Actinides in ceramics for NWS:

Combining experiments and Modeling to understand the local structural behavior

Messaoud Harfouche

Outline

- ***Introduction and generalities***
  radioactivity, metamict state and analogue minerals
- ***Structure of analogue minerals***
  collection and characterization of samples
- ***Methods used for these studies***
  experimental (XAS) and Theoretical (MD)
- ***XAS and MD Results***
  Zircon, Titanite, zirconolite and Monazite
- ***Conclusions***

Introduction and generalities

- ➲ **What is the goal?**

  Confinement matrix for HALL nuclear waste

🗁 Radioactivity and radiation damage

- 🗎 radiations α, β et γ
- 🗎 Phase transition (crystalline ⇒ amorphous)
- 🗎 So called metamict minerals

- ➲ **Analogue minerals**

- ➲ **Selection & characterization of samples**

  Zircon, Titanite Zirconolite and Monazite

Introduction

- ☐ **Over geological period of times (10^9 years), actinide bearing accessory minerals can become amorphous to x-ray.**

Amorphous = Metamict

- ☐ **Metamict minerals are natural minerals that have undergone sever radiation damage as a result of α-decay of the U and Th replacing major cations (Zr, Ca, REE …) in the original structure.**

Introduction

Zircon ……. ($ZrSiO_4$),
Monazite .. (~ $CePO_4$)
Zirconolite ($CaZrTiO_7$)
Titanite ….. ($CaTiSiO_5$)

Considered as:
natural analogues of ceramics for nuclear waste forms (Weber, 1990).

- ☐ Several samples were selected to show highly damaged structures.
- ☐ Samples were characterized using
  - ➢ Electronic microprobe
  - ➢ XRD analysis.
  - ➢ TEM

Introduction

☐ Two methods were used to investigate the behavior of natural analogues:

1. X-ray Absorption Spectroscopy (XAS) → Synchrotron
   - *XANES and EXAFS*
2. Molecular Dynamics Simulation (MD) → HPC system

Investigates:

Major elements (Zr, P, Si ….)

to validate the metamict structure(s) obtained by MD

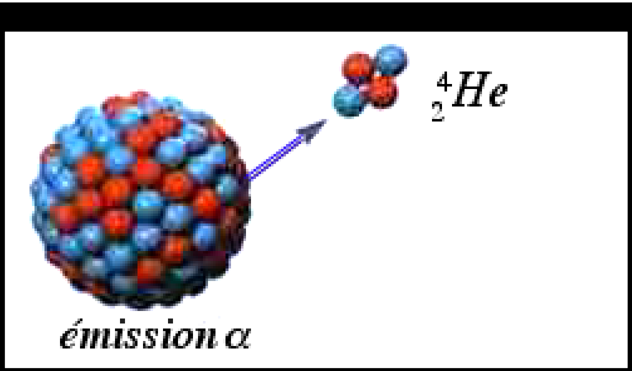
Substituted actinides (Th and U)

to understand the influence of radiation damage

Why using natural analogues ?

Ceramics	**Analogues**
High activity	Low activity
Medium period (1000 y)	Long period (billion y)
Need special environment	Easy to handle
Risk of contamination	No risk of contamination
Red experiment	Green experiment

How radiation affects the structure?

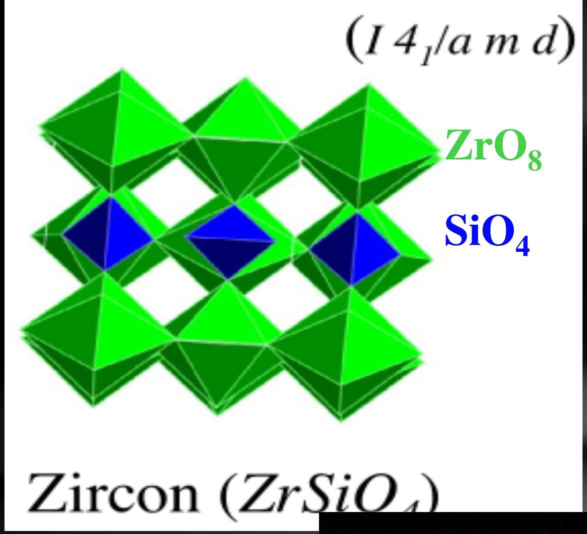


$$ {}^{A}_{Z}X \longrightarrow {}^{4}_{2}He + {}^{A-4}_{Z-2}Y $$

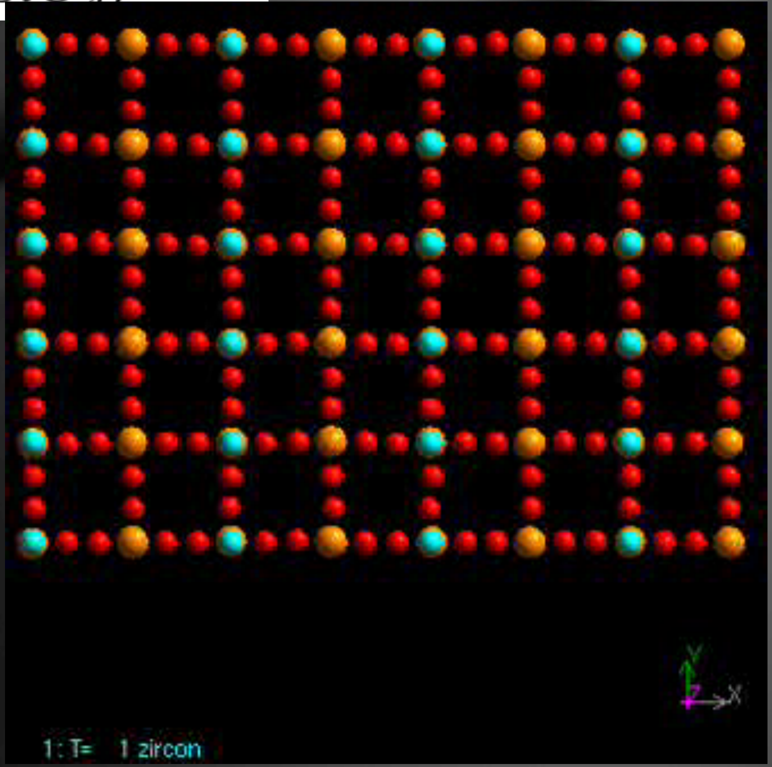
α-decay generates

E_α =~4.5MeV

E_r = ~75 keV



Simulation by:
Kostoya Trachinco



Samples

Samples Collection

Zircon

Name	Origin	Color	Age [10^9 years]	Dose α [10^{16} α/mg]
Mud Tank	Australia	Marron	*	*
Naegy	Japan	Vert - Gris	0,125	2,0[a]
Ampagabe	Madagascar	Marron	0,5 - 1,65	3,0[a]
Hittero	Norway	Blanc	0,9 – 1,64	2,0[a]
Kinkel's Quary	USA	Marron – Noir	0,3 –0,35	6,0[a]
Diamantina	Brazil	Marron		
Ural	Sri-Lanka[b]	Vert-Marron	0,32-0,42	0,2[a]
200-300	Sri-Lanka	Vert	0,32-0,42	1,3
250-350	Sri-Lanka	Vert	0,32-0,42	2,2
300-700	Sri-Lanka	Vert	0,32-0,42	1,5
Beers Kimberly	South Africa	Marron-Gris	*	*
Marasoly	Madagascar	Noir-Marron	0,5-1,65	2,0
Turvallah	KSA	Marron-Noir	*	*
Tété	Mozambique	Marron-Gris	0,5-0,6	0,6

[a] (Farges et al. 1991).

Samples Collection

Monazite

Name	Origin	Color	Age [10^9years]	Dose a [10^{16}a/mg]
FG	Madagascar	*	0,45-0,60	0,6
Governador	Brazil	Vert-Marron	0,45-0,52	0,5
Herfoss	Norway	Marron	1,0-1,02	0,9
Madiaombé	Madagascar	Marron	0,65-0,80	0,31
Marijao	Madagascar	Gris-Marron-Vert	0,35-0,45	0,35
MOAC	Brazil	*	0,41-0,49	0,4

Sources: J-M Montel (Univ. Toulouse),
J-M Le Cleac'h, Ecole Nat. Sup. Mines (Paris).

Samples Collection

Titanite & Zirconolite

Nom	Origine	Color	Age $[10^9$years$]$	Dose α $[10^{16}\alpha/mg]$
Titanite				
Bevia	Madagascar	Gris-Blanc	0,50 - 1,00	0,2
Localité inconnue	Madagascar	Vert-Marron	0,50 – 1,00	0,2
Ontario	Canada	Marron	2,60 -2,67	0,1
Capilinha	Brazil	Vert	2,68- 2,74	0,1
Zirconolite				
Palabora	South Africa	Noir	0,18-0,23	0,8
Localité inconnue	Sri-Lanka	Marron	0,32-0,42	0,9

Geological Age and Dose

Age:

$$t = T\,\frac{\ln\left(1+\frac{N_D}{N}\right)}{ln2}$$

t: Geological age
T: Half life time of the isotope
N_D: Number of dissociated atoms
N: Number of non dissociated atoms

DOSE:

$$D = 8N_{238}\left[e^{t/\tau_{238}-1}\right] + 6N_{232}\left[e^{t/\tau_{232}-1}\right]$$

D : Received dose by the sample
t : Geological age

t_{238} et t_{232} : Half-life time of ^{238}U and ^{232}Threspectively
N_{238} et N_{232} : Number of atoms per mg of ^{238}U et ^{232}Th

Minerals investigated and their structures

Structure of the minerals

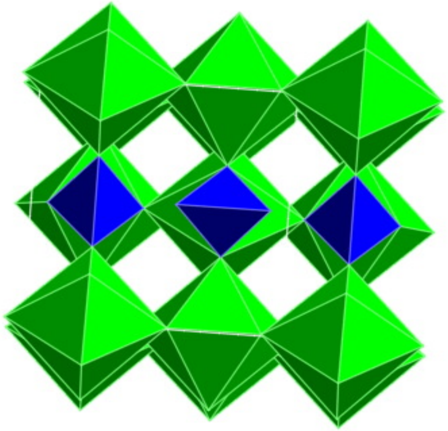
Zircon

Highly symmetric

Structure: Tetragonal

Dodecahedron (ZrO_8)$(I\ 4_1/a\ m\ d)$

Tetrahedron



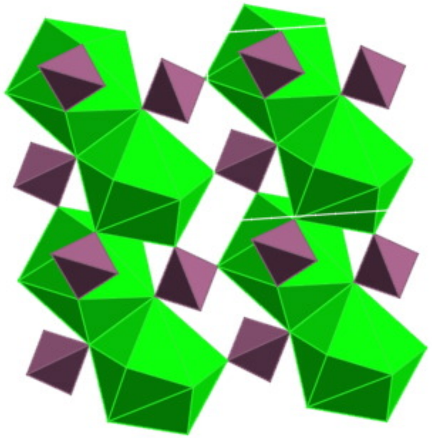
Zircon ($ZrSiO_4$)

Structure of the minerals

Monazite

Structure: **Monoclinic**

$P\,2_1/n$



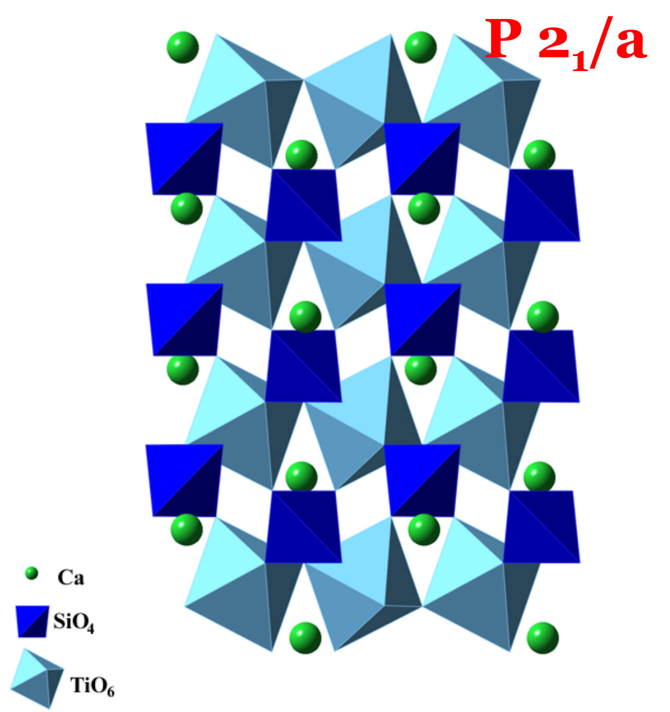
Monazite structure

(REE, PO_4)

Structure of the minerals

Titanite

Structure: Monoclinic

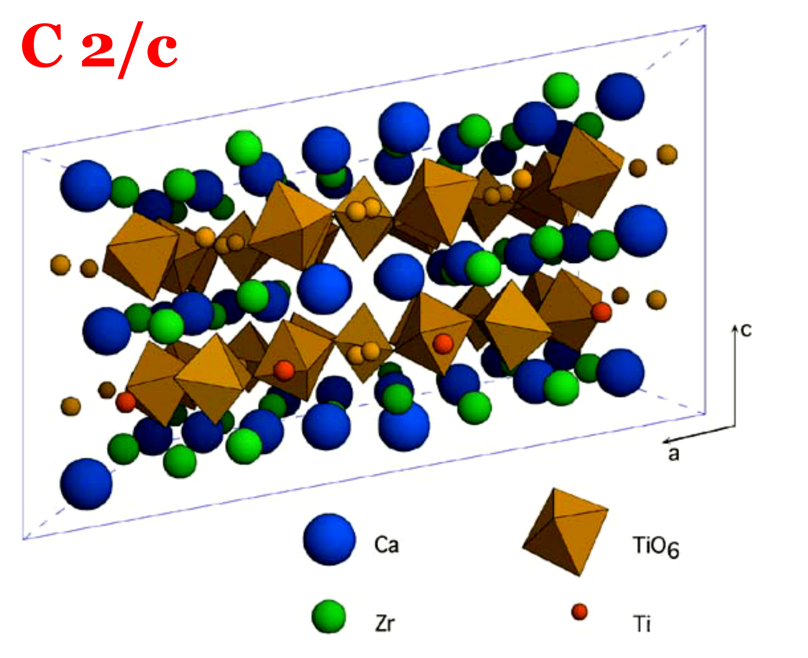


Titanite ($CaTiSiO_5$)

Structure of the minerals

Zirconolite

Structure: Monoclinic

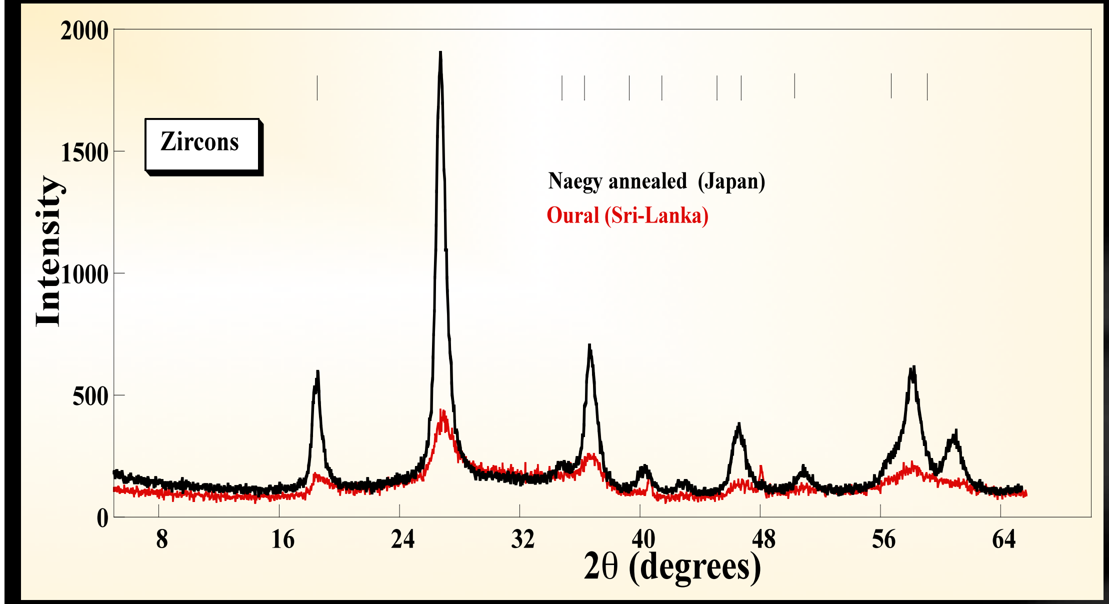


Zirconolite ($CaZrTi_2O_7$)

Samples Characterization

Sample characterization XRD

Zircon

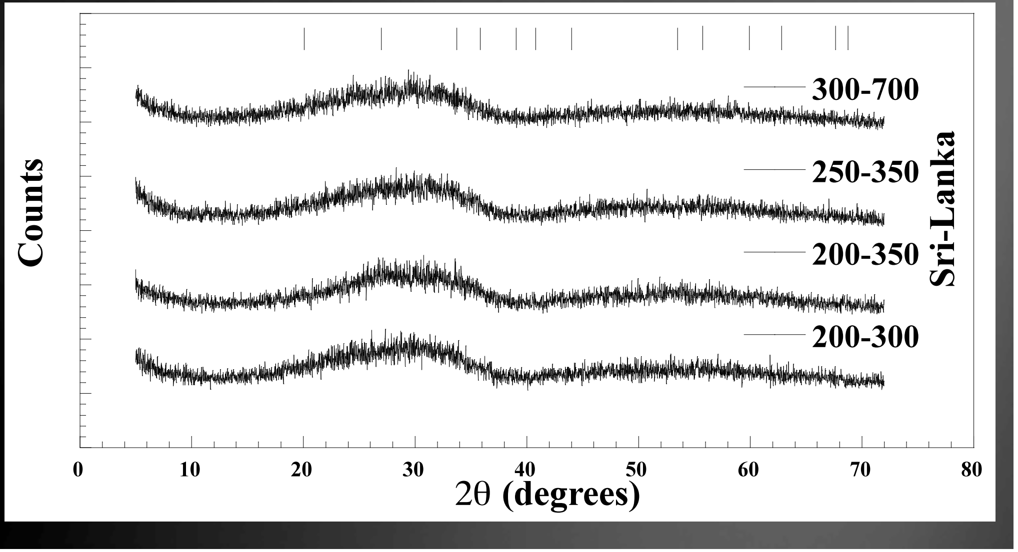


Crystalline &
Semi-crystalline

structure

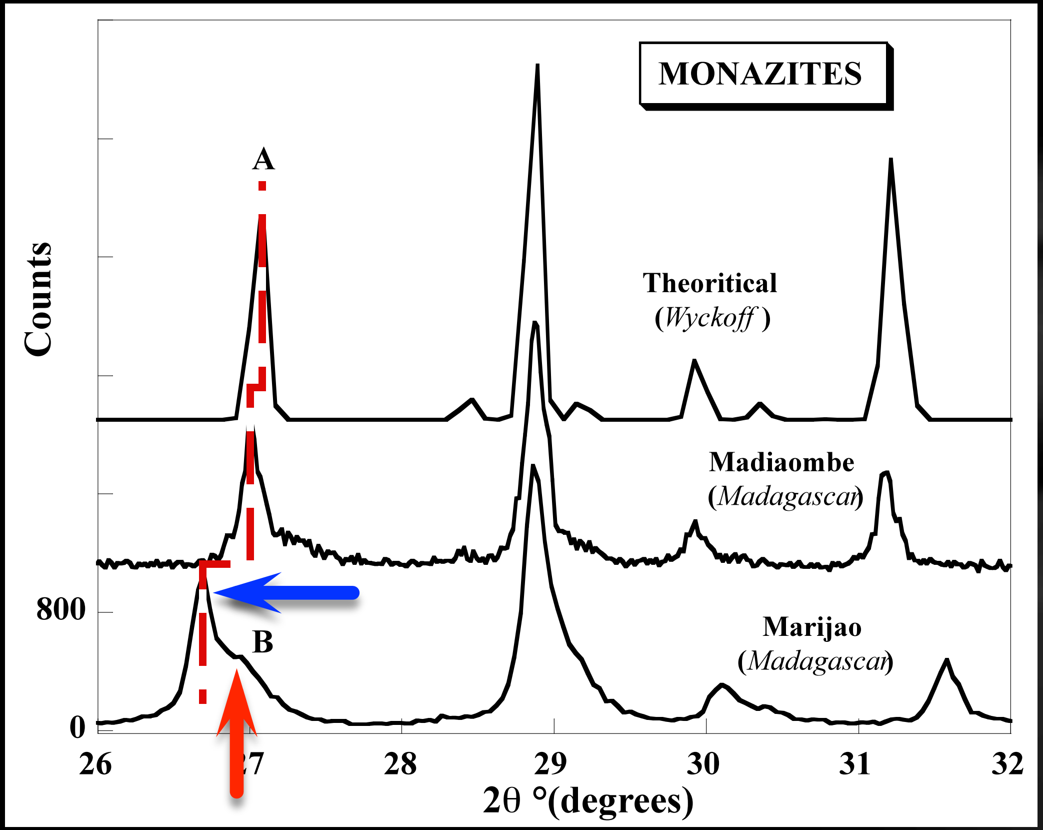
Metamict Zircons

Amorphous to x-rays



Sample characterization XRD

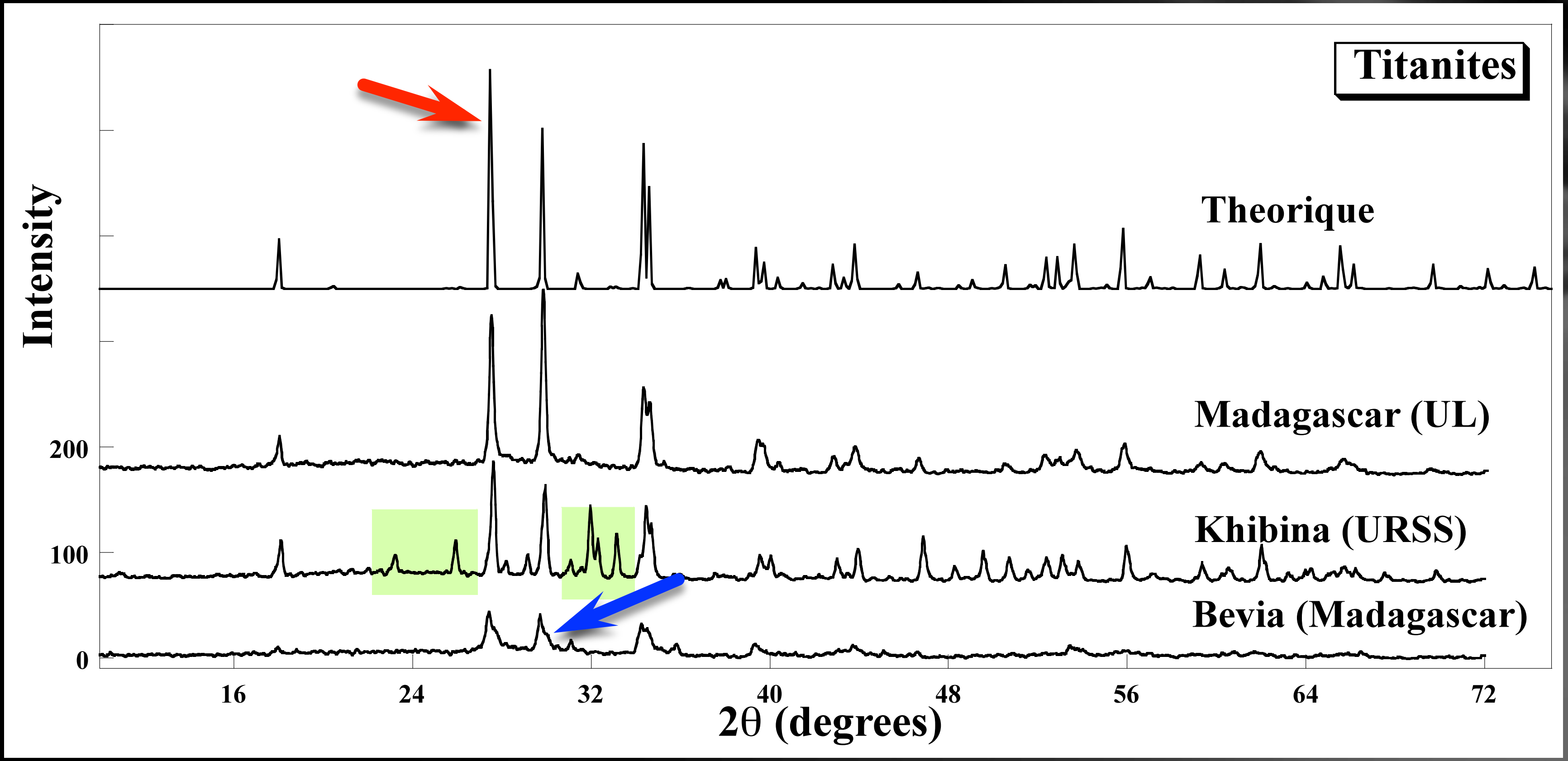
Monazite



- ✓ A shift to smaller 2θ
- ✓ B newly formed

Sample characterization XRD

Titanite



Crystalline

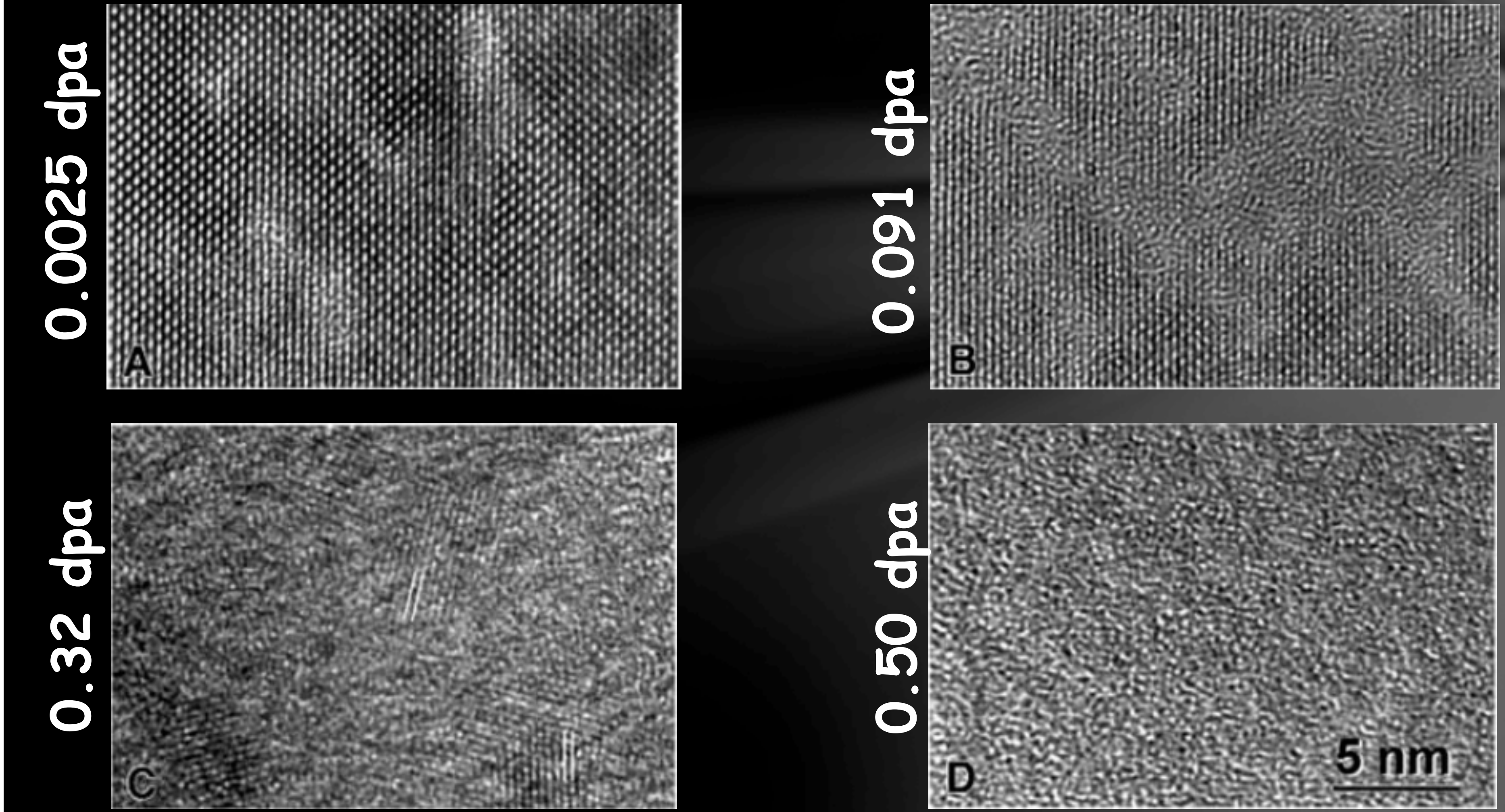
- Sharp Peaks
- High Intensity

Metamict

- Wide Peaks
- Low Intensity

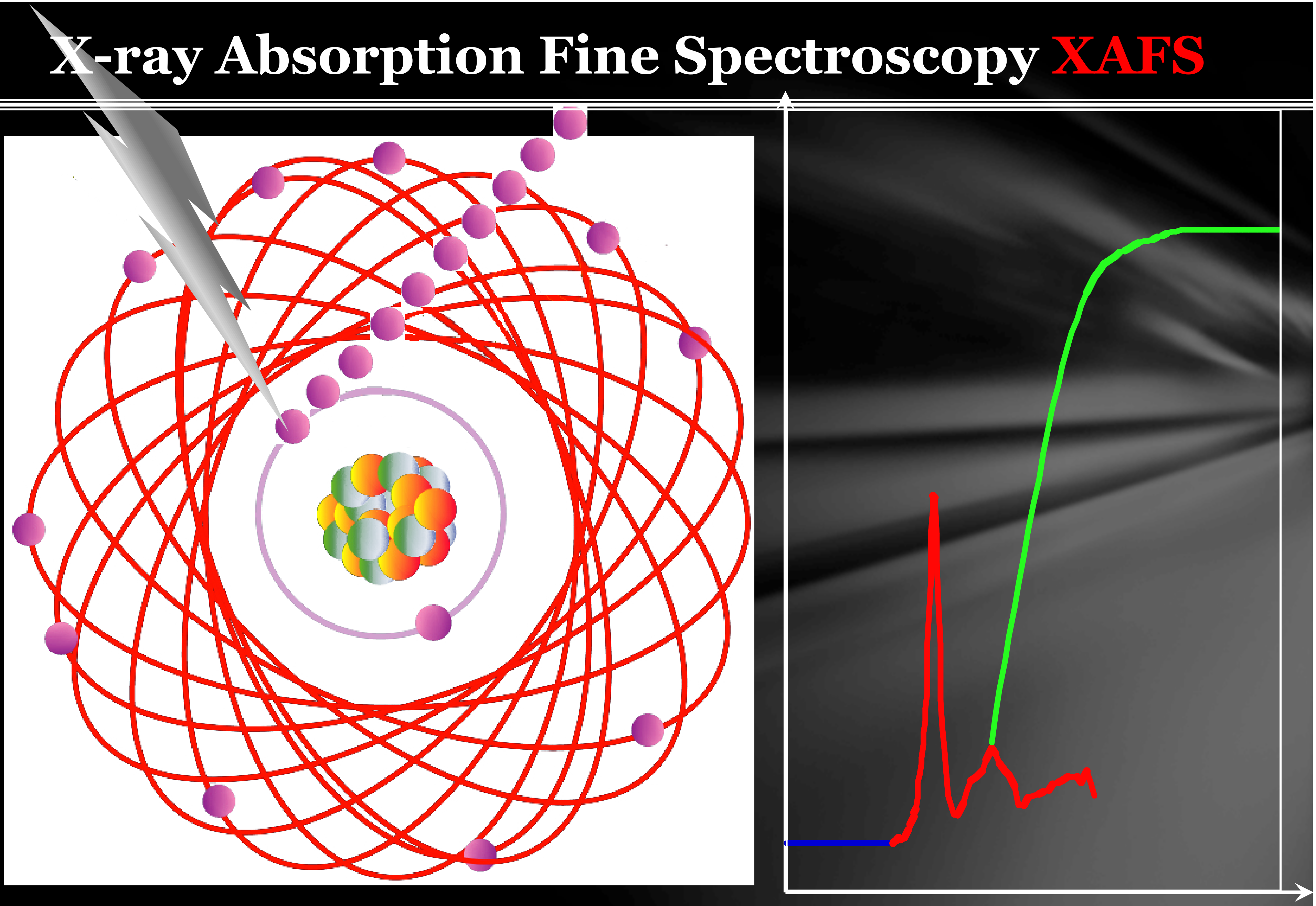
Sample characterization HRTEM

HRTEM micrographs of self-radiation damage in natural Zircons showing increased degree of amorphization with increasing dose *[Weber et al. (1994) Journal of Material Research, Vol. 9, Fig. 2, p. 690]*

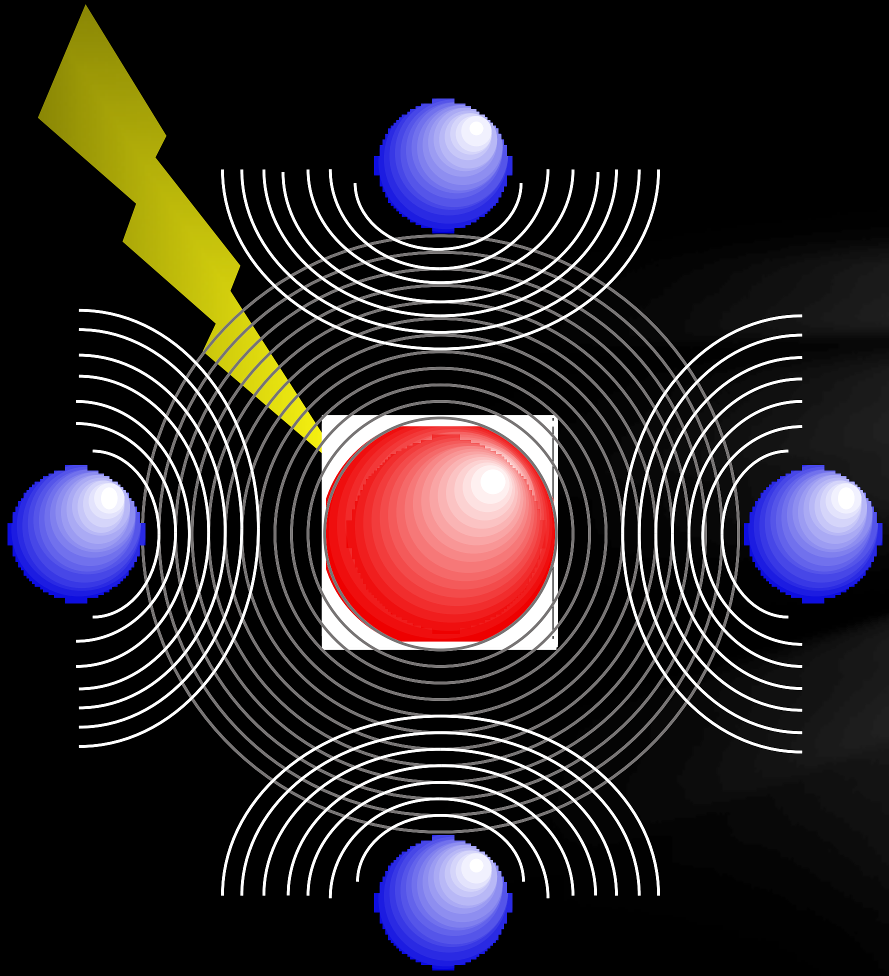


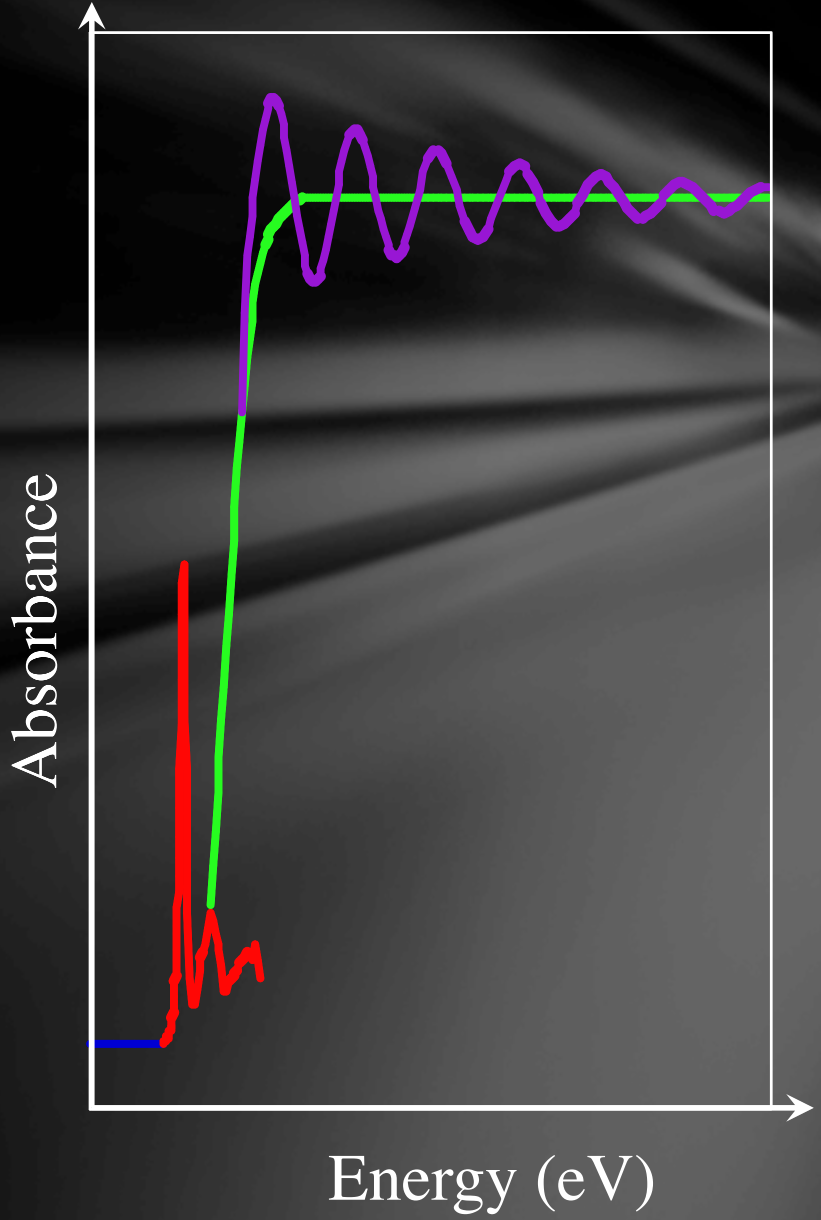
Techniques of Analyses

X-ray Absorption Fine Spectroscopy XAFS

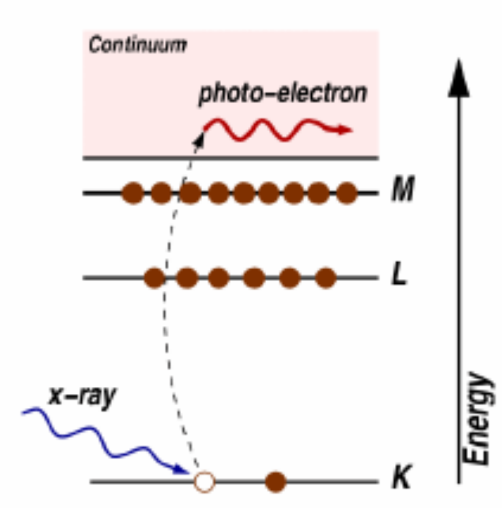


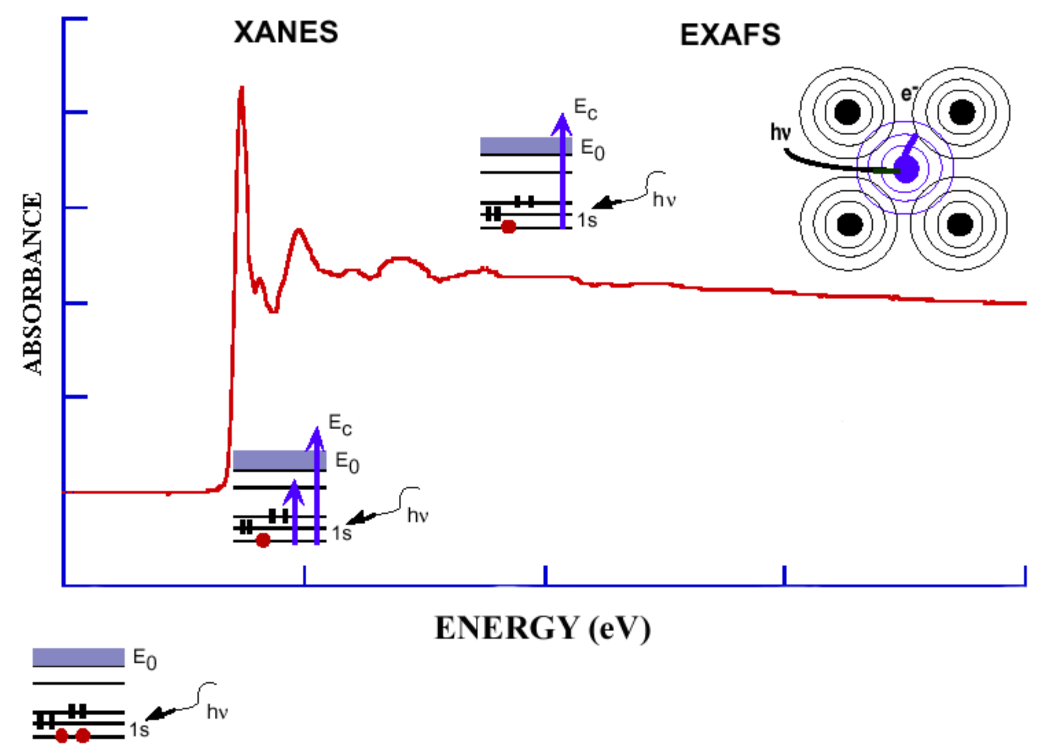
X-ray Absorption Fine Spectroscopy XAFS





Extend X-ray Absorption Fine Structure **EXAFS**





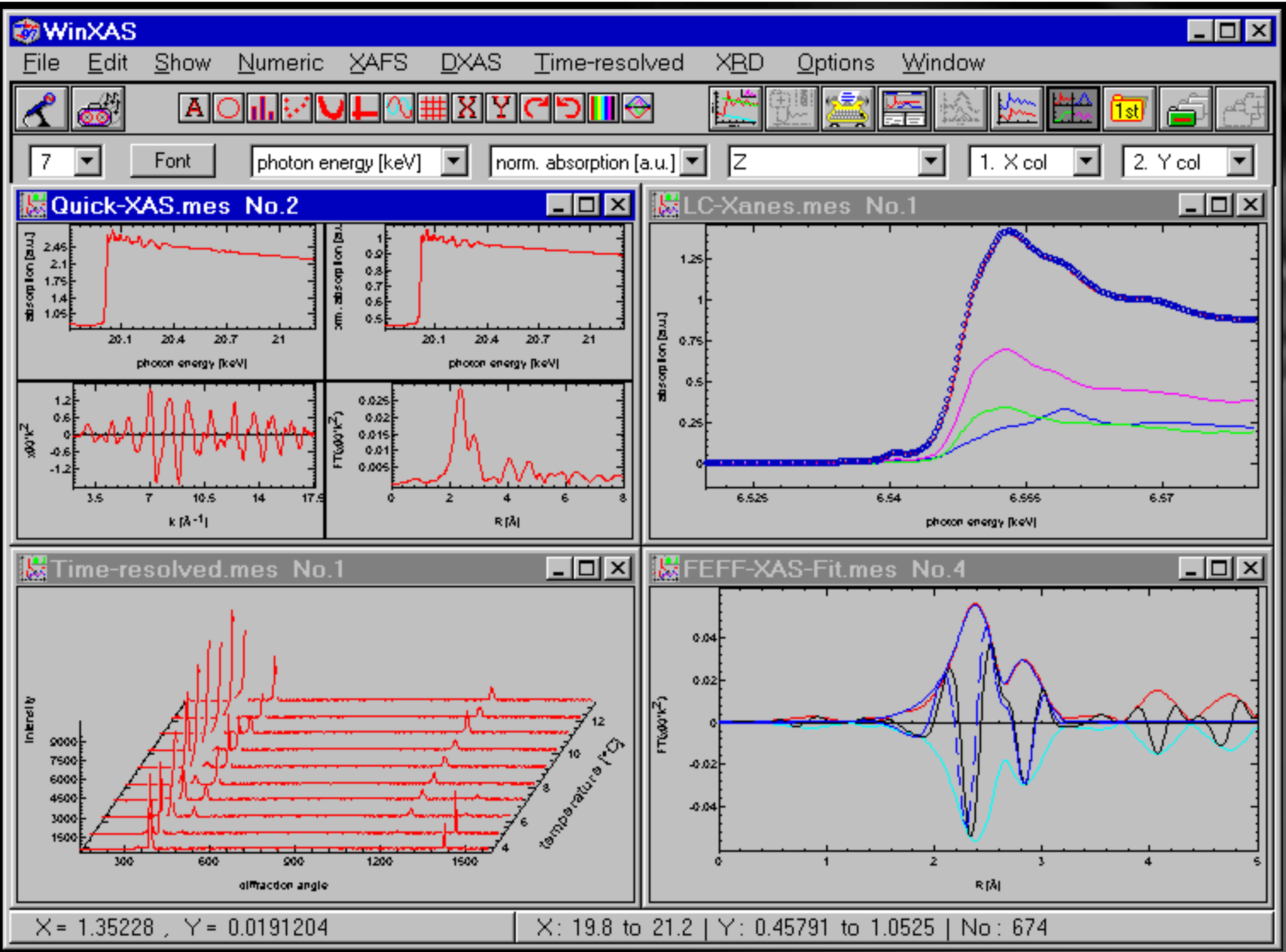
$$I_t = I_0 e^{-\mu(E)} and I_f = I_0 \cdot \mu(E)$$

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E)}$$

$$k \quad \sqrt{\frac{2m}{\hbar}(E \quad E_0)}$$

$$\chi(k) = \sum_j \left[S_0^2 R_f |F_{cw}|\right] \frac{N_j}{kR_j^2} e^{-2\left(\frac{R_j}{\lambda} + k^2 \sigma_j^2\right)} \sin\left(2kR_j + \sum \phi_j(k)\right)$$

XAFS Data Processing and Analysis



7 | photon energy [keV] | norm. absorption [a.u.] | Z | 1. X col | 2. Y col

X = 1.35228 , Y = 0.0191204 | X: 19.8 to 21.2 | Y: 0.45791 to 1.0525 | No : 674

Molecular Dynamic Simulation *(MD)*

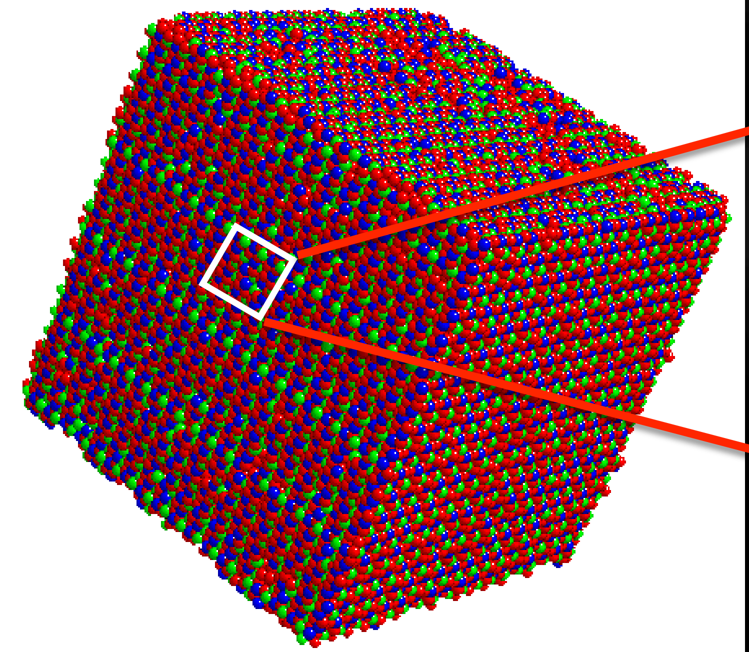
🗁 Modeling of zircon structure:

J-P Crocombette, CEA, France

- 140.000 atoms
- 3 models:

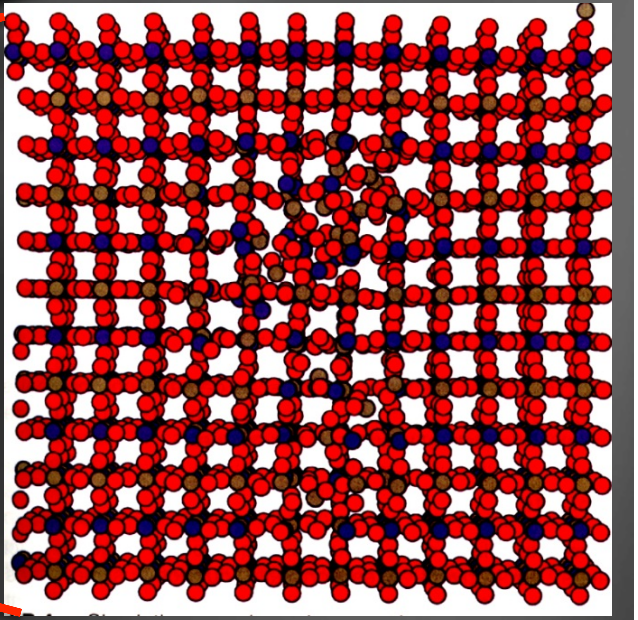
	U/Zr:
✵ 1 atom Zr => U	< 0.01 %
✵ 1000 Zr => U	4 %
✵ 3000 Zr => U	12 %

- Validation :
  - ✵ CN, Polymerization, BV
- Simulation :
  - ✵ ab-initio XAFS Calculation

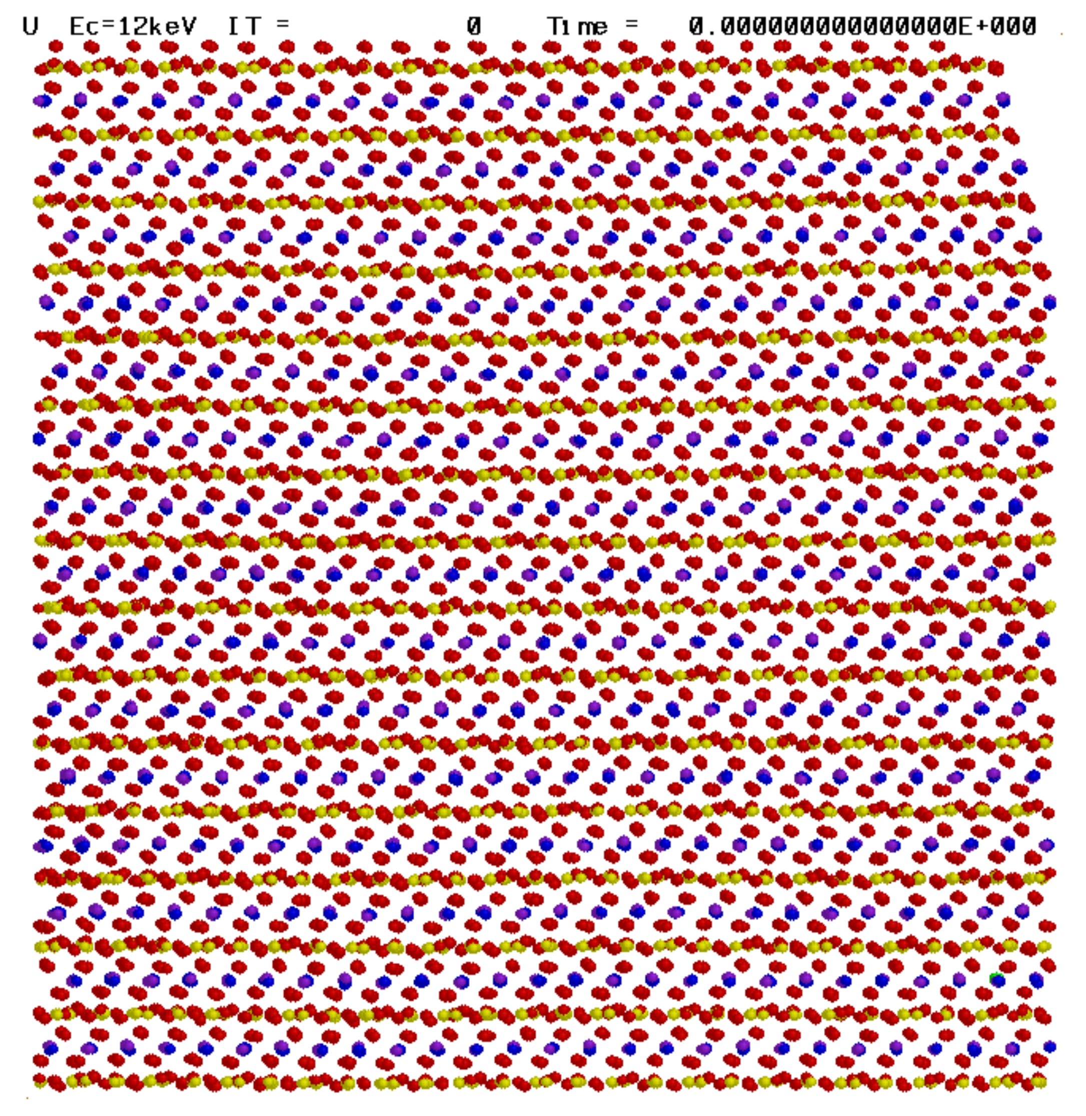


Cascades :

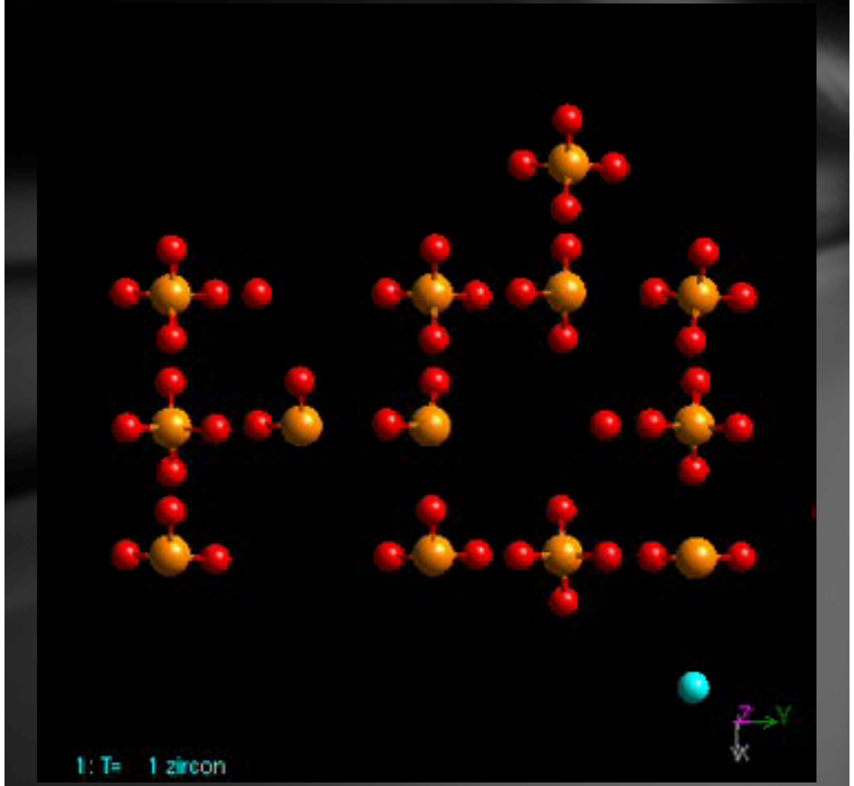
4 et 5 keV



Molecular Dynamic Simulation *(MD)*



Simulating the effect of 12 keV cascade on pure crystalline zircon structure



Zoom to the Si polyhedron

Validating
DM models

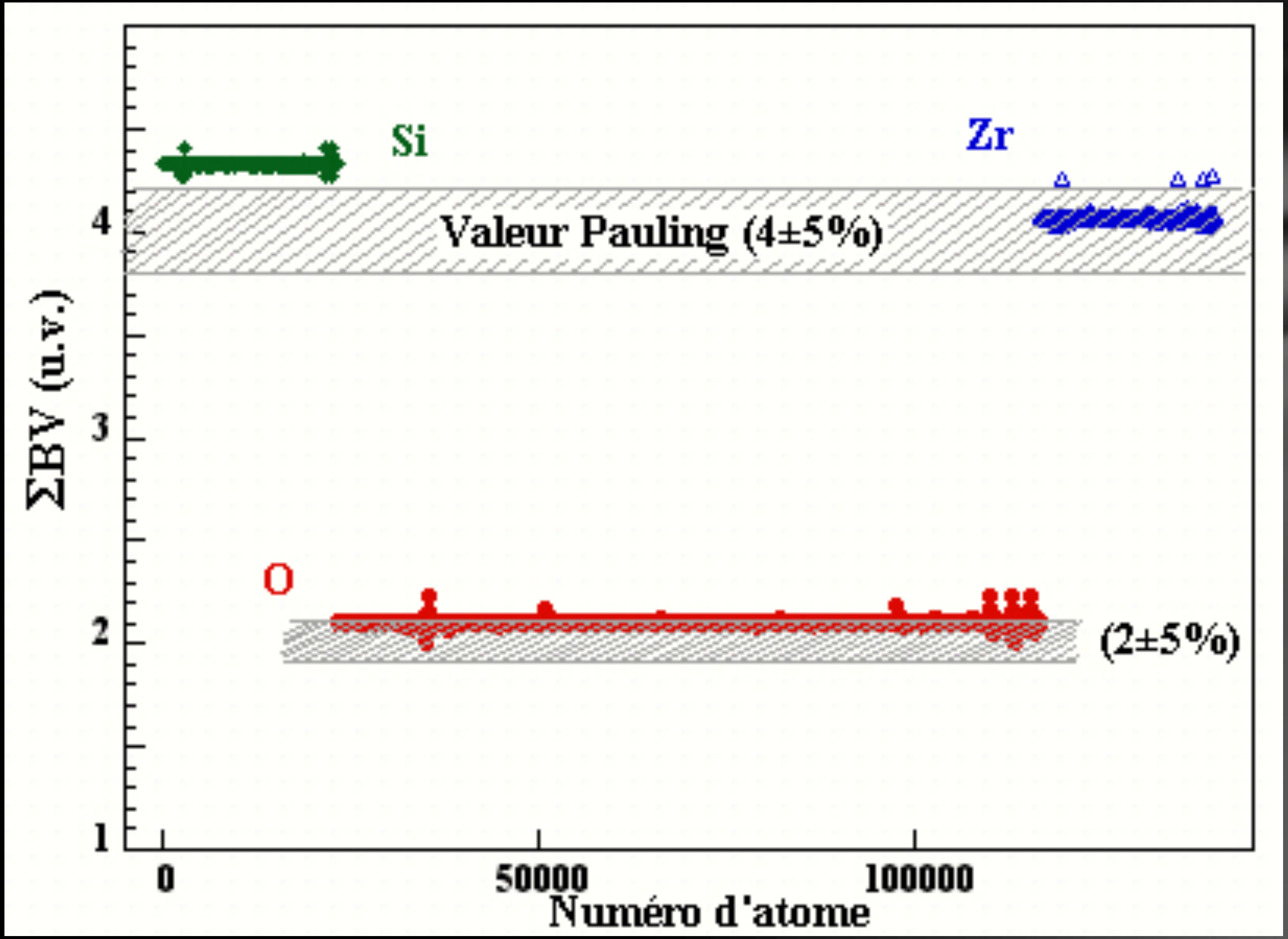
MD -validation-

$$BV \quad \exp \frac{R_0 \quad R}{0.37}$$

Brown et Altermatt (1985)

$$\sum BV = |Z|$$

Pauling (1929)

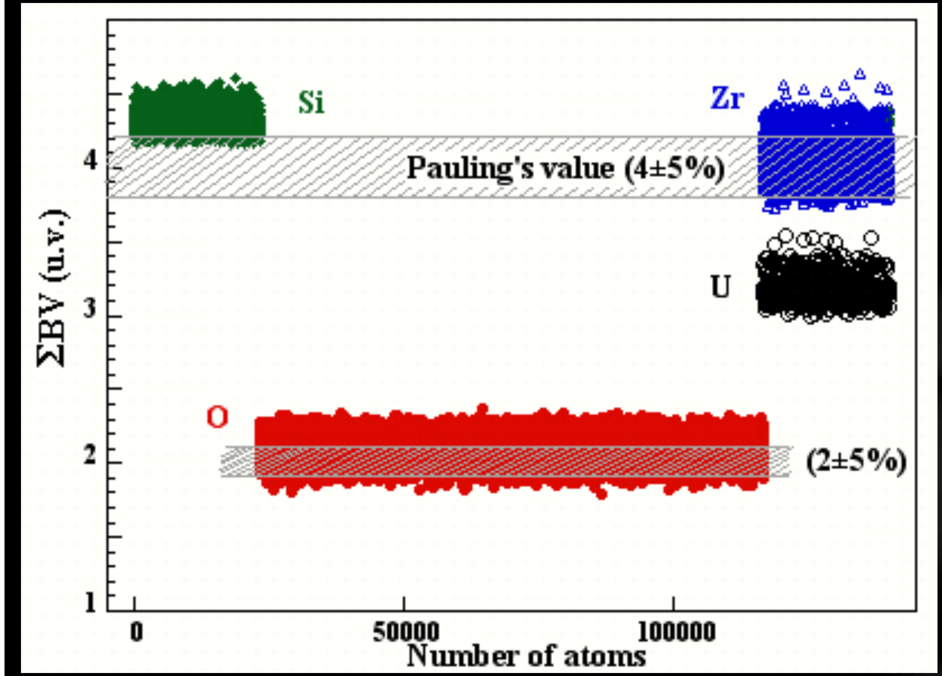


Almost pur zircon (1 U)

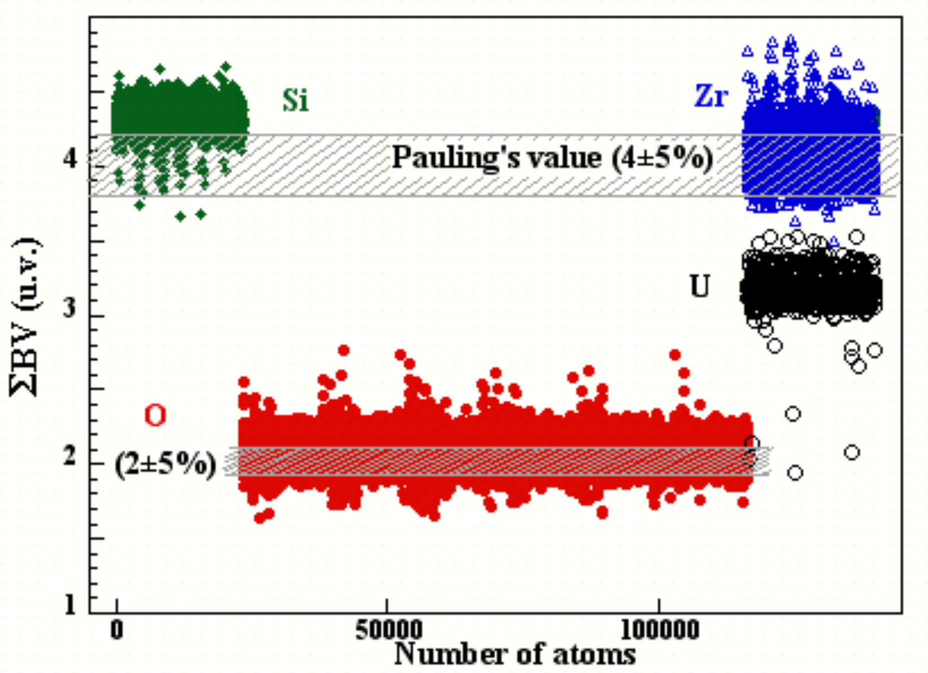
Validation of the MD models

$$BV = \exp\left(\frac{R_0 - R}{0.37}\right)$$

Brown/Altermatt (1985)



Crystalline zircon MD model with 1000 U atoms replacing Zr



MD model after a 4 keV cascade simulating radiation damage

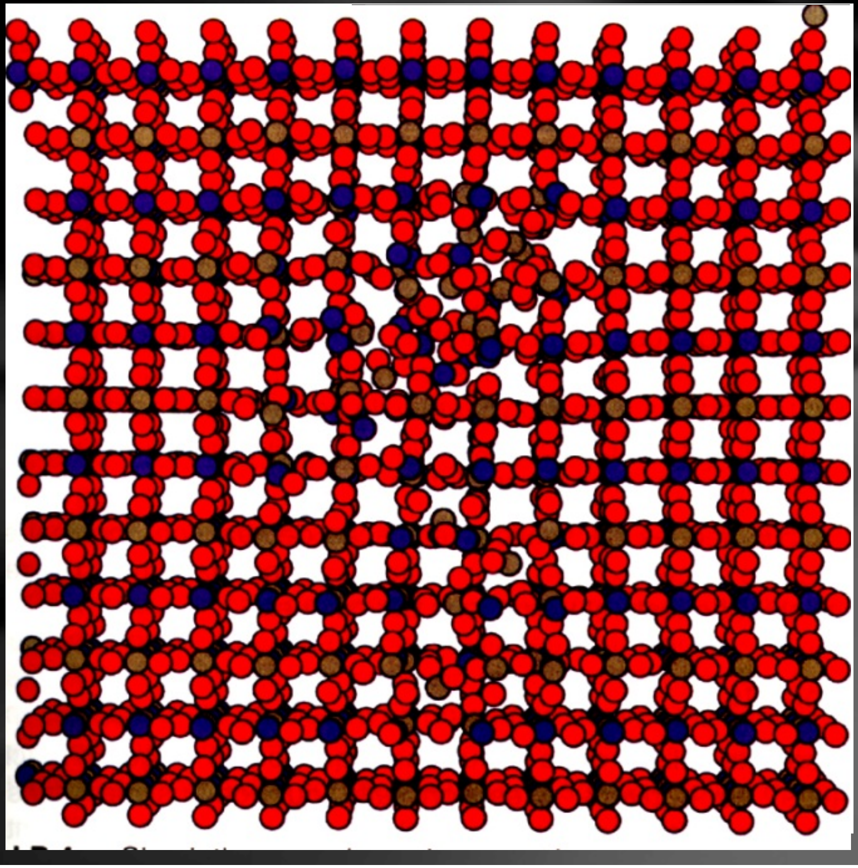
➲ BMH empirical potential over-estimate U-O interatomic distances, so ΣBV is under-estimated (ΣBV=|Z|).

➲ For Zr and O the zircon MD model (1000 U atoms) is quit good.

Validation of the MD models (Crystalline)

EXAFS over ~23 000 Zr clusters - MD - (*FEFF7 : Rehr et al*., *1999*)

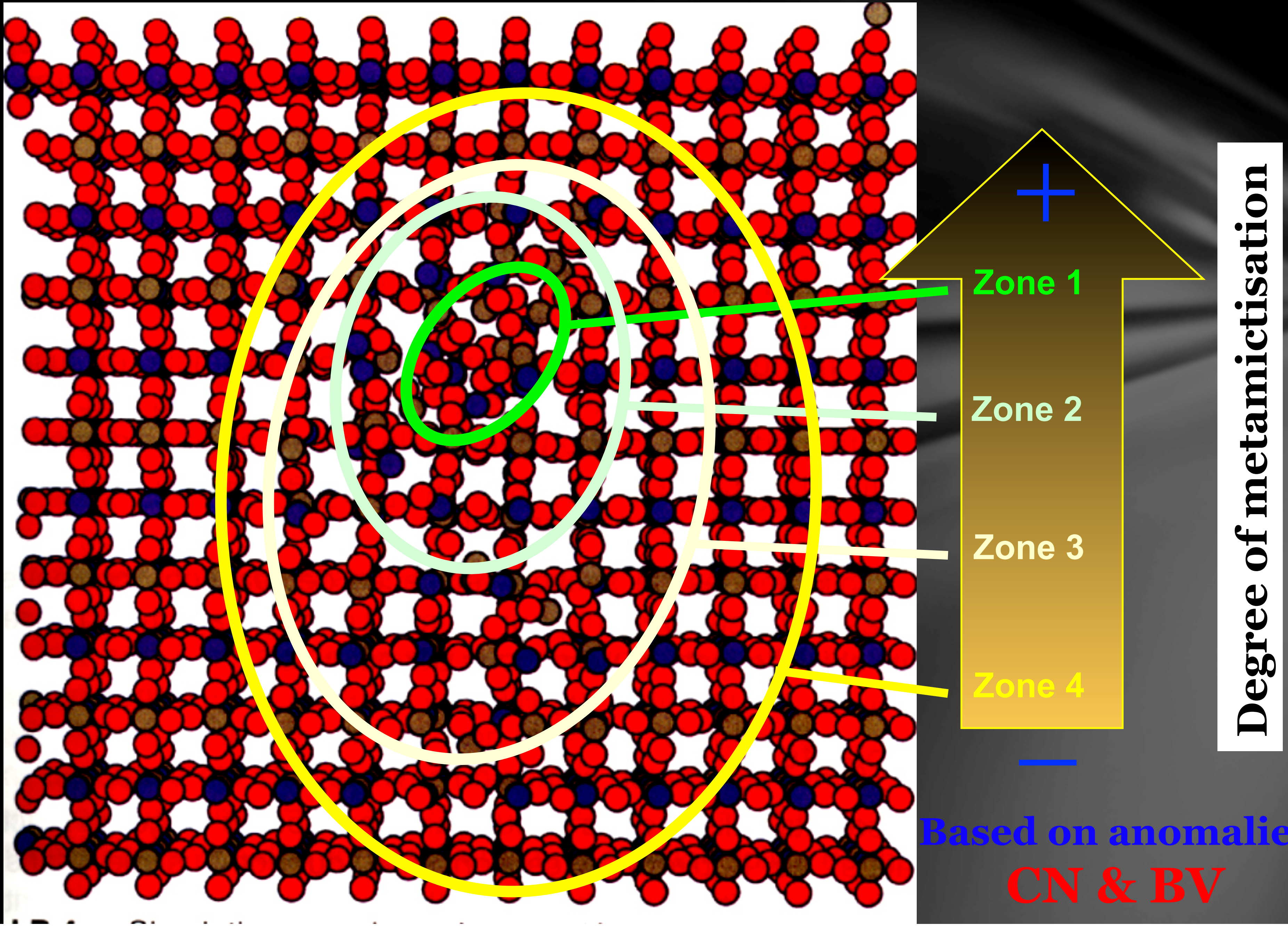
- ➢ Use the coordinates of atoms in the MD (xi, yi,zi)
- ➢ Caluculate the interatomic distaces from the absorber atom
- ➢ Generate the feff.inp file for each absorbing atom (23000 Zr = 23000 feff.inp file)
- ➢ Make the average of all feff calculation (chi)



Very good Agreement between simulation and experimental results

Validates the protocol followed - MD + FEFF -

Validation of the MD models **(Irradiated)**



+

Zone 1

Zone 2

Zone 3

Zone 4

−

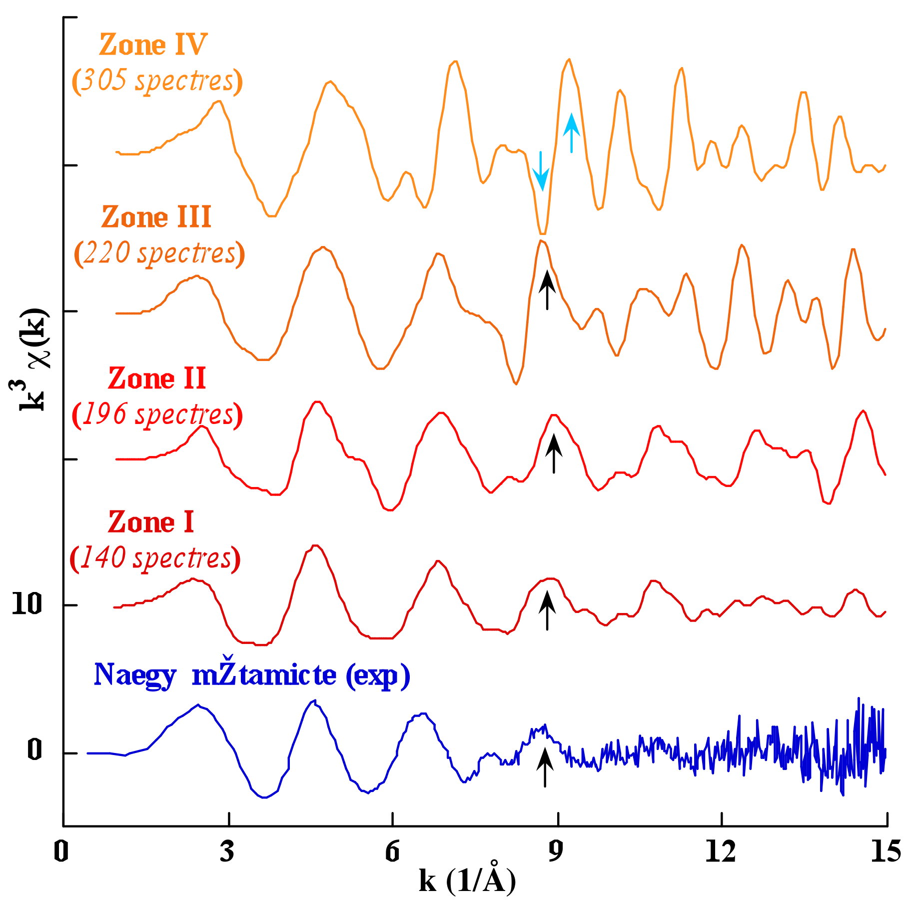
Degree of metamictisation

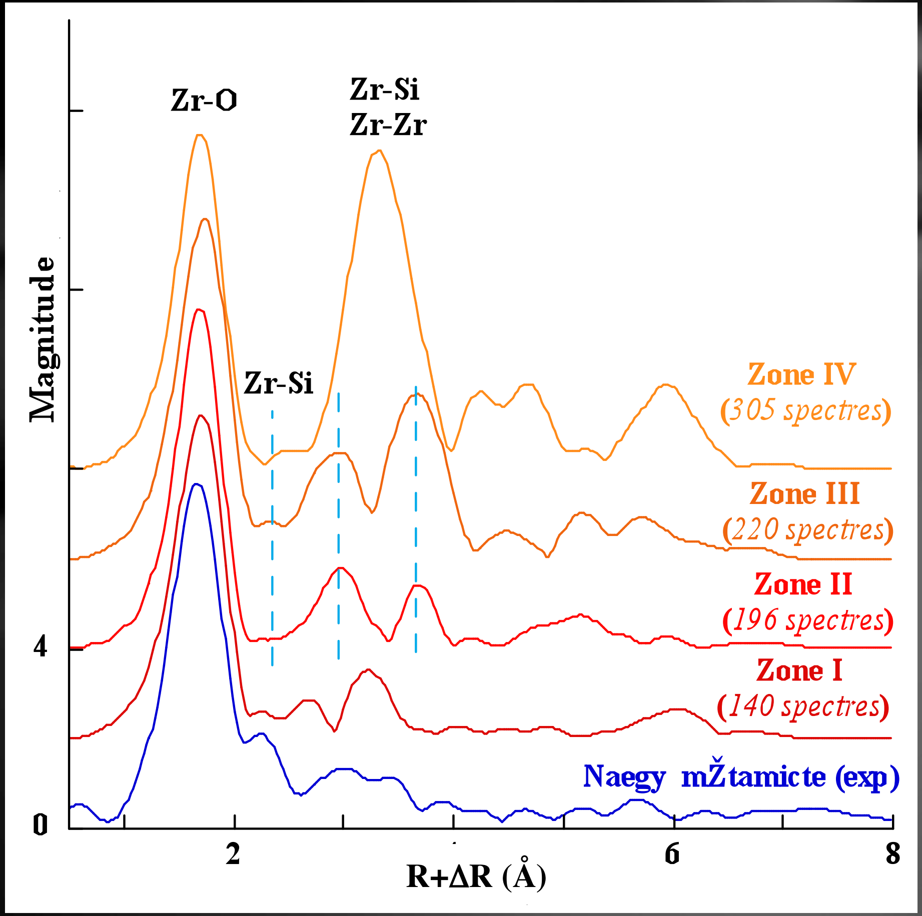
Based on anomalies

CN & BV

Validation of the MD models (Irradiated)

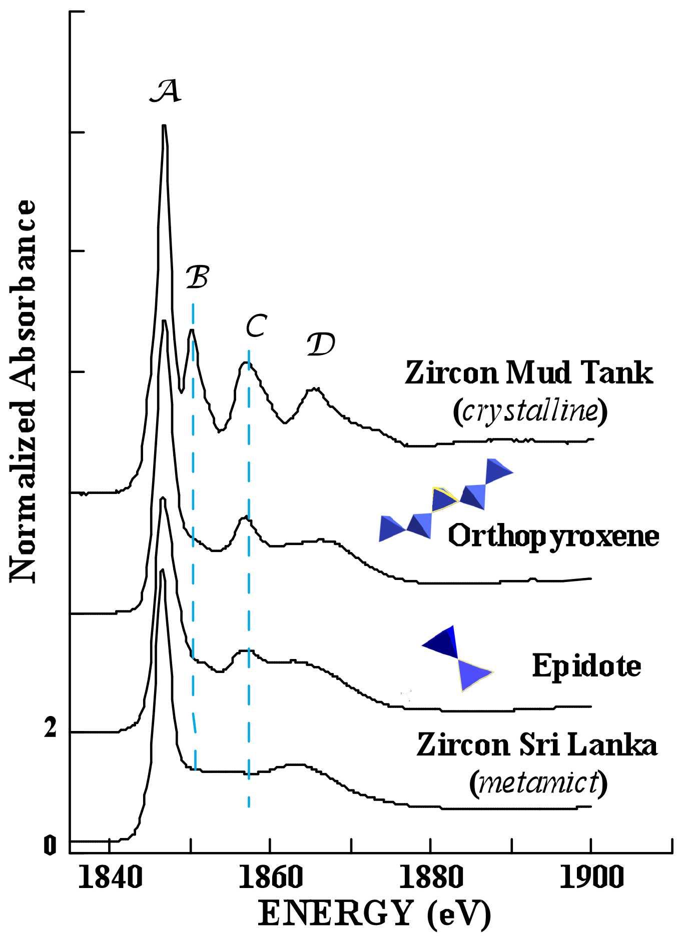
- ☐ CN ≠ 8 (5, 6, 7, 9)
- ☐ BV under/over estimated



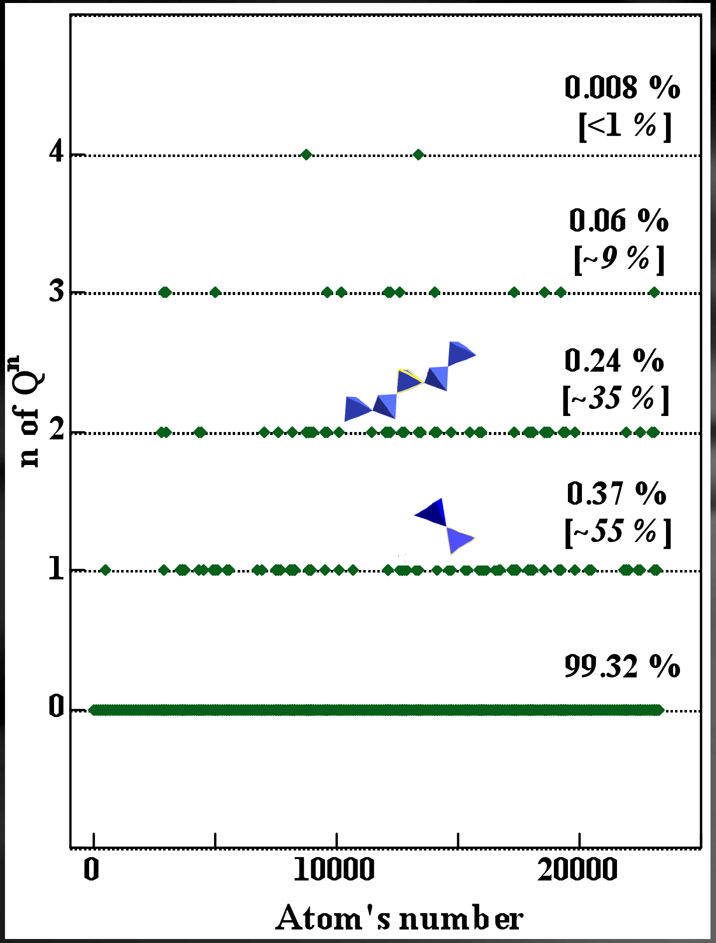


Results

Si in zircon

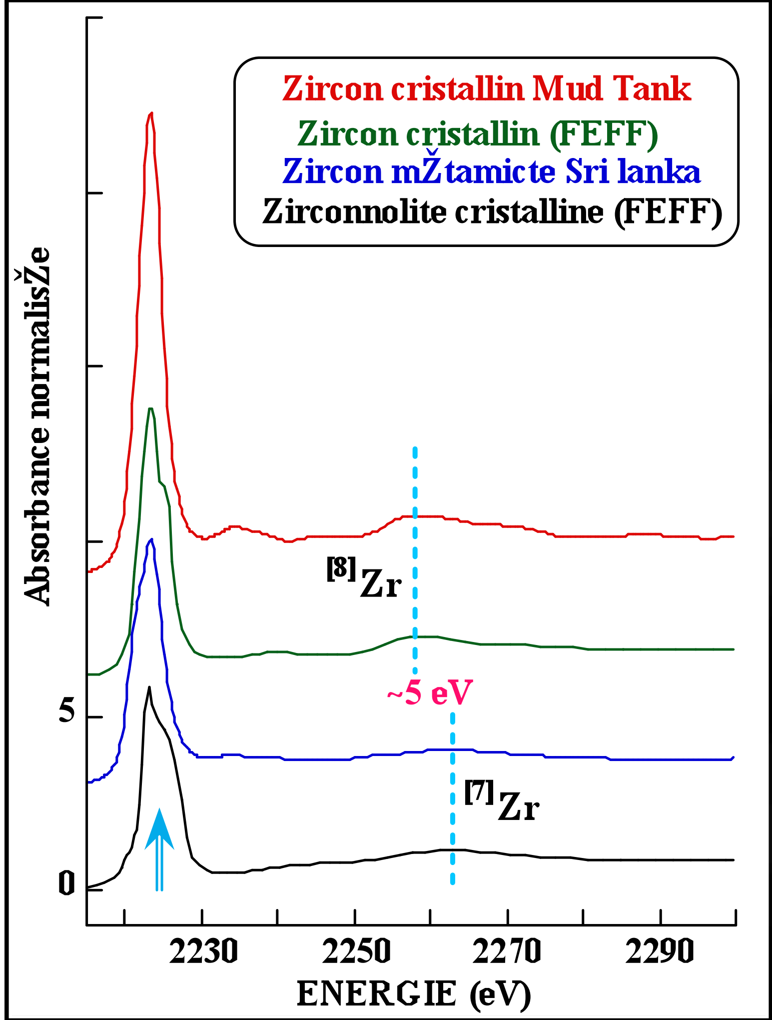


Most of polymerized SiO_n polyhedrons have 1 or 2 bridging oxygens.



MD simulation of radiation damage shows a few SiO_n polyhedrons sharing 3 or 4 bridging oxygens.

Zr in zircon



- XANES at Zr L_{III} edge
- sensitive to short range order
- $^{[8]}$Zr (crystalline) → $^{[7]}$Zr (metamict)
- coherent with Zr K edge (Farges, 1999)

➢ **Stong structural reorganisation of Si**

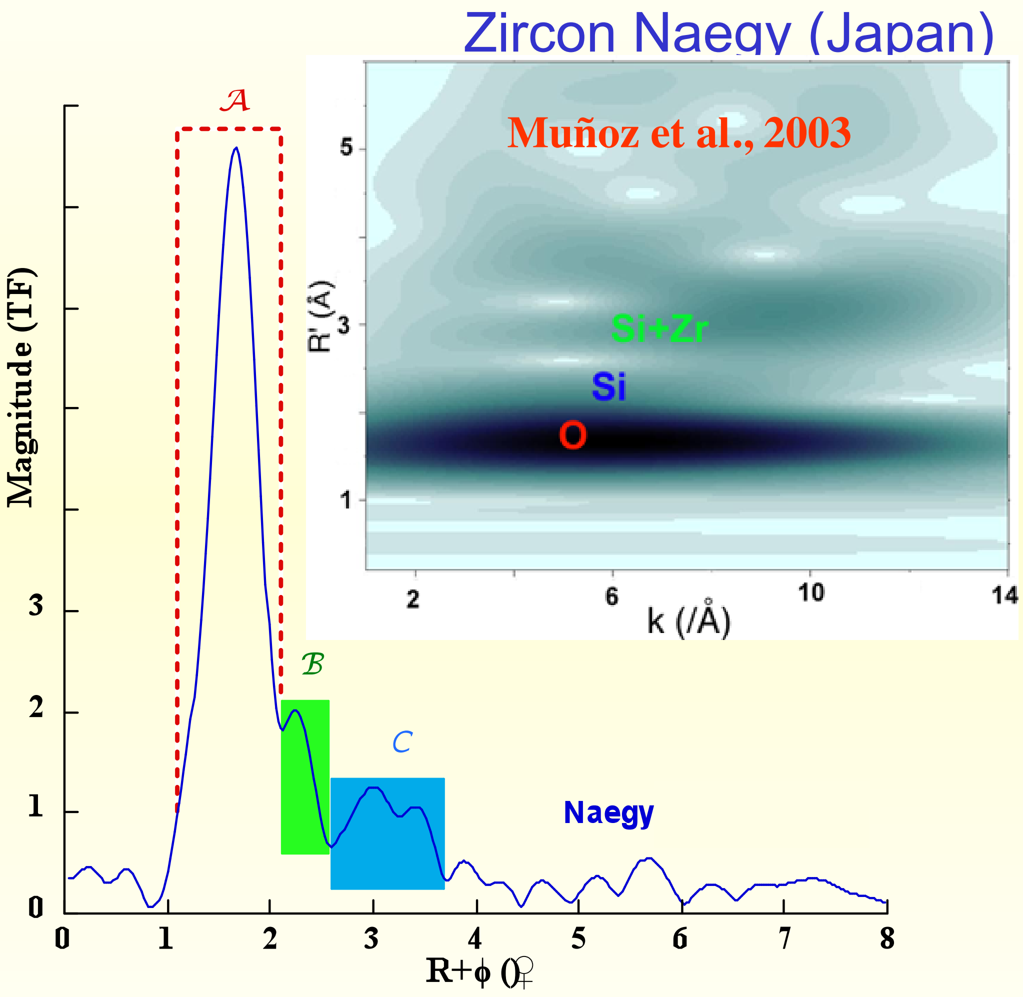
(Farges, 1994)

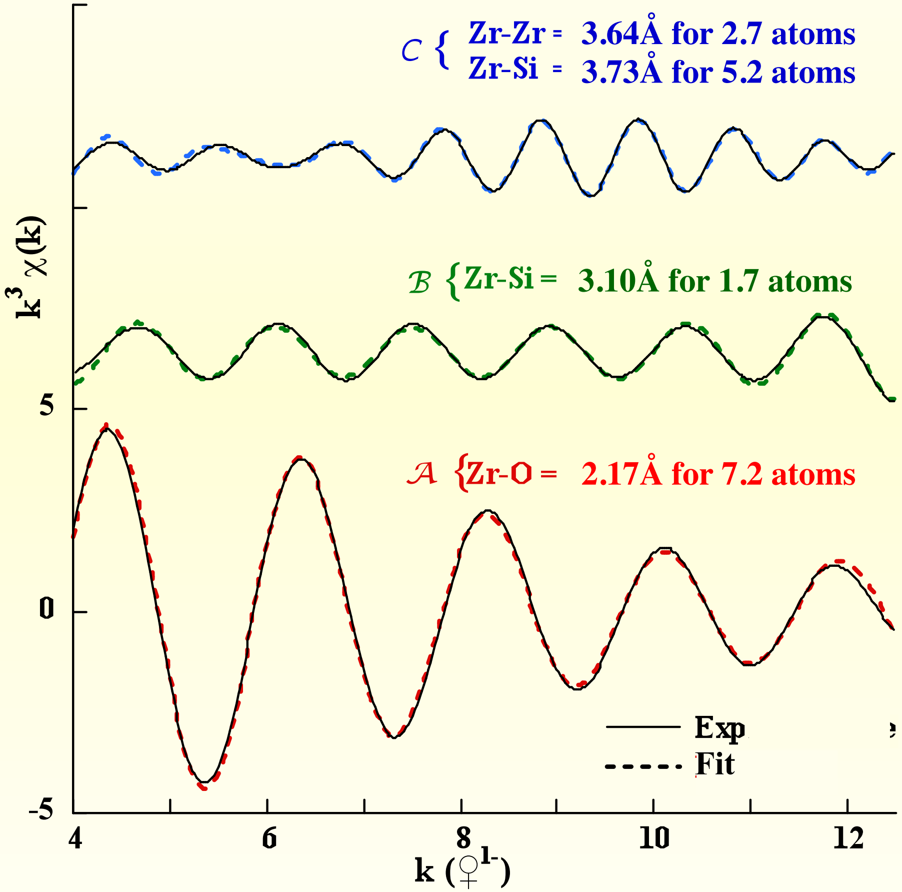
➢ **Observed by RMN/IR**

(Farnan, 1999; Zhang et al., 2000)

Data SA32 Super-Aco, LURE

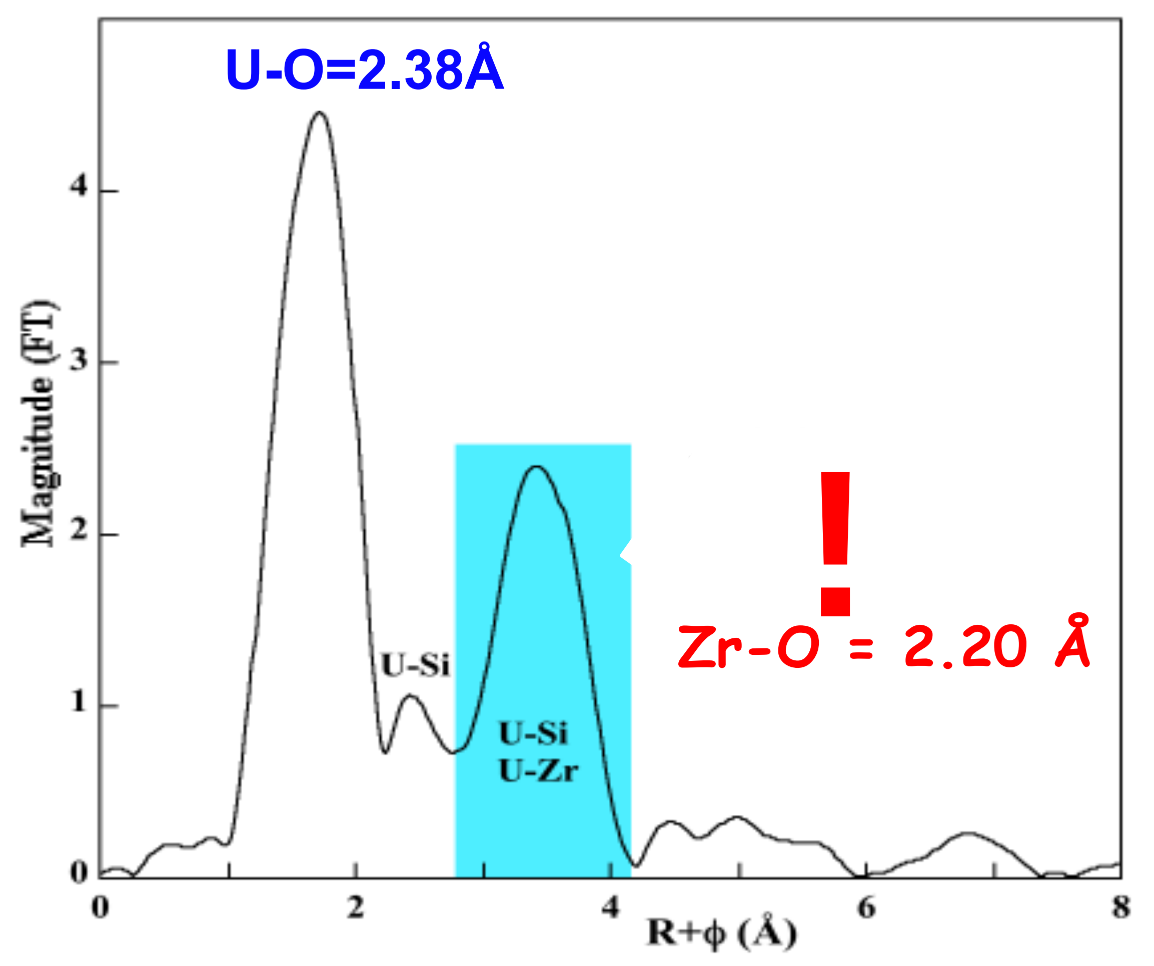
Zr in zircon





- ➢ Using amplitude and phase-shift from MD to fit exp. data
- ➢ Short (𝒜) and medium (ℬ et 𝒞) range order around Zr

U in zircon (Exp.)



$^{[8]}$U-O = 2.38 Å (oxygen 1st neighbors)

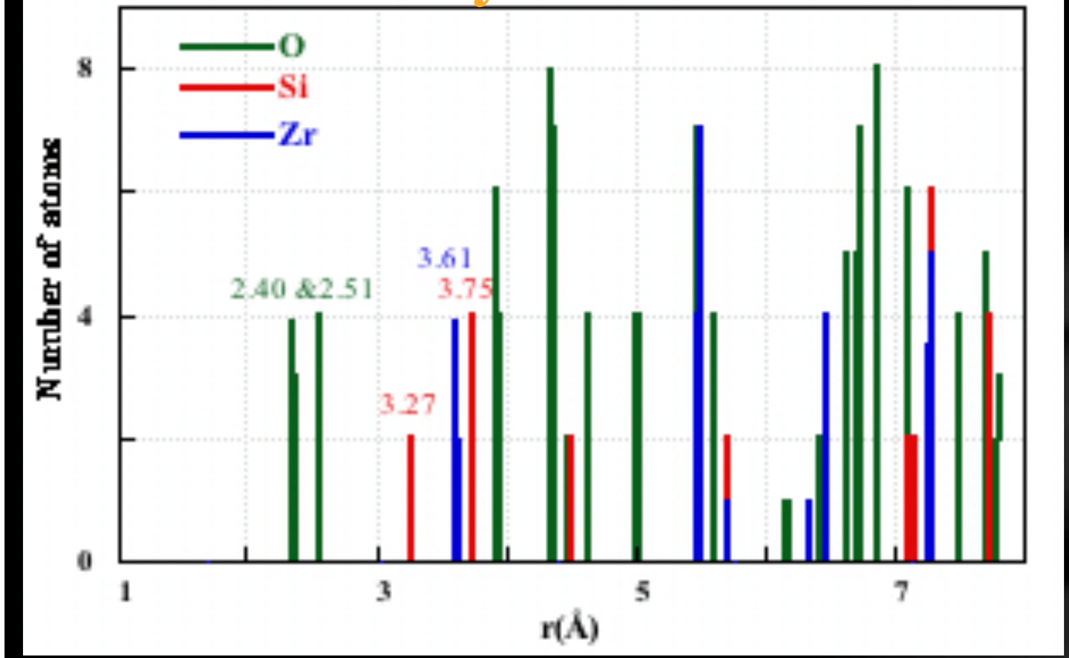
crystalline : expansion of the local structure around U

Zr appears as next neighbors ➔ U is in zircon structure

U in zircon (MD)

Diagram of the atom distribution **(Backward RDF)**

Crystalline

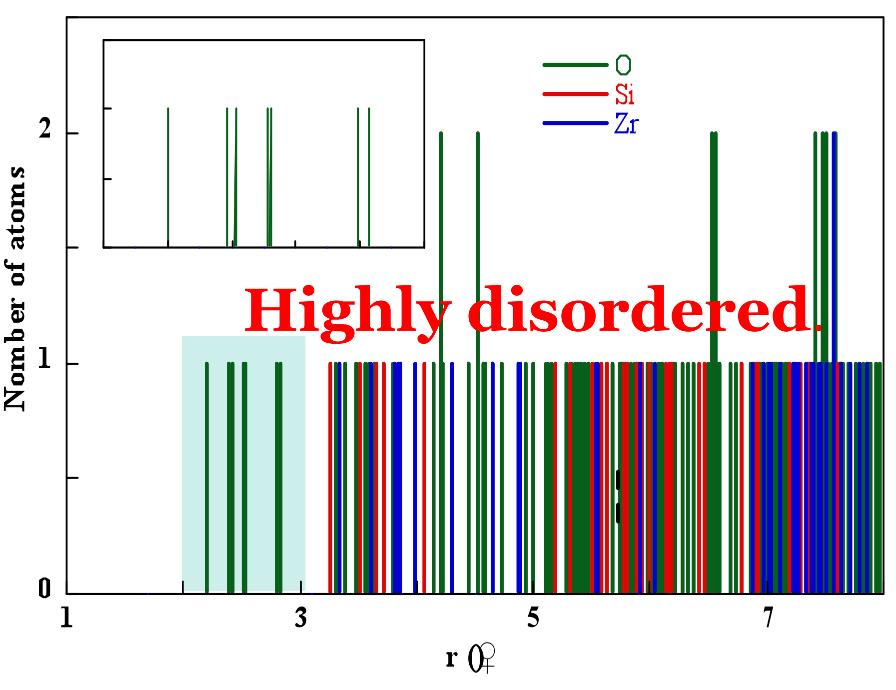


CN = 8 (2.4 and 2.51 Å)

Si short distance (3.27 Å)

Si & Zr next neighbors

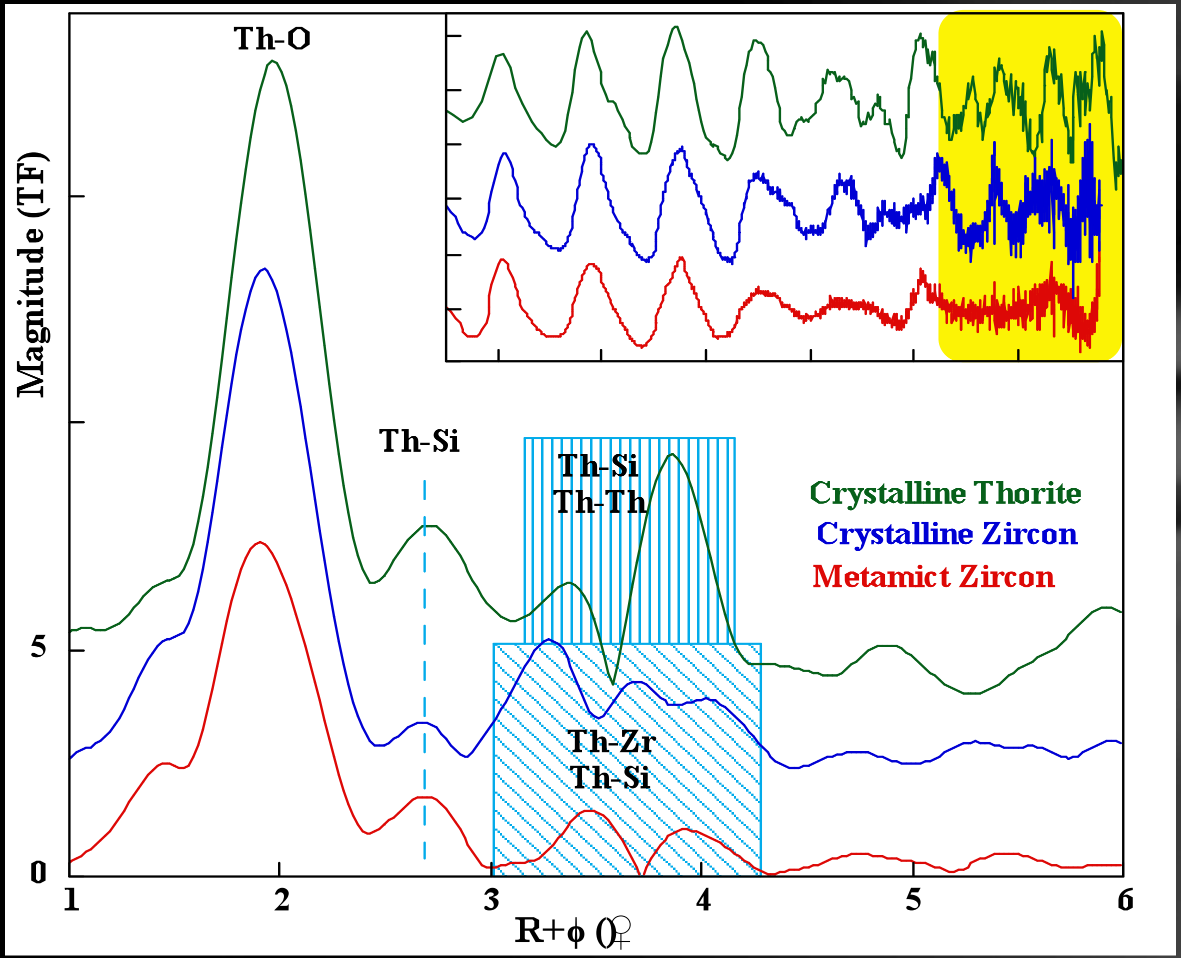
Metamict



Highly disordered.

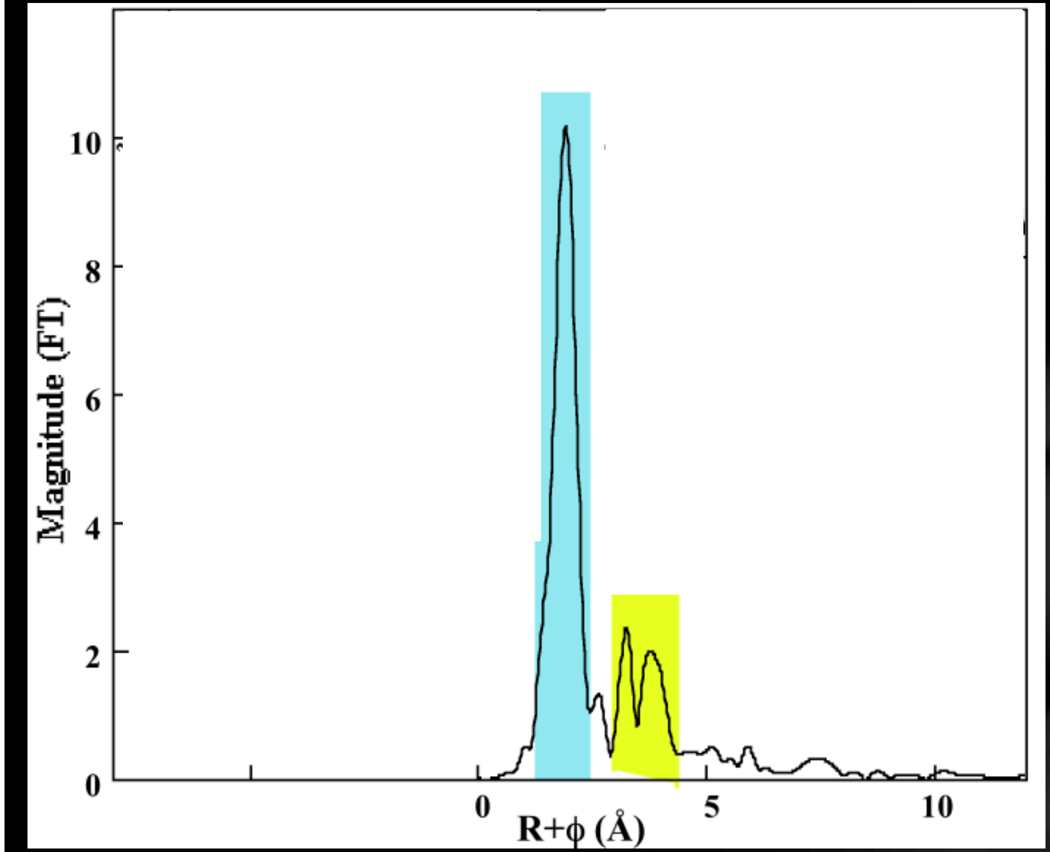
- ➢ **U in Zircon Structure**
- ➢ **Local Expansion around U**
- ➢ **High Structural Disorder**

Th in zircon

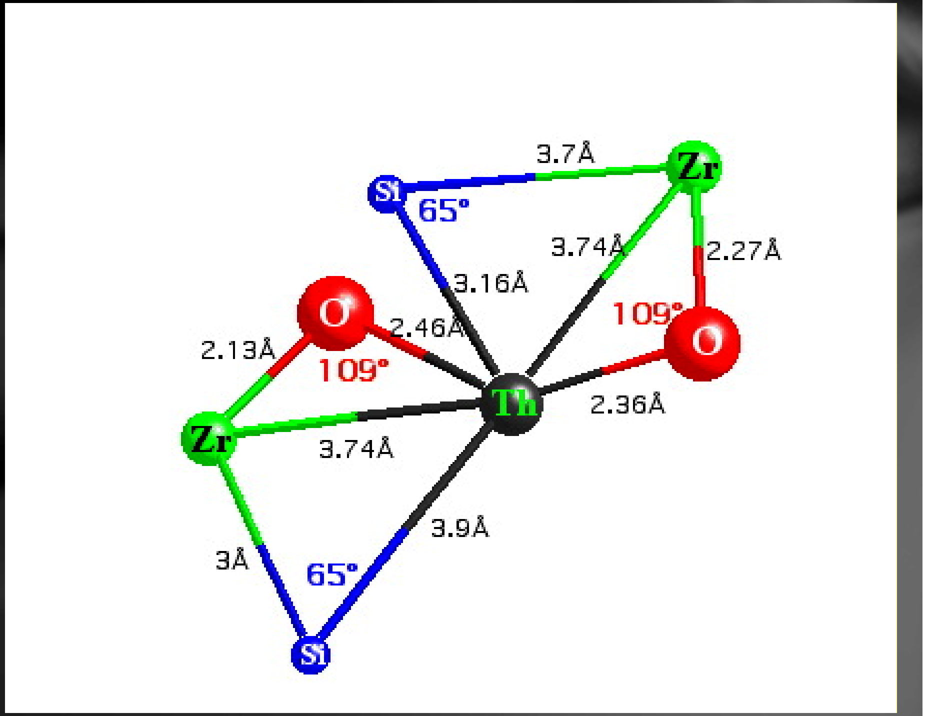


- At high *k* values, Th-site in zircon is different to that for $ThSiO_4$
- Th is not as in a Thorite-like structure, but it replaces Zr in zircon

Th in zircon



Interatomic average distances permit calculating average angles Th-O-Zr and Th-Si-Zr



Cluster ThO$_8$Si$_2$Si$_4$ (thorite-like)

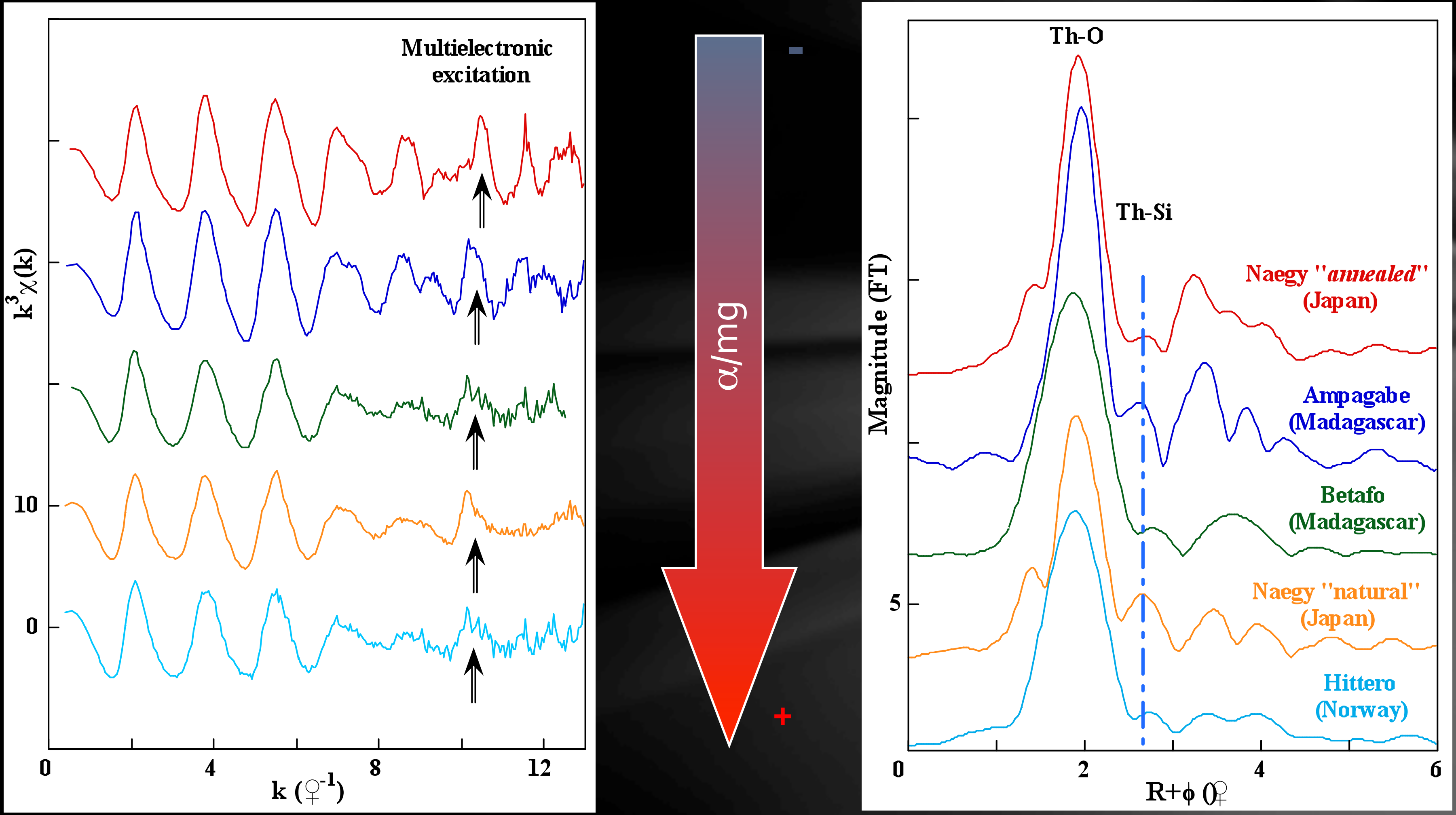
↓

Cluster ZrO$_8$Si$_2$Si$_4$ (zircon)

Zircon
- **Zr-O : 2.20 Å**
- **Zr-Zr : 3.63 Å**

Thorite
- **Th-O : 2.42 Å**
- **Th-Th : 3.90 Å**

Th in zircon



- In both crystalline and metamict zircon, Th is 8 fold-coordinated
- The local structure around Th in metamict zircon is very complex

Summerizing

- ❑ In crystalline phases, cations tend to prefer their stable coordination environment (even if redox is different).

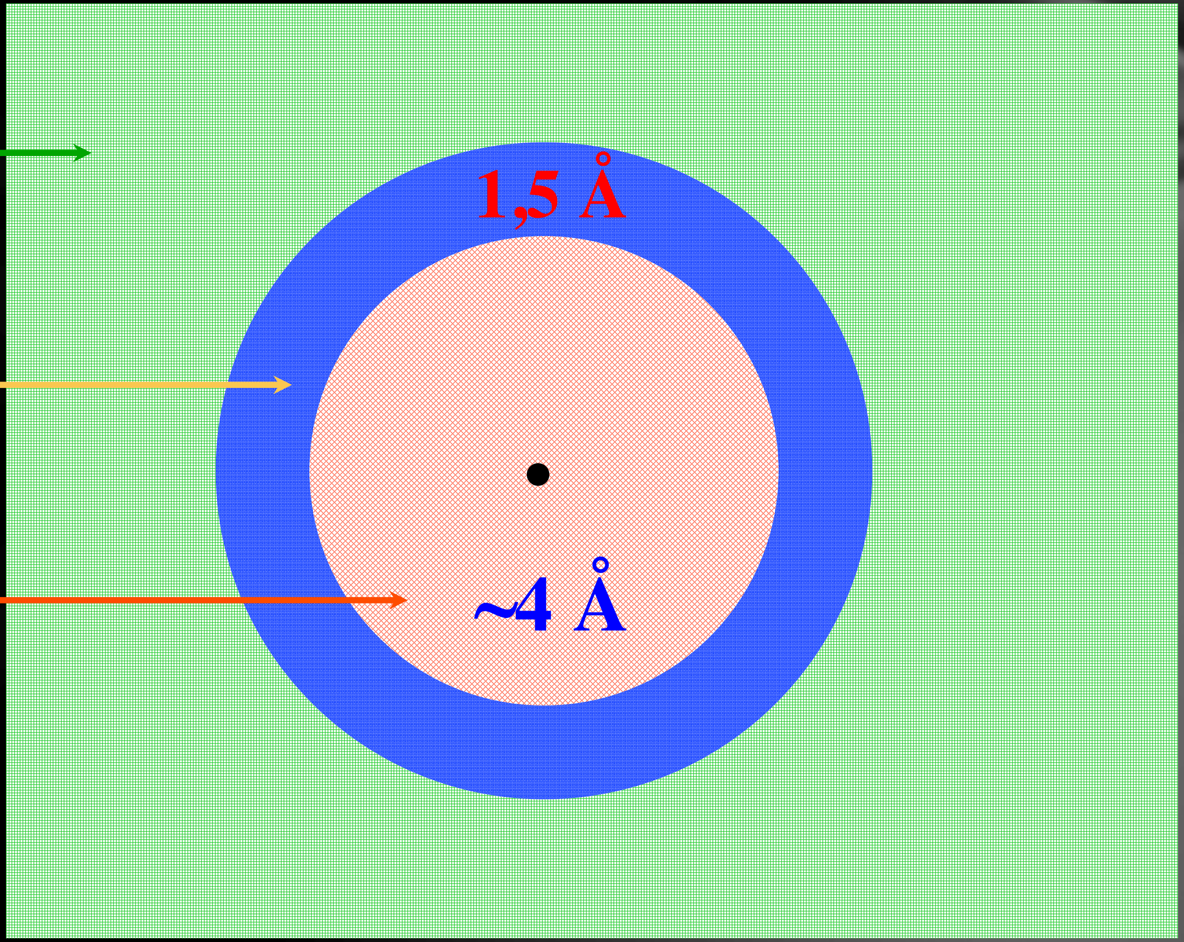
- ❑ The medium range structure around actinides in crystalline zircon shows:
  - ➢ an expanded region due to the insertion of larger actinides (up to 4 Å),
  - ➢ a compressed region between 4 and 5.5 Å,
  - ➢ the structure is back to the original crystalline zircon one above5.5 Å.

- ❑ Also, observed in natural metamict zircon and confirmed by MD.
- ❑ In metamict zircon, an average number of 7 atoms form
- ❑ The coordination polyhedron around Zr and U.

Illustation

Combining :

1. **Experimental EXAFS data Analysis**
2. **MD simulation results**



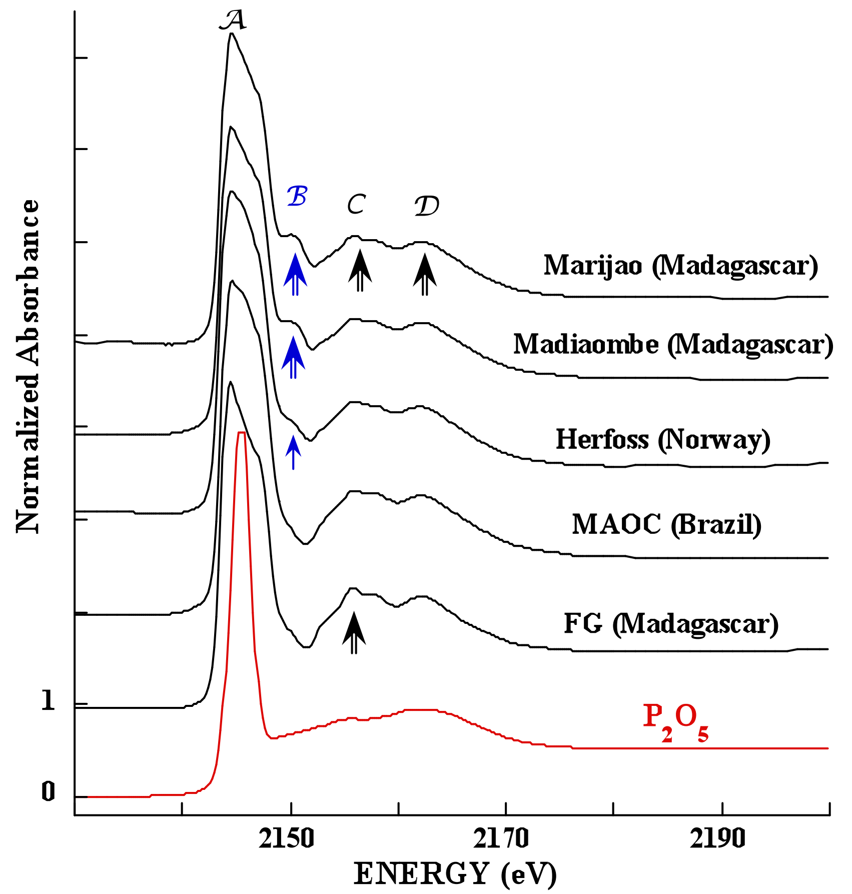
Original zircon structure

Contracted structure

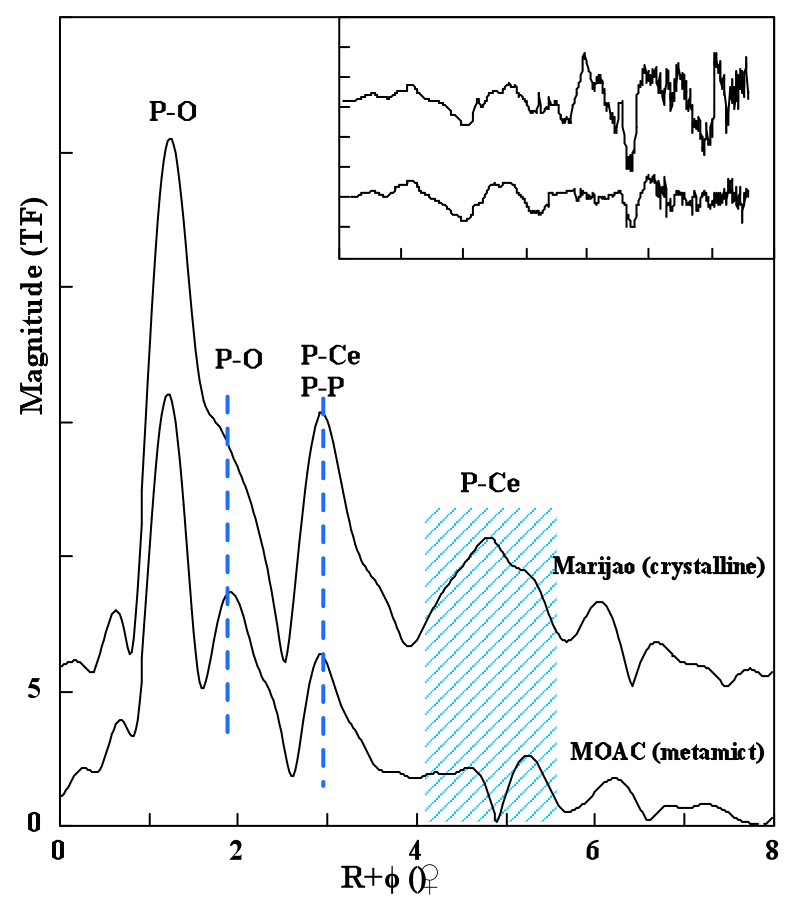
Expanded structure

Monazite

P in Monazite

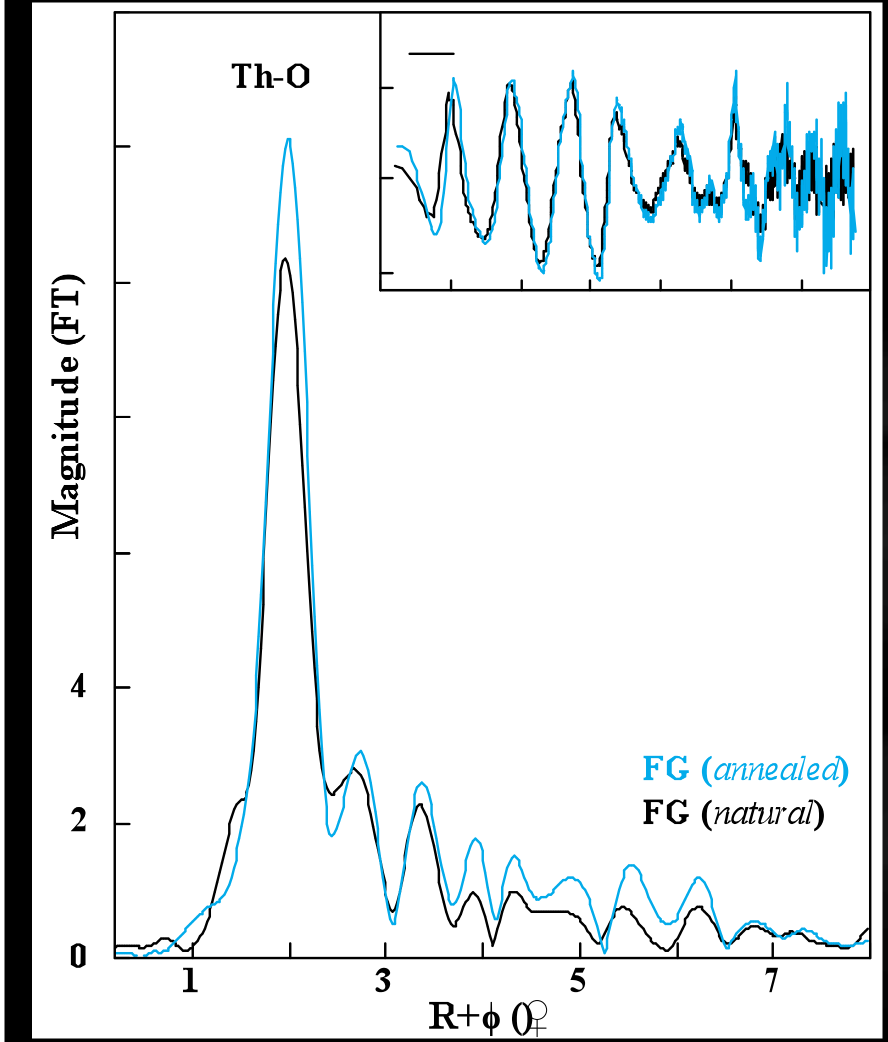


Resonance B disappears when the PO_4 tetrahedrons are polymerized



In metamict monazite, the local structure around P is distorted

Th in Monazite



❑ The local structure around Th is complex in both crystalline and metamict monazite

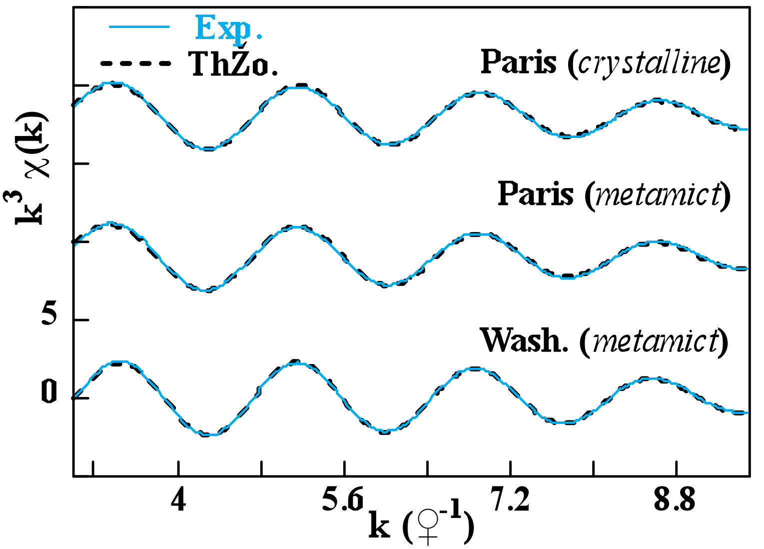
❑ Crystalline monazite ≈ Metamict monazite

❑ Unlike zircon, no expansion of the local structure around Th is observed and neither contraction

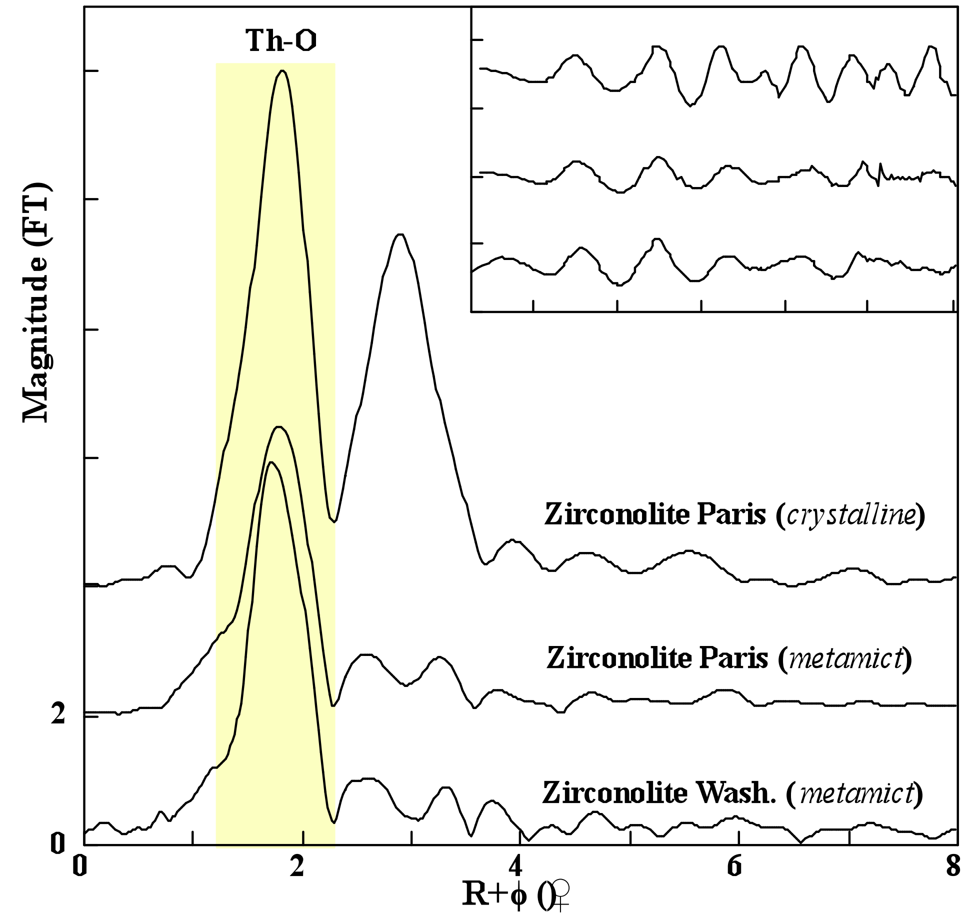
Zirconolite

Th in Zirconolite

Th substitutes to Ca site in Zirconolite structure



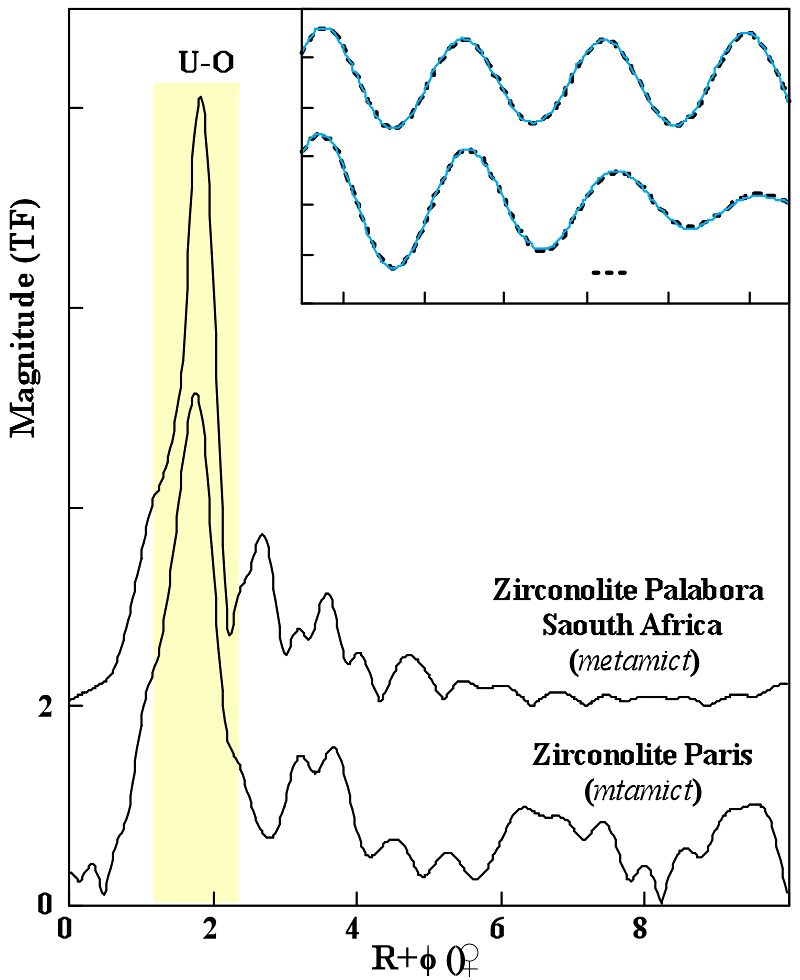
$^{[8]}$Th-O = 2.42(2) Å



- ☐ Medium and long range order is complex
- ☐ Like Zircon, it needs MD simulation to understand the local disorder (not available).

U in Zirconolite

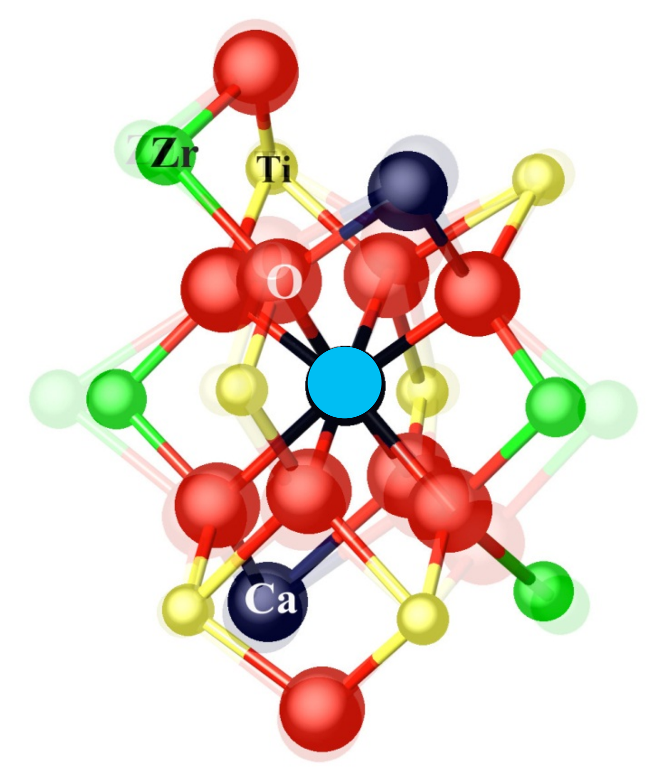
U substitutes to Ca site in Zirconolite structure



U keeps an 8 fold coordination average U-O = 2.41Å.

Knowing that:

Ca-O = 2.52 Å

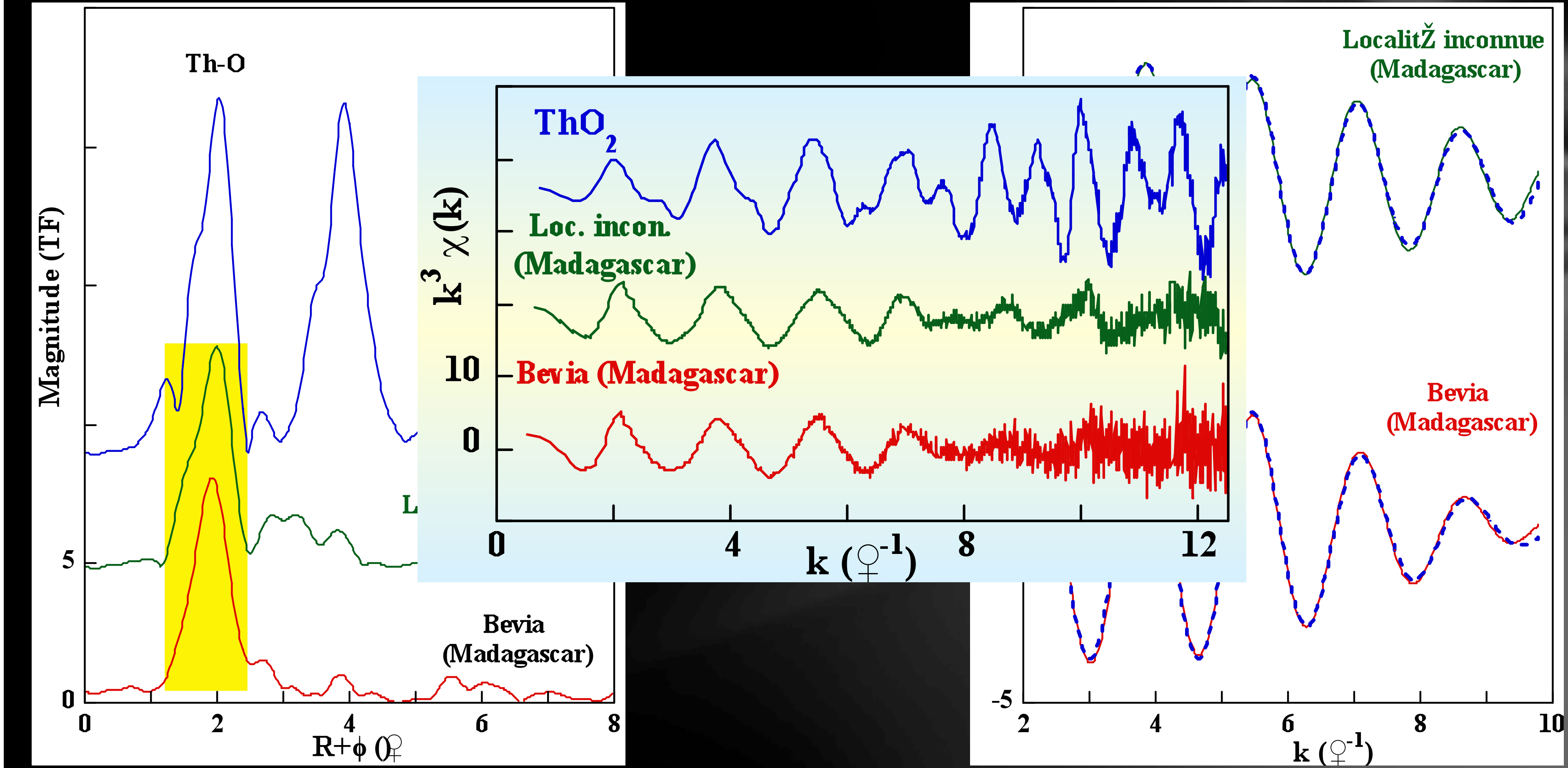


a contraction of the local structure occurs

Titanite

Th in Titanite

Th substitutes to Ca site in Titanite structure



$^{[7]}$Th-O ≈ 2.37 Å

$^{[7]}$Ca-O ≈ 2.45 Å

⟹ **Contraction**

$^{[7]}$Th ?

(≈ Th in glasses)

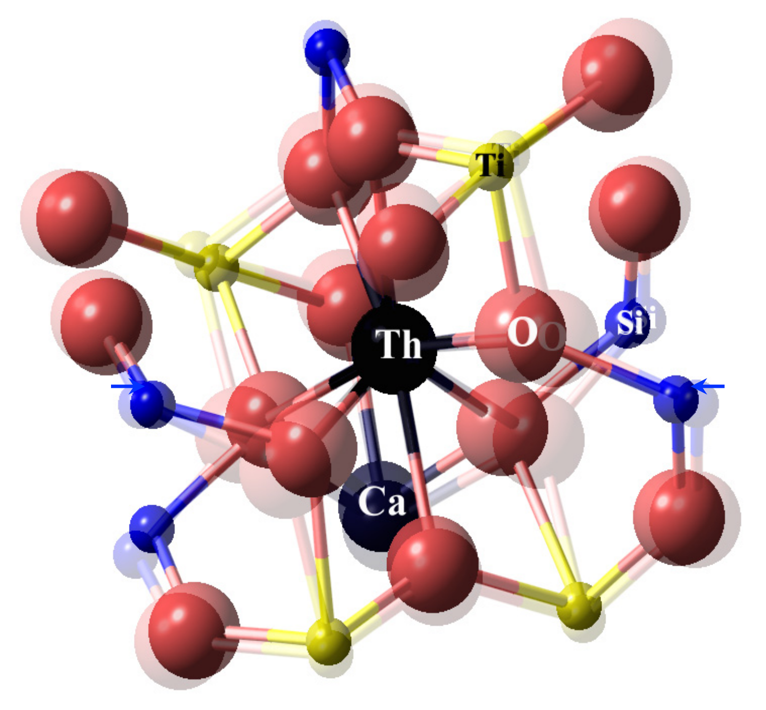
Discussion

Contraction Zone around Th in Titanite and zirconolite

❑ **Contraction even the equal ionic radius ????**

$R_{Th^{4+}}$ (1.0 Å) ≈ $R_{Ca^{2+}}$ (0.99 Å)

❑ **Electrostatic equilibrium even that Th is 4+ or Ca is 2+ ????**



Discussion

Electrostatic equilibrium & Contraction Zone

In Zirconolite and Titanite

- **Ectrostatic equilibrium impose:**
  - Substitution of P^{3+}, Al^{3+}, $Fe^{2+,3+}$, etc. to Si^{4+} et Ti^{4+} sites

- **Local contraction around Th an U is due to:**
  - $R_{substitut} > R_{substituted}$ ➡ **expansion around P, Al, Fe…**

➡ **contraction around Th/U**

Conclusion

- ❑ In crystalline phases, cations tend to prefer their stable coordination environment (even if redox is different)
- ❑ The medium range structure around actinides in crystalline zircon shows:
  - ❶ expanded region due to the insertion of larger actinides (up to 4 Å),
  - ❷ compressed region between 4 and 5.5 Å,
  - ❸ the structure is back to the original crystalline zircon one above5.5 Å.
- ❑ Observed also in natural metamict minerals and confirmed by MD
- ❑ In metamict zircon, an average number of 7 atoms form the coordination polyhedron around Zr and U.
- ❑ Inner (expanded) and outer (compressed) regions form a point defect, which reproduced a billions of times forms an aperiodic structure.

Conclusion

- ❑ In contrast to zircon, the structural changes around Th are globally much less in monazite.
- ❑ In metamict phase, polymerization of PO_n tetrahedrons (in monazite) and SiO_n (in zircon) occurs.
- ❑ A compressed region is observed around actinides in Zirconolite and Titanite due to insertion of actinides less or equal to the replaced atom (Ca).
- ❑ In some minerals, actinides do not replace major cations, but they are present as an actinide oxide-type (ThO_2, UO_2).
- ❑ MD simulation is helpful to understand the radiation damage effects on the crystalline zircon structure and results are in agreement with the experiment.
- ❑ We need MD simulation to better understand the metamict phase in monazite complex structure.
- ❑ helps also to better understand effects of disorder in EXAFS spectra

U uptake by co-precipitation and adsorption processes in cementitious systems

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Outline

- *Introduction*
  - *Waste disposal*
- *Sample preparation*
- *Results*
  - *experimental (XAS)*
- *Discussion*
- *Conclusions*

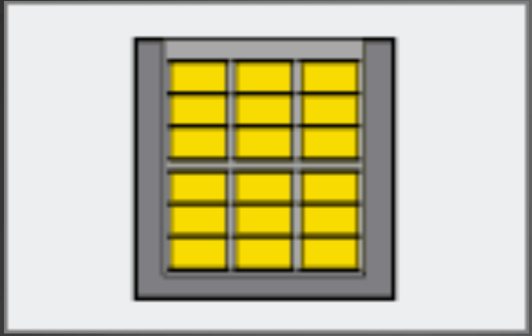
Nuclear Waste Management

Cement in the Swiss radioactive waste management program is used as waste matrix for the disposal of:

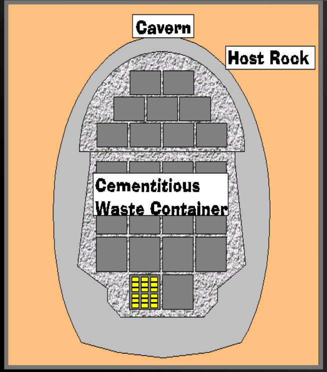
Long-lived Intermediate-level Waste

Waste package (cement & steel)

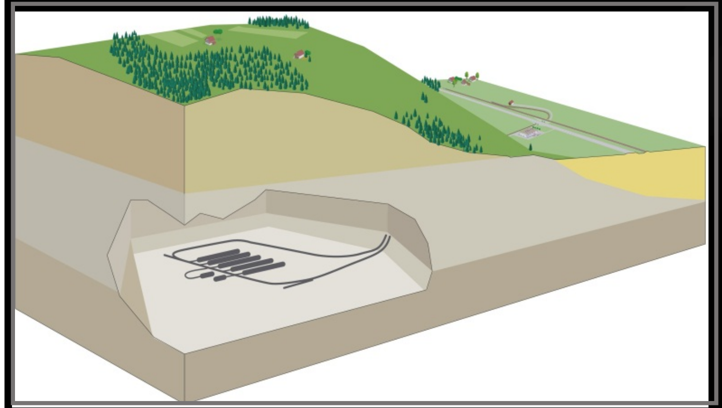
Container (concrete, mortar, steel)



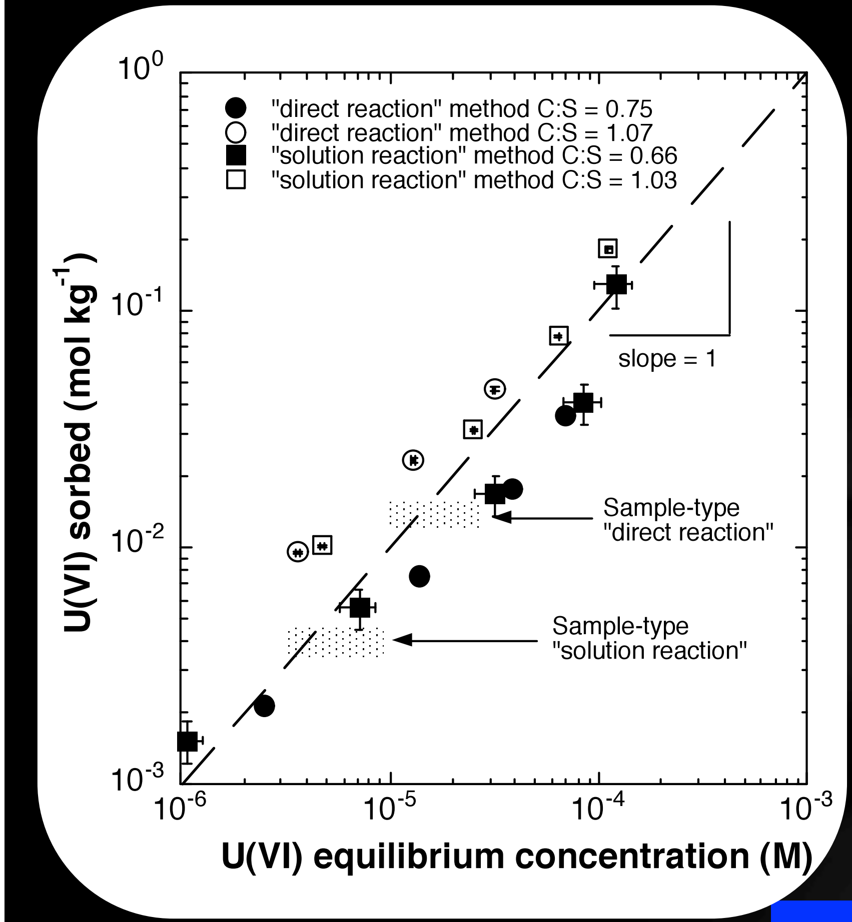
Cavern backfill (porous mortar)



Deep geological repository



U(VI) in cementitious systems



- **C-S-H phases with varying C:S ratios**
- **U(VI) loadings 1080 and 3400 ppm**
- **Sorption isotherms with ^{233}U tracer**

Solution reaction

C-S-H prepared from solutions

Direct reaction

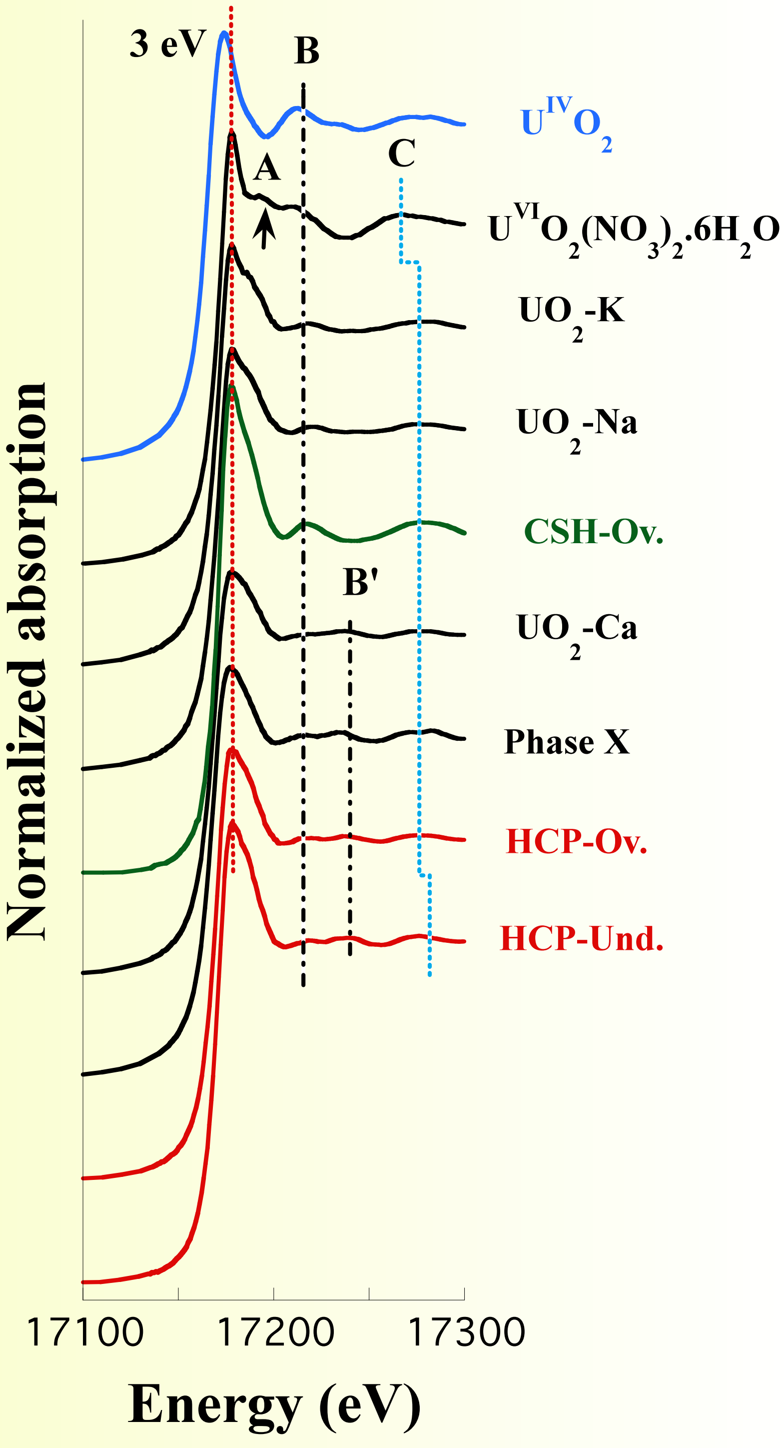
(CaO and SiO_2) used as reactants

References

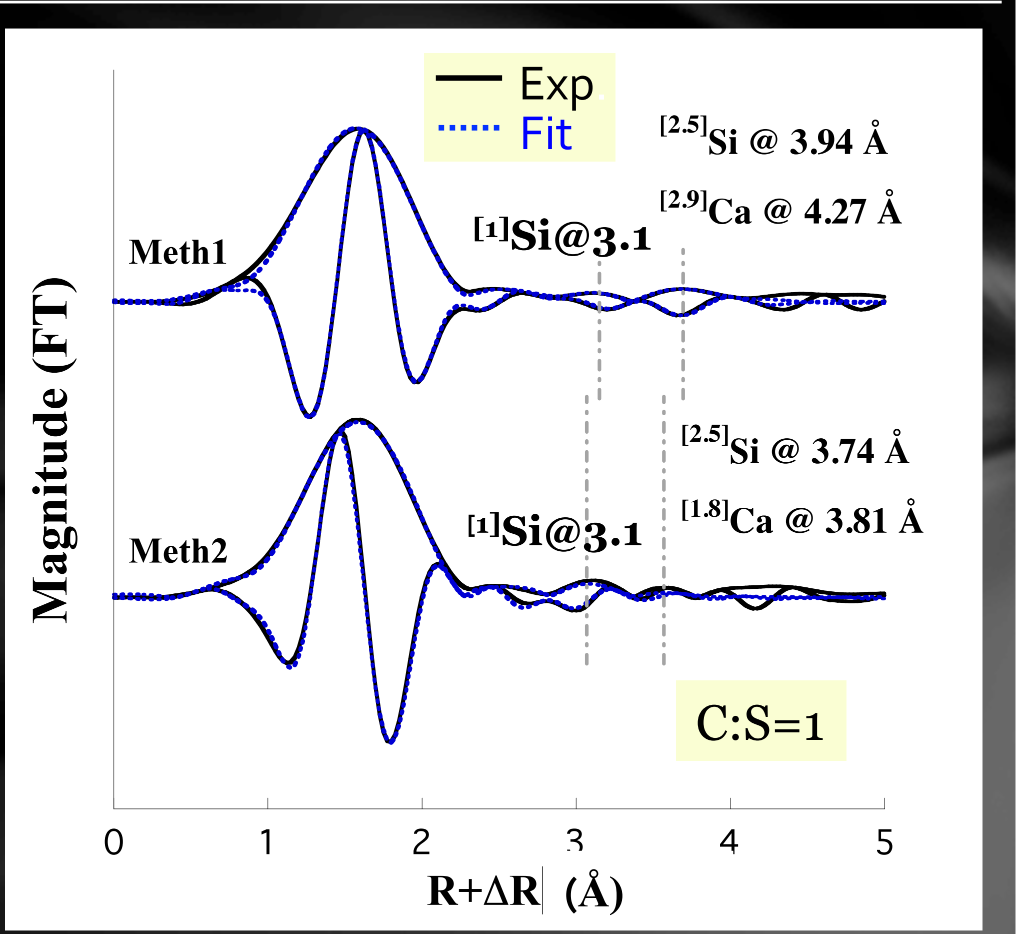
U(VI) $Ca(OH)_2$ / pH =12.5 → amorphous

U(VI) K^+/ pH =13.3 → crystallized

U(VI) Na^+/ pH =13.3 → crystallized



U(VI): adsorption process

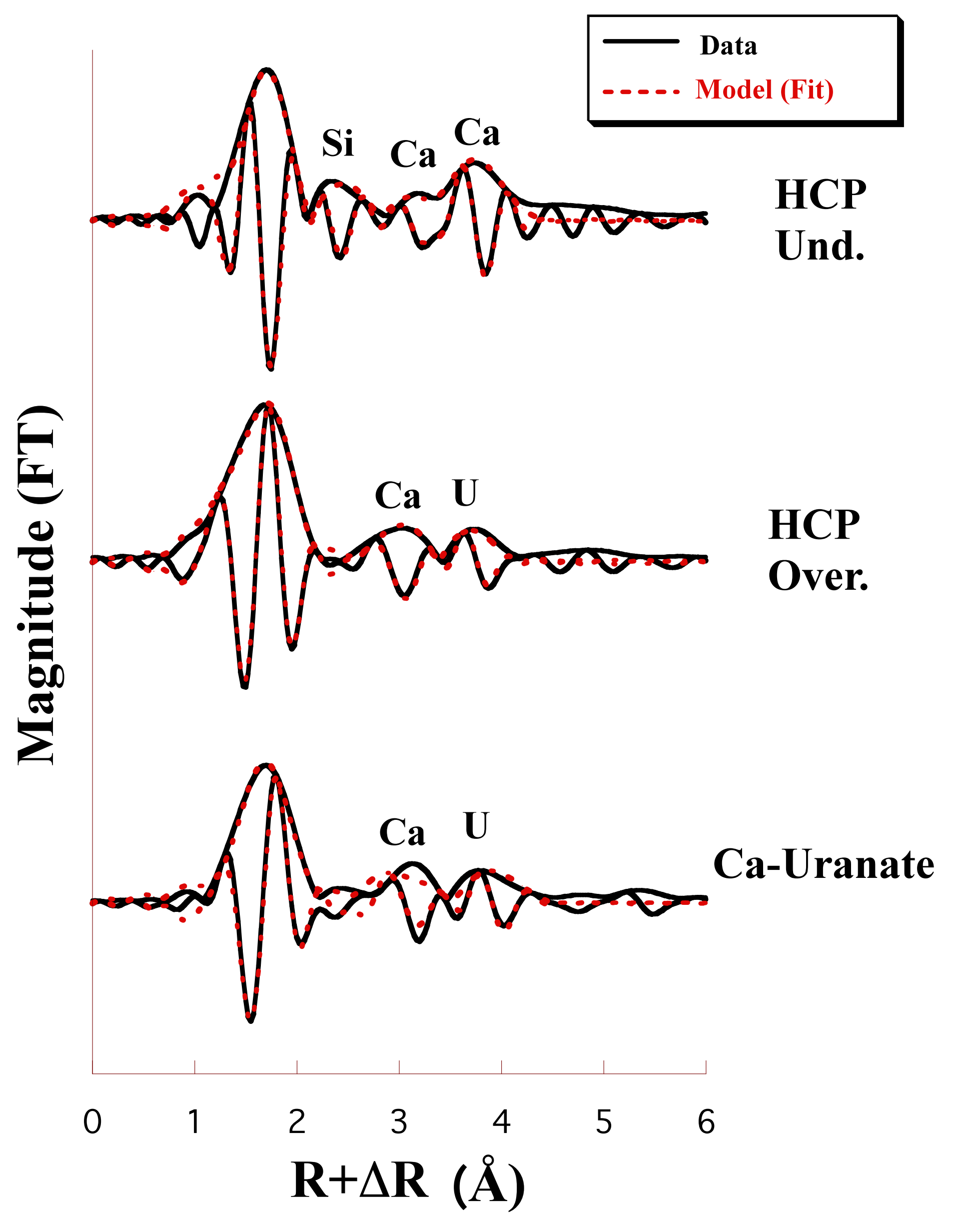


⇒ No U(VI) ➡ U(IV)

⇒ **Uranophane-like** with:

O_{ax}, O_{eq}, Si_{short}, Si_{long} and Ca

U(VI): precipitation process



[0.7]Si @3.08 Å
[0.5]Ca @3.70 Å
[2.3]Ca @4.24 Å

~~Uranophane - like~~
Edge share (SiO_4)

[1.7]Ca @3.64 Å
[1.6] U @3.80 Å

Co-precipitation
in Ca-uranate-like

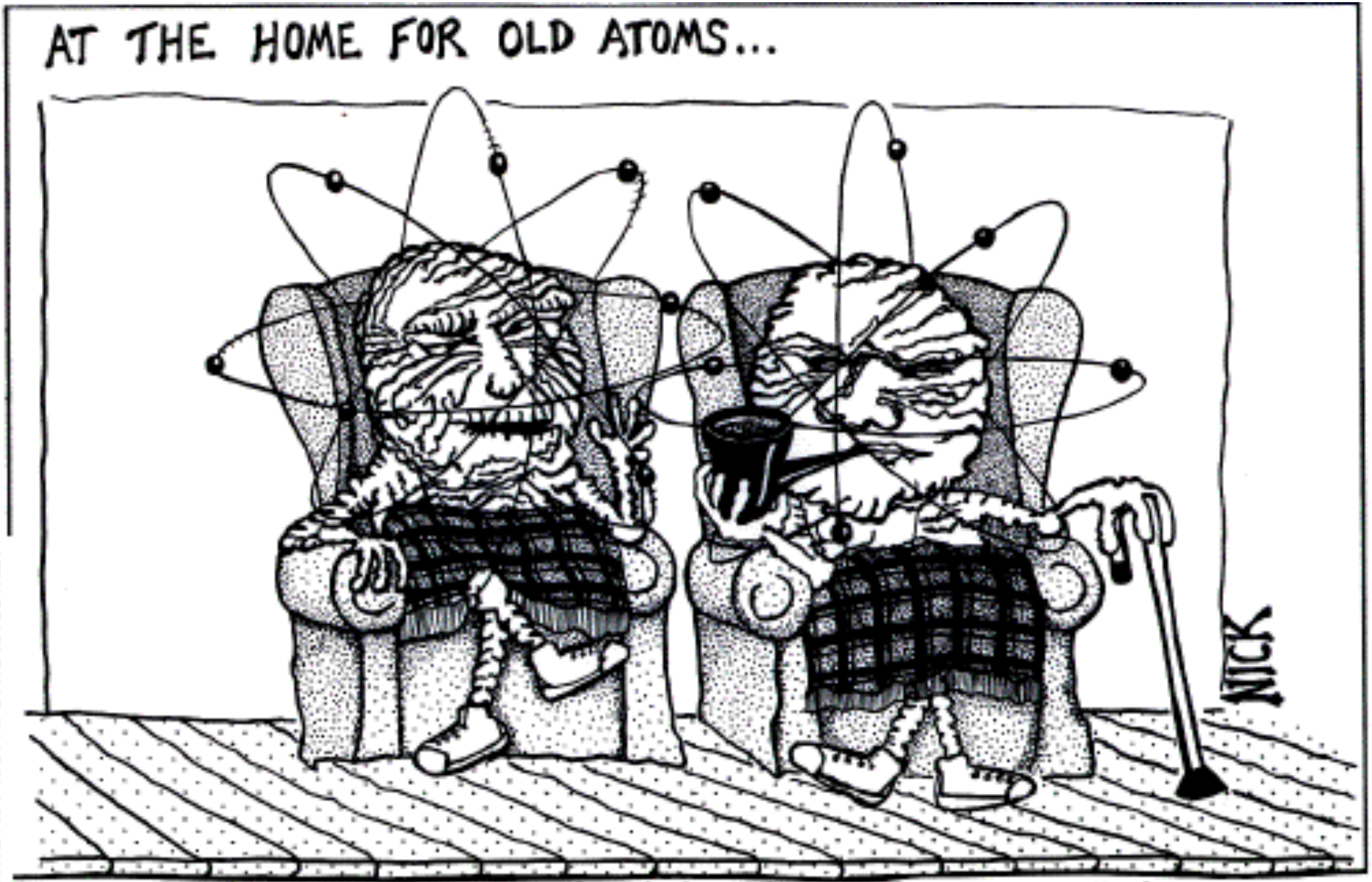
[2.0]Ca @3.62 Å
[1.8] U @3.87 Å

~~Na-uranate~~
~~K-uranate~~

Conclusion U(VI) in cementitious systems

- ☯ Uranium linked to C-S-H structure and under-saturated H-C-P via the Si atom
- ☯ Sharing the SiO_4 tetrahedron edge
- ☯ In CSH, U is present as uranophane- like

- ❑ In over-sat. HCP, U precipitates in Ca-uranate-like form
- ❑ Neither Na-, K-uranate structures were observed



"When I was young I used to feel so alive, so dangerous..! In fact, would you believe that I started out life as a Uranium-238 ? Then one day I accidentally ejected an alpha particle, and that's where it all began. Now look at me, a spent old atom of Lead-206. It seems that all my life since then has been nothing but decay, decay, decay...."