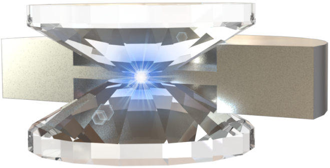
High Pressure X-ray Raman Scattering at ID20

Ch. Sahle

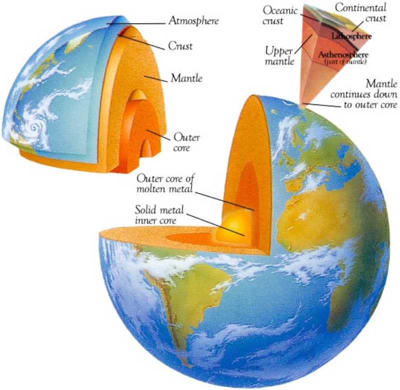
The European Synchrotron

June 18, 2019

x-ray spectroscopy at high pressure



- need for diamond anvil cells
- conventional XAS for absorption edges in the hard x-ray regime
- XAS fails for in situ study of absorption edges in the soft x-ray regime



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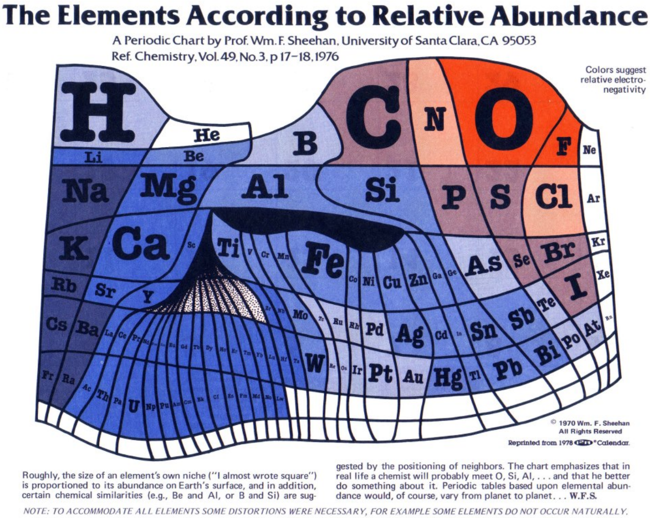

- light elements are especially abundant in the Earth
- need spectroscopic tools to study low-Z elements at extreme conditions

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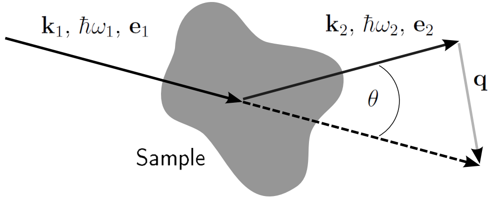
non-resonant inelastic x-ray scattering



- incoming photon ($\mathbf{k}_1$, $\hbar\omega_1$, $\mathbf{e}_1$)
- outgoing/scattered photon ($\mathbf{k}_2$, $\hbar\omega_2$, $\mathbf{e}_2$)
- scattering angle Θ
- energy transfer $\hbar\omega = \hbar\omega_1 - \hbar\omega_2$
- momentum transfer $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$

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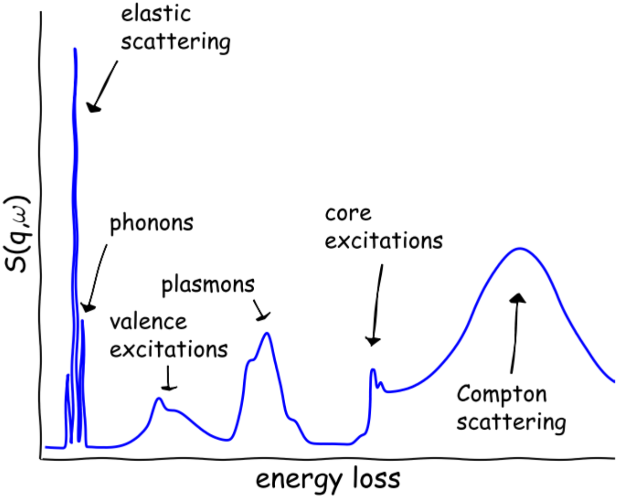
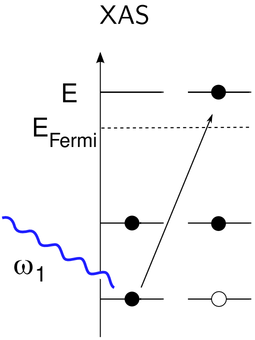
the dynamic structure factor $S(q, \omega)$

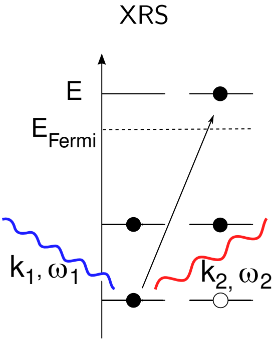


adapted from S. Huotari

- core excitations main focus of the ID20 XRS end-station

x-ray Raman scattering (XRS) spectroscopy





- photon is absorbed
- **primary energy** in the order of x-ray absorption edge

- photon is scattered inelastically
- **energy loss** in the order of x-ray absorption edge

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which edges are accessible?

element	Z	edge	energy transfer [eV]
He - Si	2 – 14	K	20 - 1800
N - Cu	7 – 29	$L_{2,3}$	40 - 1100
Ar - Cu	18 – 29	$M_{2,3}$	15 - 120
Ba - Yb	56 – 70	$N_{4,5}$	90 - 200
La - U	57 – 92	$O_{2,3/4,5}$	15 - 100

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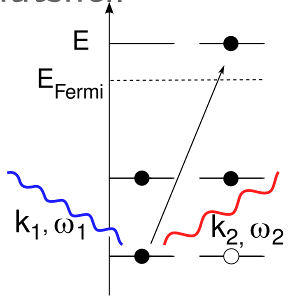
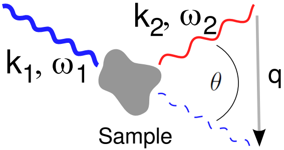
X-ray Raman Scattering in a nutshell

- **inelastic** scattering of **hard x-rays** from core electrons
- **energy transfer** in the order of soft x-ray absorption edges
- **primary energies** are in the range $5 - 15\ \mathrm{keV}$
- high **bulk sensitivity**, samples under **extreme conditions**
- **high momentum transfer** accessible
- **no saturation**, **no** sample **self/over absorption**





W. Schülke, Oxford (2007) ; Ch. Sahle et al. J. Synchrotron Rad. (2015).

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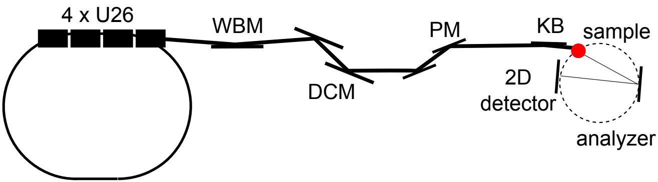
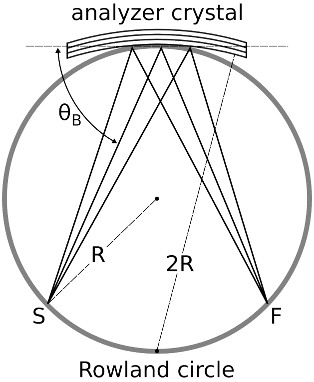
ID20 - inelastic scattering I



- XRS is a photon hungry technique
- photons from 4 consecutive undulators
- 72 spherically bent analyzer crystals (large solid angle of detection)



- point-to-point focus
- 72 individual Rowland circles

S. Huotari et al. J. Synchrotron Rad. (2017); Ch. Sahle et al. J. Synchrotron Rad. (2015); Ch. Sahle et al. J. Synchrotron Rad. (2017); Ch. Sahle et al. J. Synchrotron Rad. (2017); google: ID20 ESRF

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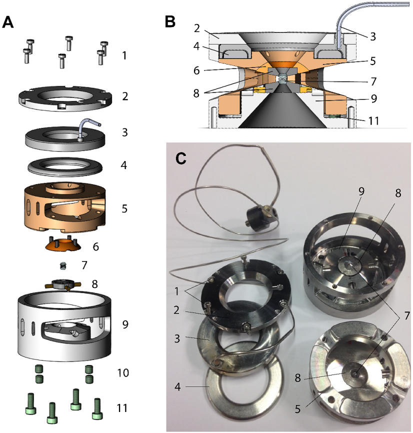
high pressure instrumentation at ID20



→ presentation of J. Jacobs (Thu. 11 am)

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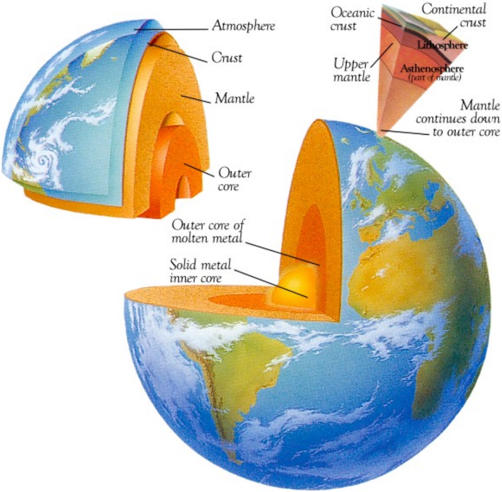
compression mechanism in a-SiO_2

a-SiO_2 - silica and silicates

- ca. 45 wt.% of the earth is made up of SiO_2
- scarce information about even simplest silicates (SiO_2, $MgSiO_3$)
- density, structure, melting at pressure



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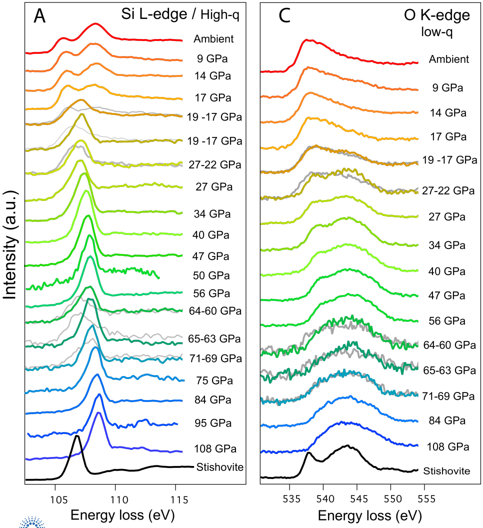
experimental data: Si $L_{2,3}$ and O K-edge



- transition at 20 GPa
- change in shape and edge onset around 60 GPa

S. Petitgirard et al. Geochem. Persp. Let. (2019) 9, 32-37.

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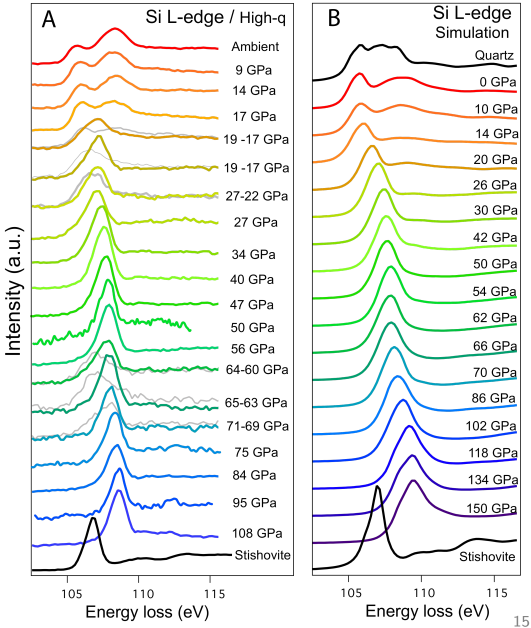
simulation data: Si $L_{2,3}$

- structures from AIMD
- spectra from OCEAN

M. Wu Sci. Rep. (2012), J. Vinson Phys. Rev. B (2011), K. Gilmore Comp. Phys. Comm. (2015).



simulation data: O K

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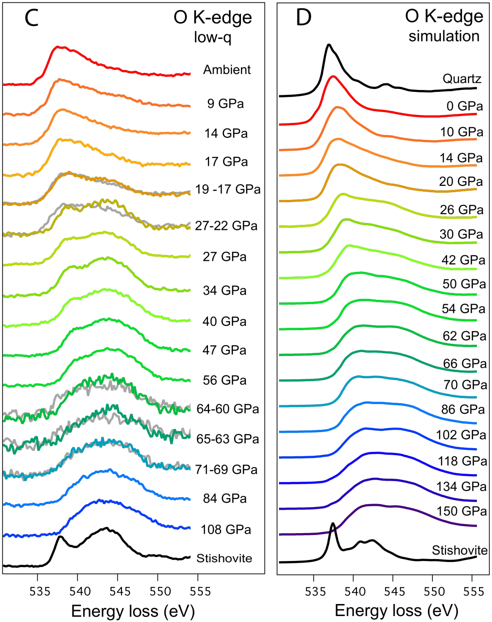
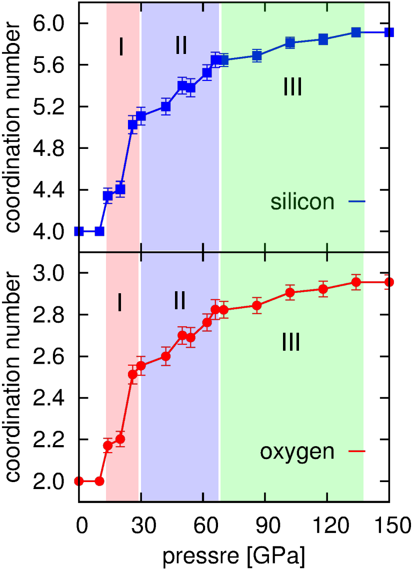
- spectra from OCEAN

M. Wu Sci. Rep. (2012), J. Vinson Phys. Rev. B (2011), K. Gilmore Comp. Phys. Comm. (2015).



MD model: coordination numbers

- three distinct regions
- I: 4- to 5-fold
- II: 5- to 6-fold
- III: 6-fold



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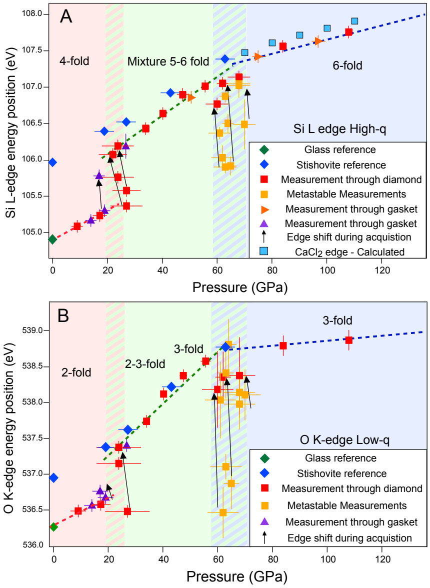
experimental data: edge onset

- three distinct regions
- comparison with well known 4- and 6-fold standards
- 6-fold state reached, but not exceeded for $p > 60$ GPa

S. Petitgirard et al. Geochem. Persp. Let. (2019) 9, 32-37.



compression mechanism in carbonatitic glass

- carbon cycle of the Earth
- carbonates and carbonatites
- pressure-dependence of physical properties (density, viscosity, electronic conductivity, etc.)

- $K_2Mg(CO_3)_2$ glass as analogue for the melt
- one of very few quenchable carbonatites
- O K-edge as proxy for C-O bonding/chemistry

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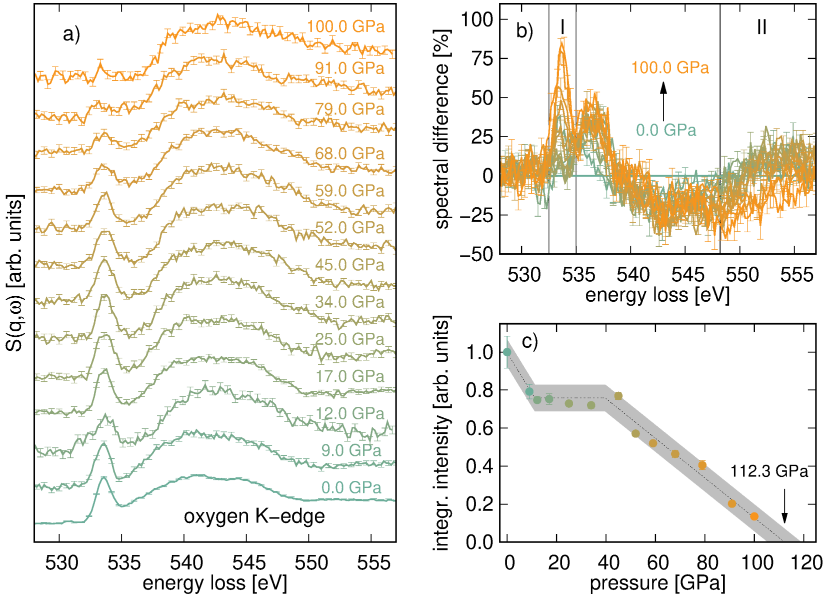
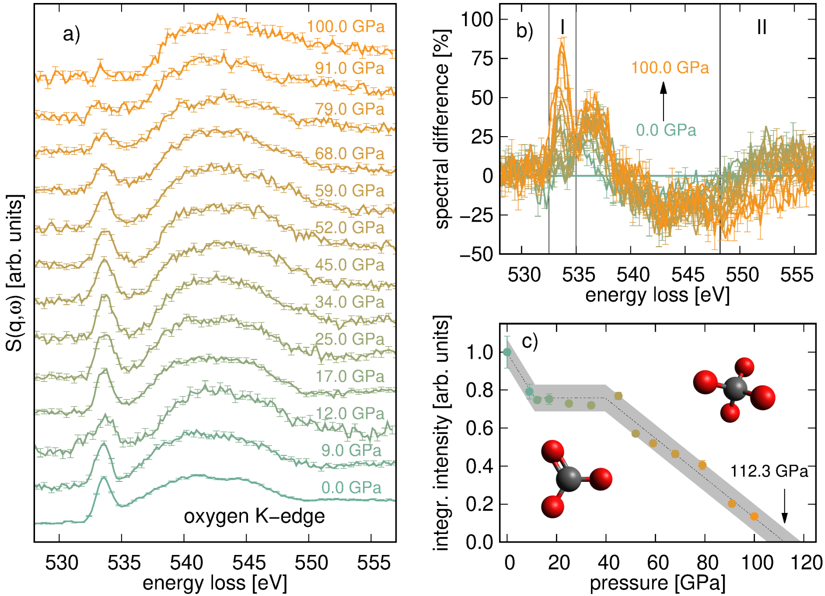


a)
100.0 GPa
91.0 GPa
79.0 GPa
68.0 GPa
59.0 GPa
52.0 GPa
45.0 GPa
34.0 GPa
25.0 GPa
17.0 GPa
12.0 GPa
9.0 GPa
0.0 GPa
oxygen K−edge
S(q,ω) [arb. units]
energy loss [eV]
b)
I
II
100.0 GPa
0.0 GPa
spectral difference [%]
energy loss [eV]
c)
112.3 GPa
integr. intensity [arb. units]
pressure [GPa]

ESRF


a)
100.0 GPa
91.0 GPa
79.0 GPa
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45.0 GPa
34.0 GPa
25.0 GPa
17.0 GPa
12.0 GPa
9.0 GPa
0.0 GPa
oxygen K−edge
S(q,ω) [arb. units]
energy loss [eV]
530
535
540
545
550
555
b)
I
II
100.0 GPa
0.0 GPa
spectral difference [%]
100
75
50
25
0
−25
−50
energy loss [eV]
c)
112.3 GPa
integr. intensity [arb. units]
1.0
0.8
0.6
0.4
0.2
0.0
pressure [GPa]
0
20
40
60
80
100
120

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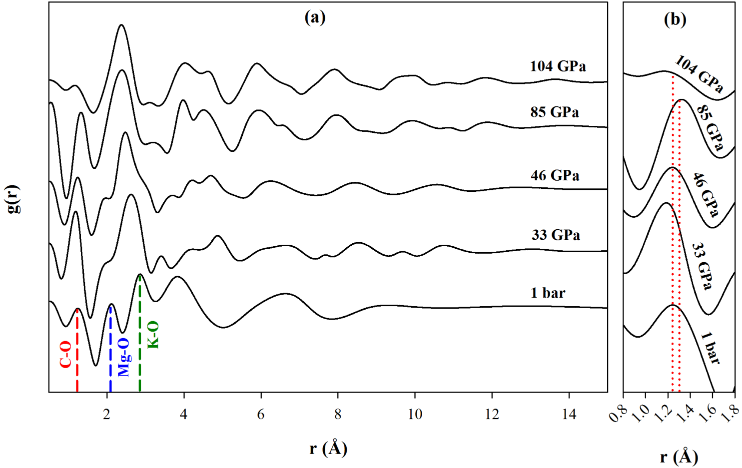
PDF analysis from ID15a and ID15b



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thanks to

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- **V. Cerantola** of XFEL (former ESRF), Hamburg
- **M. Hanfland, M. di Michiel, J. Jacobs** of ESRF, Grenoble
- **K. Gilmore** of BNL (former ESRF), Brookhaven
- **C. Sternemann, C. Weis** of TU Dortmund, Dortmund
- **G. Spiekermann, M. Wilke** of Uni Potsdam, Potsdam

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thank you and hope to see you at ID20