School on
Synchrotron Light Sources
and their Applications

ICTP

6 - 17 December 2021
An ICTP Virtual Meeting
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SESAME

Synchrotron-light for Experimental Science and Applications in the Middle East

~~XAFS Beamline at SESAME and~~ Applications

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SESAME

UPEM UNIVERSITÉ PARIS-EST MARNE-LA-VALLÉE devient l'université Gustave Eiffel

Actinides in ceramics for NWS:

Combining experiments and theory to understand the local structural behavior

Messaoud Harfouche

Acknowledgment
Francois Farges,
Jean-Paul Crocombette

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.

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

Investigation:

Major elements (Zr, P, Si ….)

to validate the metamict structure(s) obtained by DM

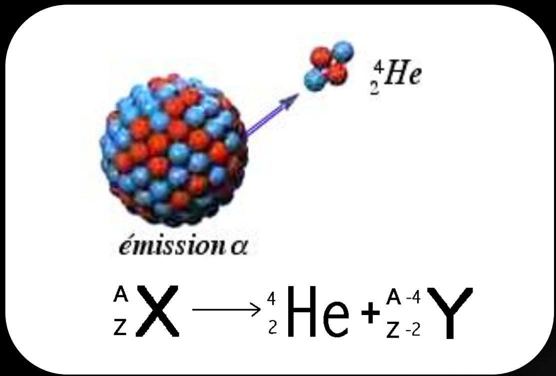
Substituted actinides (Th and U)

to understand the influence of radiation damage

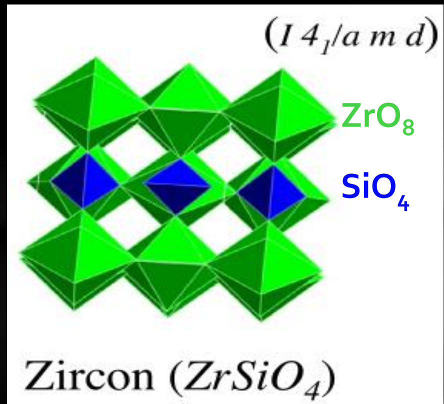
Why using natural analogues ?

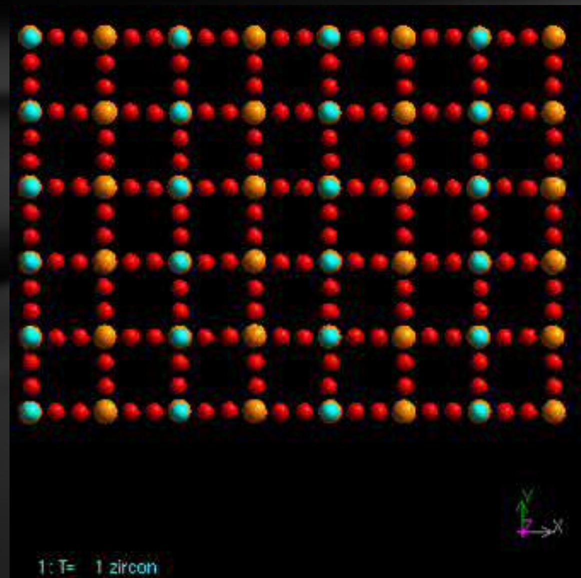
Ceramics	Analogues
High activity	Low activity
Medium period	Long period
Need special environment	Easy to handle
Risk of contamination	No risk of contamination
Red experiment	Green experiment

What causes the damage?



α-decay generates
E_{α} =~4.5 MeV
E_{r} = ~75 MeV





Influence of an α-decay on zircon structure
(by Trachenko et al., 2000)

Samples

Structure of the minerals

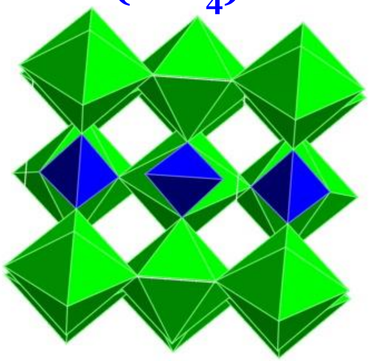
Zircon

Highly symmetric

Structure: Tetragonal

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

Tetrahedron (SiO_4)



Zircon ($ZrSiO_4$)

Geological Age and Dose

AGE:

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

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

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

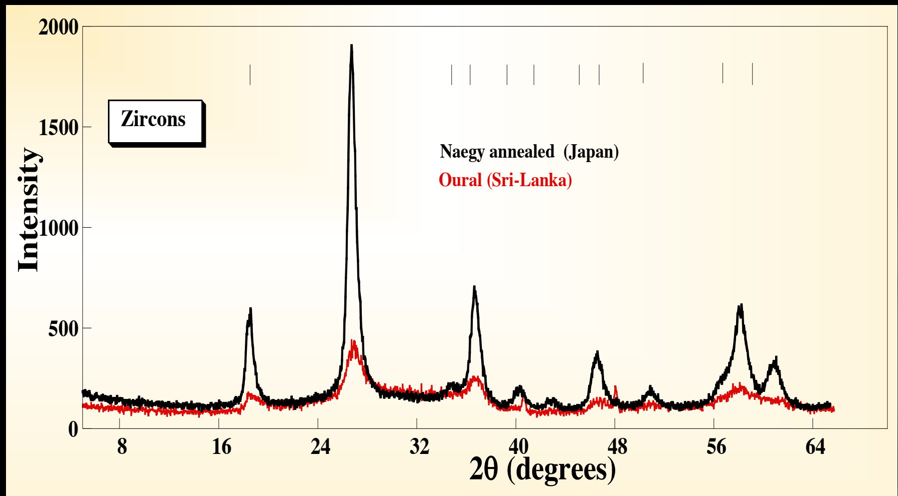
[a] (Farges et al. 1991).

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

Samples Characterization

Sample characterization XRD

Zircon

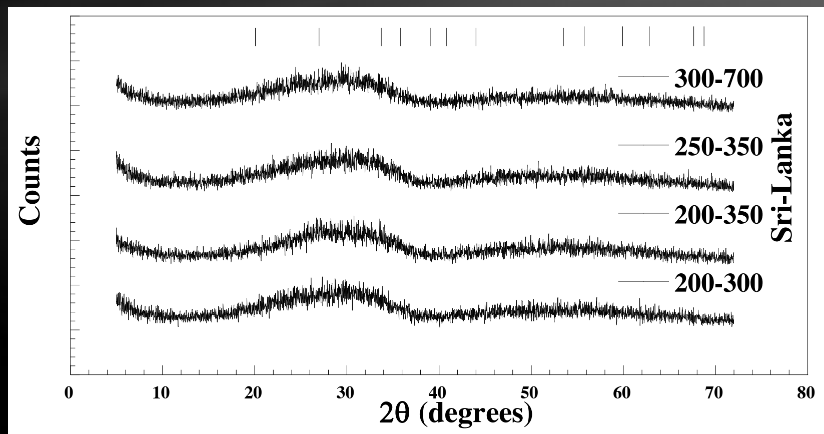


Crystalline &
Semi-crystalline

structure

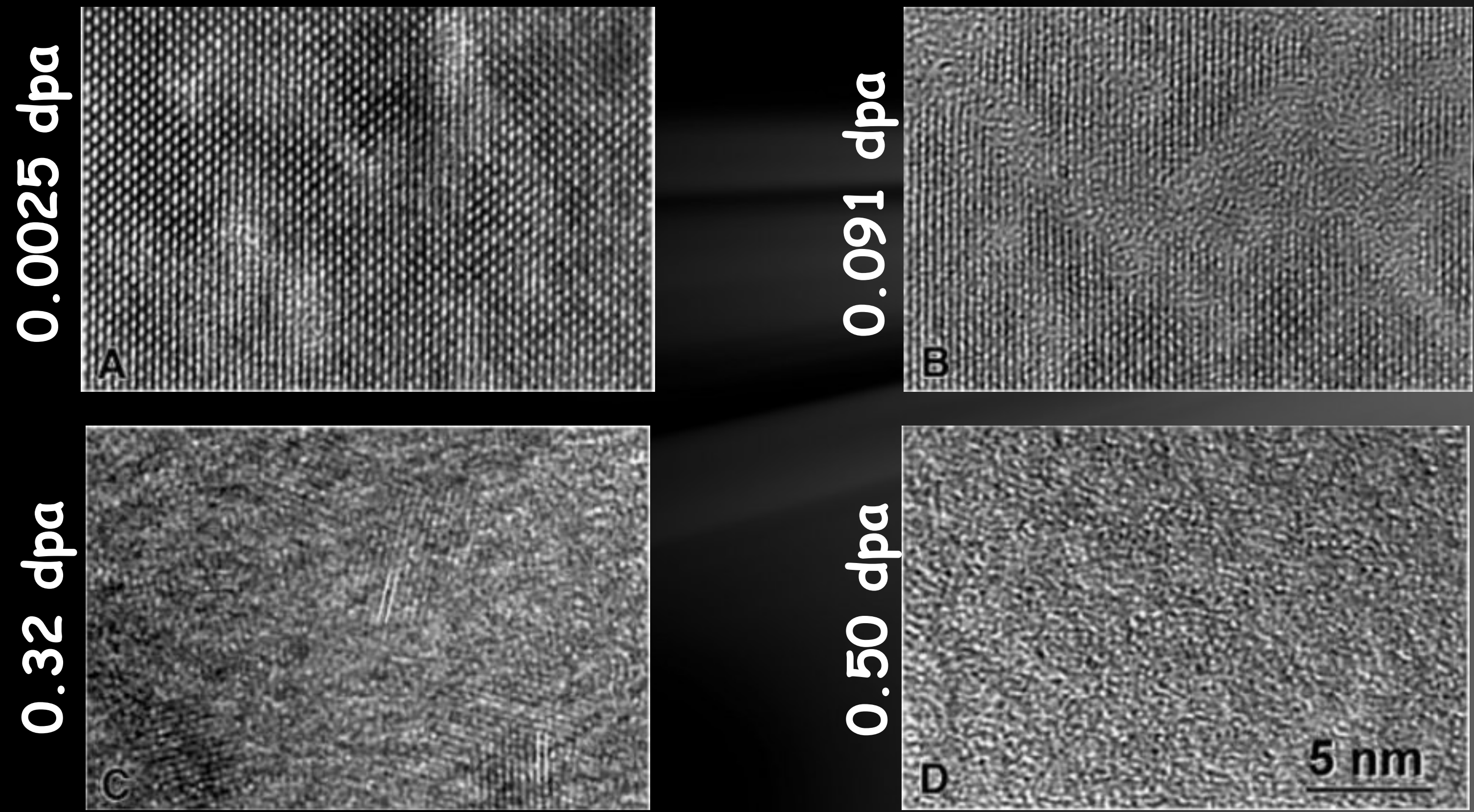
Metamict Zircons

Amorphous to x-rays



Sample characterization HRTEM

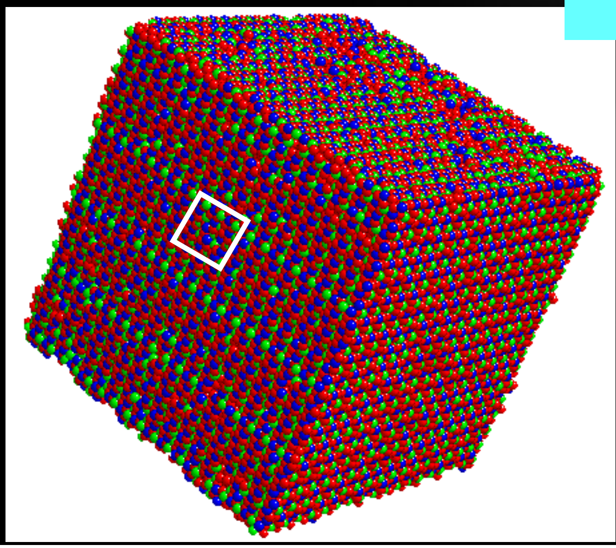
HRTEM micrographs of self-radiation damage in natural Zircons showing increased degree of amorphization with increasing dose *[Weber et al. (1994) Journal of Material Research, Vol. 9, Fig. 2, p. 690]*



Molecular Dynamic *(MD) Simulation*

- Modeling of zircon structure:
  - 140.000 atoms
  - 3 models:

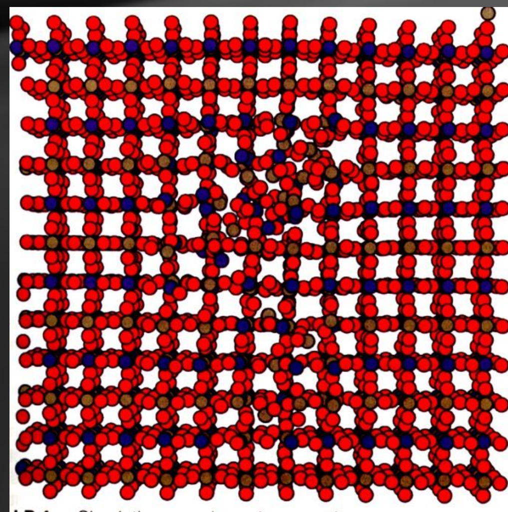
Model	U/Zr:
✵ 1 atom Zr => U	< 0.01 %
✵ 1000 Zr => U	4 %
✵ 3000 Zr => U	12 %



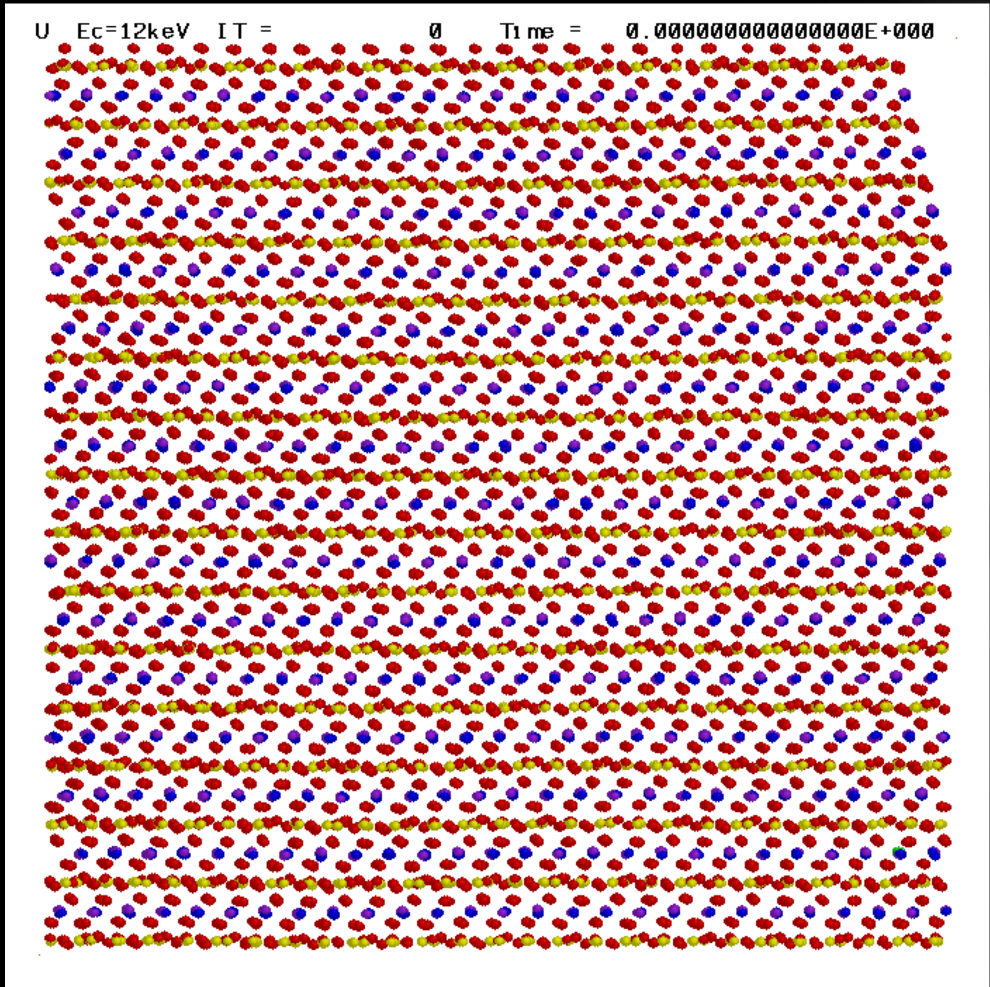
- Validation :
  - ✵ CN, Polymerization, BV
- Simulation :
  - ✵ ab-initio XAFS Calculation

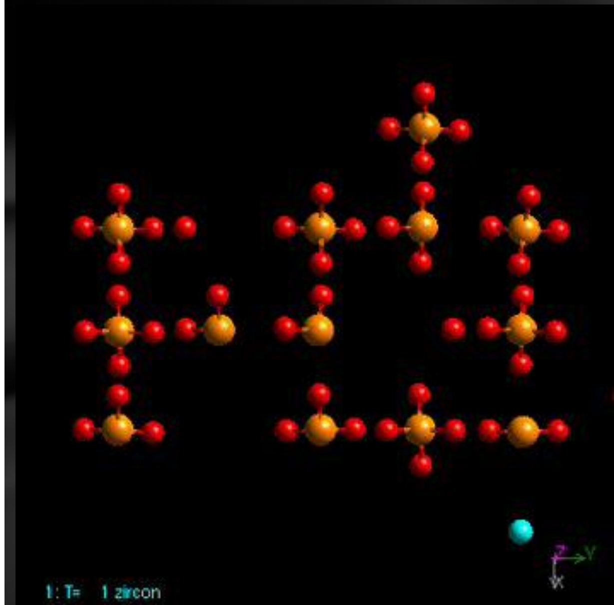
Cascades :

4 et 5 keV



Jean-Paul Crocombette (CEA, France)



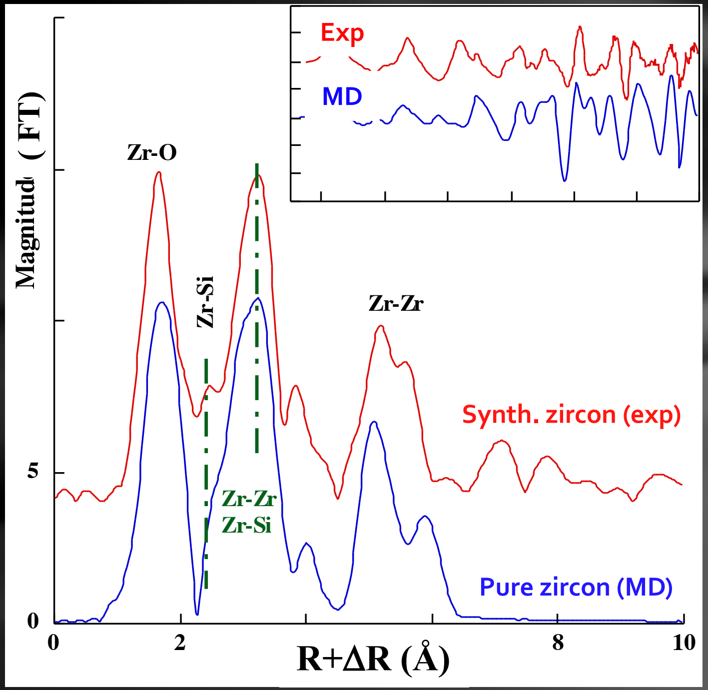


Validating DM models

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 (x_i, y_i, z_i)
- 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)

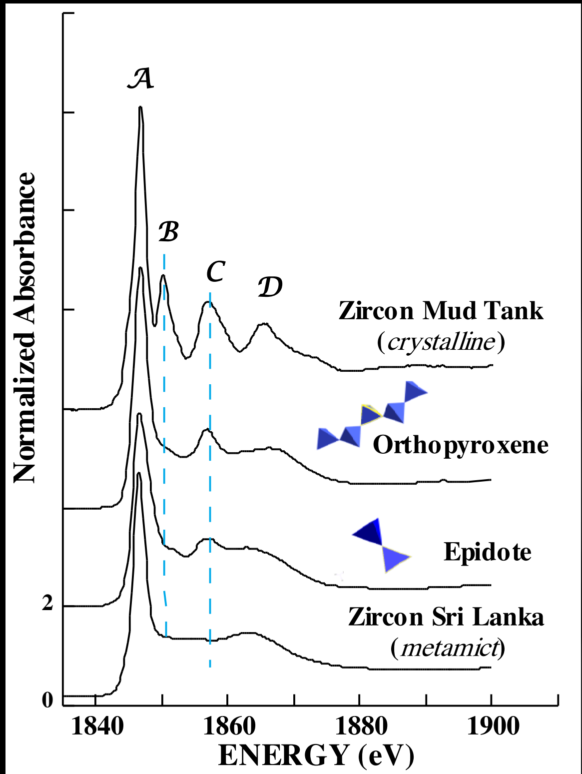


Very good Agreement between simulation and experimental results

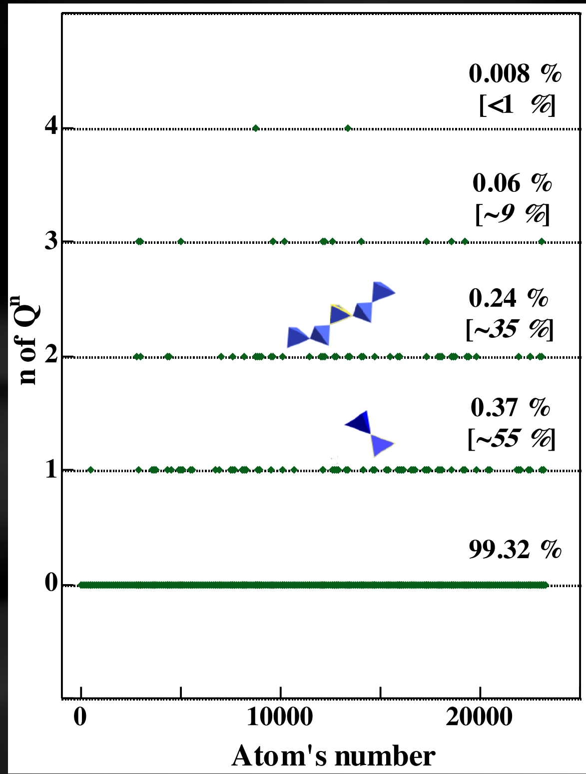
Validates the protocol followed - MD + FEFF -

Results

Si in zircon

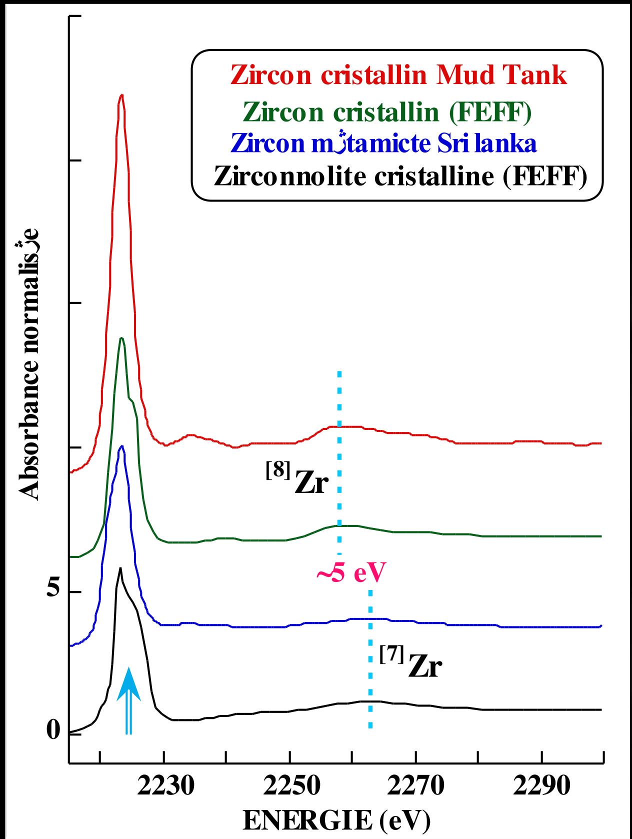


Most of polymerized SiO_n polyhedrons have 1 or 2 bridging oxygens.



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

Zr in zircon

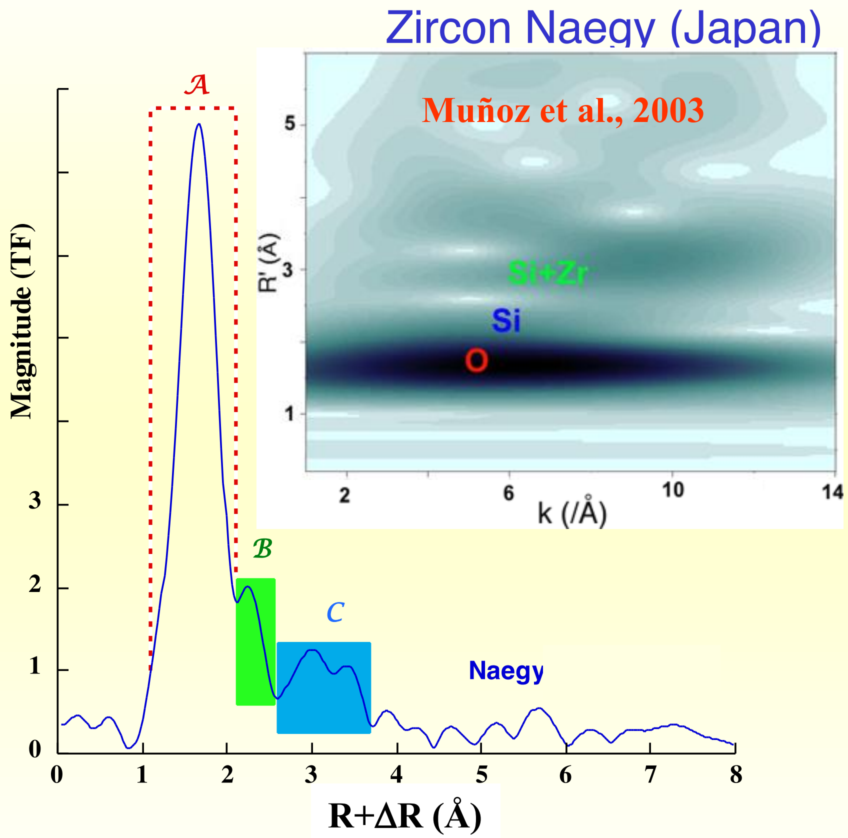


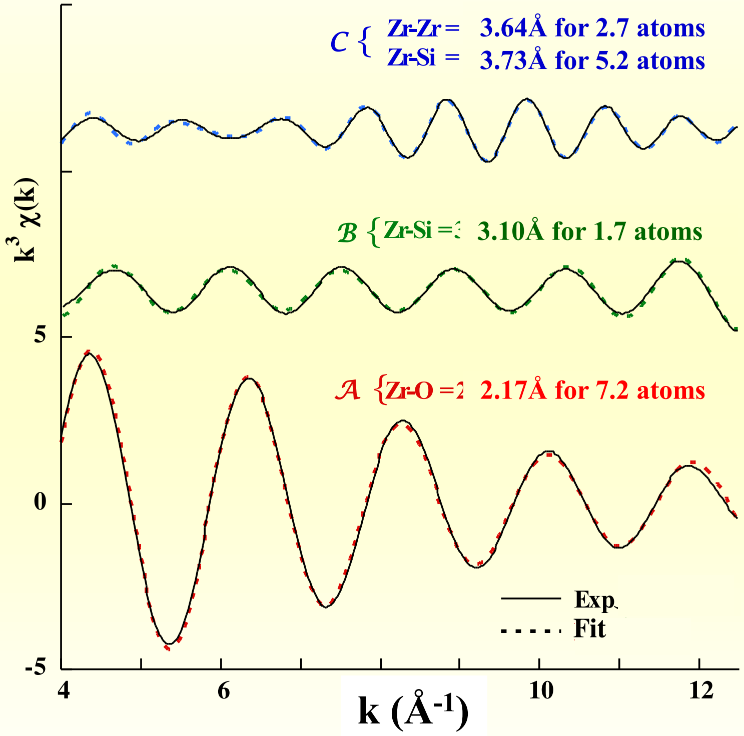
- XANES at Zr L_{III} edge
- sensitive to short range order
- [8]Zr (crystalline) ⇨ [7]Zr (metamict)
- coherent with Zr K edge (Farges, 1989)

> **Stong structural reorganisation of Si**
> (Farges, 1994)
>
> **Observed by RMN/IR**
> (Farnan, 1999; Zhang et al., 2000)

Data SA32 Super-Aco, LURE

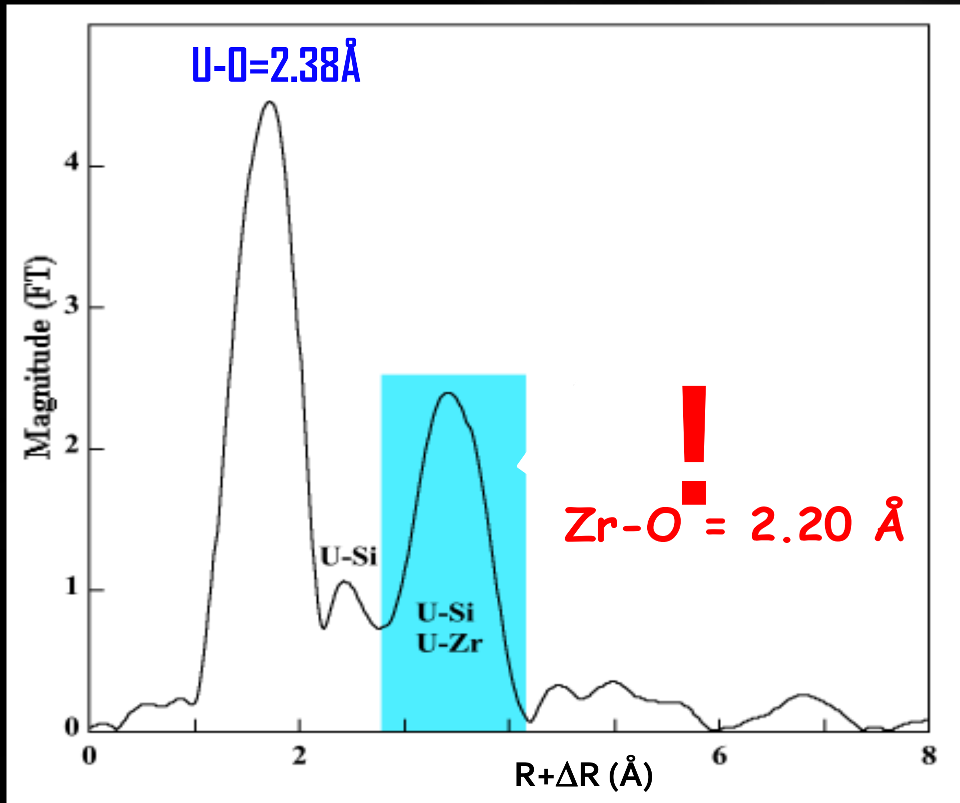
Zr in zircon





- 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)

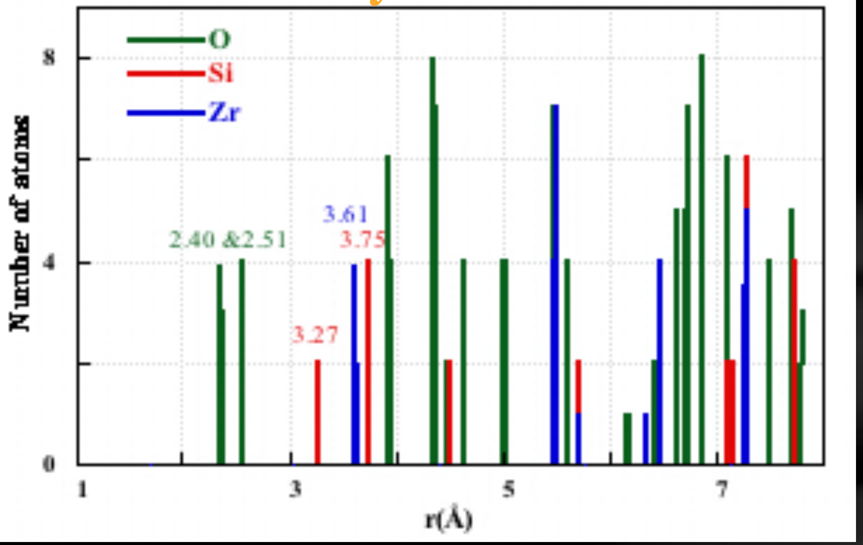
crystalline : expansion of the local structure around U

Zr appears as next neighbors ➔ U is in zircon structure

U in zircon (MD)

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

Crystalline

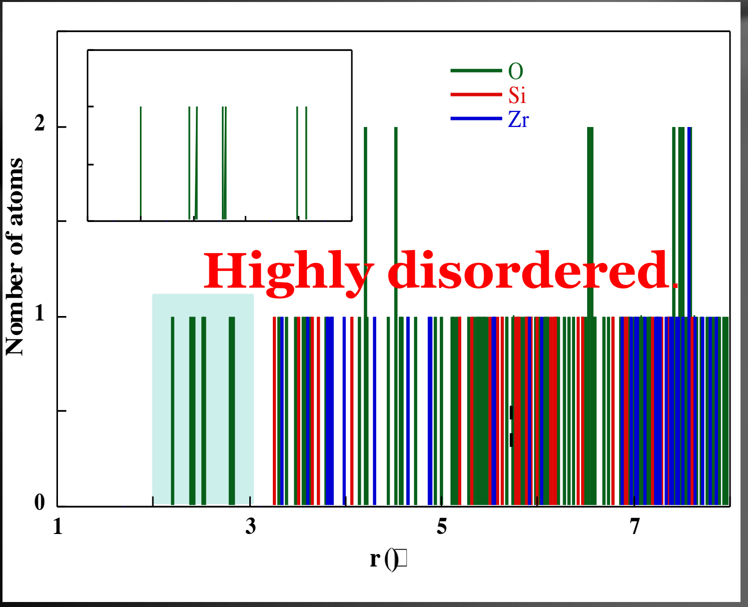


CN = 8 (2.4 and 2.51 Å)

Si short distance (3.27 Å)

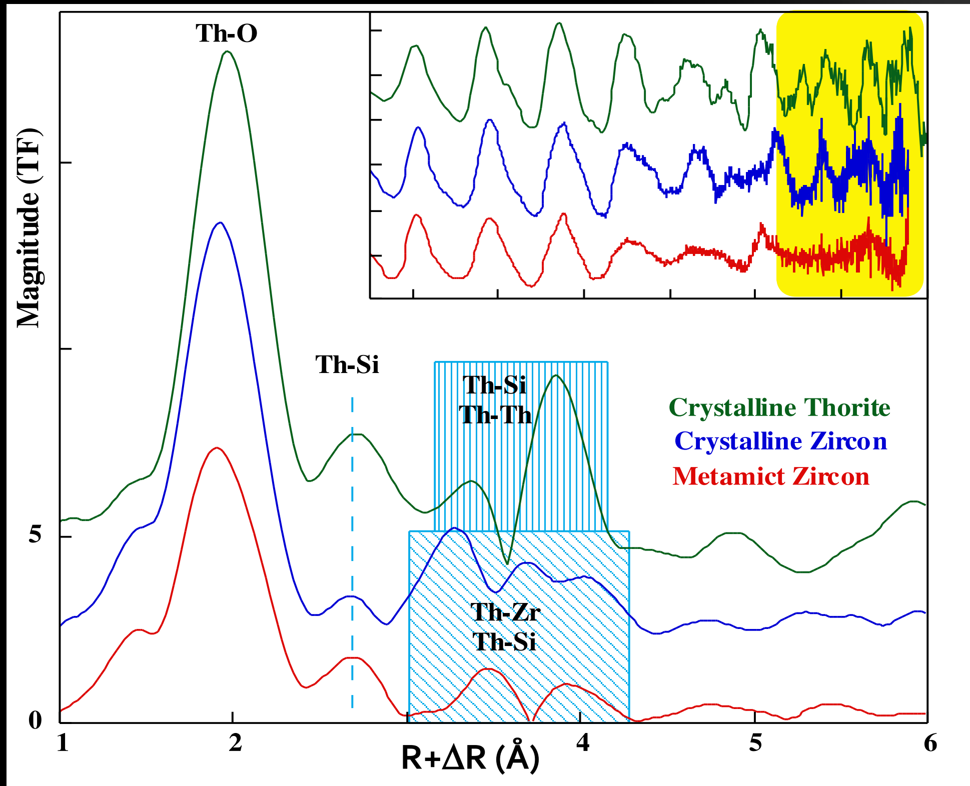
Si & Zr next neighbors

Metamict



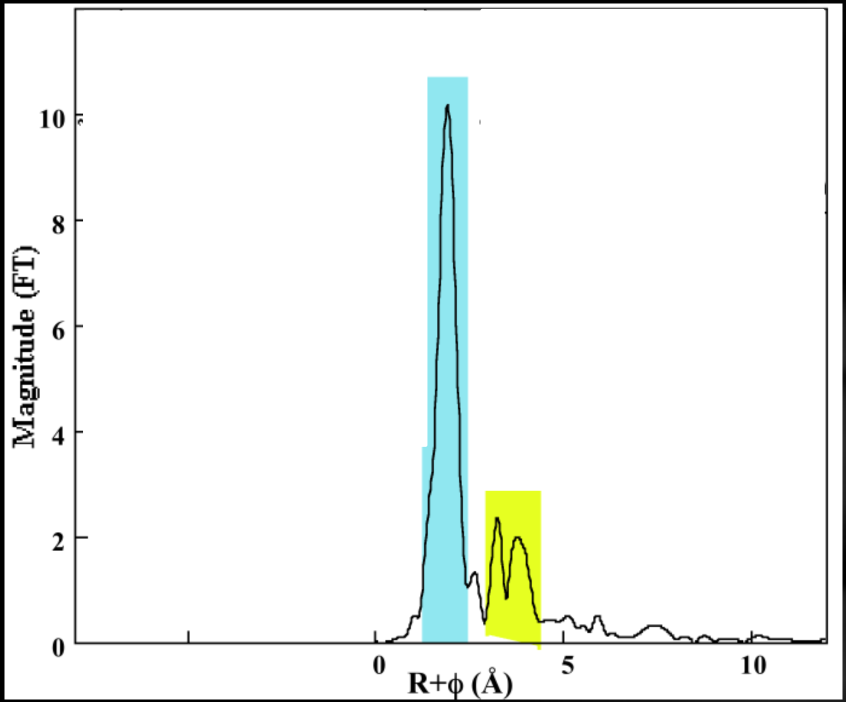
- U in Zircon Structure
- Local Expansion around U
- High Structural Disorder

Th in zircon

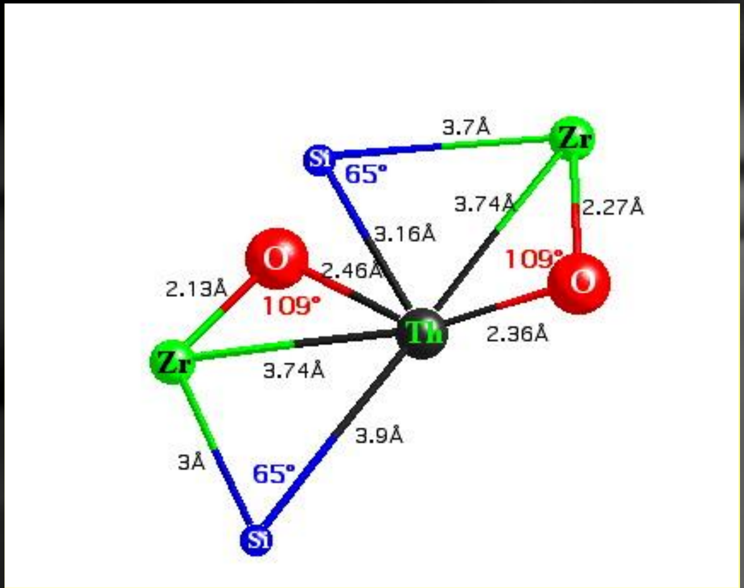


- At high *k* values, Th-site in zircon is different to that for $ThSiO_4$
- Th is not as in a thorite-like structure, but it replaces Zr in zircon

Th in zircon



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



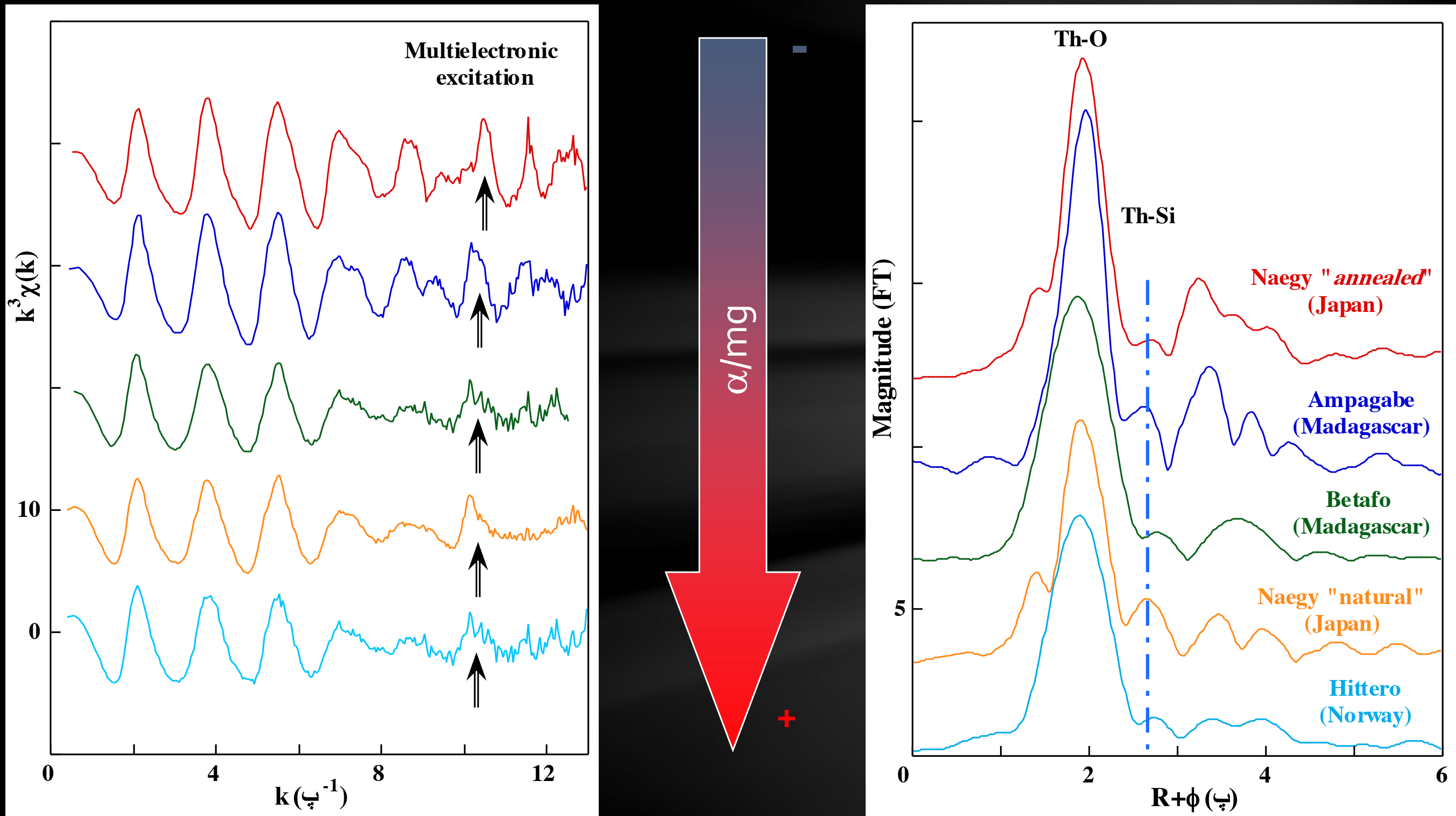
Cluster $ThO_8Si_2Si_4$ (thorite-like)

↓

Cluster $ZrO_8Si_2Si_4$ (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).

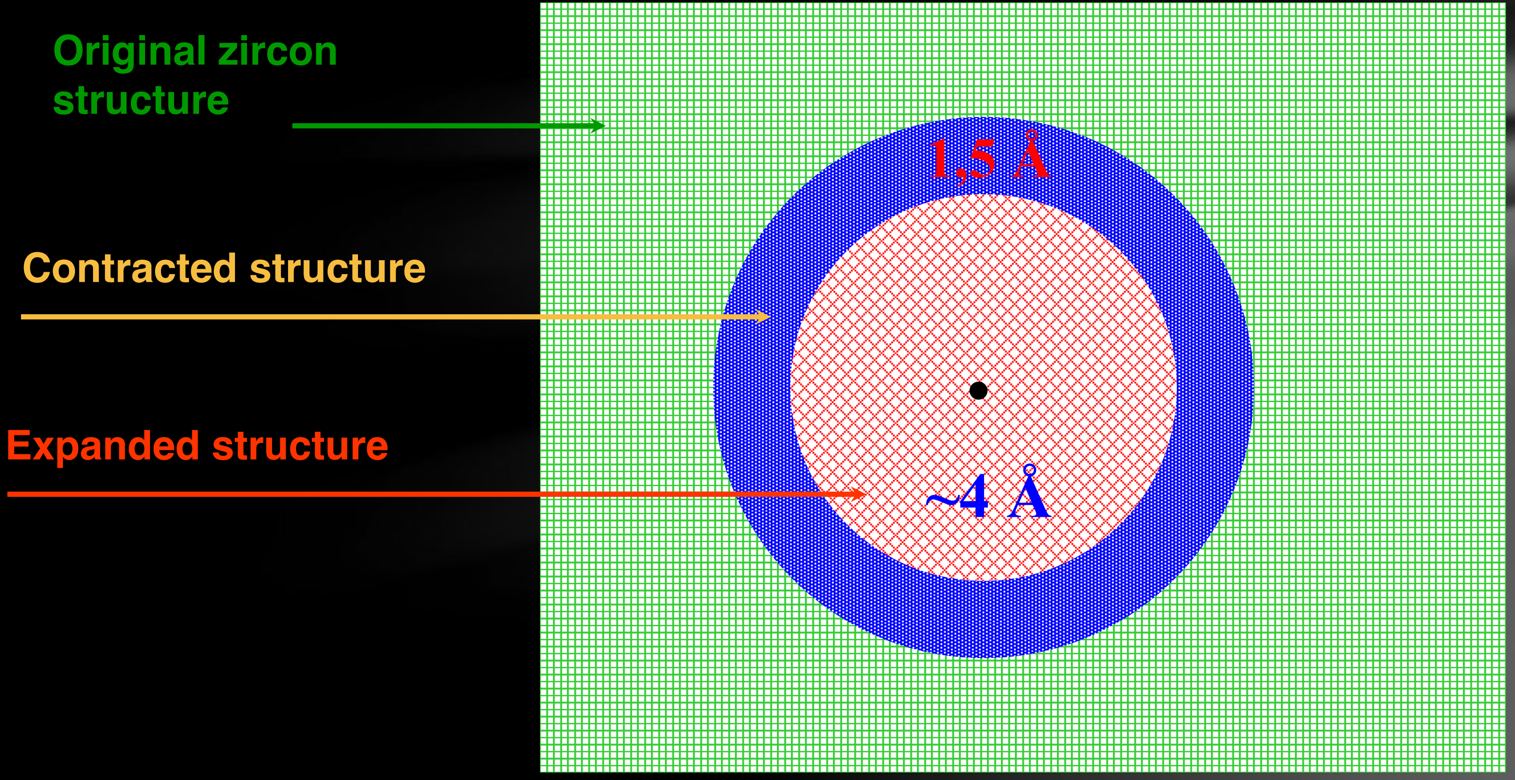
- ❑ The medium range structure around actinides in crystalline zircon shows:
  - ➢ an expanded region due to the insertion of larger actinides (up to 4 Å),
  - ➢ a compressed region between 4 and 5.5 Å,
  - ➢ the structure is back to the original crystalline zircon one above5.5 Å.

- ❑ 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**



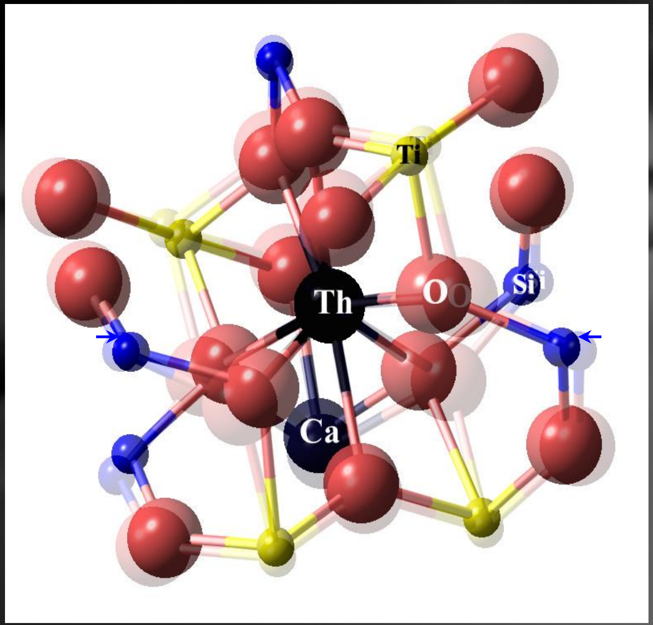
Discussion

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+ ????**



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

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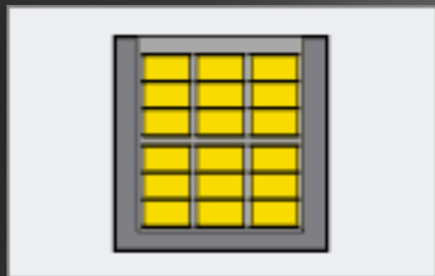
Nuclear Waste Management

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

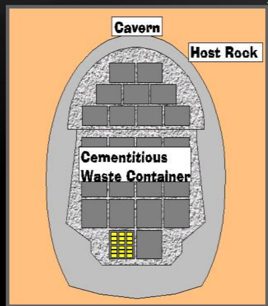
Long-lived intermediate-level waste (ILW)

Waste package (cement & steel)

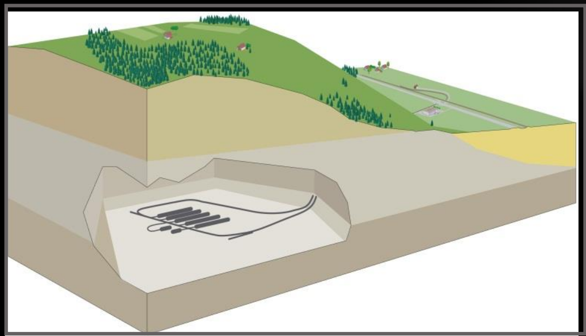
Container (concrete, mortar, steel)



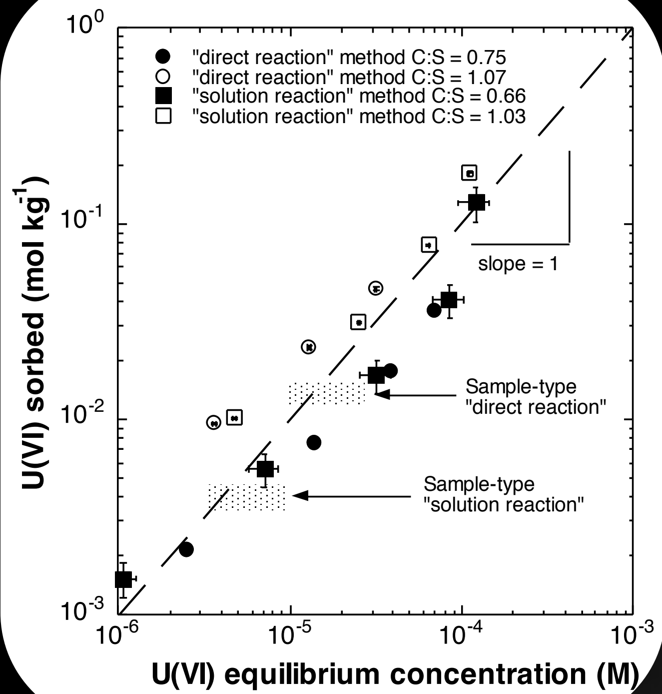
Cavern backfill (porous mortar)



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

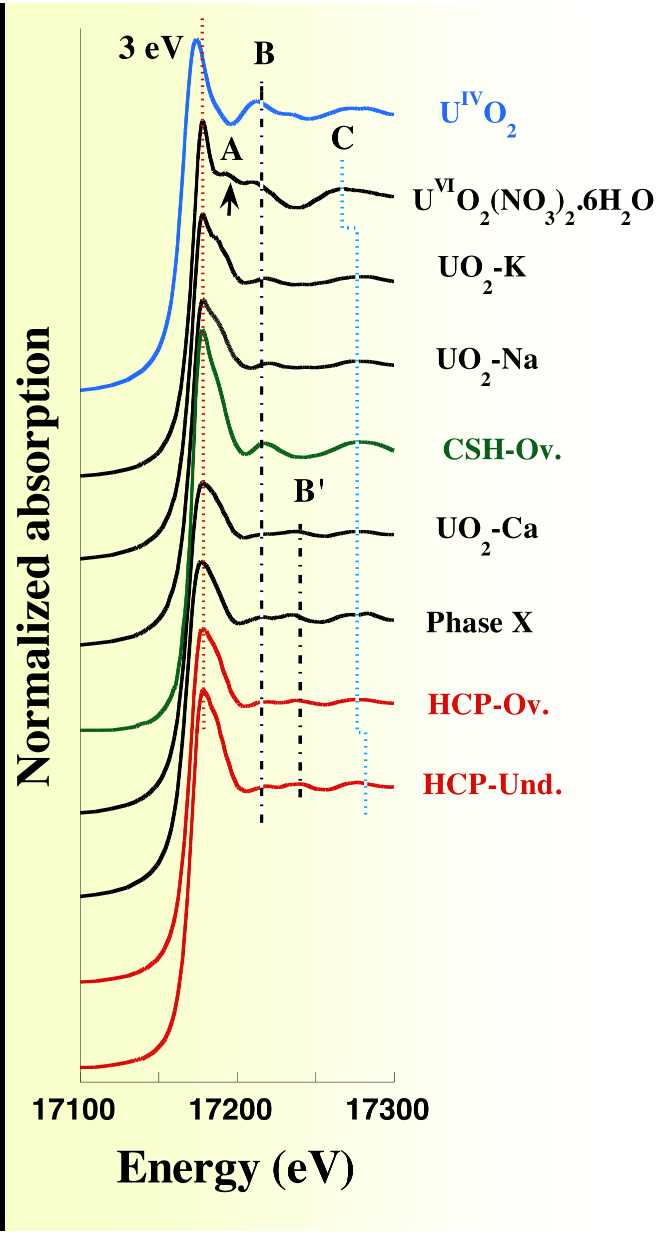
(CaO and SiO_2) used as reactants

References

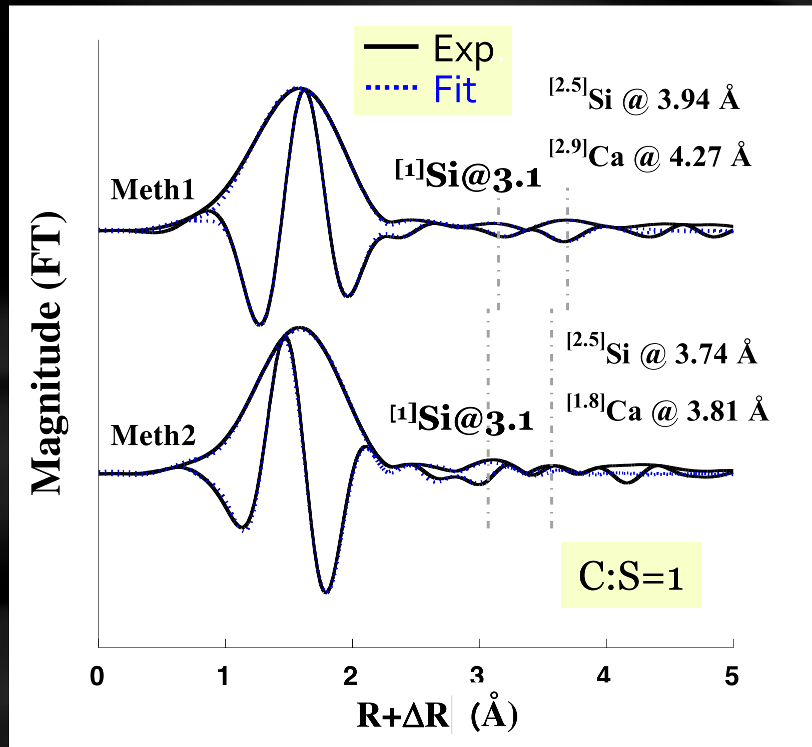
U(VI) $Ca(OH)_2$ / pH =12.5 → amorphous

U(VI) K^{+}/ pH =13.3 → crystallized

U(VI) Na^{+}/ pH =13.3 → crystallized



U(VI): adsorption process

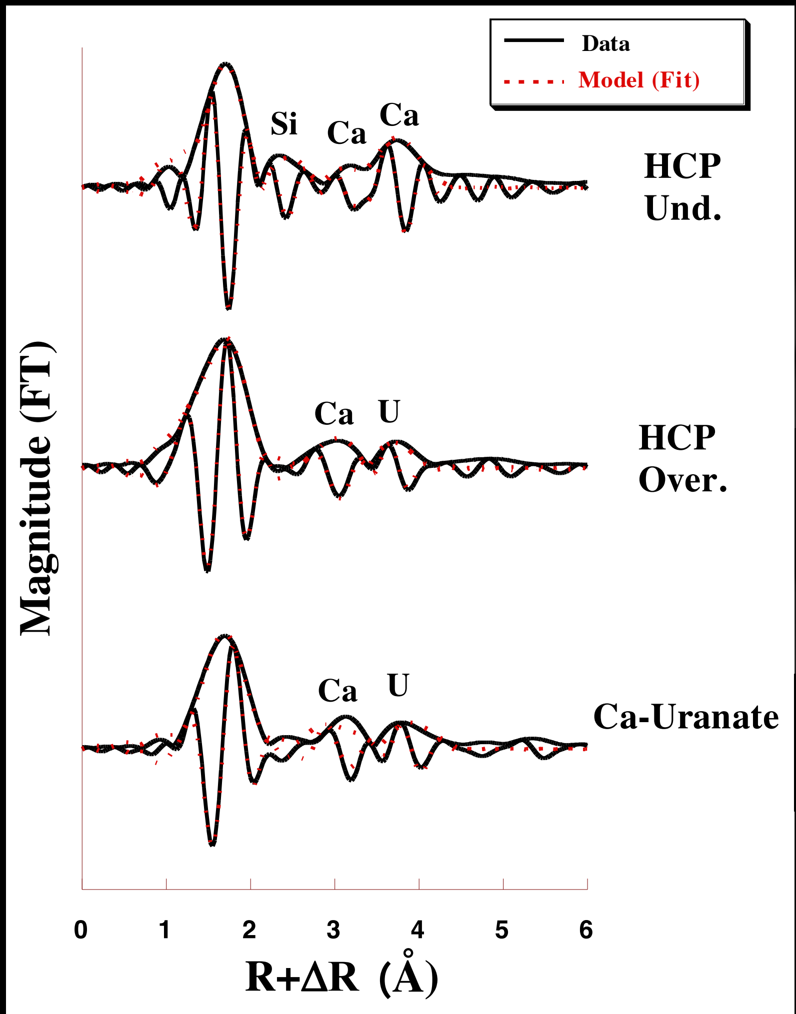


⇒ No U(VI) ➡ U(IV)

⇒ Uranophane-like with:

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

XAFS measurements of Cr ~~V, and As~~ within the various mixtures of oil shale ash solidifying additives

Jordan

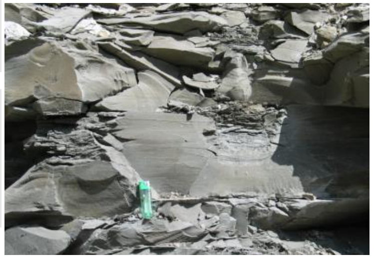
T. El Hassan, A. Al-Darabee, W. Sakhnah

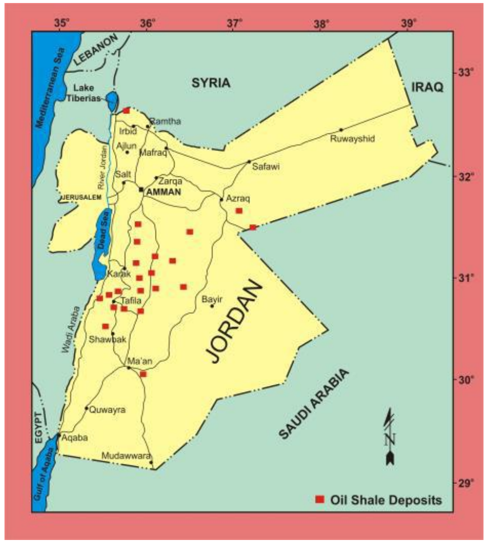
Visit of **JAEC's Commissioner** & Chairman of the Jordanian National Committee of SESAME (**JNC**)

XAFS measurements of Cr ~~V, and As~~ within the various mixtures of oil shale ash solidifying additives

Jordan has huge highly organic matter -rich oil shale resources. Total Organic Carbon (17.39 - 22%)

Jordan is utilizing the oil shale, that would create huge ash tailings containing high concentrations of trace elements.

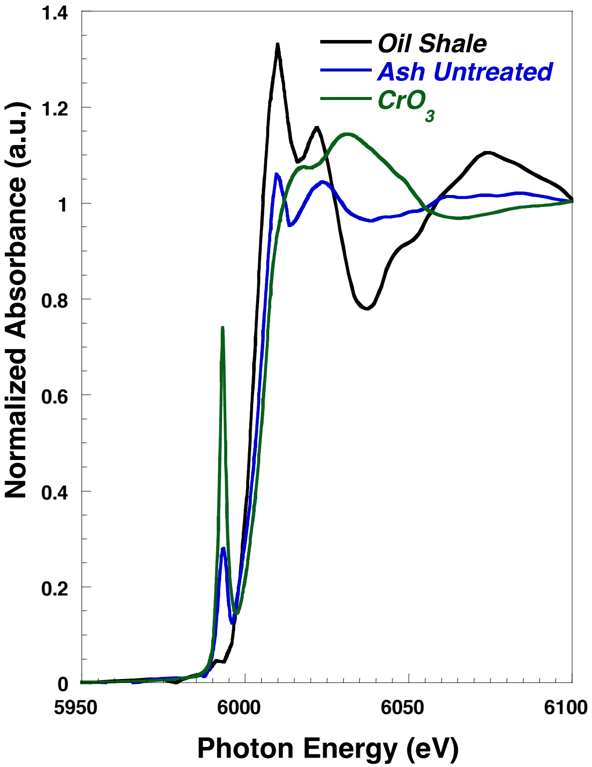


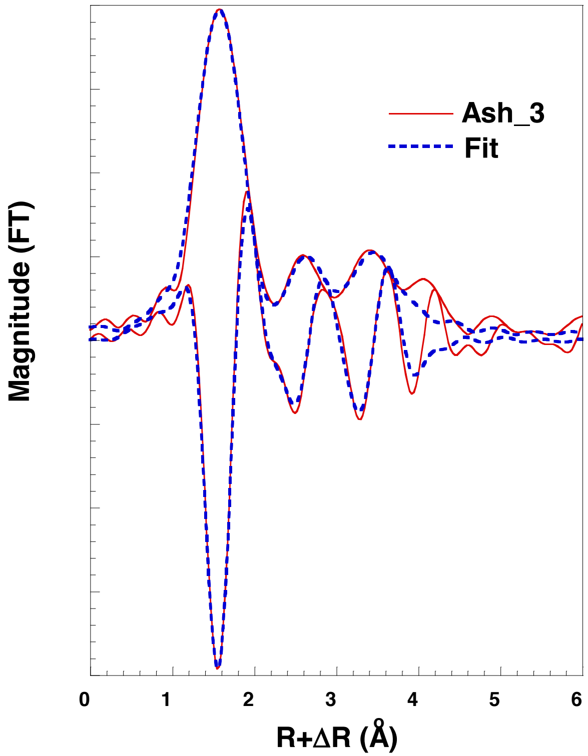


through the interaction with rainwater it would form solutions resembling acid mine drainage. This leachate might reach soil, plants beside the surface and groundwater resources, thus causing hazardous pollution.

Therefore, attempts were made to find suitable mixture of additives with the ash in order to solidify the toxic elements with higher oxidation states.

XAFS measurements of Cr ~~V, and As~~ within the various mixtures of oil shale ash solidifying additives



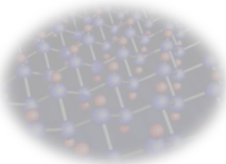


Ligand	N (atom)	R (Å)	s^2 (Å^2)	ΔE (eV)
Cr-C	6.0	2.03	0.0002	4
Cr-Cr	0.7	2.72	0.003	
Cr-Cr	4.1	3.70	0.008	
Cr-C	4.2	3.9	0.008	

Cr is not in an oxide

BUT

in an **organic** form



Thank you For Your Attention