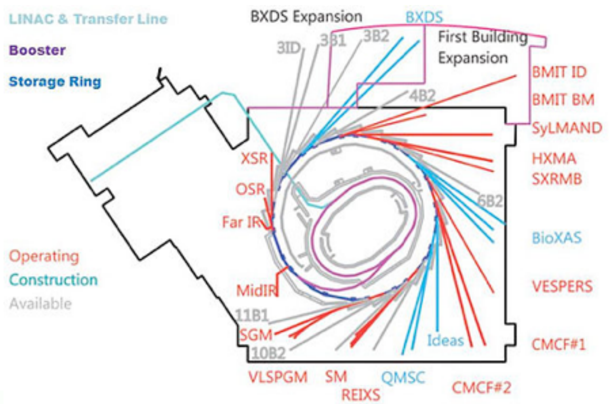
X-ray absorption spectroscopy: a structural point of view

Georges Calas, Laurent Cormier, Laurence Galoisy, Gérald Lelong
Institut de Minéralogie, Physique des Matériaux et Cosmochimie
Université P&M Curie, Paris

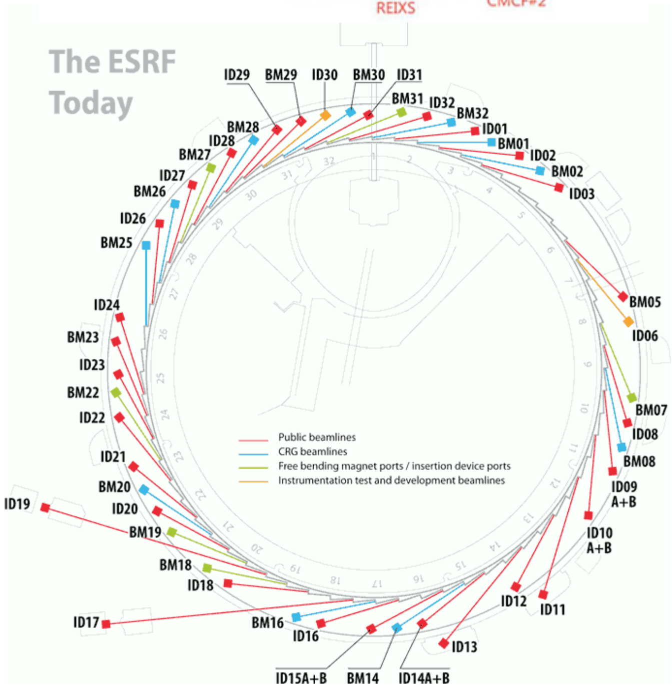
1. Measuring x-ray absorption spectra

- Pioneer measurements using x-ray tubes (bremsstrahlung)
- Synchrotron radiation extracted from a storage ring ("parasitic use": coexistence with particle physics)
- Now, dedicated large user facilities (6,500 scientists/year at ESRF; 30% projects involving industrial participation)
- Interest for multicomponent materials: chemical selectivity, partial radial distribution functions+ site symmetry/coordination numbers (+ redox)

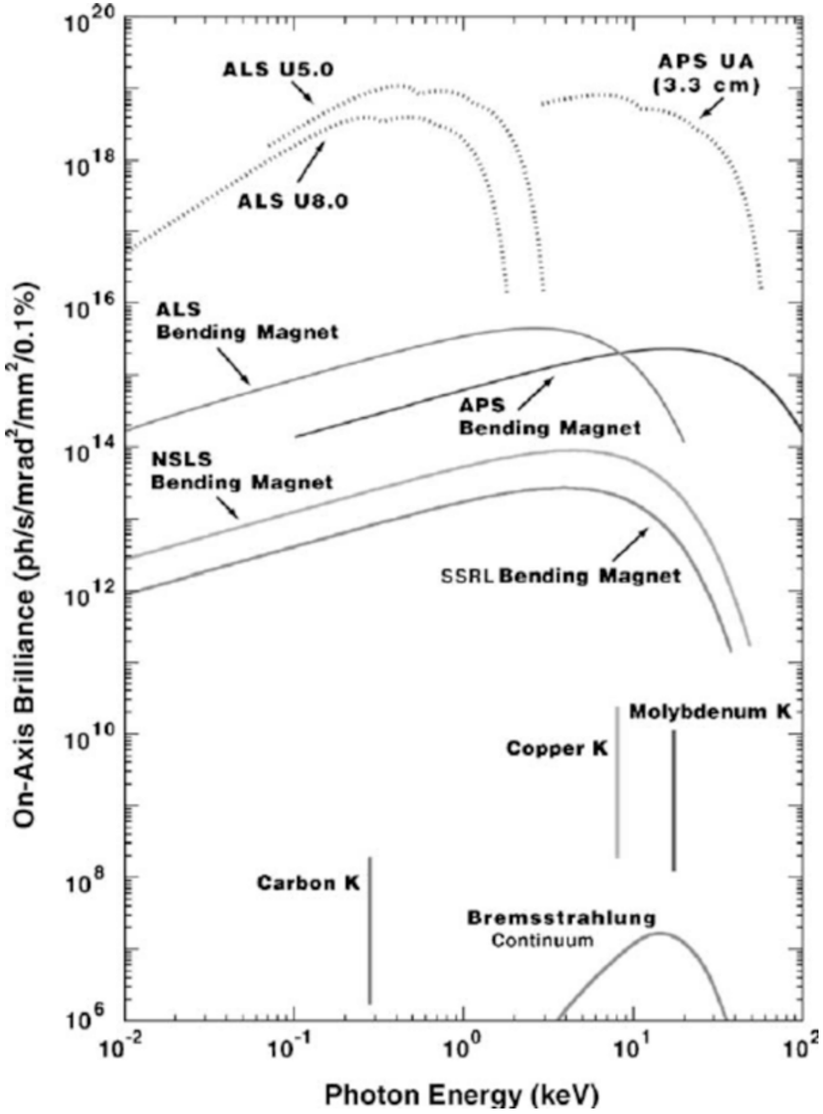
You first need a synchrotron…



CLS, Saskatoon



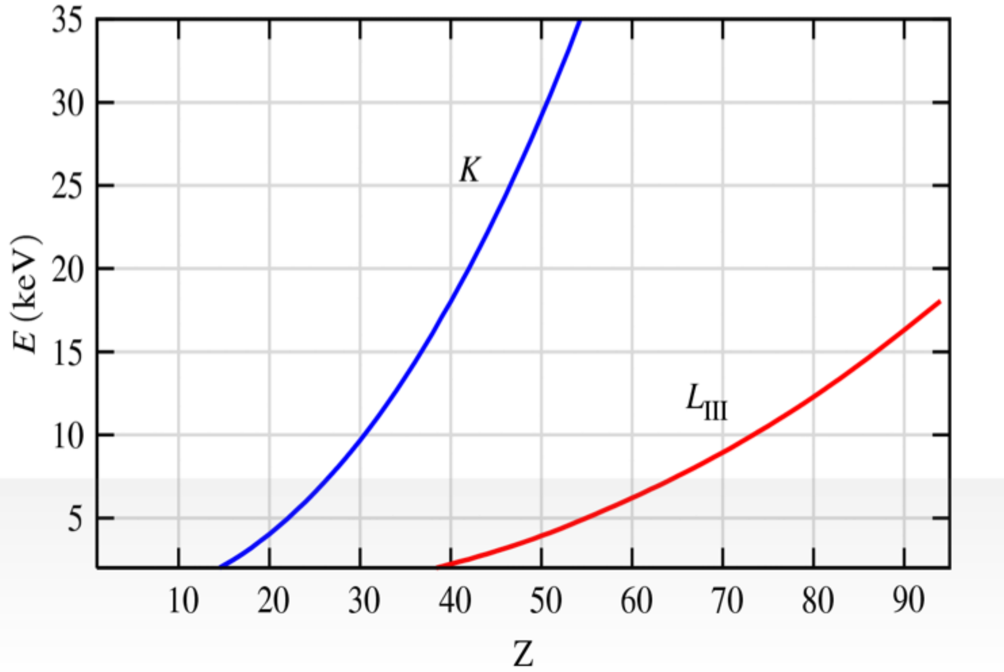
ESRF, Grenoble

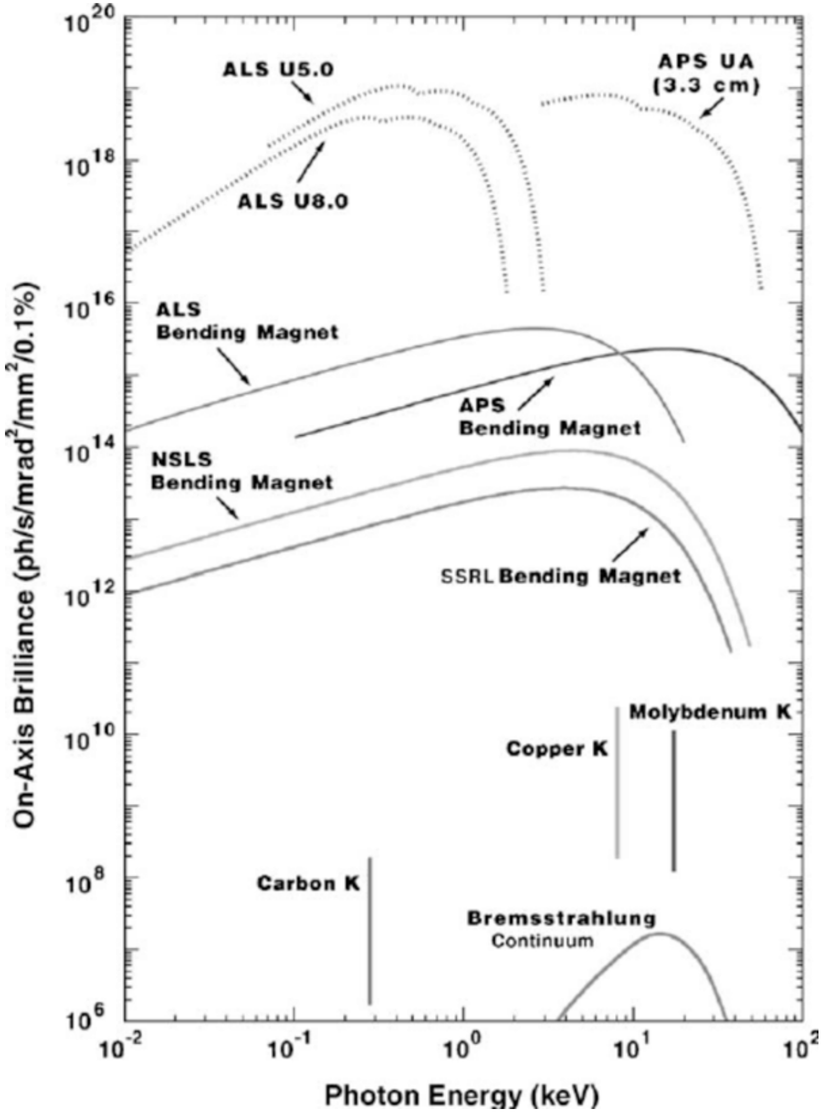


Energy characteristics for various rings

… You have then to choose the right one

X-ray absorption energy increases with Z (K-, L- or M-edges)

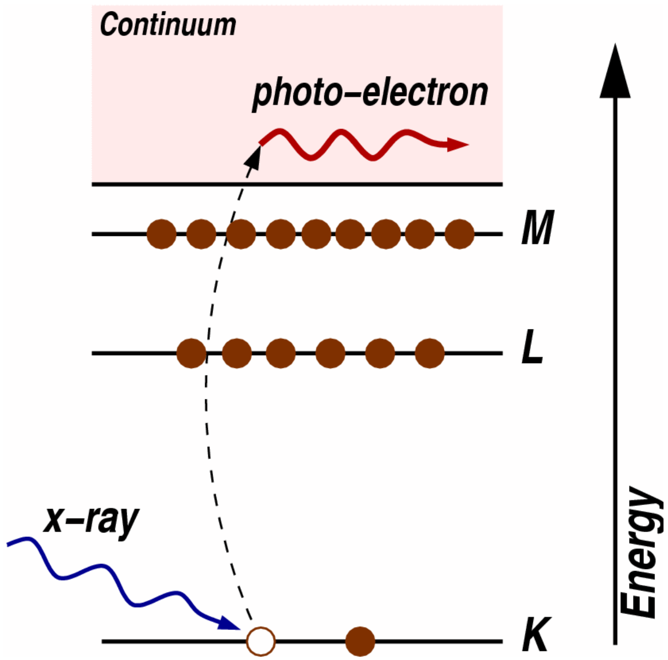




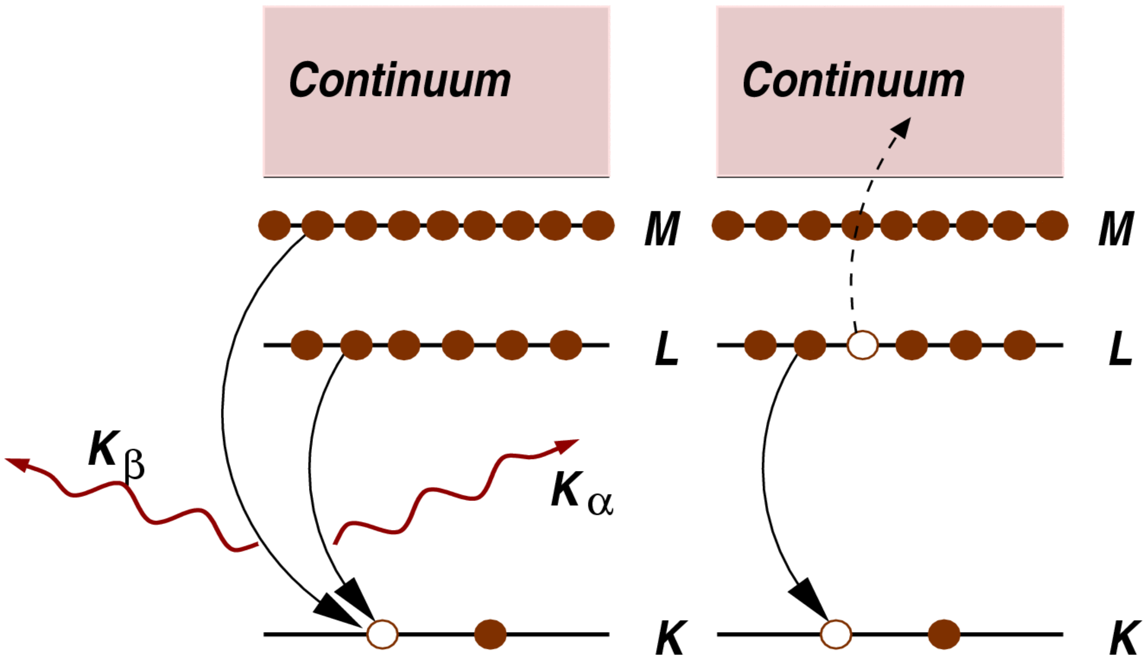
(Newville, 2004)

Choice depends on E, sample environment, detection systems… + selection!

The X-ray absorption process



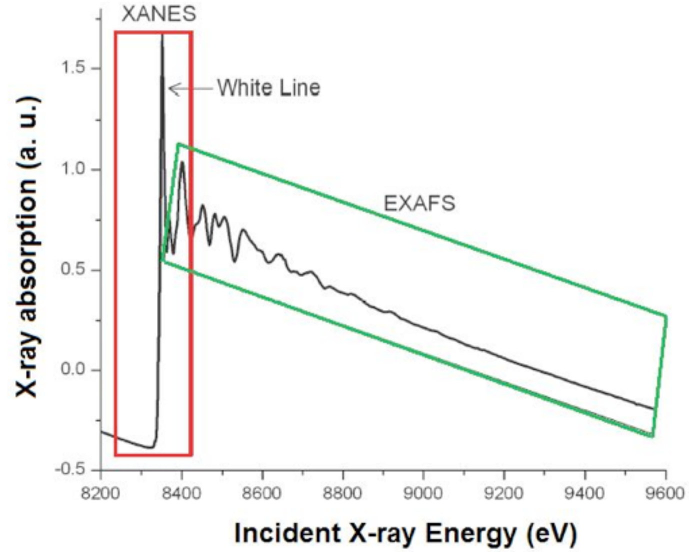
Photon absorption



Filling the hole

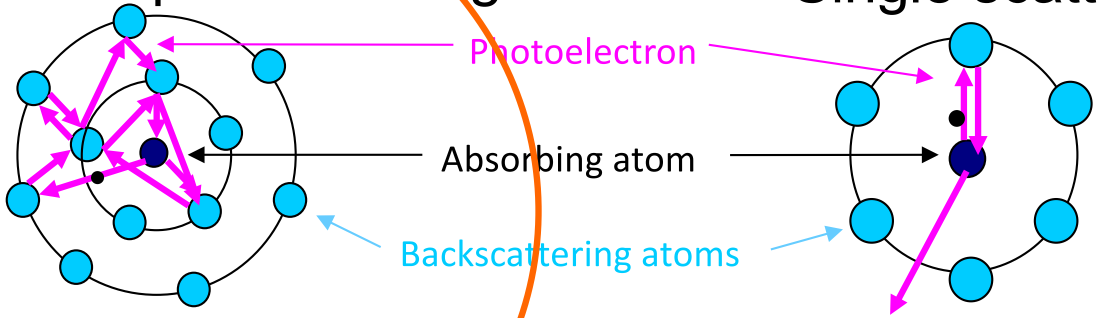
(Newville, 2004)

X-ray Absorption Spectroscopy: two regions



Bound states+
Multiple scattering

Single scattering

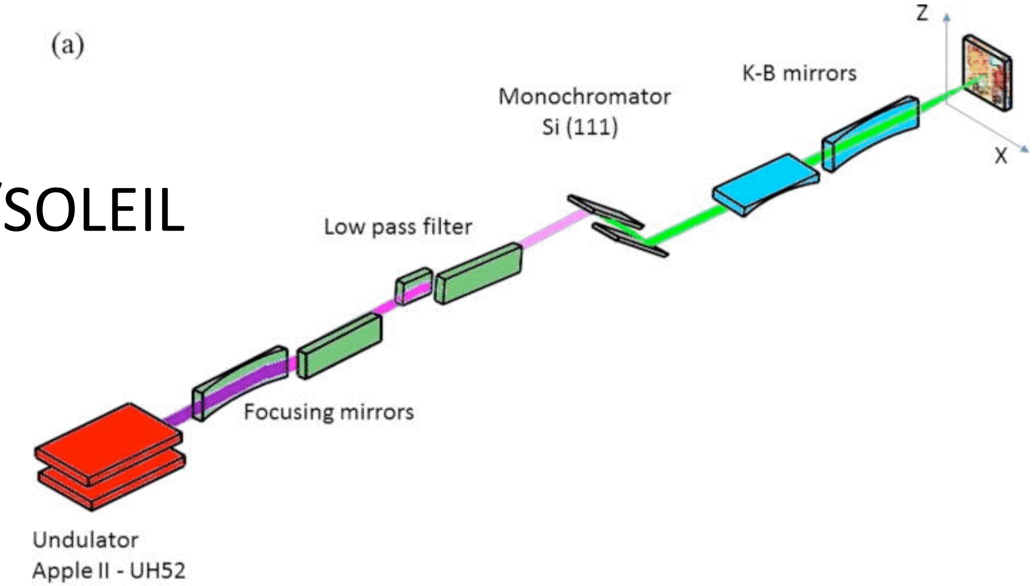


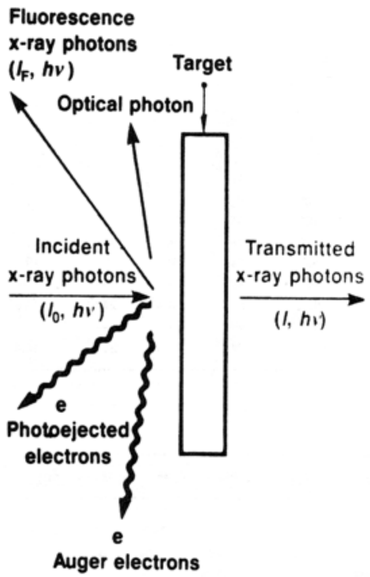
XANES
X-ray Absorption
Near Edge Structure

EXAFS
Extended X-ray Absorption
Fine Structures

Experimental settings

The µXAS setting @LUCIA/SOLEIL





"Classical" detection schemes

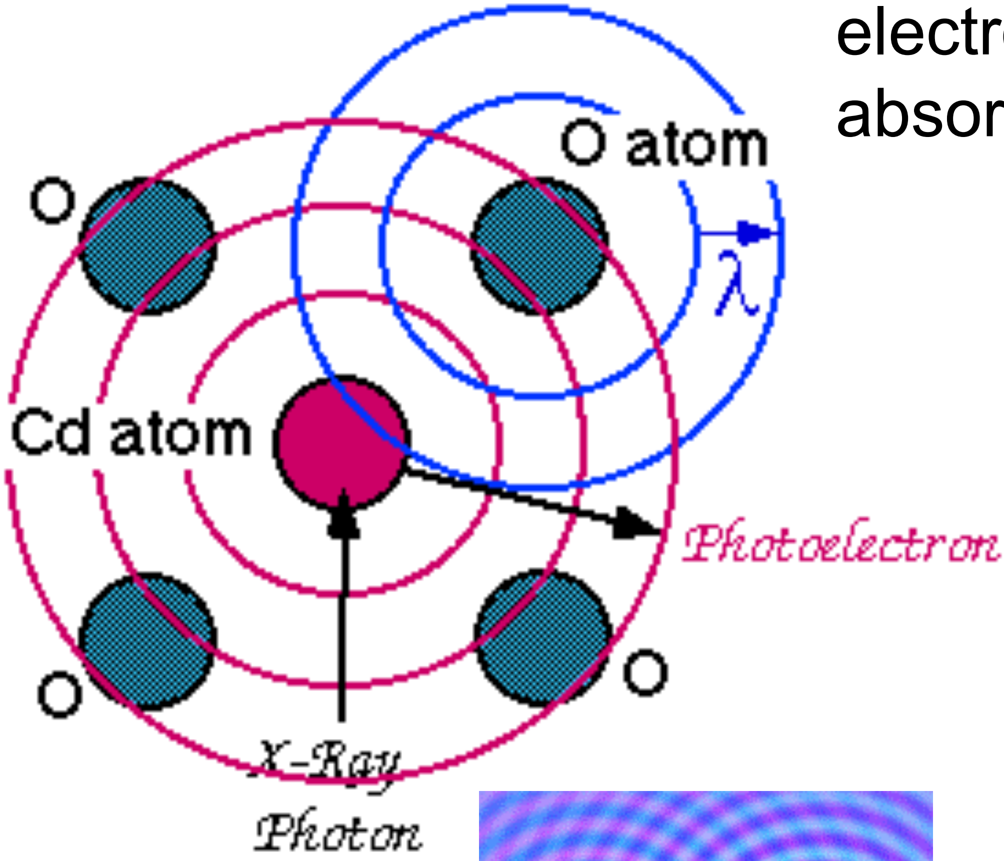
µ-XAS including mapping
High T (anharmonic effects)
High P

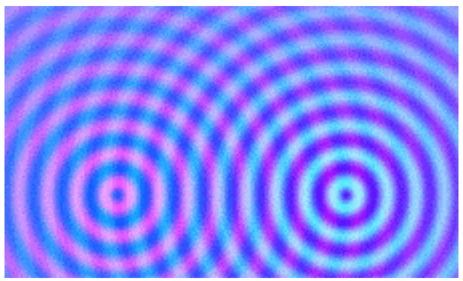
More recently:
- *High-Energy Resolution Fluorescence Detected XAS (HERFD)*

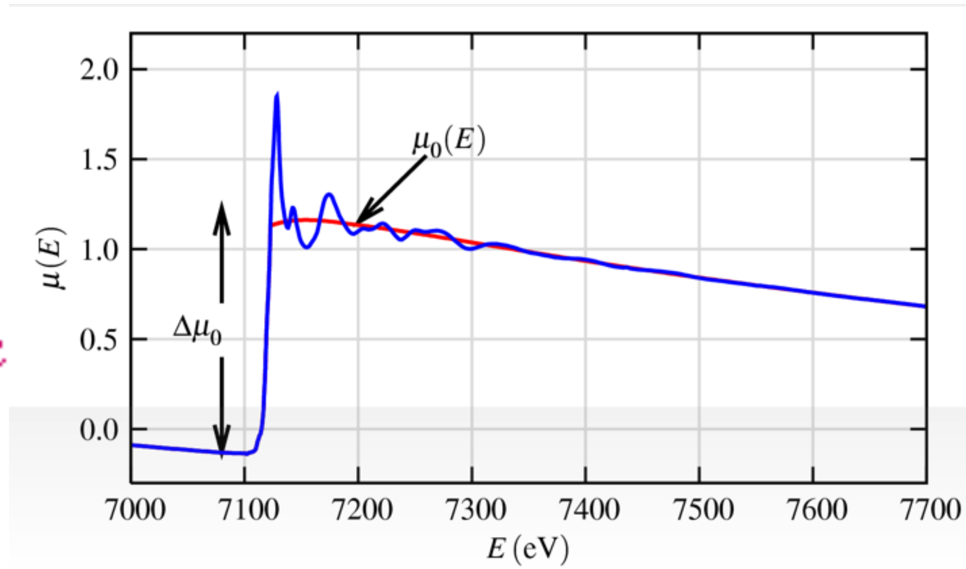
- *Inelastic X-ray scattering (IXS)*

EXAFS (1)

Interference phenomenon between outgoing and backscattered photo-electron wave= modulation of the absorption function







EXAFS (2)

Interatomic distance R_j and coordination number N_j
Scattering amplitude $f_j(k)$: types of neighbors

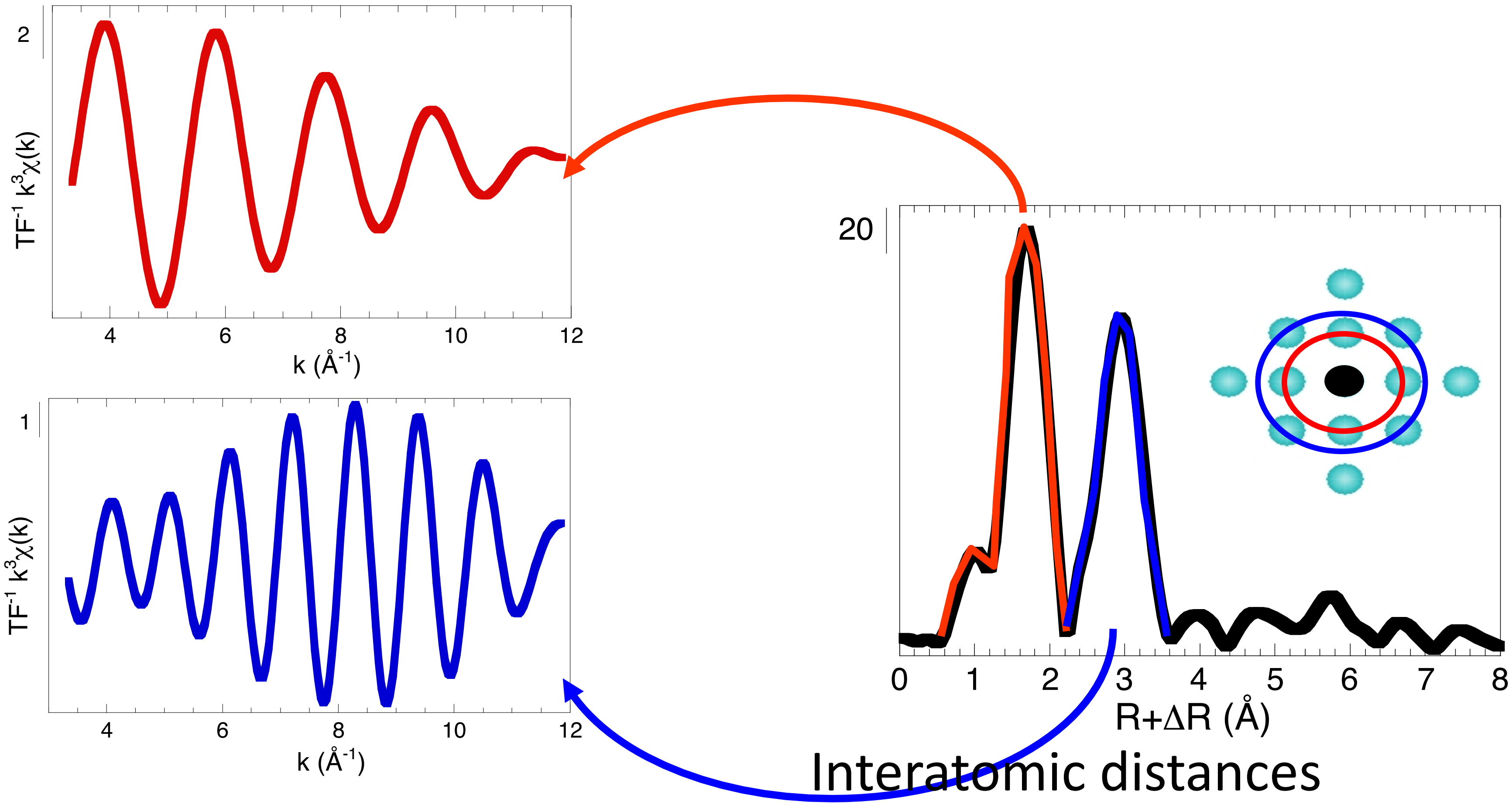
$$\chi(k) = \sum_j \frac{N_j}{kR_j^2} f_j(k) \exp\left(-2\sigma^2 k^2\right) \exp\left(\frac{-2R_j}{\lambda}\right) \sin(2kR_j + 2\delta + \theta)$$

- Damping: Debye Waller term and mean free path

- Phase shift: depends also on the type of neighbors

EXAFS (3)

Fourier filtering



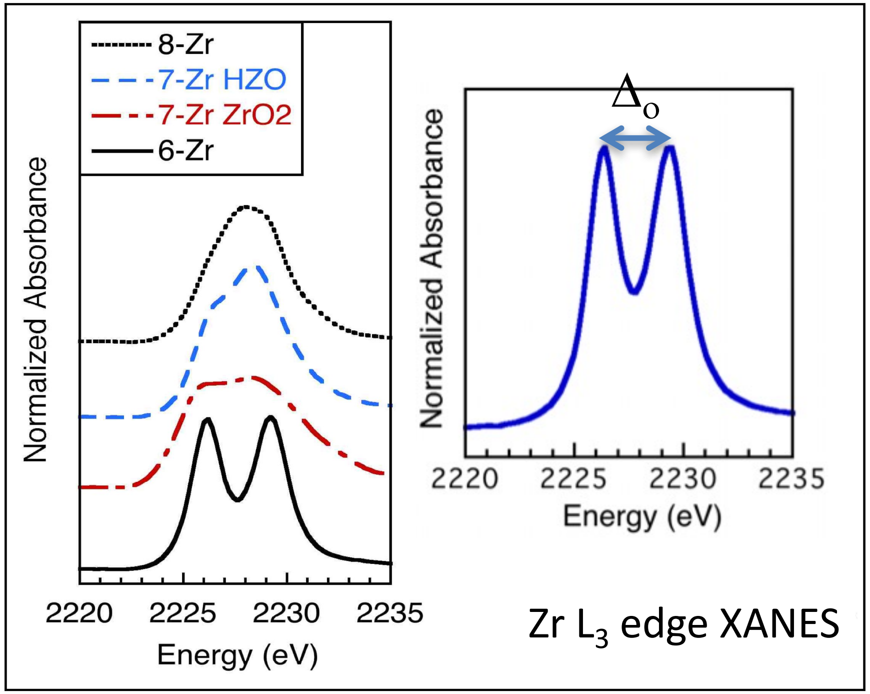
Wavevector space

Interatomic distances
(uncorrected for phase shift)

2. A large diversity of sites in glasses: XANES

Structural aspects: coordination number and site geometry

Cations: a well-defined site geometry (1)

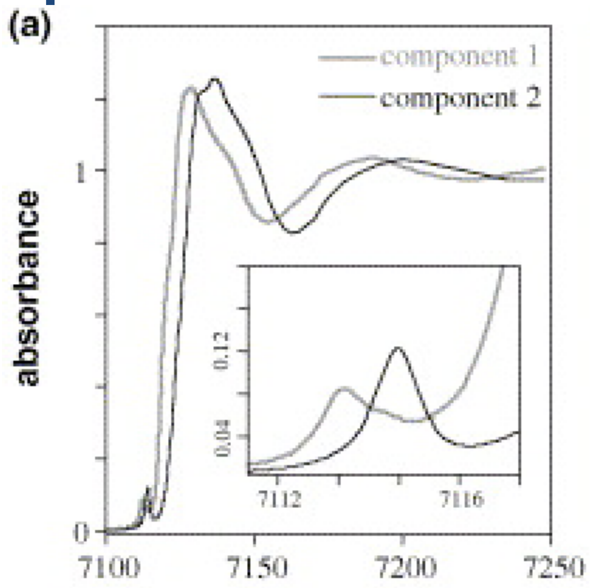


Zr L_3-edge XANES in a borosilicate glass: Zr in an octahedral site

Lorentzian ("natural shape") components = regular octahedra

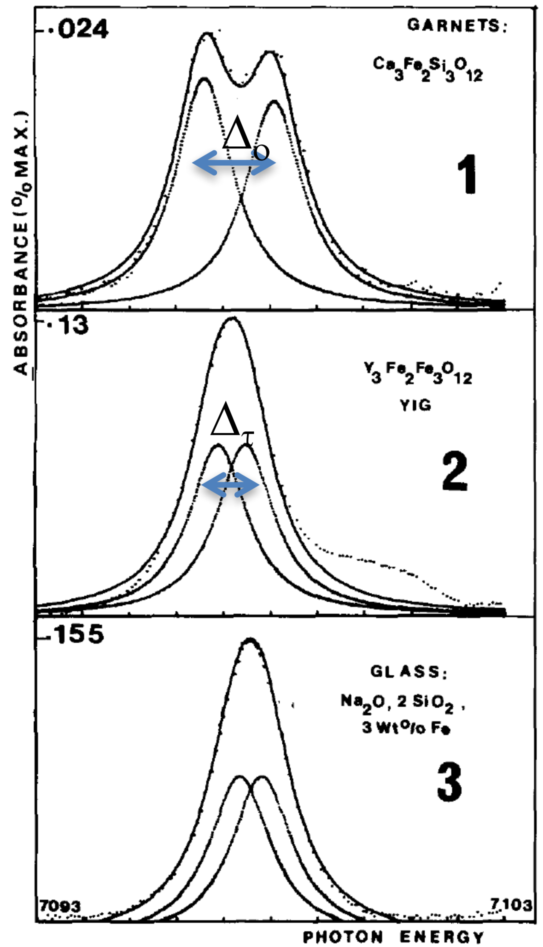
(Galoisy et al., 1999)

Cations: a well-defined site geometry (2)



Photon energy (eV)

Fe K-edge XANES: Fe^{2+} and Fe^{3+}



Pre-edge features on the low-energy side of K-edges of transition metal ions = transitions to 3d-derived empty levels.

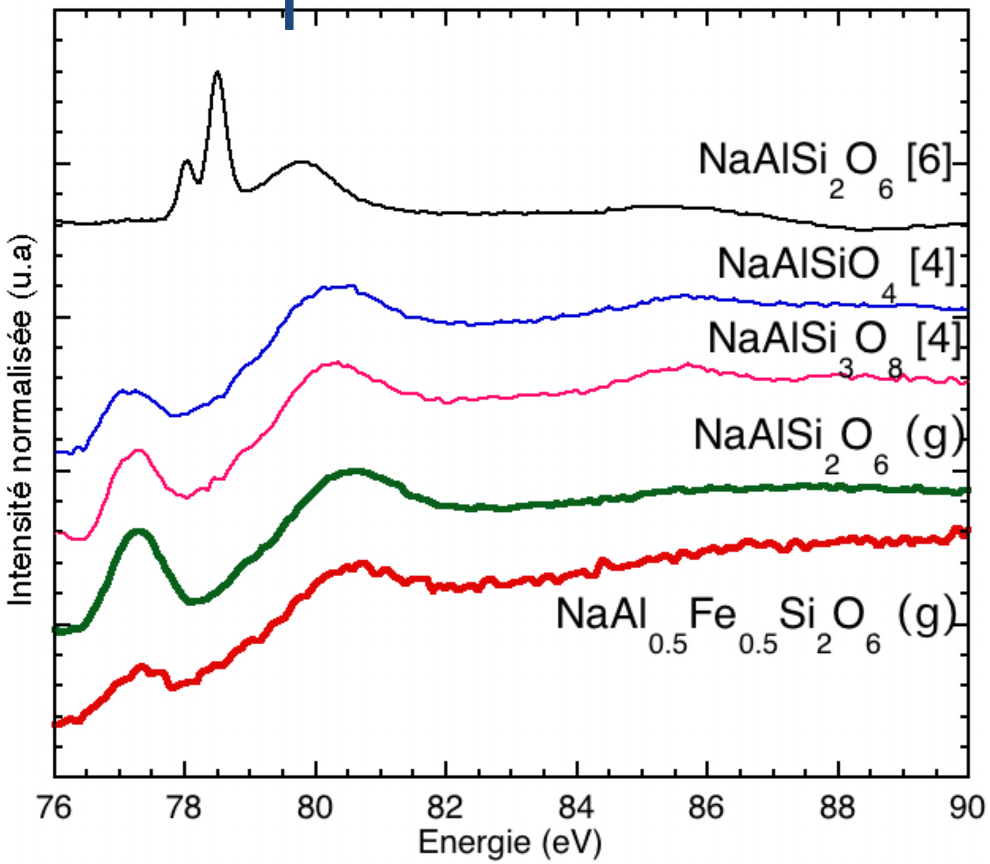
Crystal-field splitting of Fe^{3+} pre-edge features: Fe^{3+} in tetrahedral symmetry

(Farges et al., 2012)

(Calas and Petiau, 1983)

Al coordination: $L_{2,3}$-edge XANES

CLS (PGM beamline)



Crystalline references

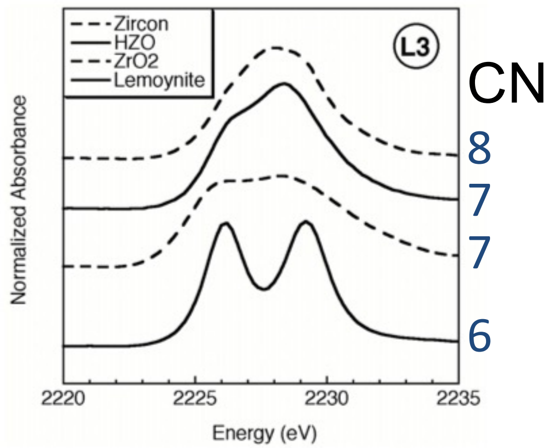
Glasses (Fe-bearing: problems with NMR)

Tetrahedral Al^{3+} : confirms a network-forming position in Fe-bearing jadeite-composition glasses ($NaAlSi_2O_6$)

(Weigel et al., 2008)

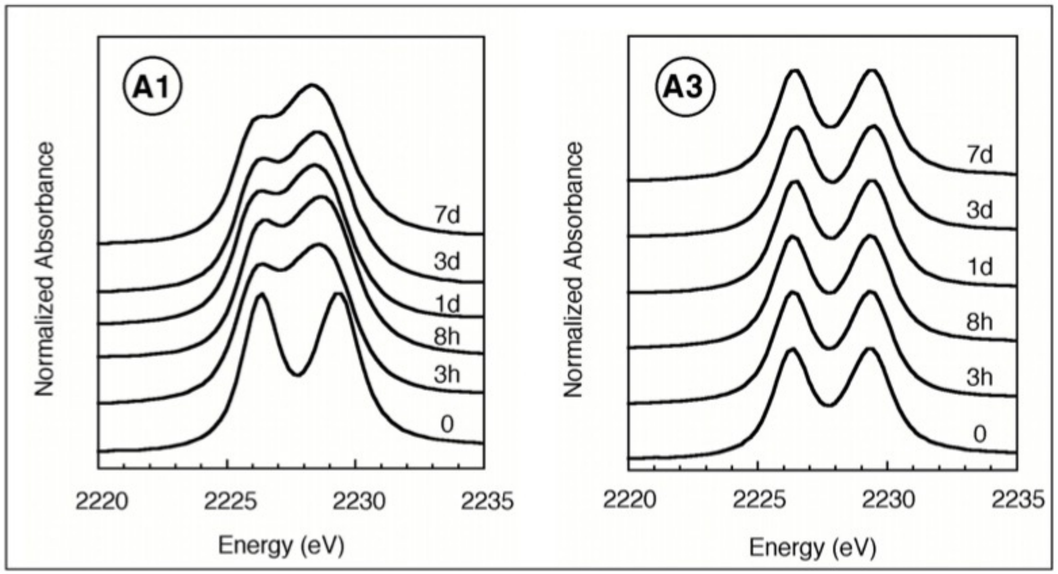
Evolution of glass surface during leaching : Zr L-edge XANES

Surface detection (total electron yield)



Crystalline references: dependence of XANES on coordination number (CN)

Deionized water: CN from 6 (glass) to 7 (after corrosion)



Saturated Conditions: CN=6

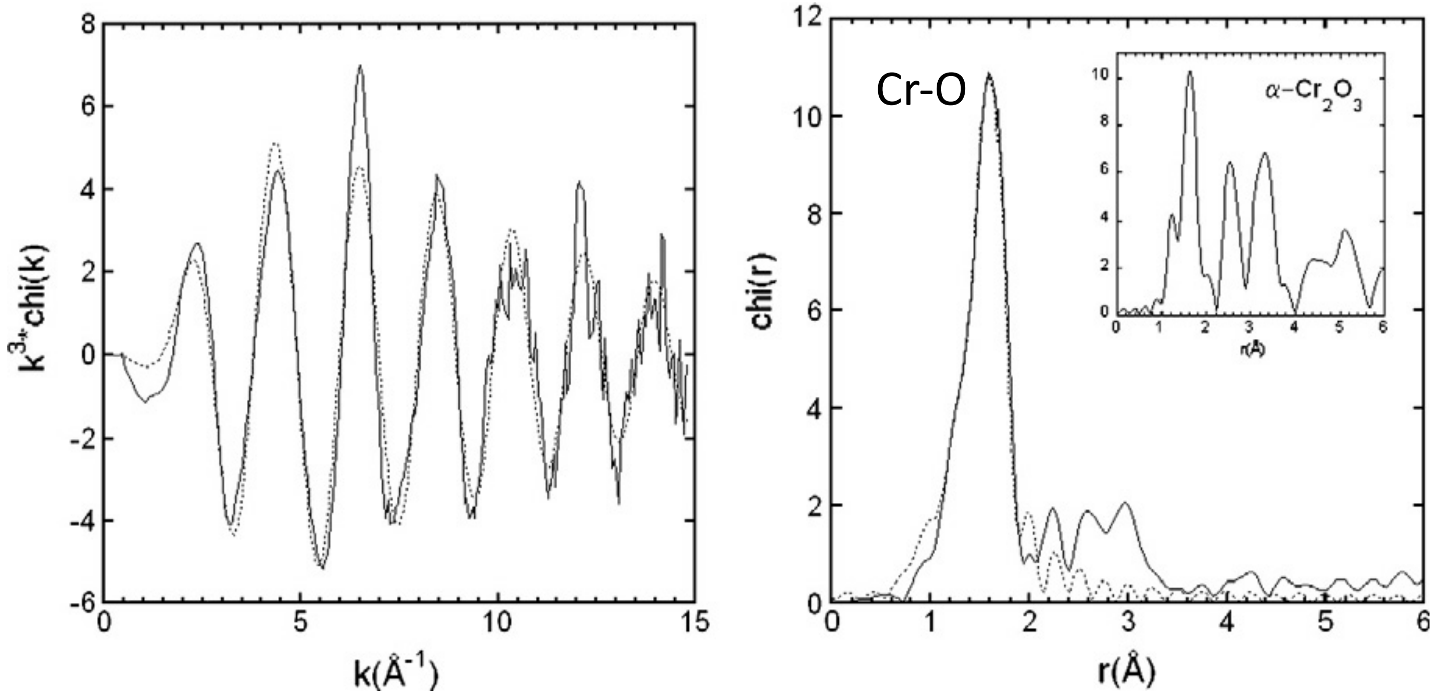
(Pelegrin et al., 2010)

3. A large diversity of local structures: EXAFS

- cation-ligand (oxygen) distances
- nearest and next-nearest neighbors

Radial information = well-defined sites

Cr K-edge EXAFS on $Na_2O \cdot 2SiO_2$ glass (1 wt% Cr^{3+})



-1 main contribution= Cr-O

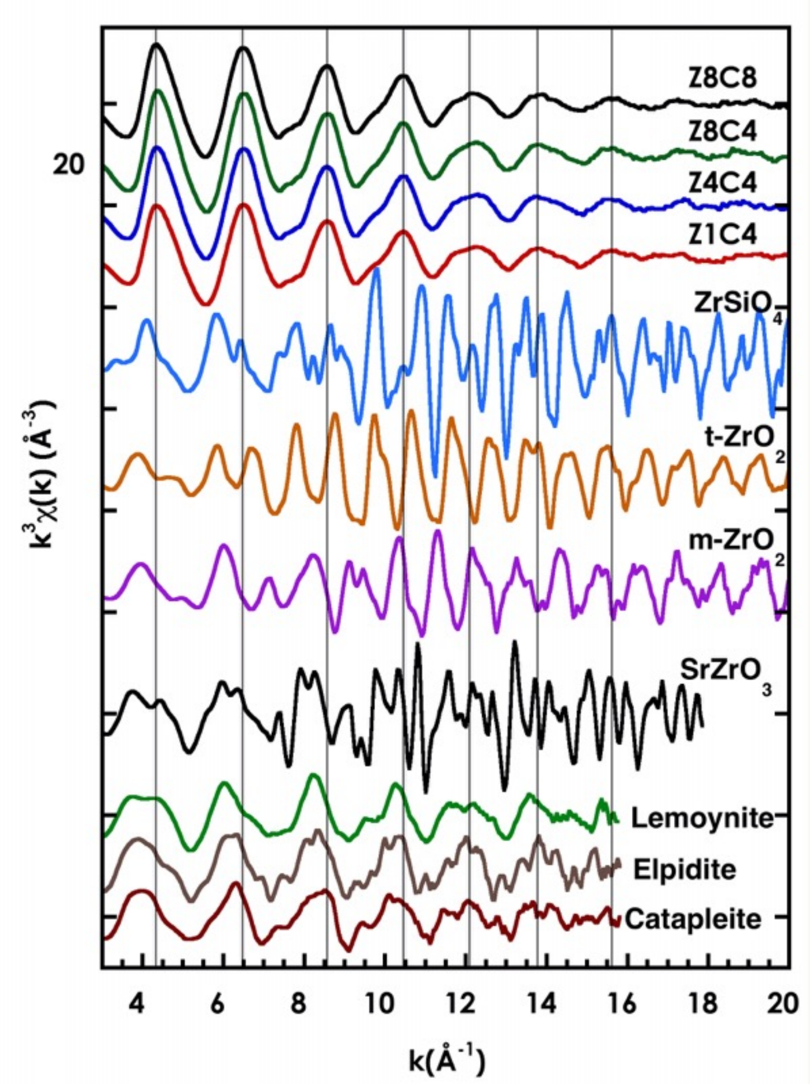
- d(Cr-O)=1.99Å= relaxed distances as in crystals
- similar Cr-O distances in most glasses

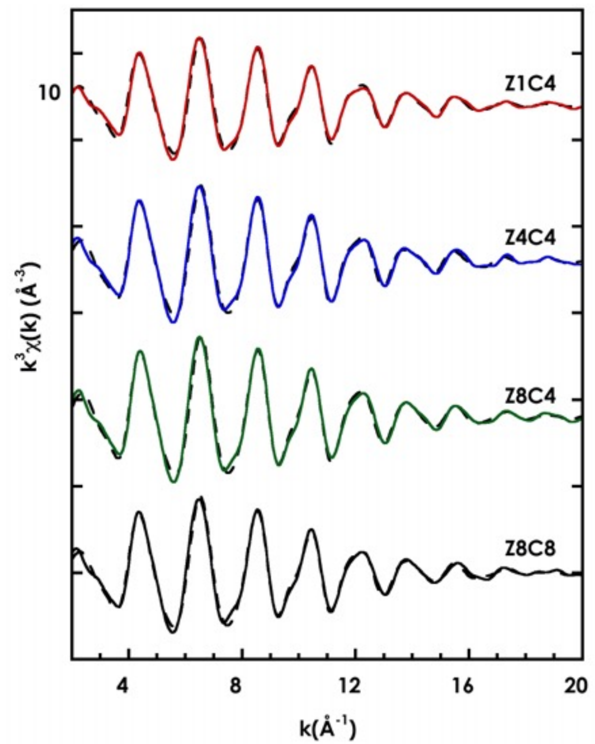
(Villain et al., 2010)

Improving the information

Zr K-edge EXAFS in borosilicate glasses

Large E range (17700-21200eV): improves data accuracy

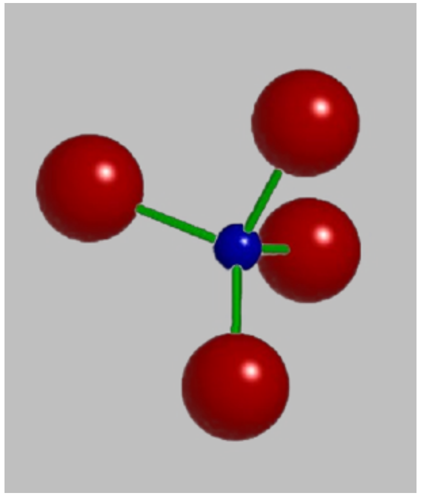




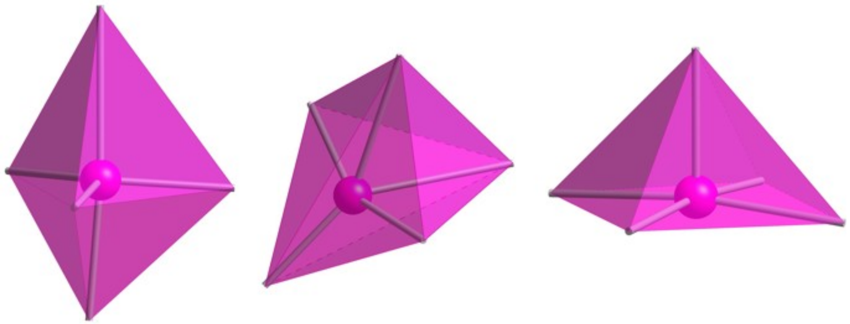
Zr-octahedra distort with increasing [Zr]: still a random distribution?

(Jollivet et al., 2013)

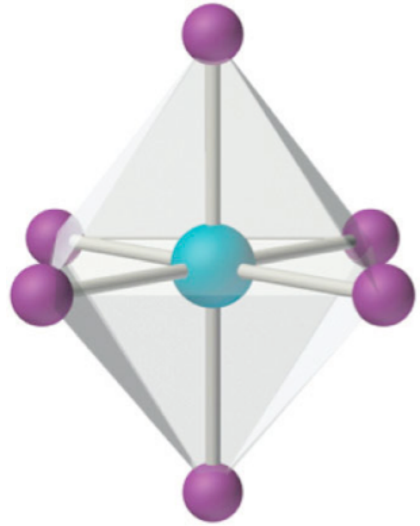
A large diversity of sites



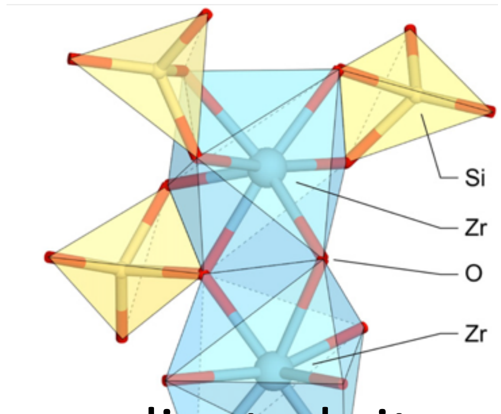
Tetrahedra ± distorted (Zn, Ni, Fe^{3+})



Abundant 5-coordinated sites (Ni, Fe^{2+} and Fe^{3+}…)



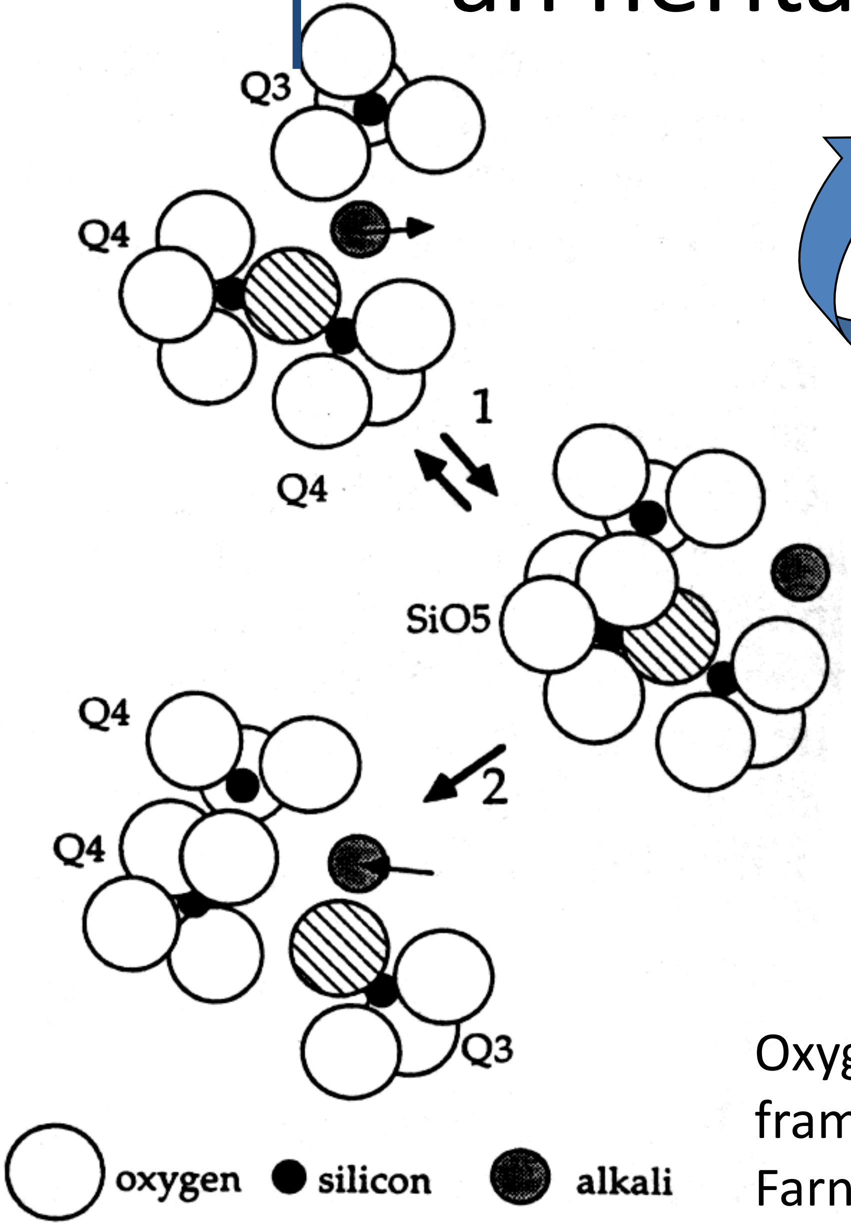
Regular octahedra (Cr^{3+}, Zr^{4+})

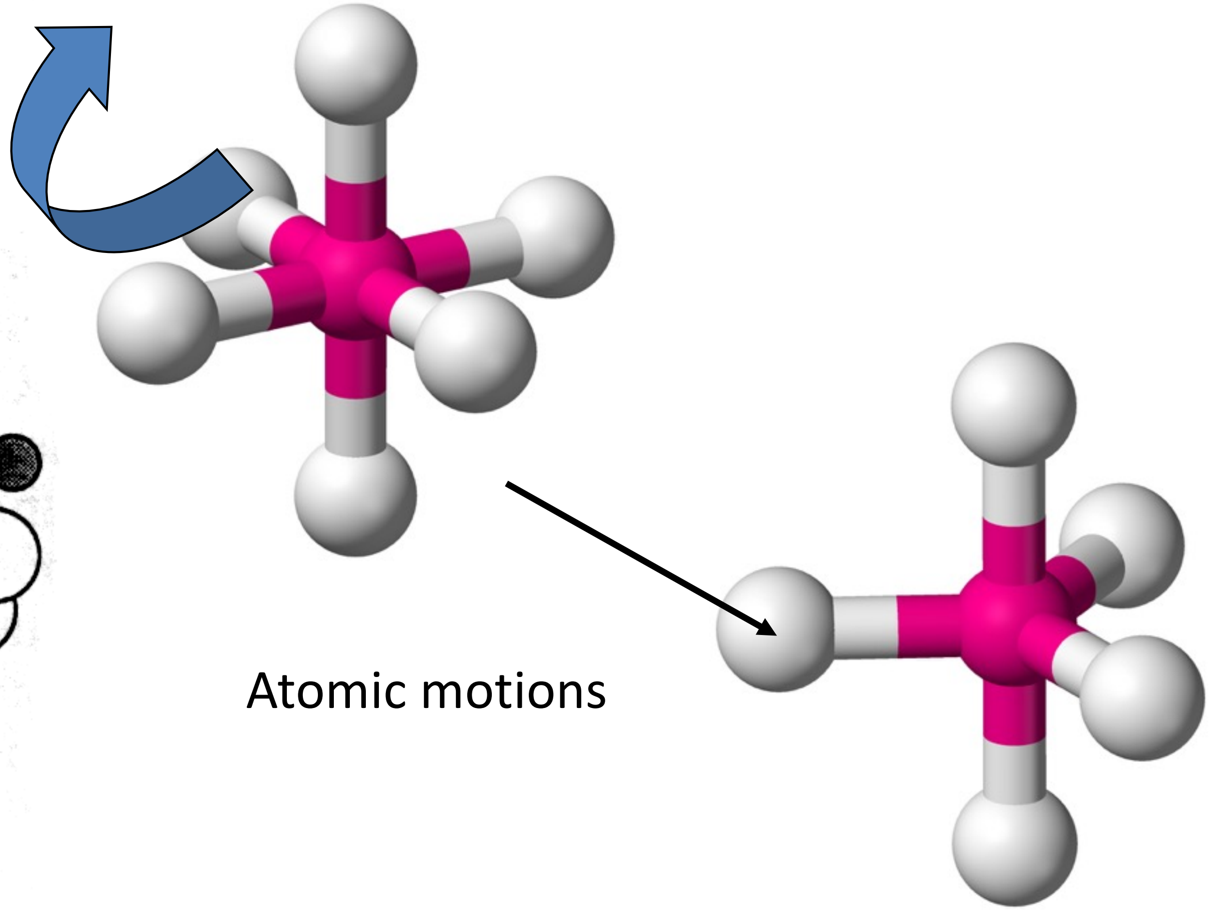


7-coordinated sites (Zr^{4+})

Small coordination number vs. crystals

Exotic coordinations: an heritage of the molten stage?



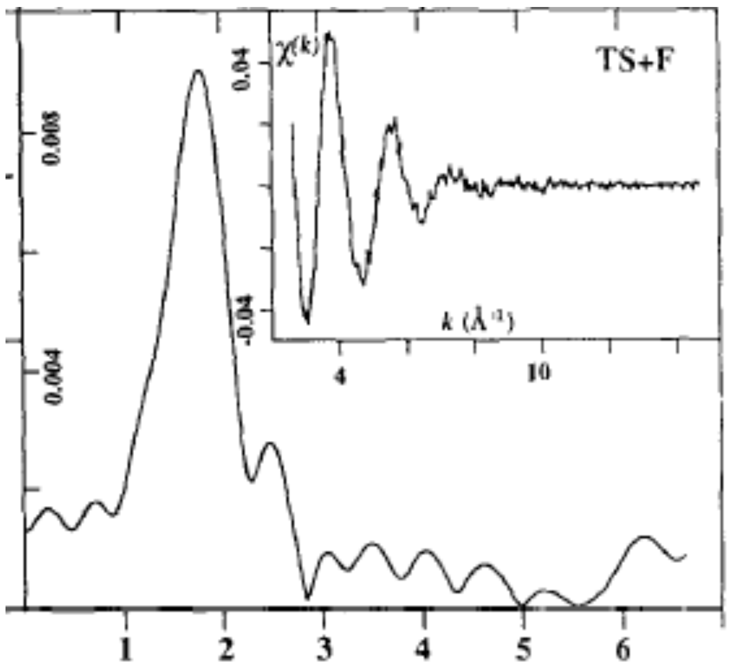


Atomic motions

Oxygen motion in the polymeric framework and viscous flow (after Farnan & Stebbins, 1994)

Uranium speciation in glasses: a peculiar behavior

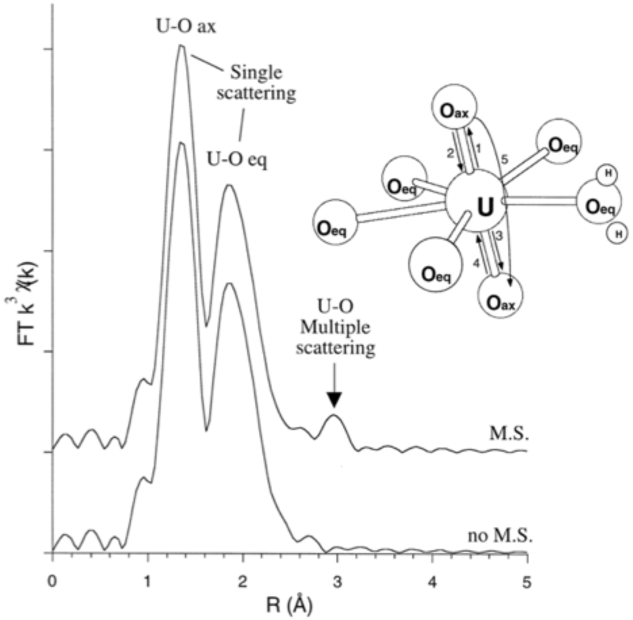
- U(VI) as uranate species: different from the uranyl groups UO_2^{2+}. Explains optical properties (color, luminescence)
- U as uranyl species in gels = speciation change during glass alteration.



Glass

(Petit-Maire et al., 1986)

Gel

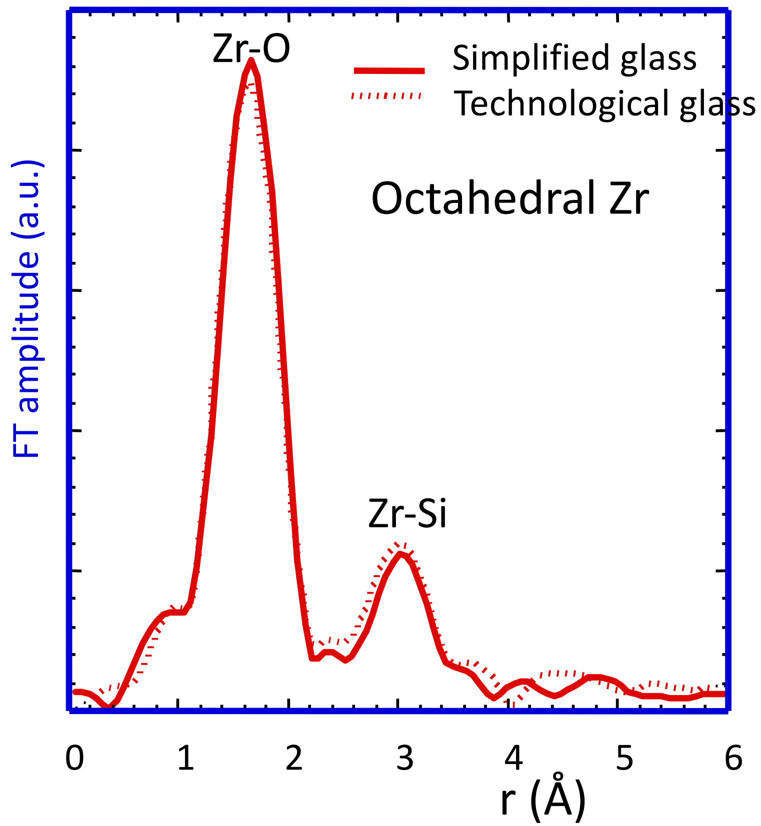


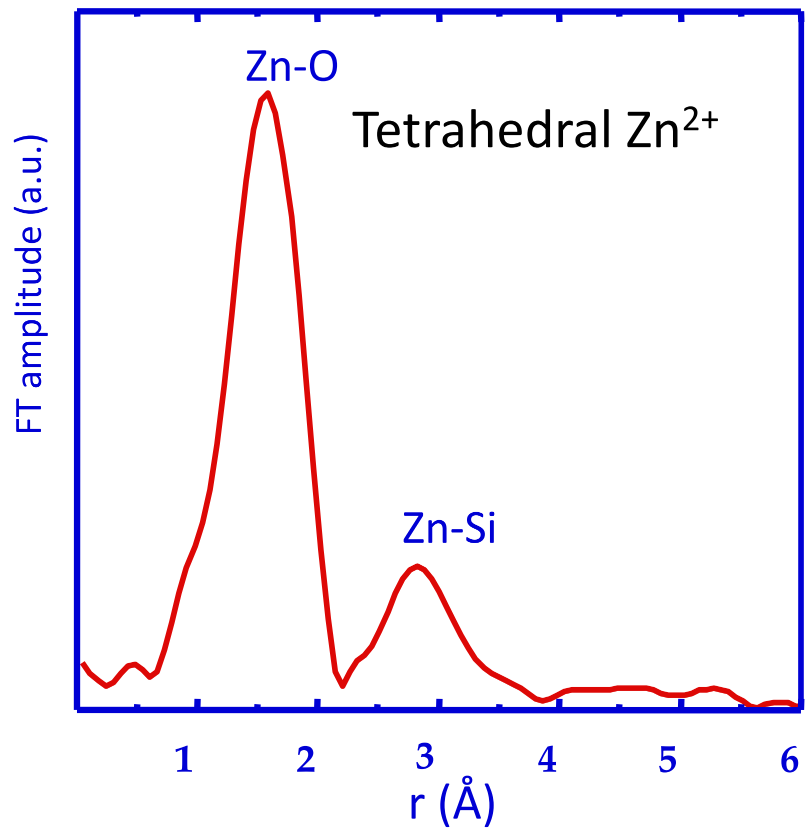
(Jollivet et al., 2002)

4. Beyond the coordination shell

EXAFS: The structural role of transition elements: connection of cations with glass structure?

Radial information: connection with glass framework



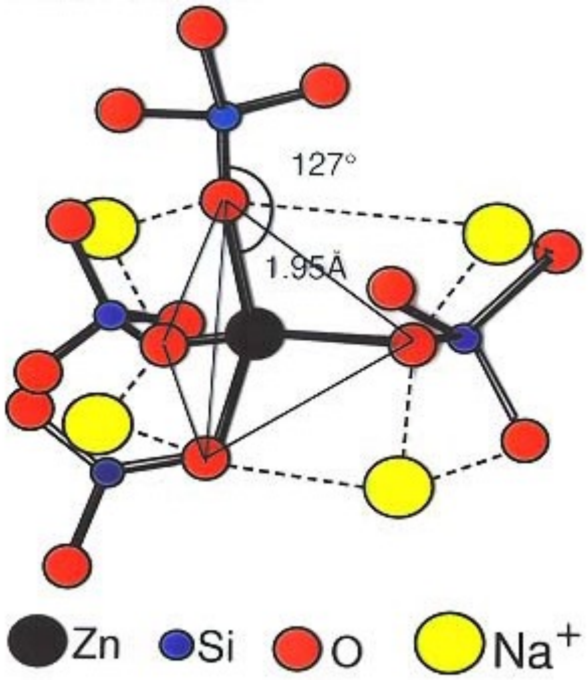


Presence of stable local topologies; importance of radial disorder at larger distances.

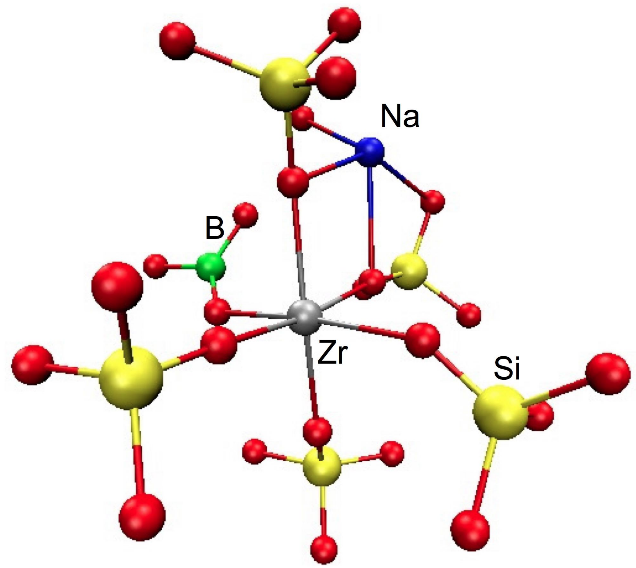
(Galoisy et al., 1999)

(Le Grand et al., 2000)

Cations in glasses: Structural role



Stabilizing role of Zn, Zr,Ti…, provided adequate charge compensation.
Increases mechanical properties and enhancing chemical durability.



Zn^{2+} = Network-forming position

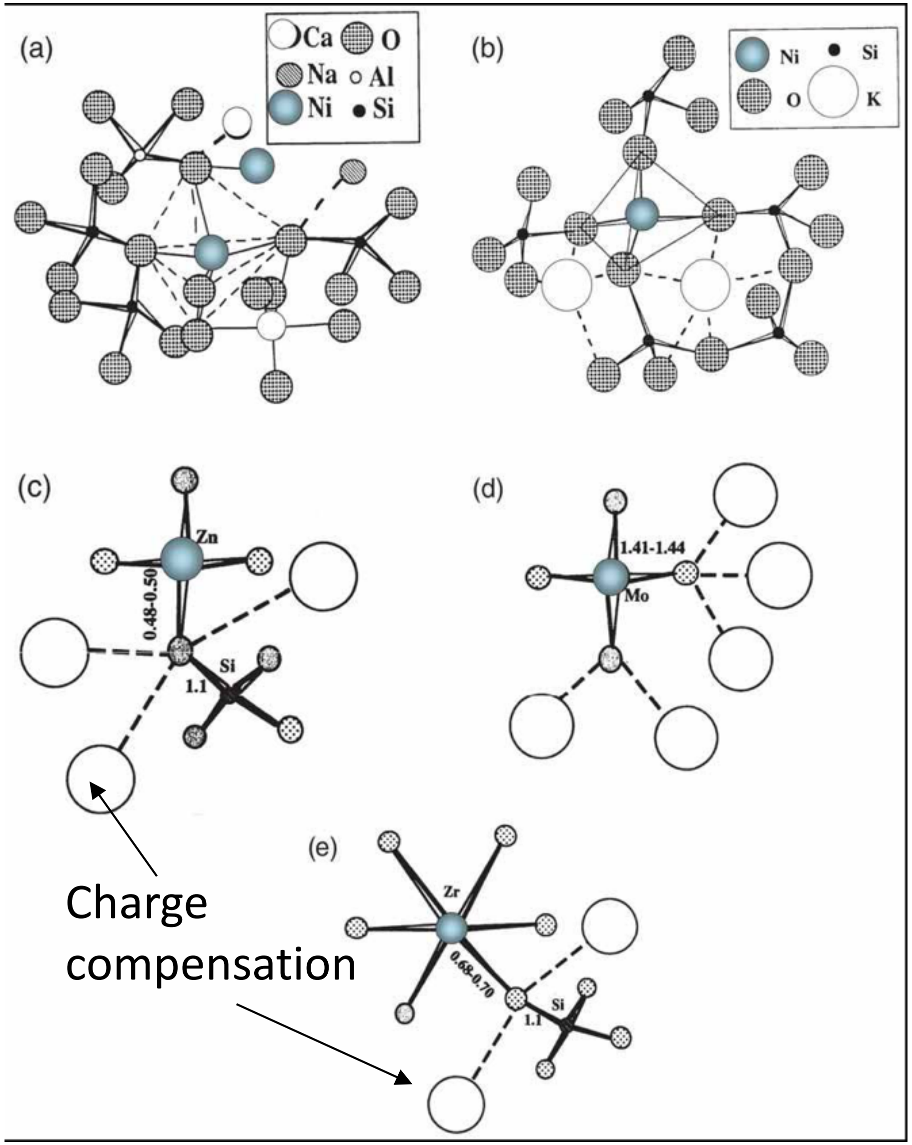
Zr^{4+} = Networking role of Zr^{4+} :

- Na^{+} serves for local charge compensation
- prevents Zr clustering

(Le Grand et al., 2000)

(Ferlat et al., 2006)

Cations in glasses: Structural role



Low coordination numbers: agreement with XANES

Ni: CN=4, 5

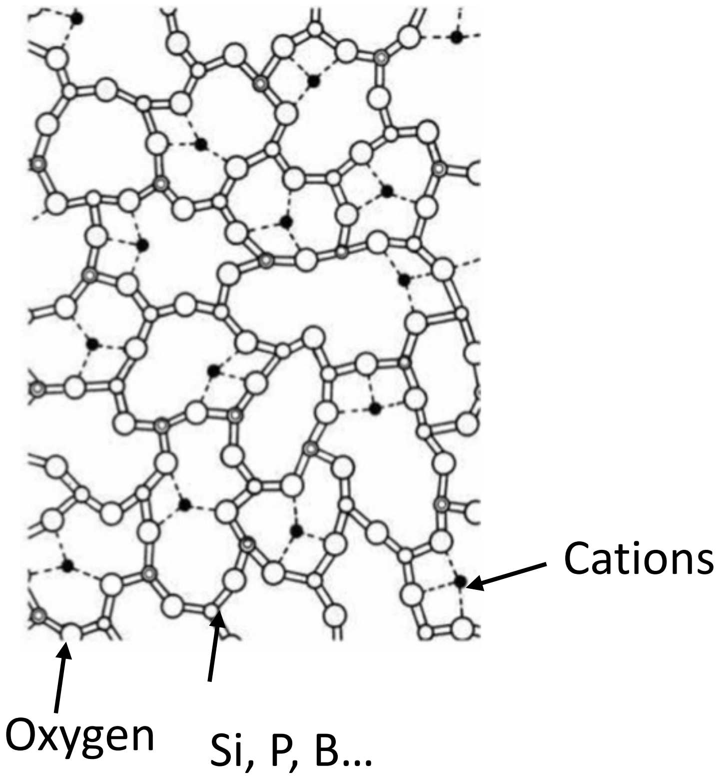
Zn: CN=4

Mo^{VI}: CN=4

Zr: CN=6

(Greaves and Sen, 2007)

Results at variance with earlier speculations



Organization of some order at short range around cations.
Confirms Pauling rules
Incompatible with just filling the holes of a random network

A figure that may get a glass spectroscopist upset …

4. A few examples of applications of EXAFS in glasses

Cations in glasses: competition for charge compensation

Intermediate (network formers/networking) elements in glasses

Al

Zr

Zn

B

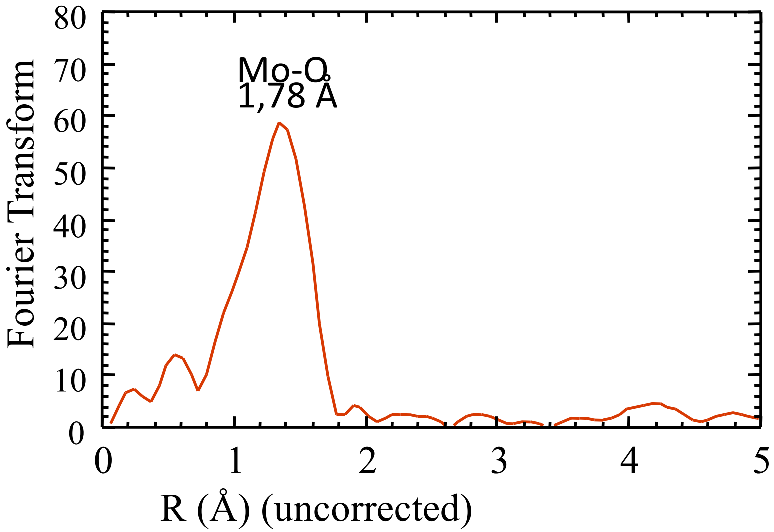
Decreasing priority for charge compensation around intermediate elements

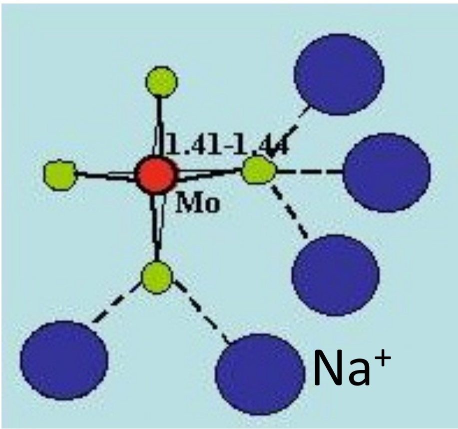
Increasing the concentration of a more competitive intermediate element will force a less competitive cation to change coordination and its influence on glass properties, as

- nucleating or stabilizing role: Zr, Zn, Ti…).
- links with glass stability relative to dissolution

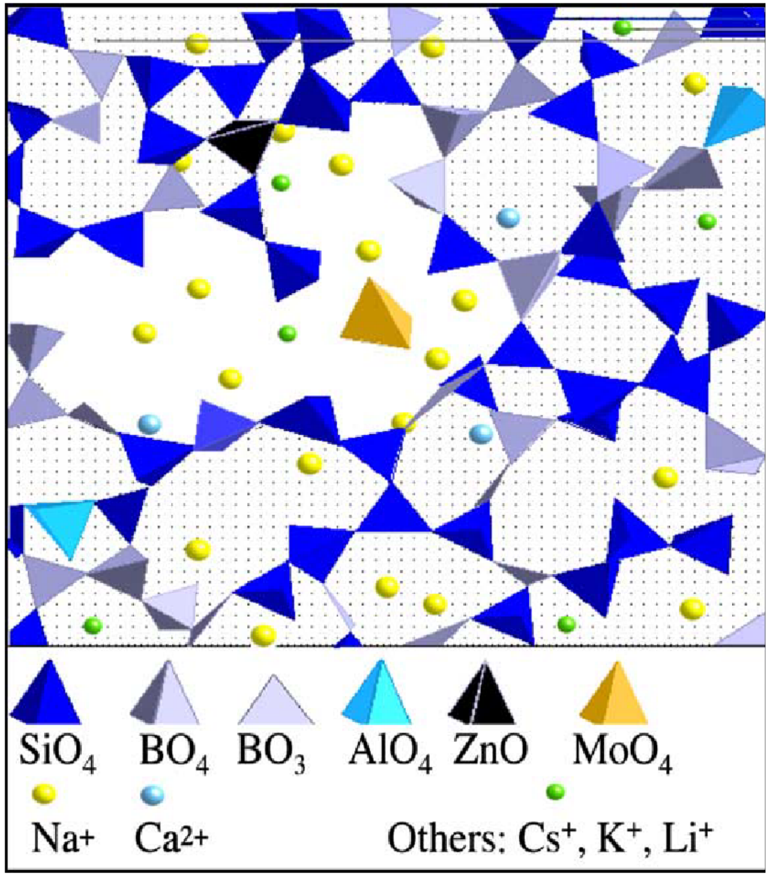
(Cormier et al., 2000)

Cations in glasses: heterogeneous distribution





Molybdate groups non connected to the glassy network.

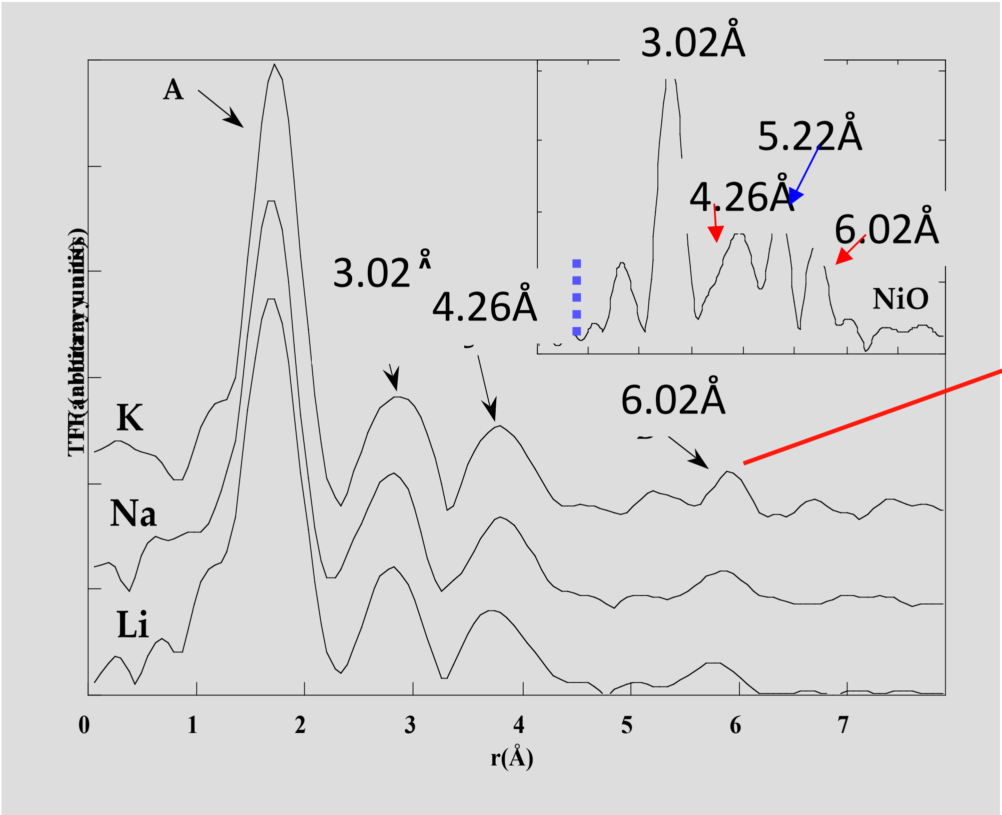


Model of a Na–Ca alumino-borosilicate glass (nuclear glass analog): neutron scattering/calculations on a simplified.

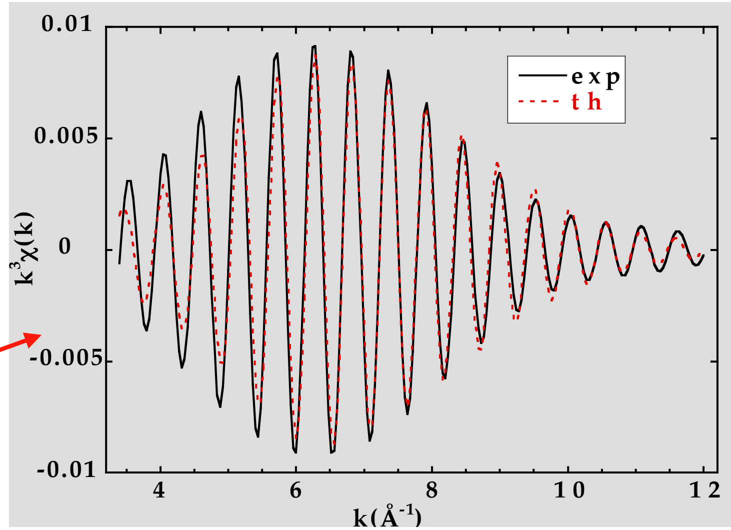
(Calas et al., 2003)

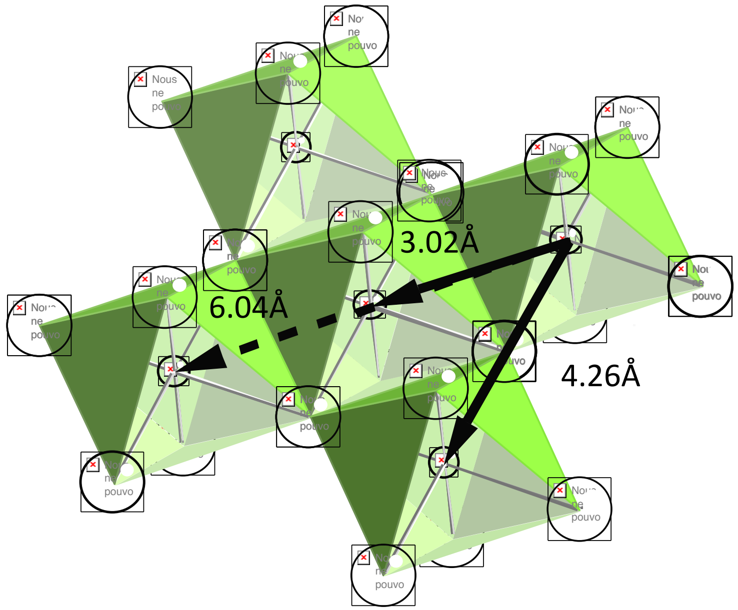
From site connections to clustering

Ni in low-alkali borate glasses



Multiple scattering



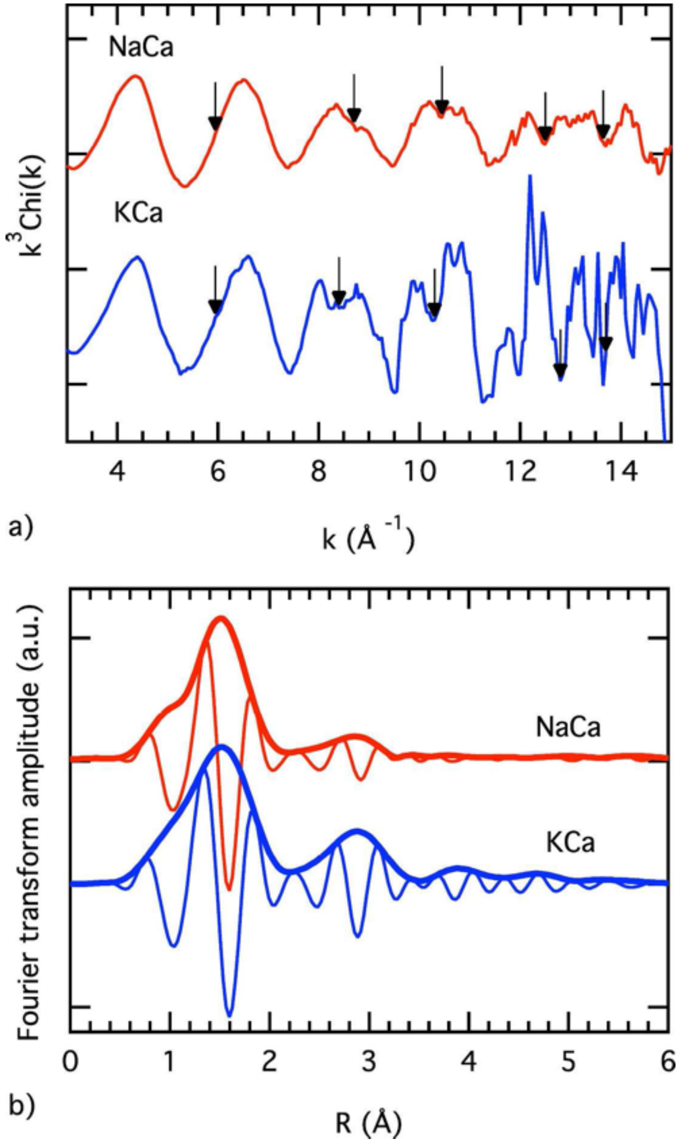


NiO clusters≈ c-NiO but the 5.22Å distance is lacking

Similar behavior for Co and Zn

(Galoisy et al., 2001)

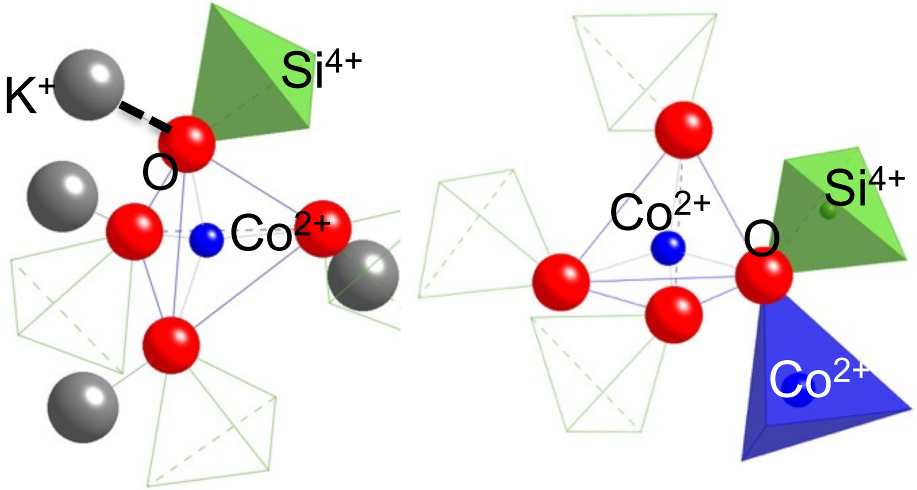
Cobalt in glasses



Proportion of tetrahedral Co^{2+} is larger in the KCa glass than in the NaCa glass. More Si second neighbors in the former.

Two models are possible:

(i) a network-forming position (ii) "tricluster"

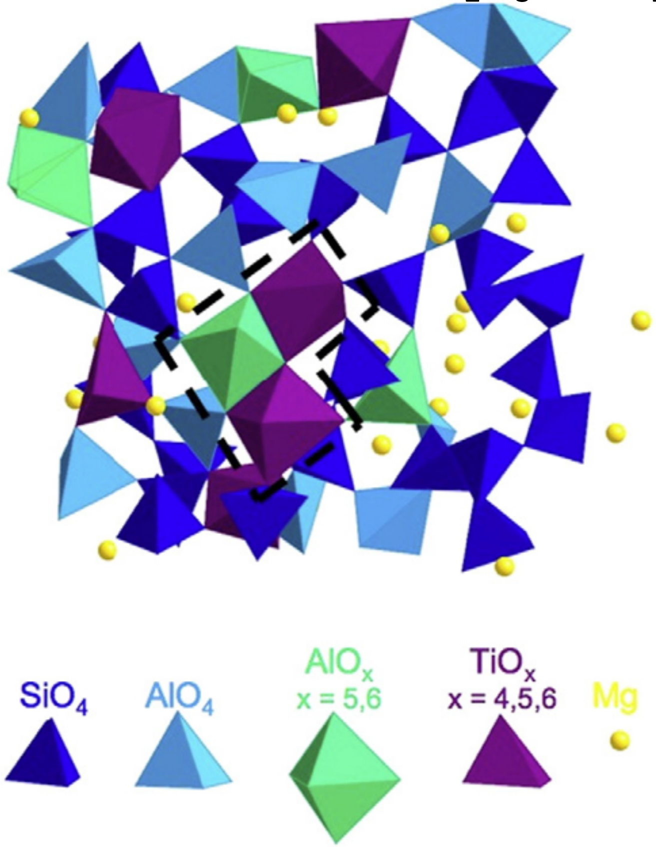


What is a glassy network?

(Hunault et al., 2014)

Glass structures as a nucleating precursor

Ti sites in $2MgO–2Al_2O_3–5SiO_2$ glass

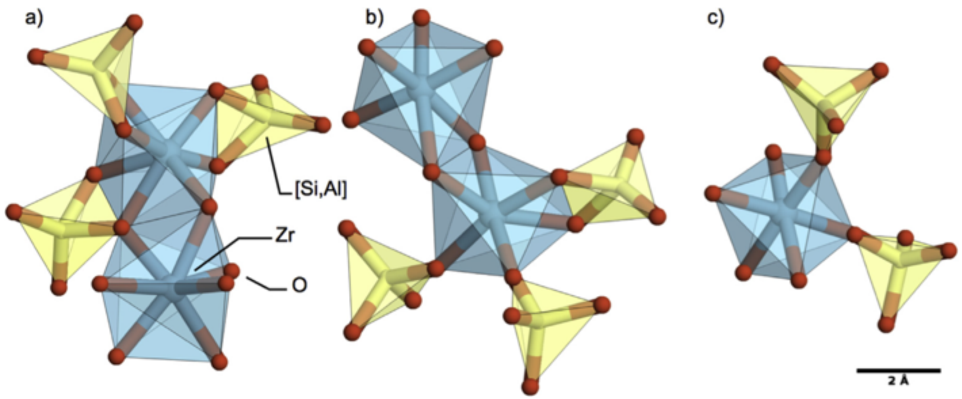


Preferential Ti-Al site linkages in the glass : similar to Al_2TiO_5 phases.

(Guignard et al., 2010)

Zr sites in aluminosilicate glasses:

Mg, Zn, Ca	Li	Na
Nucleation	Nucleation	***No nucleation***



CN7 CN6 CN6

Zr-Zr linkages **No Zr-Zr links**

Importance of the medium range structure to rationalize nucleation properties.

(Cormier et al., 2015)