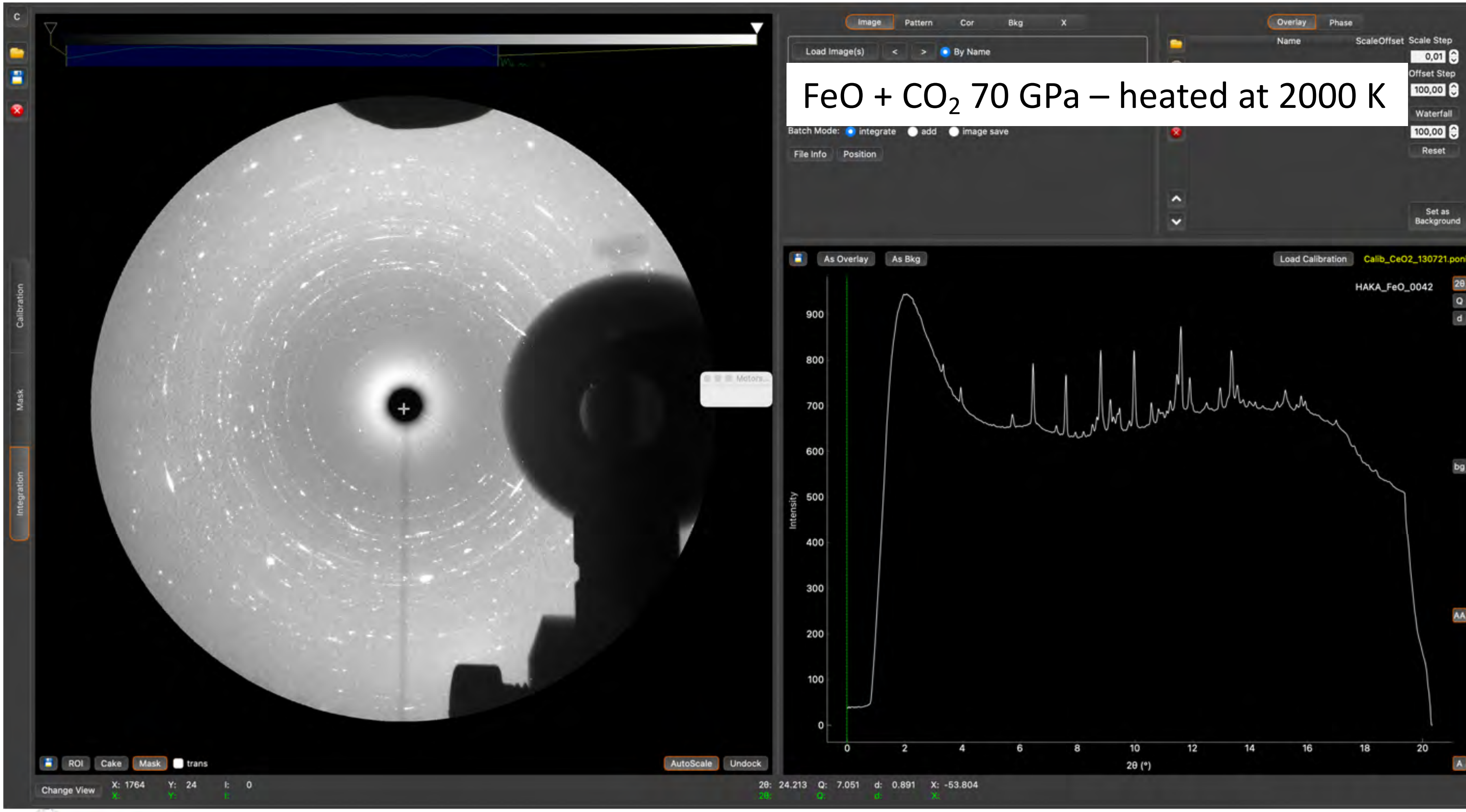
In Situ X-Ray Diffraction Experiments



In Situ X-Ray Diffraction Experiments

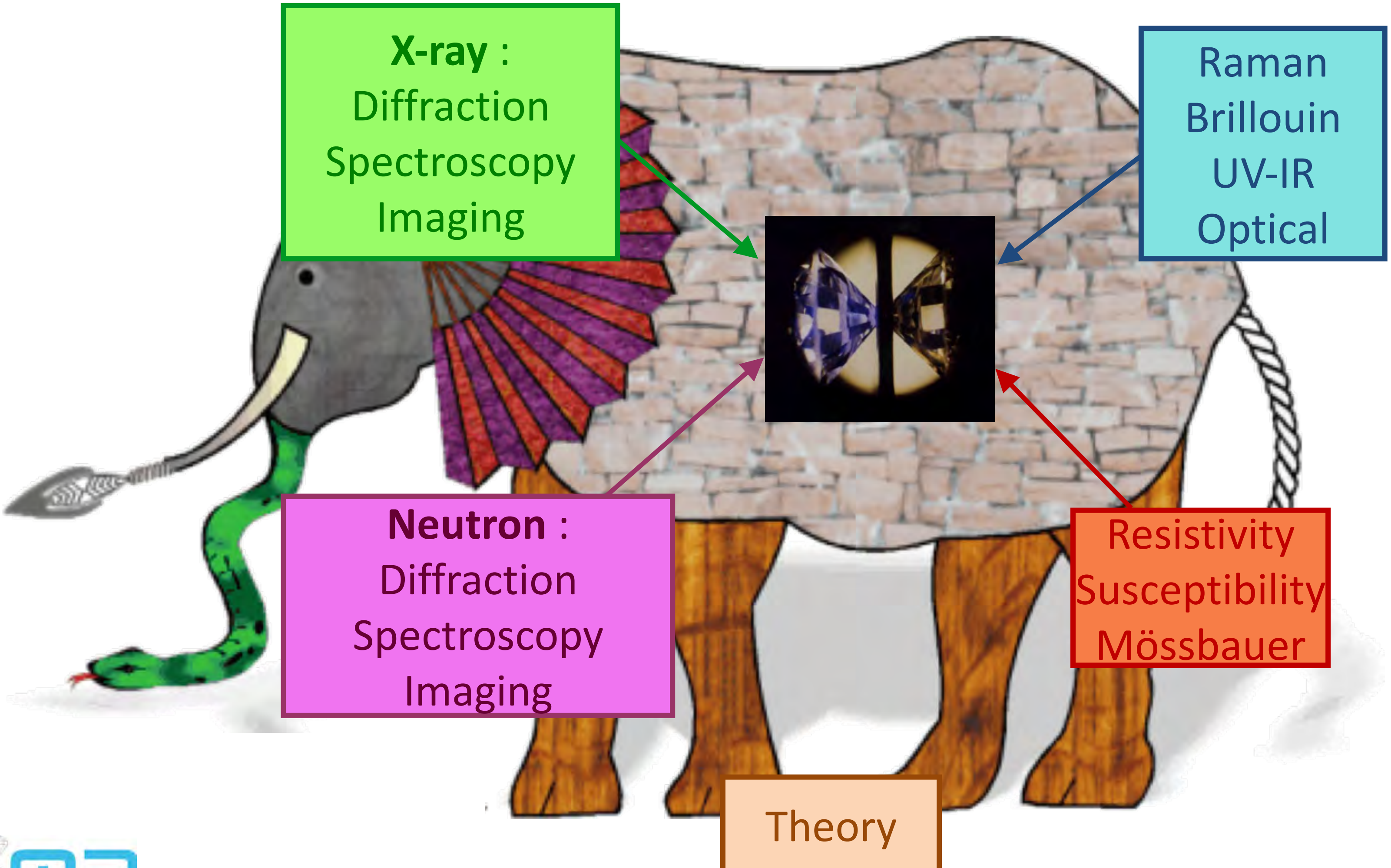


In Situ X-Ray Diffraction Experiments



FeO + CO_2 70 GPa – heated at 2000 K

Integration of Multiple in situ Probes



Analytical Techniques Examples

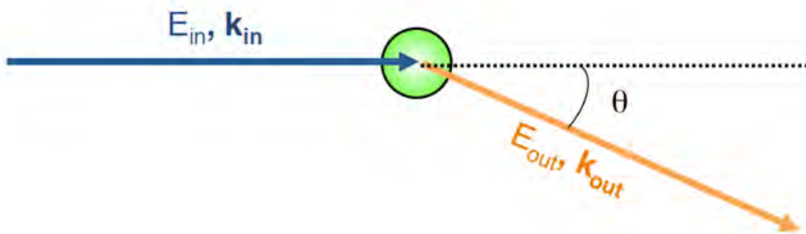
In Situ Analyses:

- The routine technique : what can we do with X-Ray Diffraction (XRD) ?
- **Crystallo-chemistry description techniques**
- How do we measure V_P V_S at HP-HT ?

Ex Situ Analyses:

- Transmission Electron Microscopy (TEM)

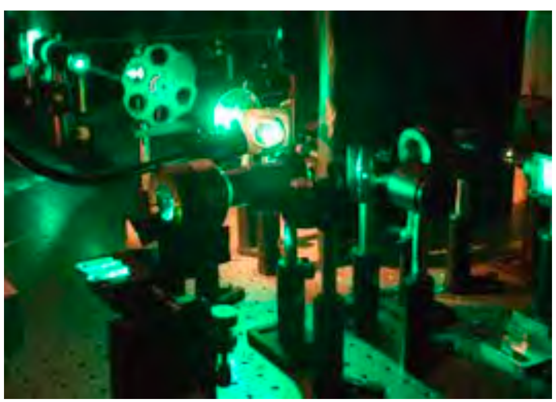
Inelastic Scattering of Light by **Optical** Phonon : **Raman** Spectroscopy

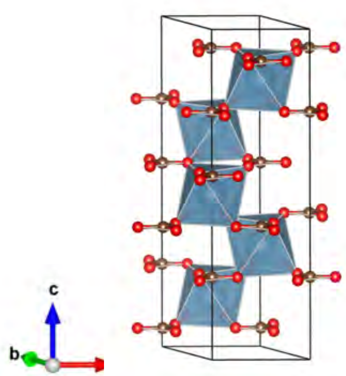


Lattice or molecular vibrations:
- Energy transfer $E = E_{out} - E_{in}$
- Spatial deviation $\theta \neq 0$

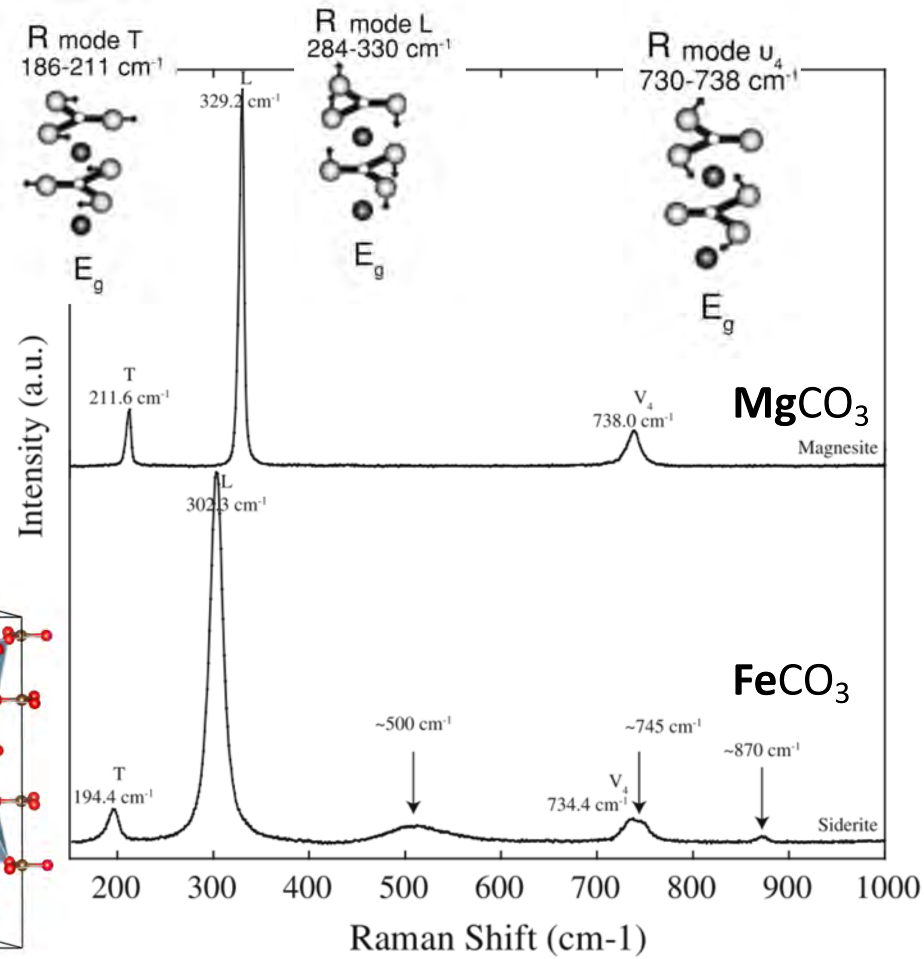
➢ Sensitive to the chemical composition
➢ molecular arrangement

Phase identification/transition



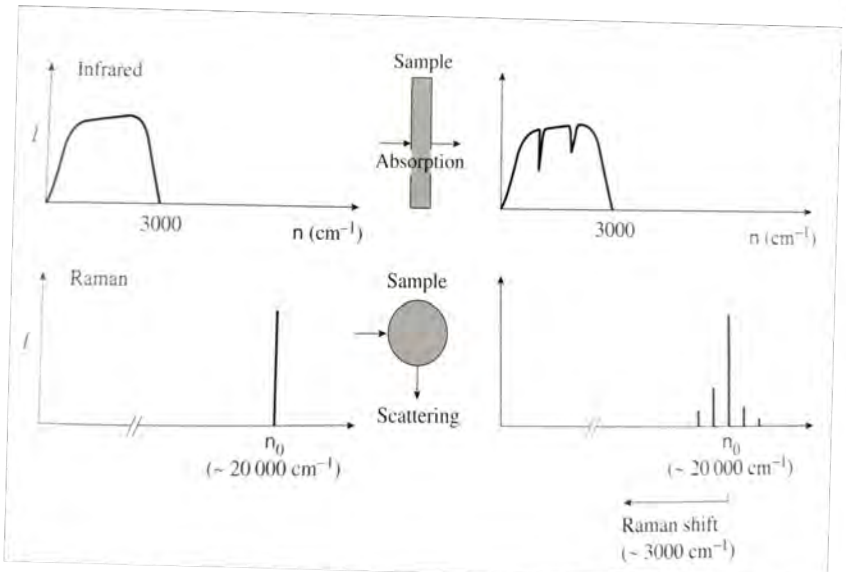


« Calcite » Structure

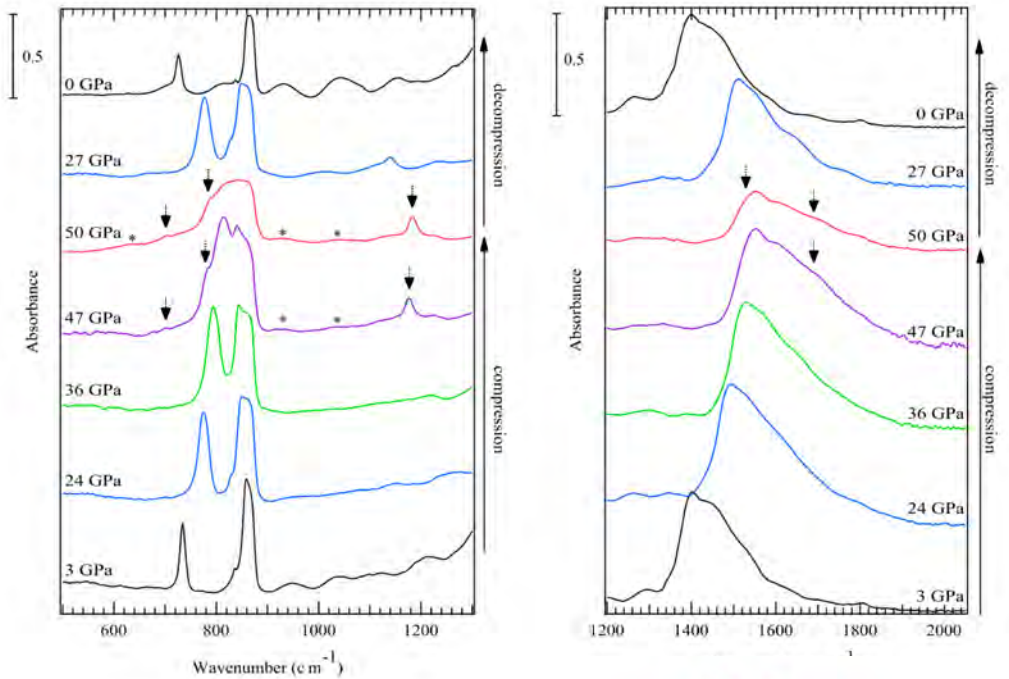


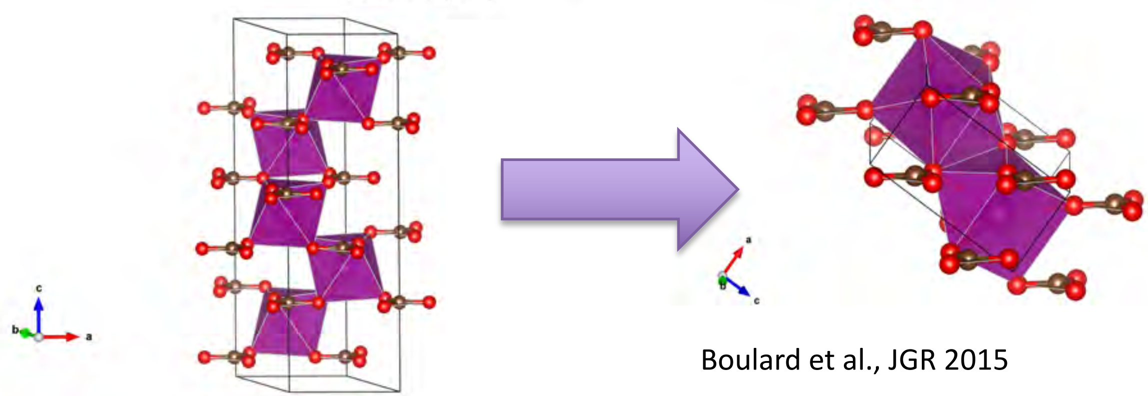
Boulard et al., PCM, 2013

Other Vibrational Spectroscopy: IR Spectroscopy



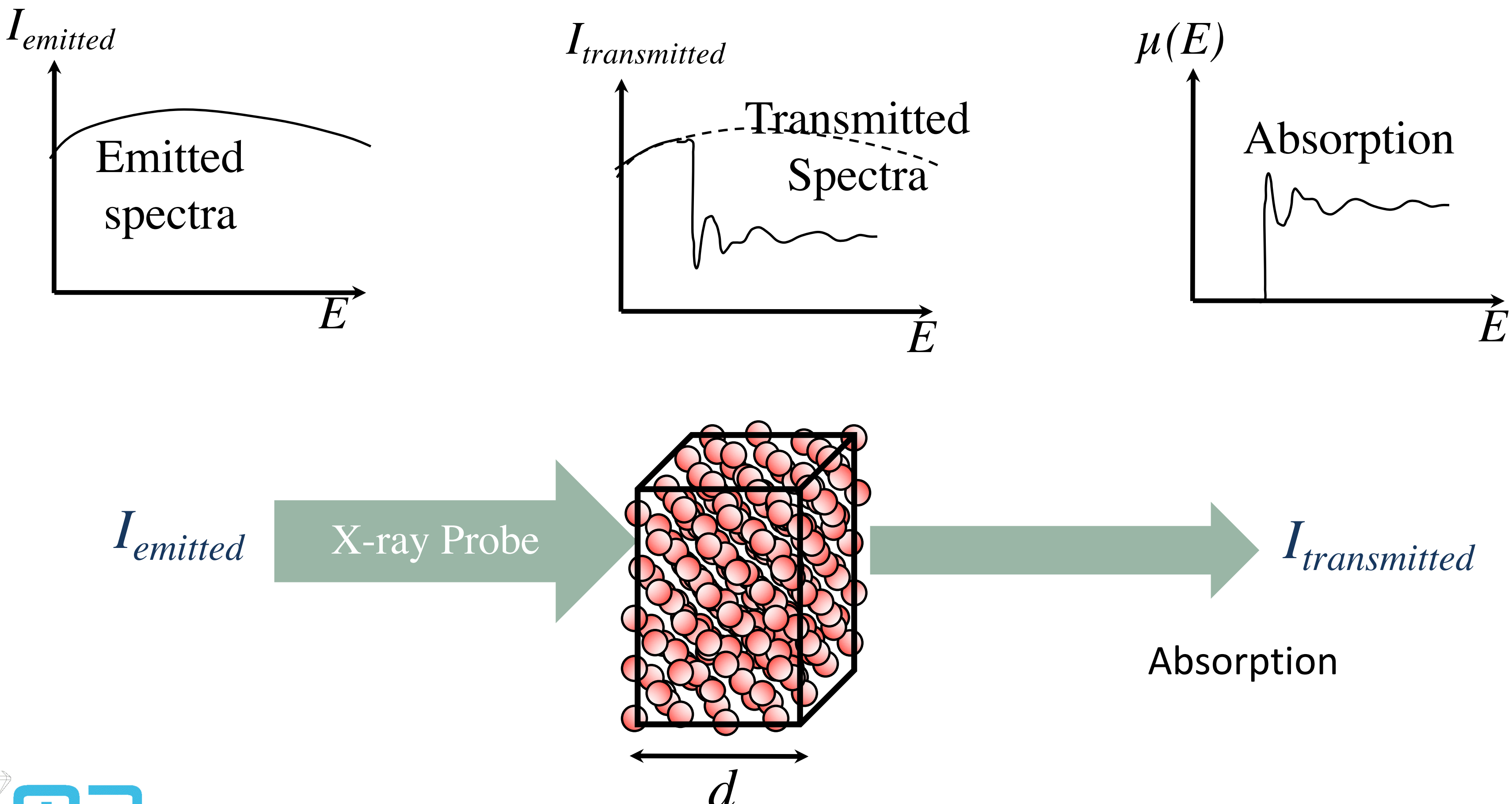
$MnCO_3$



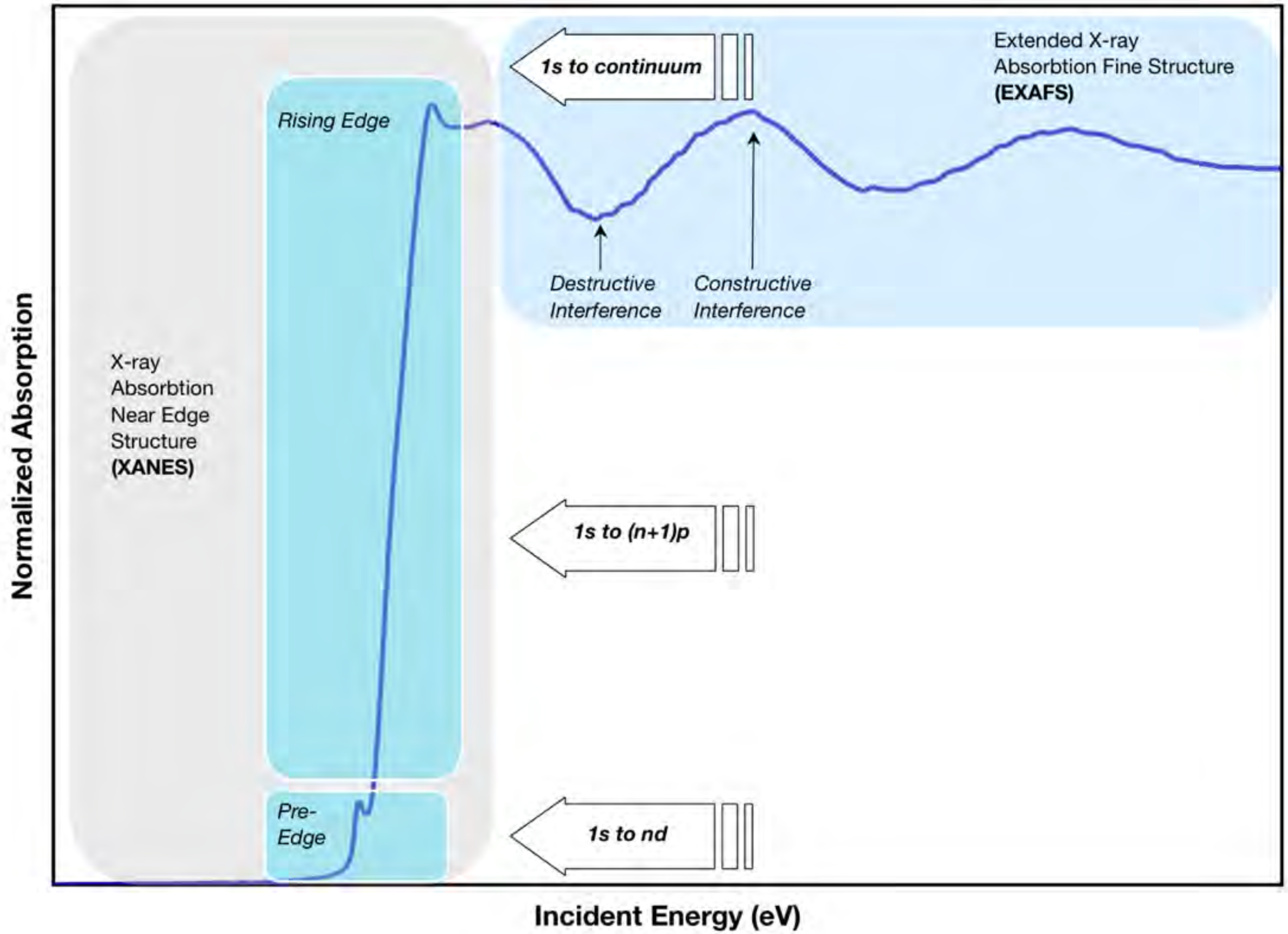


Boulard et al., JGR 2015

X-Ray Absorption

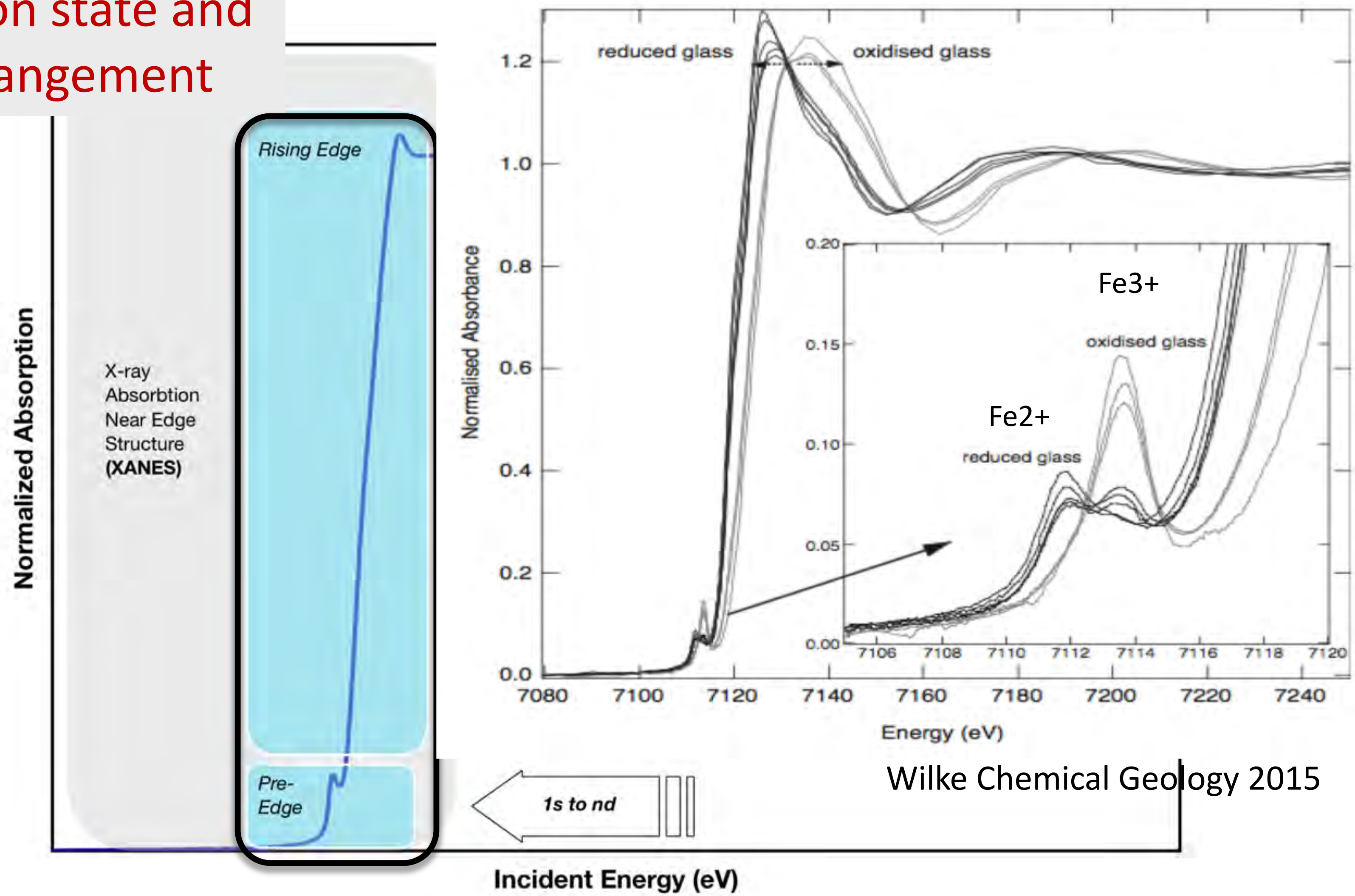


X-Ray Absorption



X-Ray Absorption

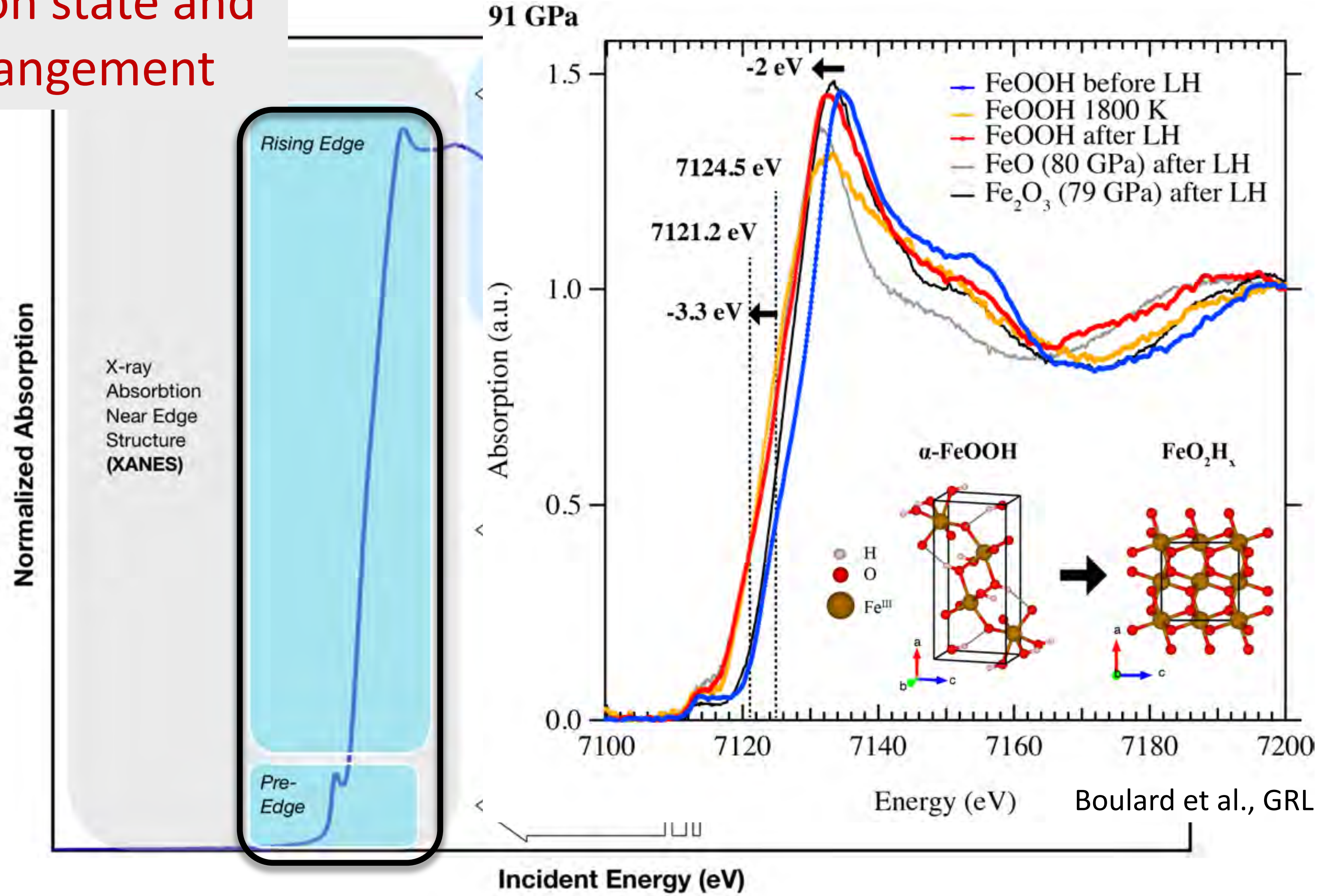
Oxydation state and local arrangement



Wilke Chemical Geology 2015

X-Ray Absorption

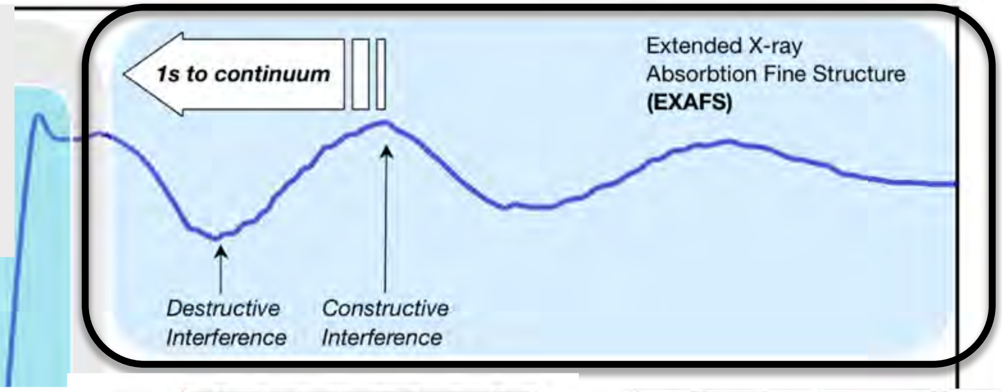
Oxydation state and local arrangement

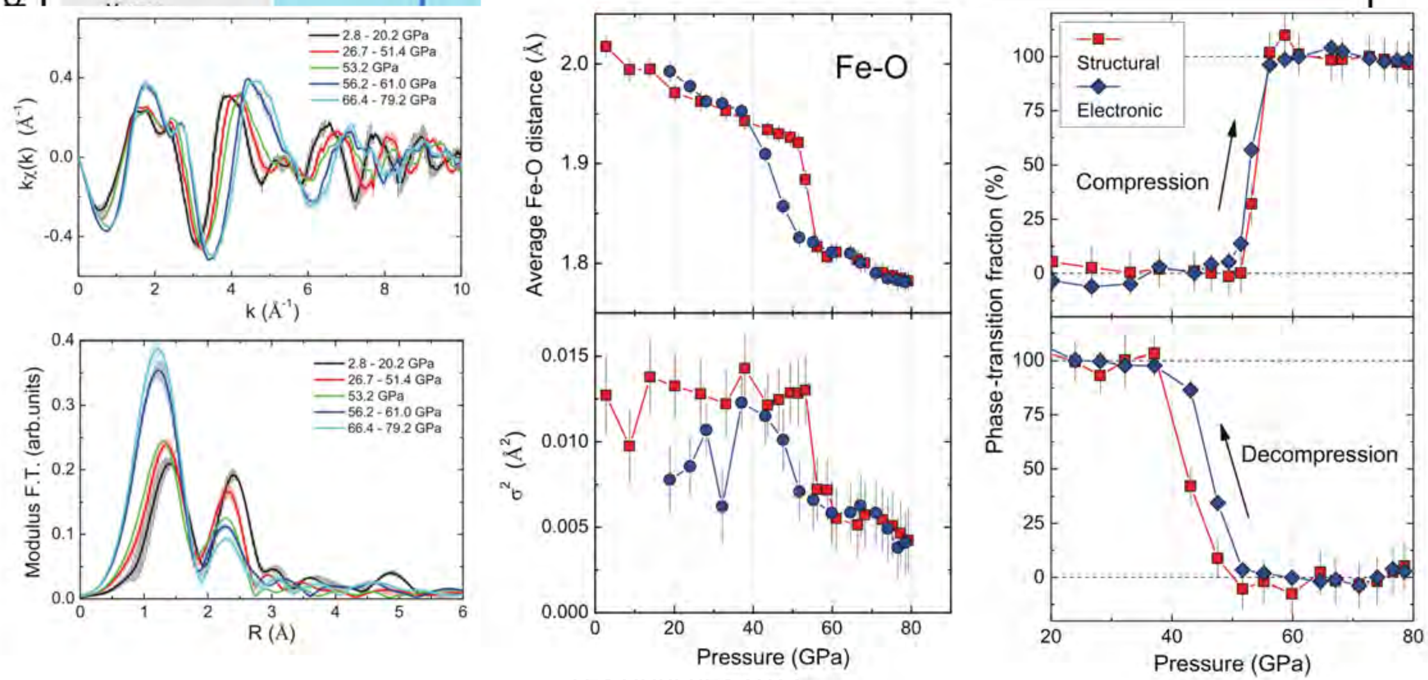


Boulard et al., GRL 2019

X-Ray Absorption

Coordination shell (number, distances, disorder)

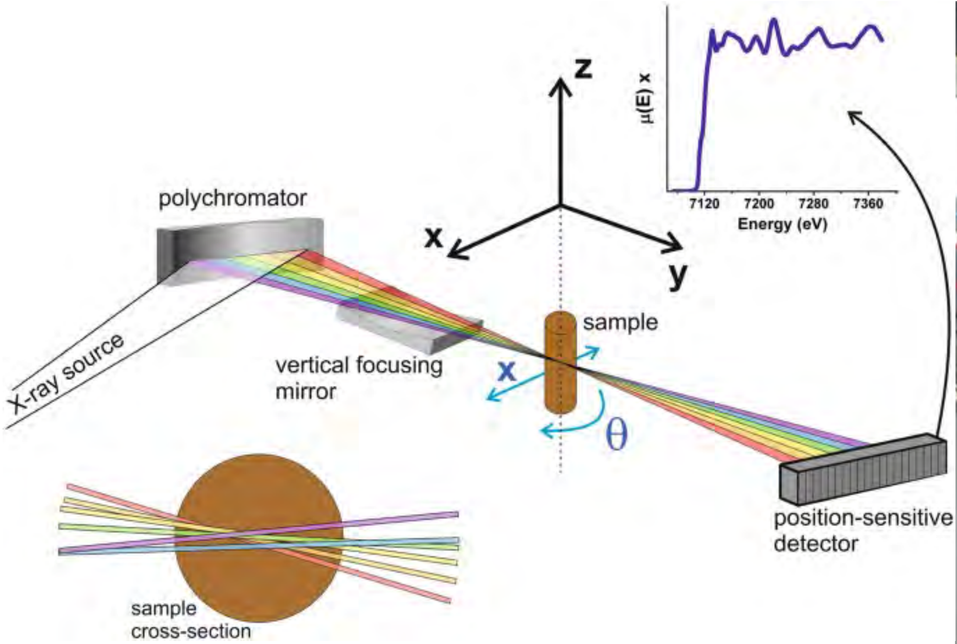


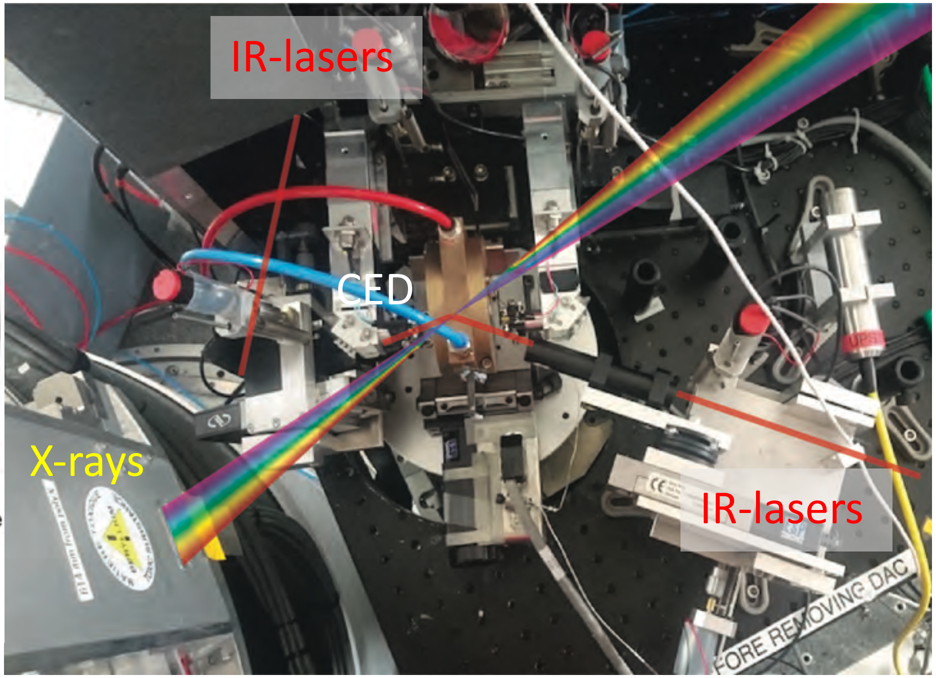


Fe_2O_3

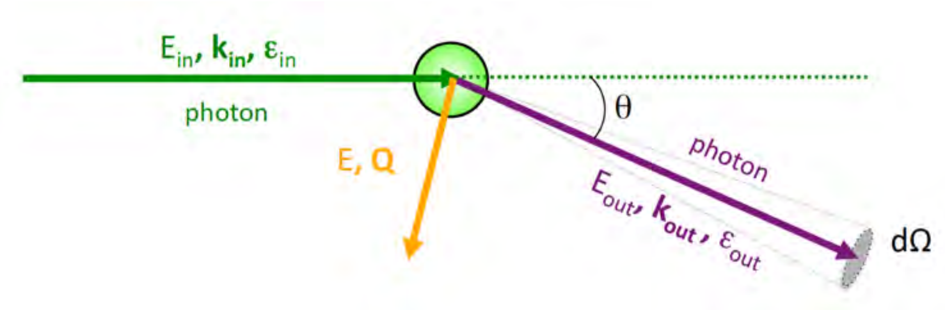
Sanson et al. PRB 2016

X-Ray Absorption





Accessing Light Elements : X-Ray Raman = Inelastic Scattering of X-Rays

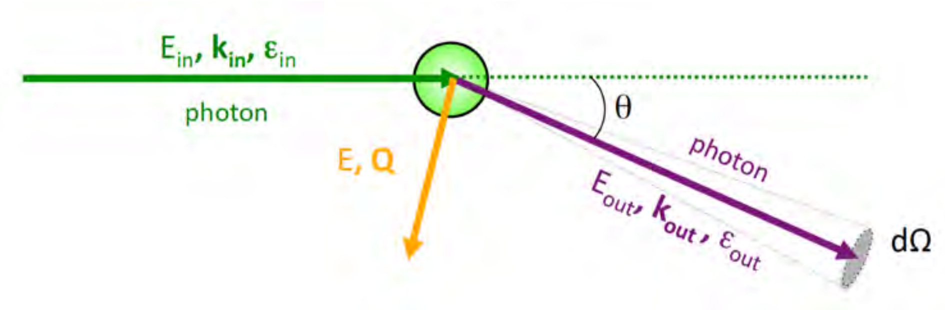


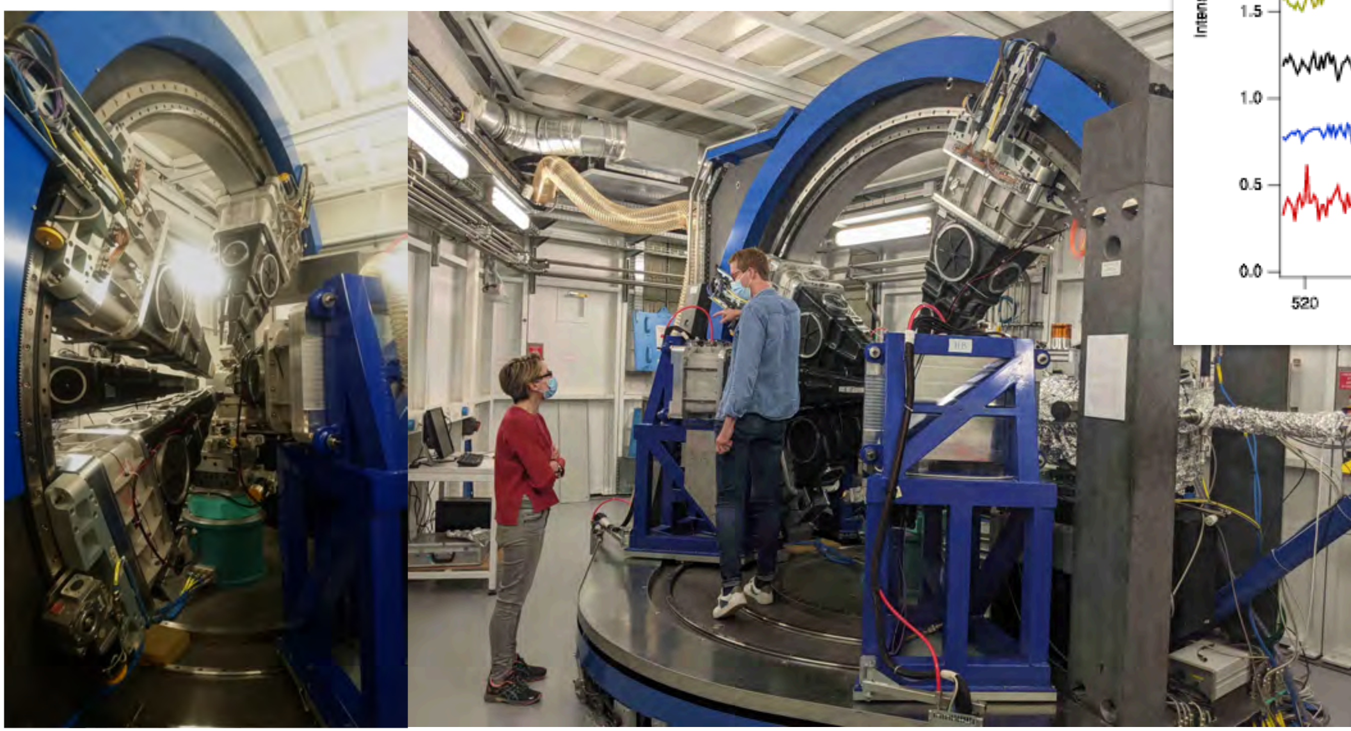
- Energy Transfer $E = E_{out} - E_{in}$
- Momentum Transfer $Q = (k_{out} - k_{in}) = 2k\sin(\theta/2)$

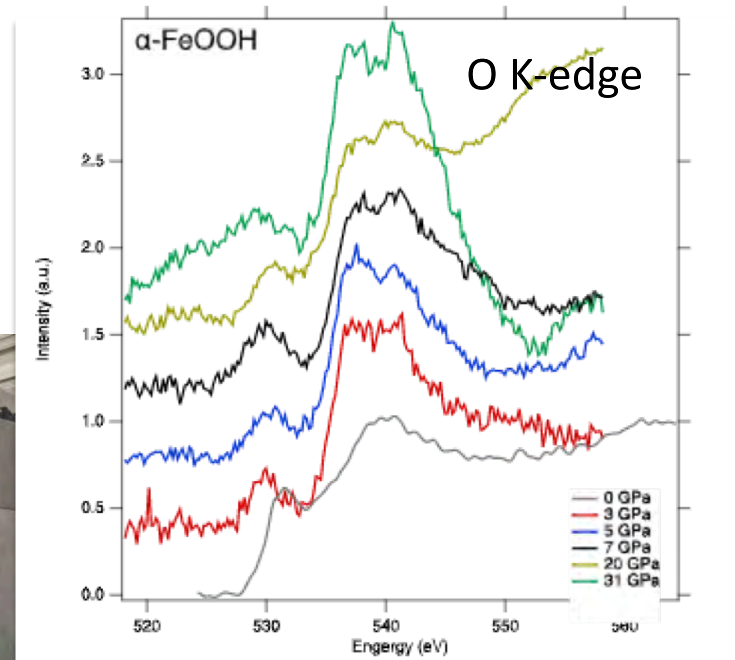
Measure:

Energy of the scattered photons (E) for different directions of the scattered photons Q

Accessing Light Elements : X-Ray Raman = Inelastic Scattering of XRays







Boulard et al., in prep.

Analytical Techniques Examples

In Situ Analyses:

- The routine technique : what can we do with X-Ray Diffraction (XRD) ?
- Crystallo-chemistry description techniques
- **How do we measure V_P V_S at HP-HT ?**

Ex Situ Analyses:

- Transmission Electron Microscopy (TEM)

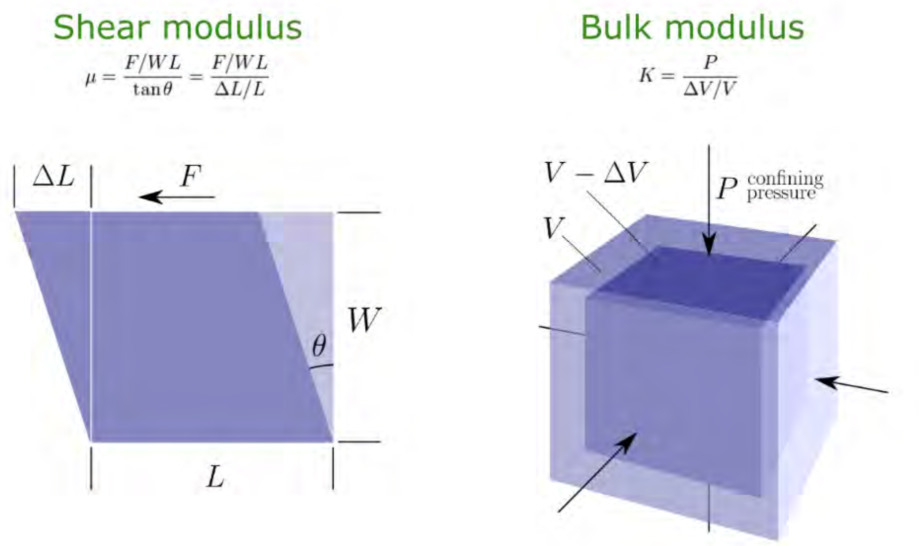
V_P V_S Determination at HP-HT

Compressional wave velocity :

$$V_P = \sqrt{(K + \frac{4}{3}\boldsymbol{G})/\rho}$$

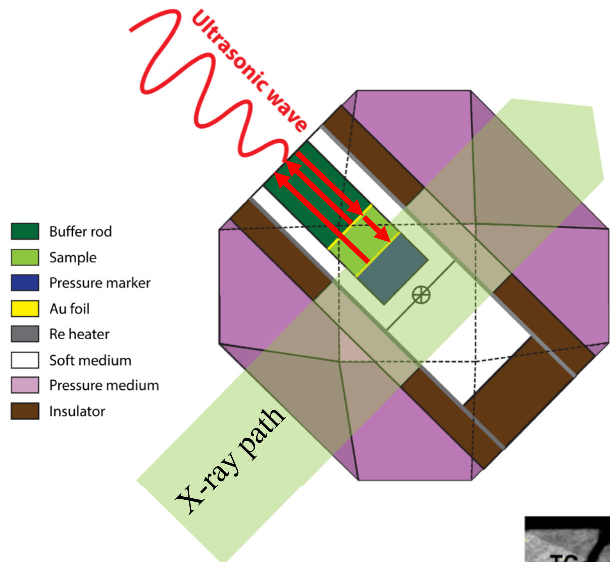
Shear wave velocity :

$$V_S = \sqrt{\boldsymbol{G}/\rho}$$



Shear Modulus G:
no volume change, but describes a material's change in shape as a response to shear stresses

UltraSonic Accoustic : MHz

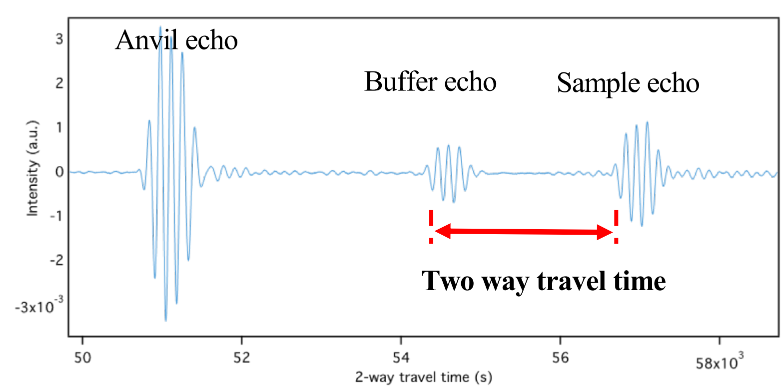


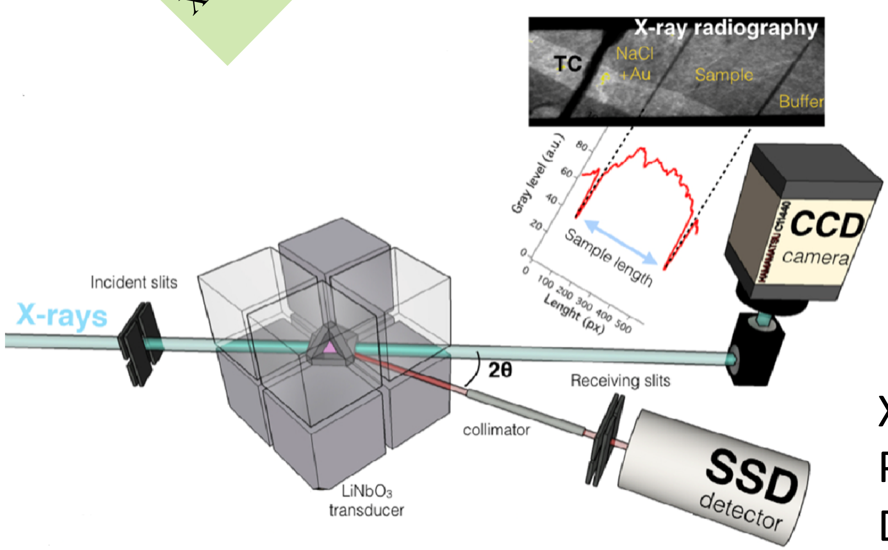
Sample Thickness : 1 mm

Microcrsytal > 500 µm

- ➢ Multi-Anvils Experiments
- ➢ Limited in P - T

Ultrasonic signal (P wave 60 MHz)



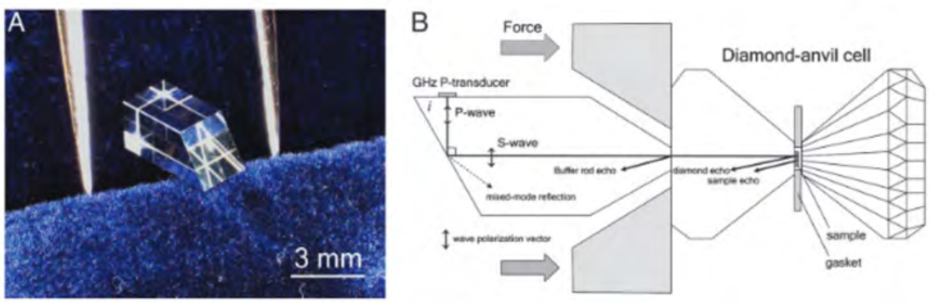


XRD = Pressure and Density

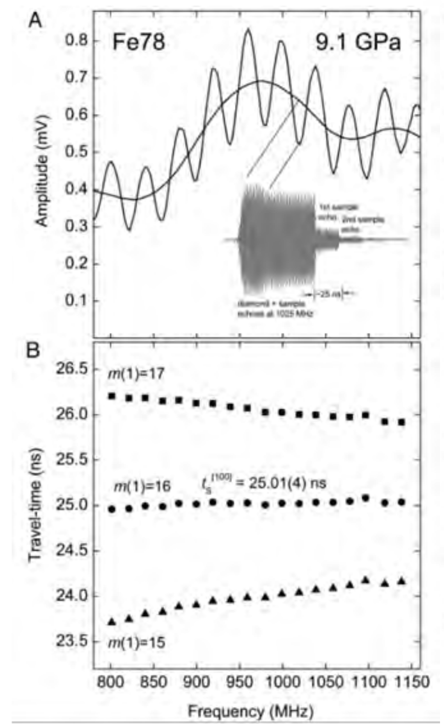
$$V_P = \frac{2L}{t_P}$$

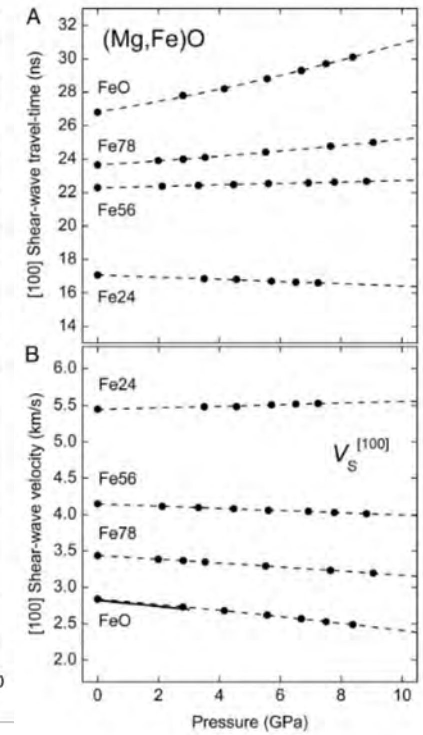
UltraSonic Accoustic : GHz

In Diamond Anvil cell :



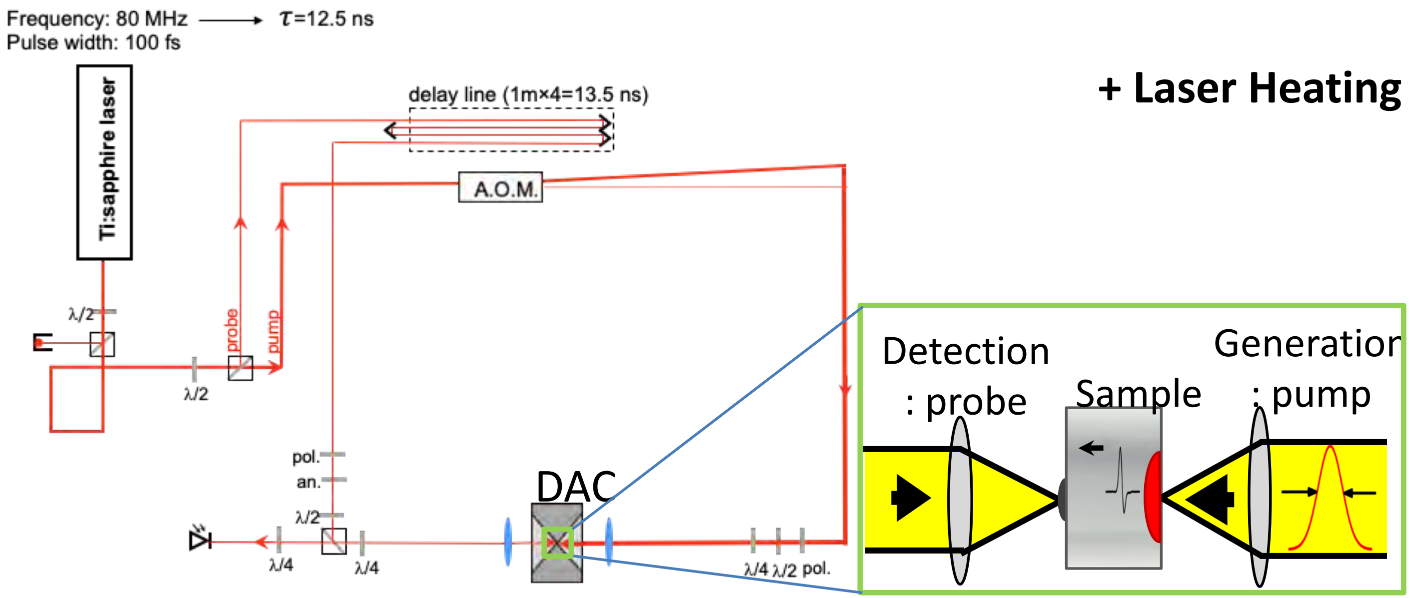
Jacobsen et al., PNAS 2004





- seismic heterogeneity in Earth’s lower mantle may result from compositional variations rather than phase changes in (Mg,Fe)O

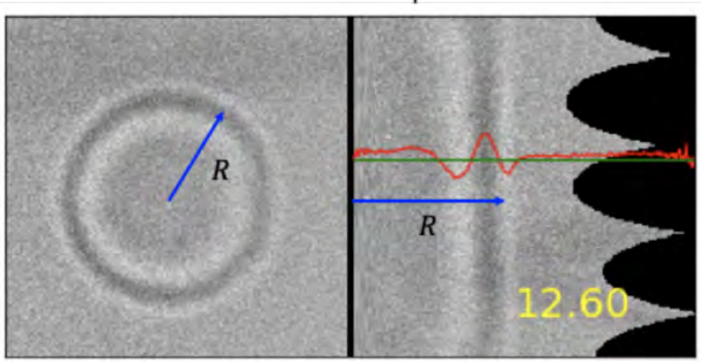
Picosecond Accoustic

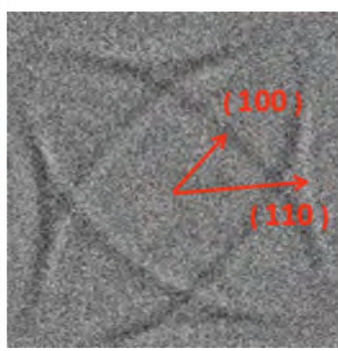


+ Laser Heating

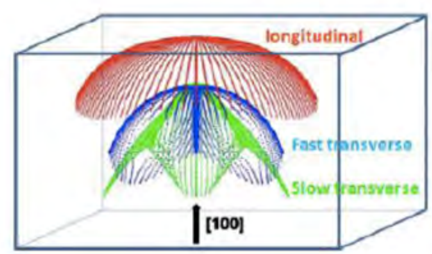
Raw image

Transformation to polar coordinates



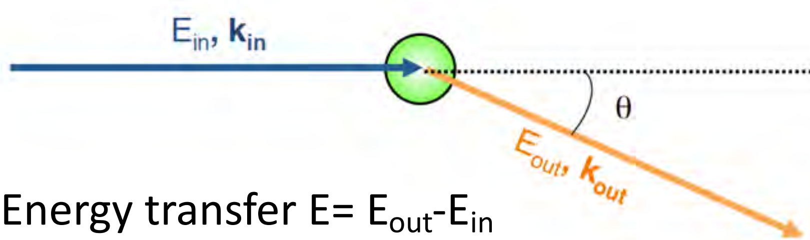


Values refined from inversion:
Density = 3.67 g/cm^3
Elastic constants:
$C11$ = 305.5 GPa
$C12$ = 96.2 GPa
$C44$ = 158.2 GPa
Sample thickness = 110.33 µm

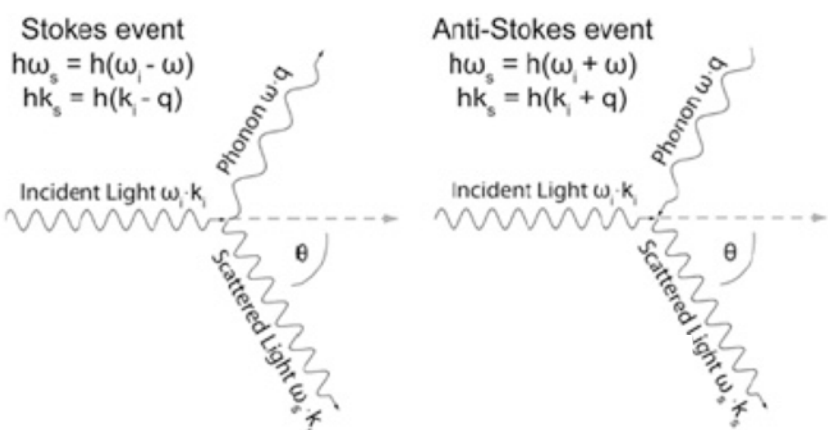


Brillouin Spectroscopy

Inelastic light scattering by accoustic phonons

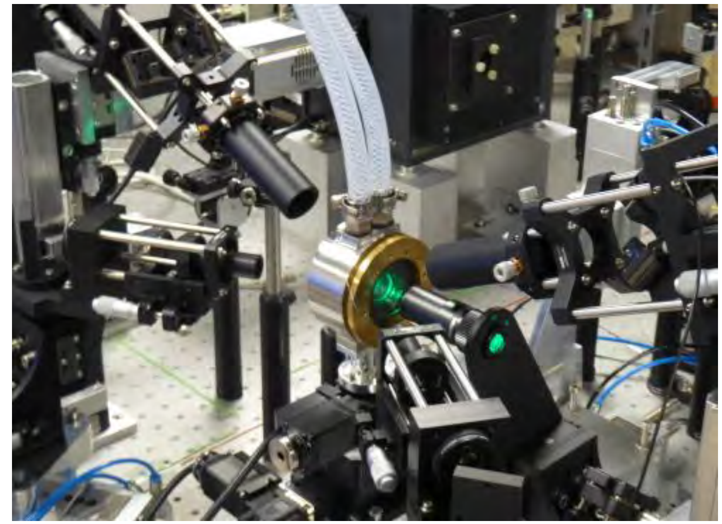


Energy transfer E= E_{out}-E_{in}
k(wave vector)
Spatial deviation $\theta \neq 0$



Photon loses energy to create a phonon

Photon gain energy by absorbing a phonon



Refractive index sample
Need Transparent samples

Phase velocity

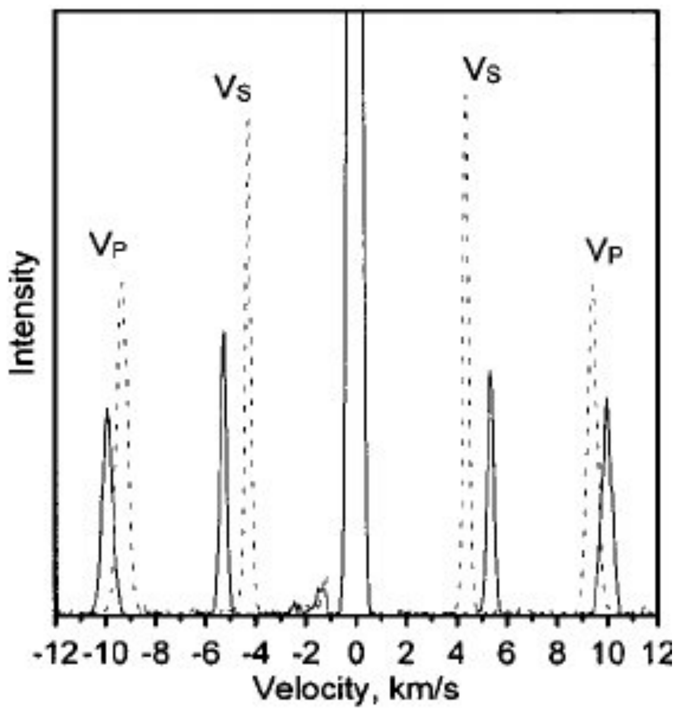
$$\Delta\omega_B = \pm \frac{4n\pi}{\lambda_0} v \sin\left(\frac{\theta}{2}\right)$$

Frequency shift

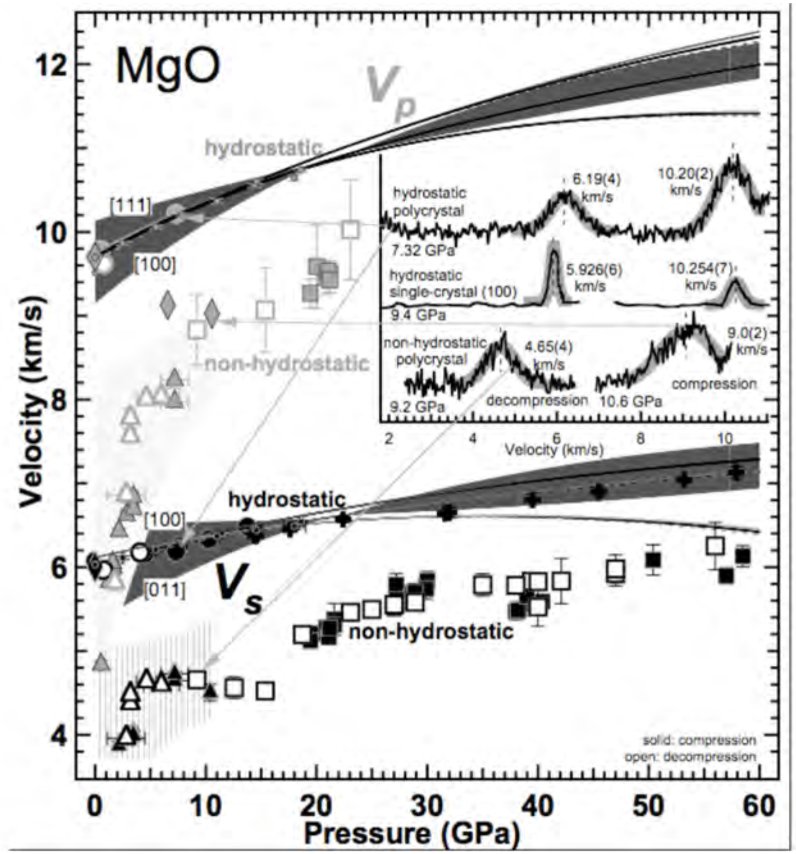
Wavelength incident light

Brillouin Spectroscopy

MgO



Sinogeikin et al., Rev. Sci. Ins., 2000



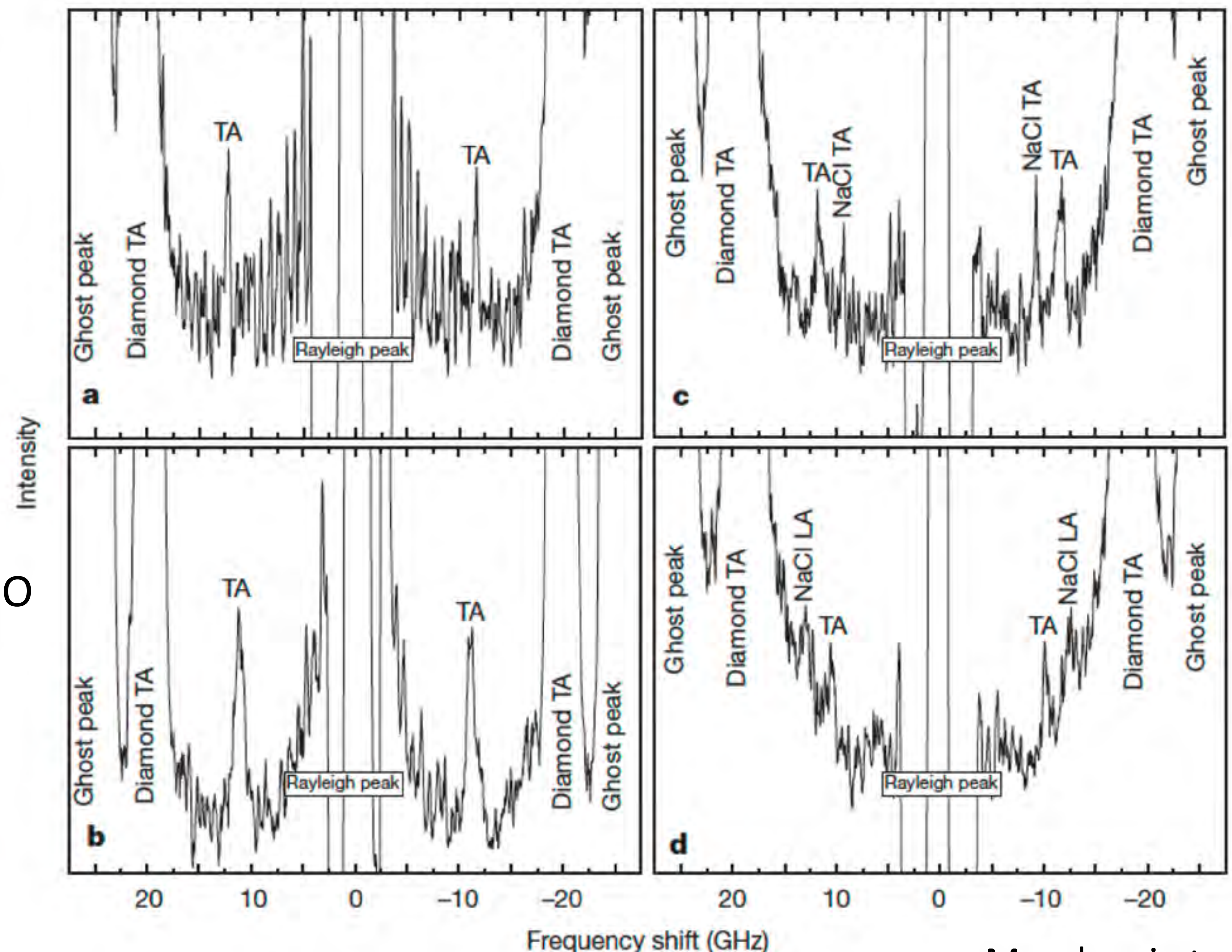
Gleason, PhD thesis 2010

Brillouin Spectroscopy

Through Laser Heated Diamond Anvil cell

MgSiO$_3$
P=95 GPa
T=300 K

MgSiO$_3$
P=91 GPa
T=2700 K

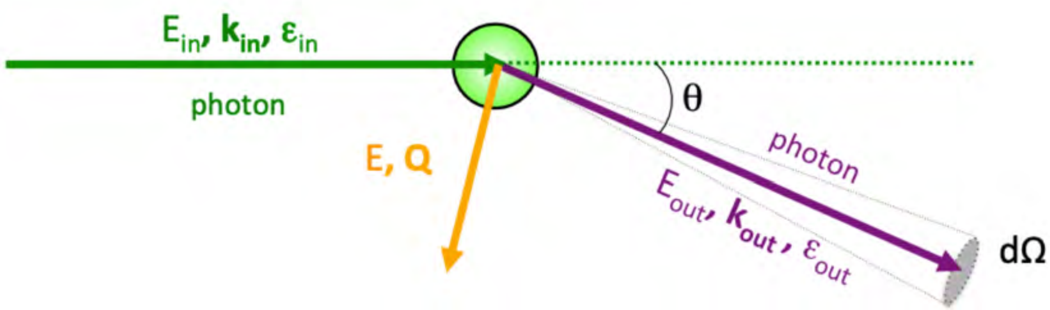


(Mg$_{0.92}$Fe$_{0.08}$)O
P=86 GPa
T=300 K

MgO
P=48 GPa
T=2700 K

Murakami et al., Nature 2012

Inelastic X-Ray Scattering (IXS)

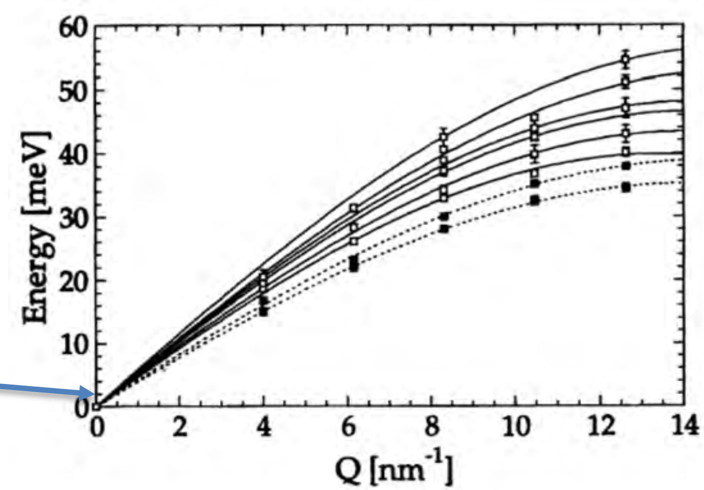


- Energy Transfer $E = E_{out} - E_{in}$
- Momentum Transfer $Q = (k_{out} - k_{in}) = 2k\sin(\theta/2)$

Measure:
Directional of the scattered photons => Q
Energy of the scattered photons => E

No coupling

Brillouin



Fiquet et al., Science 2001

Analytical Techniques Examples

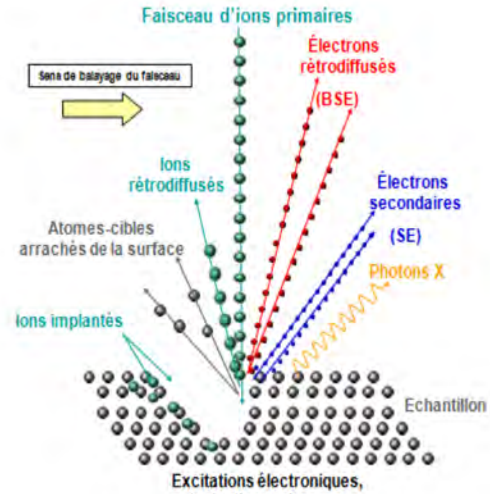
In Situ Analyses:

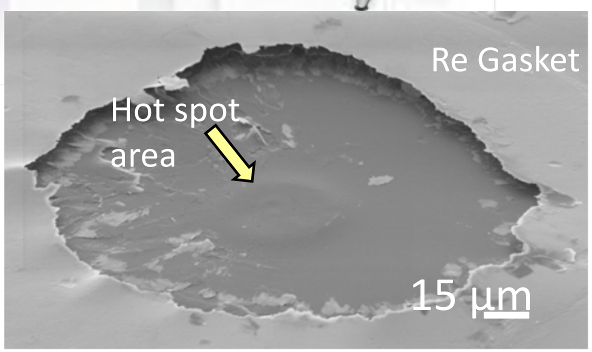
- The routine technique : what can we do with X-Ray Diffraction (XRD) ?
- How do we measure V_P V_S at HP-HT ?
- What elses ?

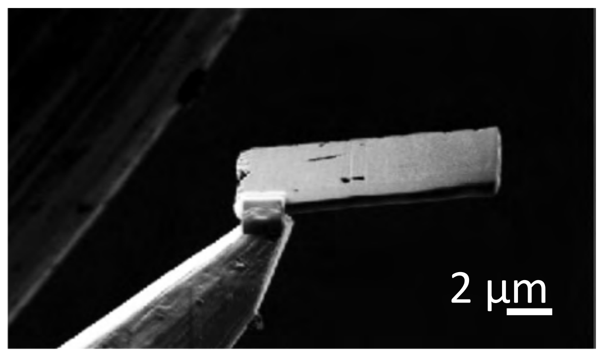
Ex Situ Analyses:

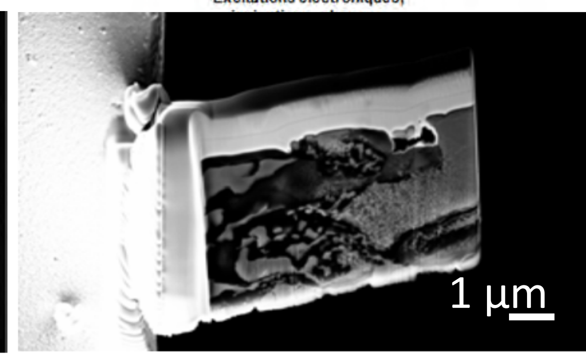
- **Transmission Electron Microscopy (TEM)**

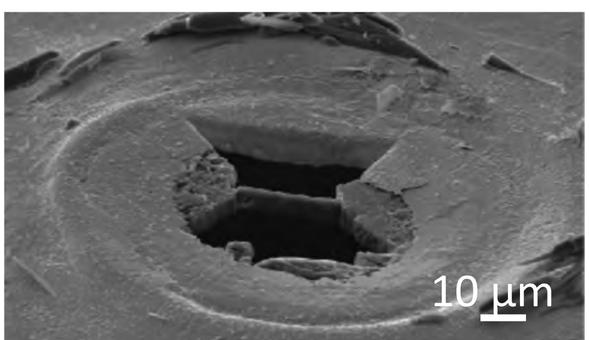
Ex situ Analyses : Sample Preparation by FIB

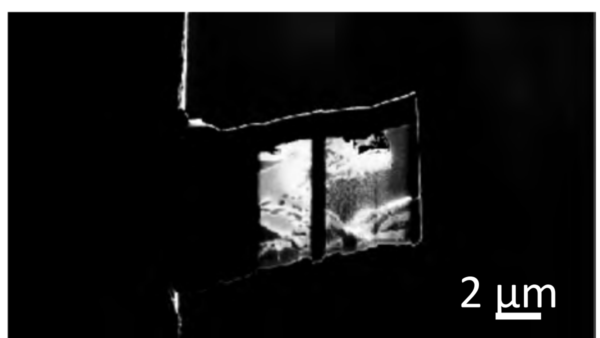


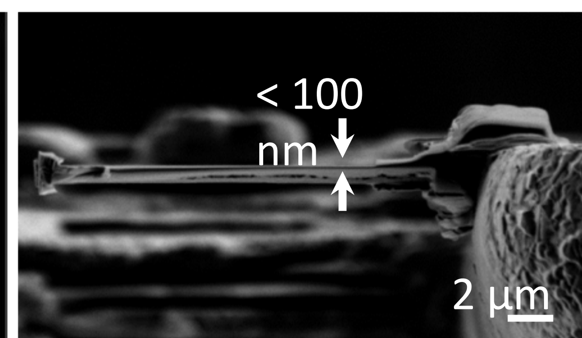




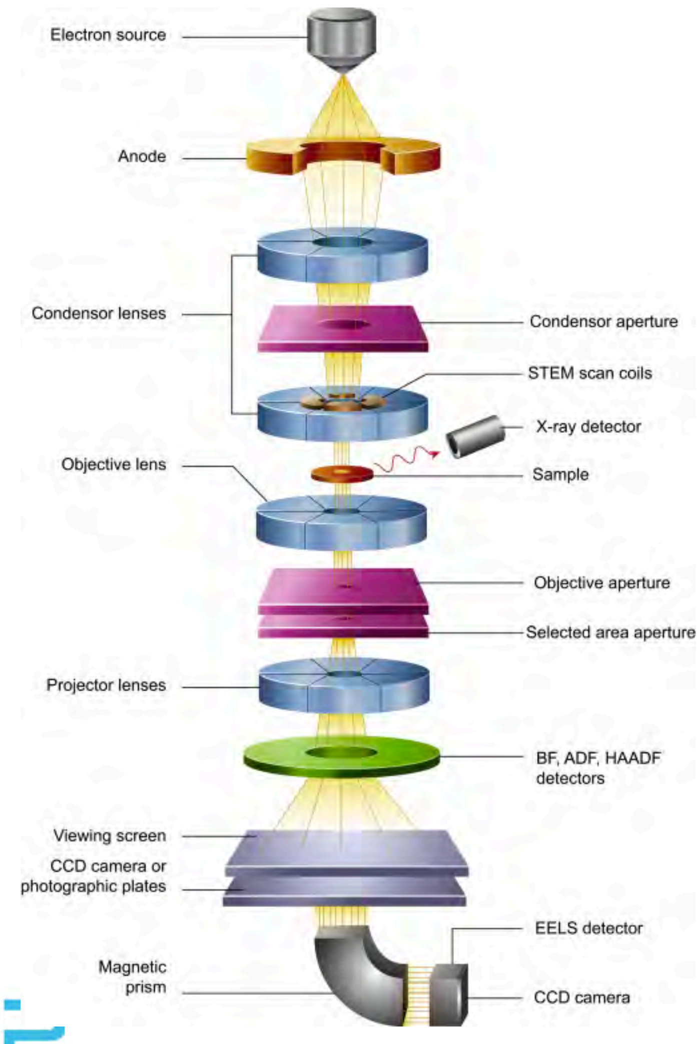








Transmission Electron Microscopy



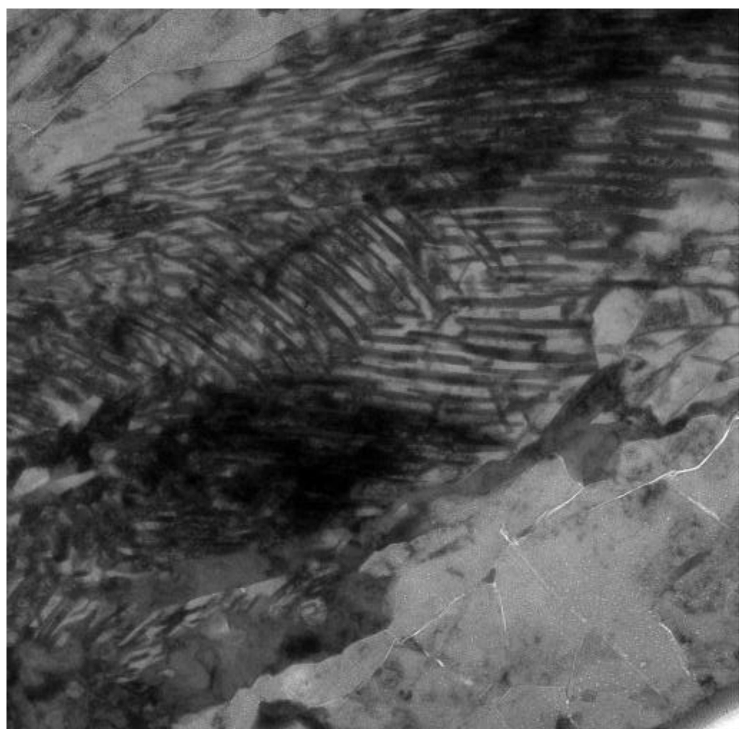
Transmission Electron Microscopy

Incident e- beam

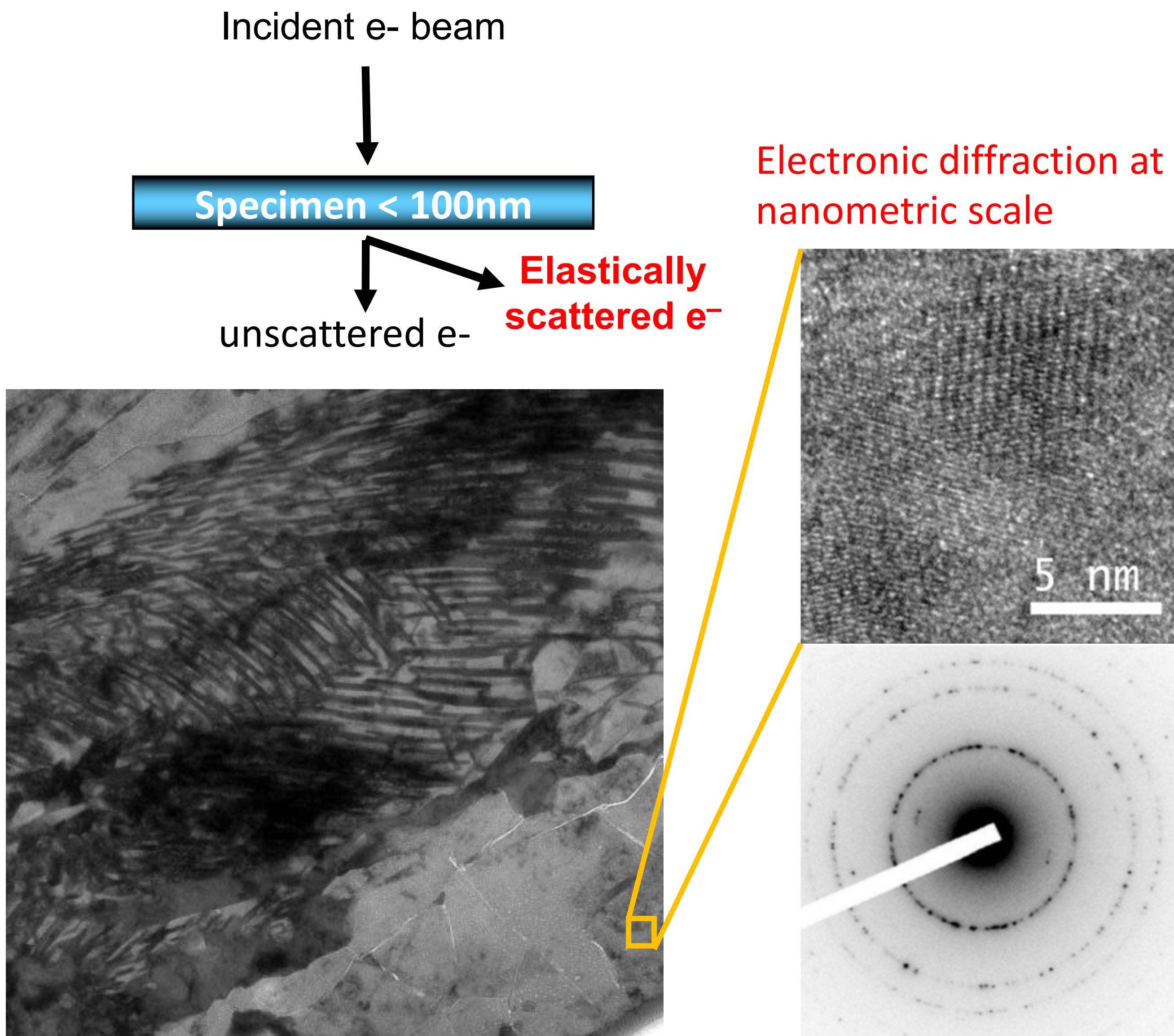
Specimen < 100nm

Bright Field Imagery

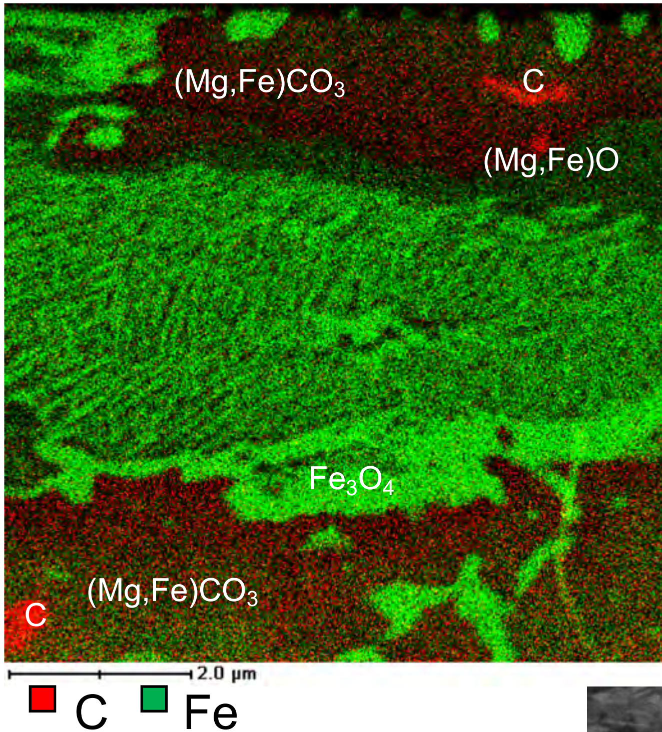
unscattered e-



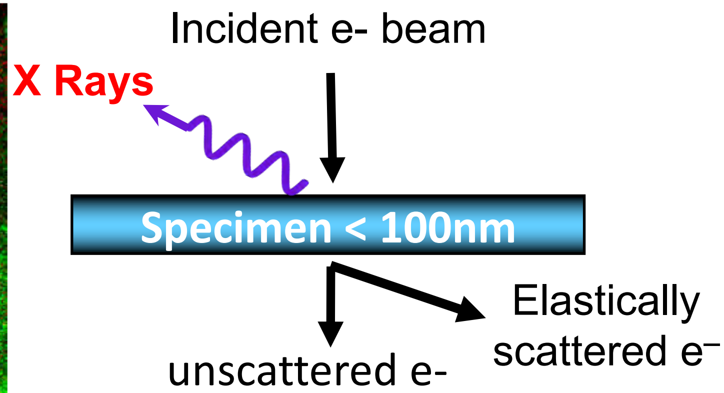
Transmission Electron Microscopy

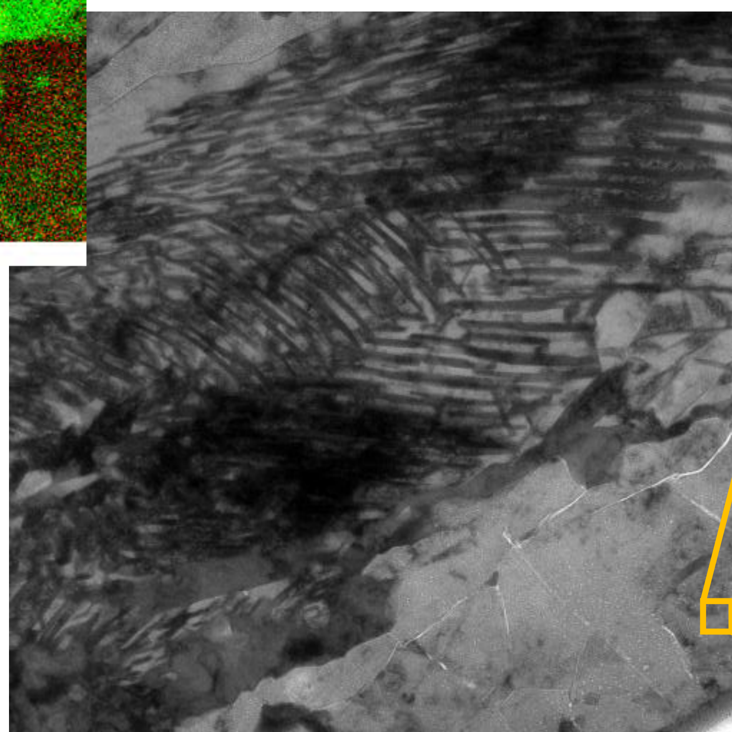


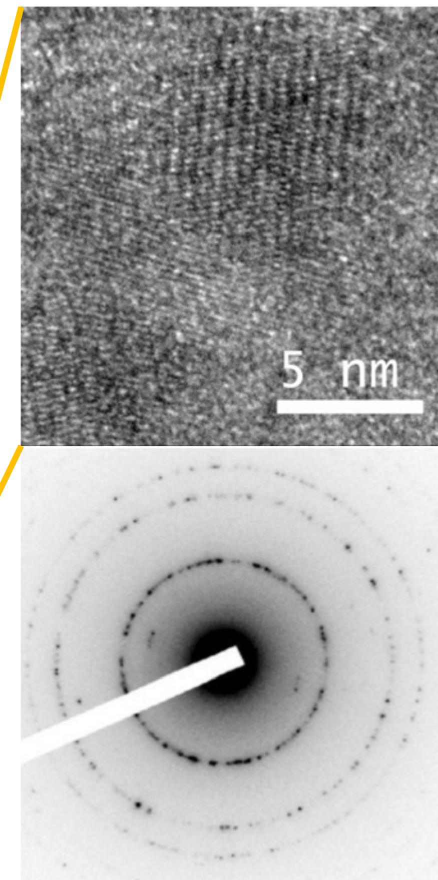
Transmission Electron Microscopy



XEDS : Major elements chemical analyses







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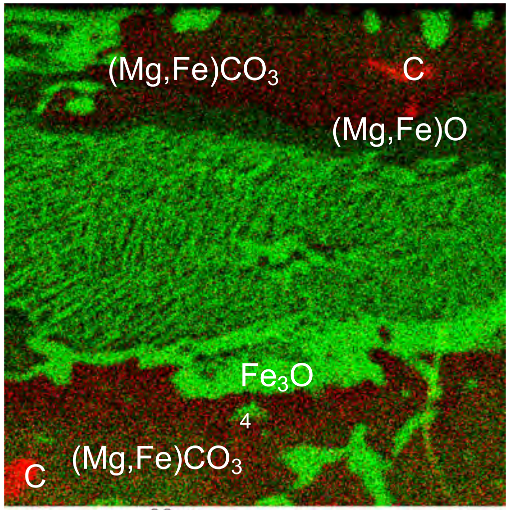
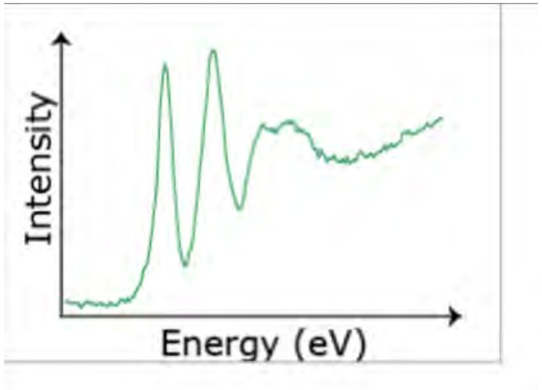
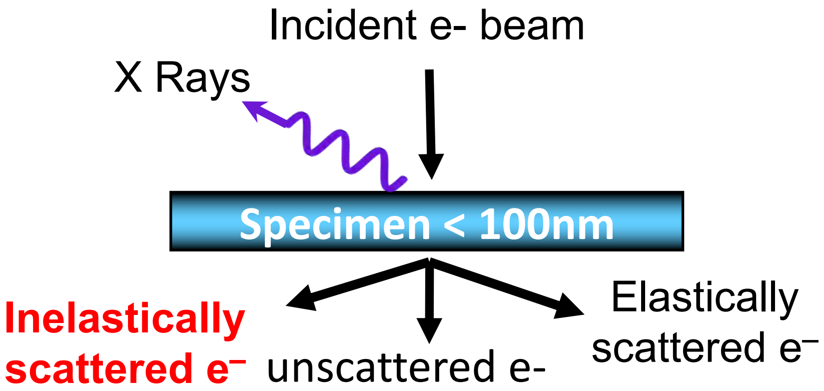
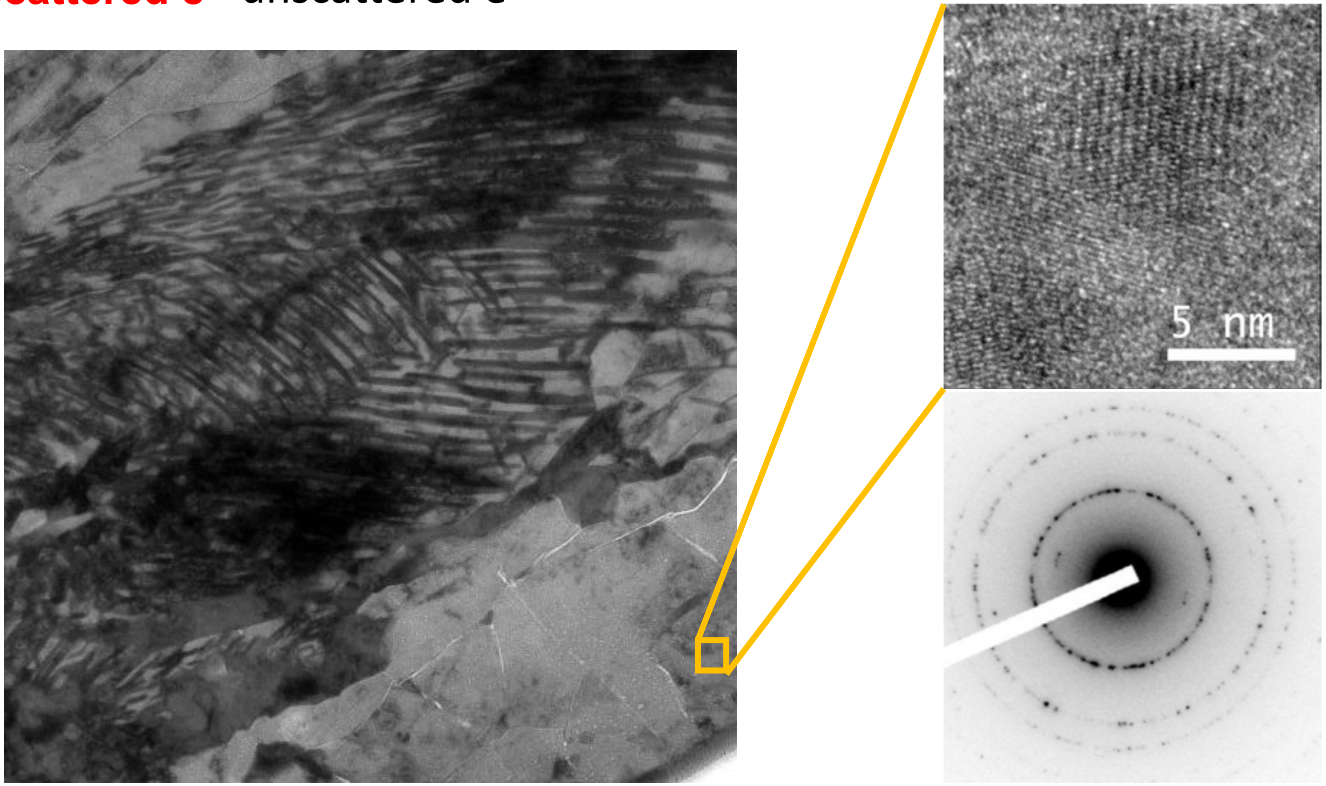
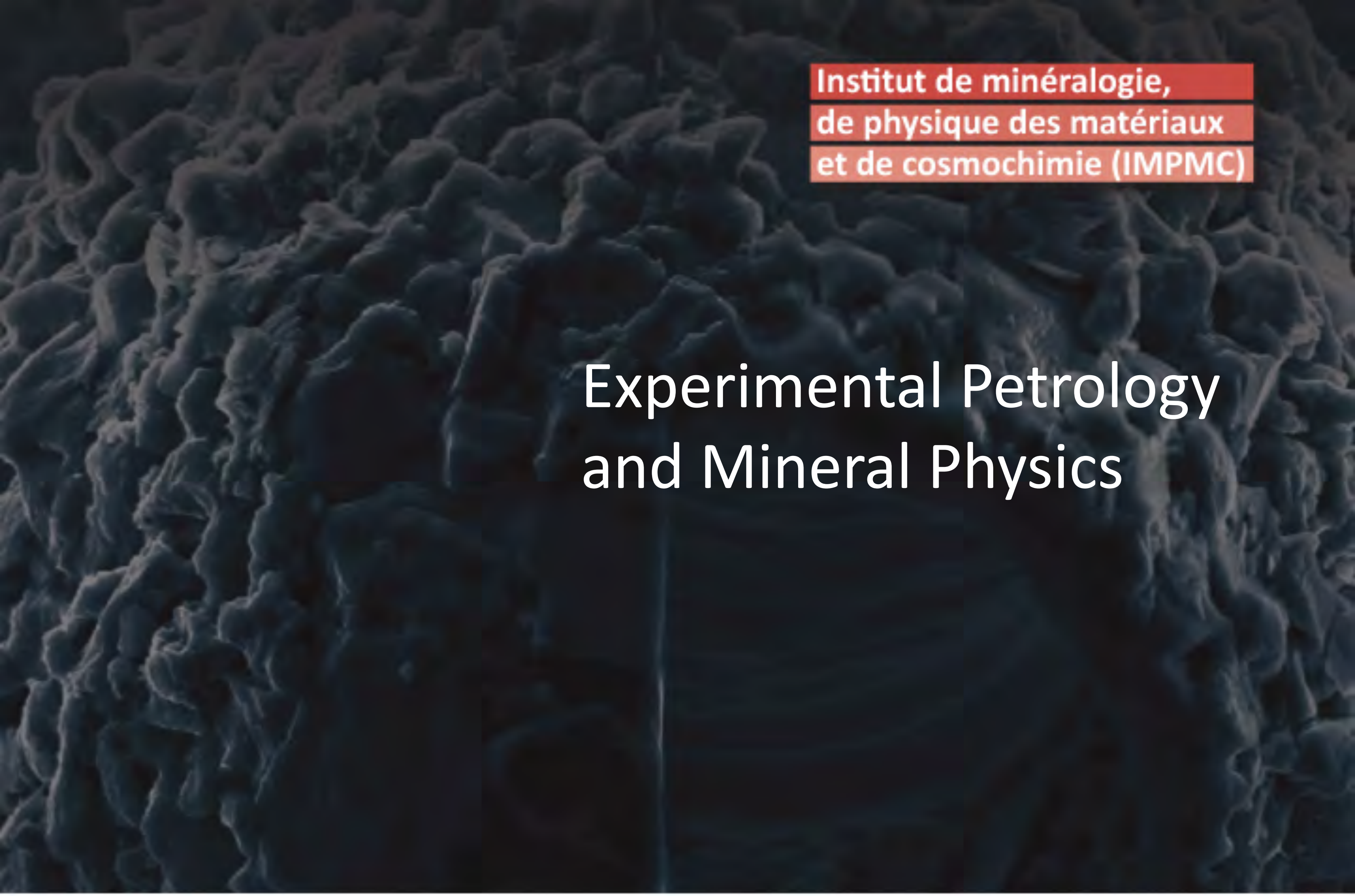


Electron Energy Loss Spectroscopy (EELS) : Element speciation, local environment of elements + EFTEM imagery









Institut de minéralogie,
de physique des matériaux
et de cosmochimie (IMPMC)

Experimental Petrology and Mineral Physics

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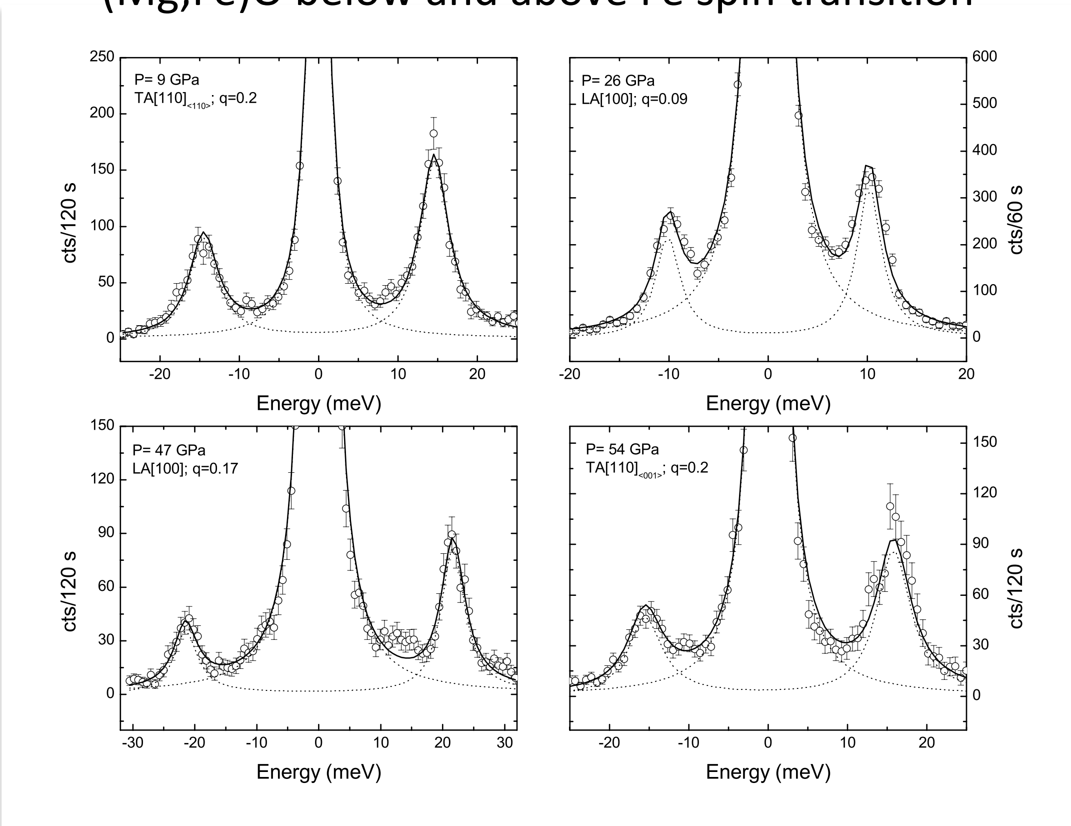
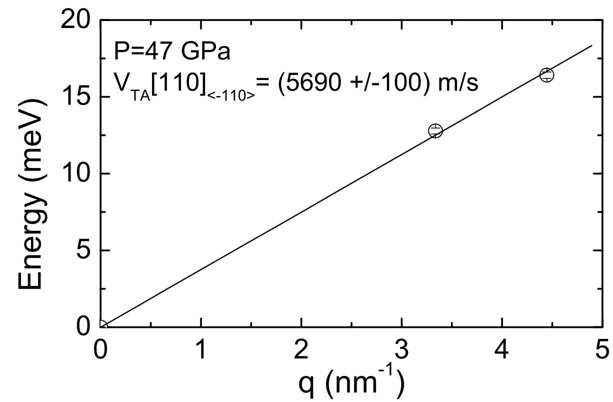
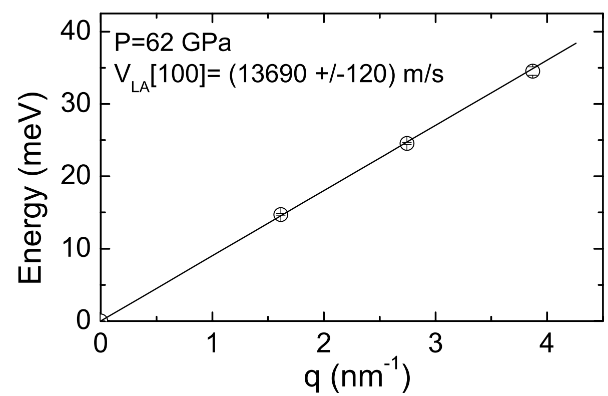
Inelastic X-Ray Scattering (IXS) from Phonons

(Mg,Fe)O below and above Fe spin transition







Antonangeli et al., Science 2011

Pauling Rules

- 1 First rule: the radius ratio rule: sum of the ionic radii -> cation-anion distance, cation-anion radius ratio -> coordination Nb and shape
- 2 Second rule: the electrostatic valence rule : local neutrality sum of strenghths of the electrostatic bonds equals the charge of the anion.
- 3 Third rule: sharing of polyhedron corners, edges and faces : sharing corners does not decreases stability as much as others .
- 4 Fourth rule: crystals containing different cations: if different cations in the crystal, cation with high valency and small CN tend not to share polyhedron elts with another one.
- 5 Fifth rule: the rule of parsimony: nb of constituents in a crystal tends to be small

Birch-Murnaghan

Equation of State: Third Order Birch-Murnnaghan

$$P(V) = \frac{3B_0}{2}\left[\left(\frac{V_0}{V}^{7/3}\right) - \left(\frac{V_0}{V}^{5/3}\right)\right]\left\{1 + \frac{3}{4}(B'_0 - 4)\left[\left(\frac{V_0}{V}^{2/3} - 1\right)\right]\right\}$$

$$B_0 = -V\left(\frac{\partial P}{\partial V}\right)_{P\ =\ 0}$$

$$B'_0 = \left(\frac{\partial B}{\partial P}\right)_{P\ =\ 0}$$