Ongoing XAS collaboration between SCK•CEN and Aalto University

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STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

Outline

- **Background**
- Examples of actinide studies
- Fuel lab introduction
- Collaboration possibilities

Background

- Personal interest towards synchrotron methods since PhD work on III-V semiconductors
  - Photoluminescence blue shift as a function of In-N bonds in GaInAsN
  - These things can be ACTUALLY measured!

- Visiting scientist at the UW-Madison, USA
  - SSRL and collaboration with S. Conradson (complexity of UO_{2+x} ....)

- Arrival to SCK•CEN in 2014
  - Productive PhD students in newly established fuel laboratory
  - Storage full of samples ready for further analysis
  - Collaboration with R. Bes

Background

- UO_2 and its derivatives are the main fuel used in the light water reactors globally
  - 450 reactors online, 58 under construction (158 ordered or planned)*)
  - 150 tons of U per reactor per year (→ 65 000 t/year)*)

- Nuclear fuel – complex system
  - Simple binary fluorite consisting of U and O
  - ~100 years of studies – simple oxidation of UO_2 still remains a subject of debate

- Spent nuclear fuel – the most complex system on Earth
  - Crystal damage from fissions
  - Alternating chemical environment from fission products
  - Extreme radiotoxity

*) http://www.world-nuclear.org/information-library/facts-and-figures/world-nuclear-power-reactors-and-uranium-requireme.aspx

Background

SCIENTIFIC REPORTS

OPEN

Direct observation of pure pentavalent uranium in U_2O_5 thin films by high resolution photoemission spectroscopy

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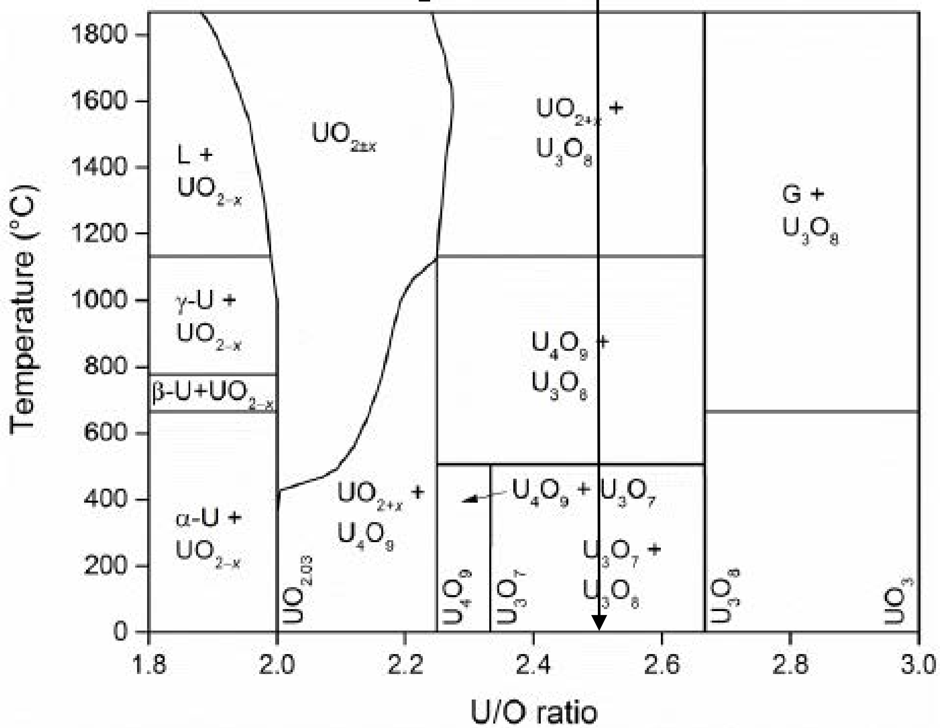
T. Gouder, R. Eloirdi & R. Caciuffo

Oxidation of UO_2



G. Leinders (PhD Thesis, https://lirias.kuleuven.be/handle/123456789/546279)

→ Understanding the behavior of (spent) fuel is a challenge

Spent fuel inventory

Heavy metal atoms	
U	238.00
Np	237.00
Pu	240.00
Am	242.00
Cm	244.00
Cf	249.00

Fission products	
Li	6.94
Be	9.01
C	12.01
Zn	65.37
Ga	69.72
Ge	72.59
As	74.92
Se	78.96
Rb	85.47
Sr	87.62
Y	88.91
Zr	91.22
Nb	92.91
Mo	95.94
Tc	97.00
Ru	101.07
Rh	102.91
Pd	106.40
Pd	106.40
Ag	107.87
Cd	112.40
In	114.84
Sn	118.69
Sb	121.75
Te	127.60
Ba	137.34
La	138.91
Ce	140.12
Pr	140.91
Nd	144.24
Pm	145.00
Sm	150.40
Eu	151.96
Gd	157.25
Dy	162.50
Tb	158.92
Ho	164.93
Er	167.26
Tm	168.93
Yb	173.04
Pb	207.19

Gaseous and volatile fission products	
H	1.00
He	4.00
Br	79.09
Kr	83.80
I	126.90
Xe	131.29
Cs	132.91

J. Spino, P. Peerani / Journal of Nuclear Materials 375 (2008) 8–25

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Examples of actinide studies

- Challenges (mainly) due to radioactivity
  - Transport of samples
    - Can become costly and time consuming
    - Exempt limit for U and Th = 1000 Bq → sample mass < ~1 g
    - Optimization required (and sometimes possible)
  - Preparation of samples
    - Double sealing required (Kapton)
    - 10 – 20 mg of UO_2 in BN
    - No powder allowed (pressed pellet)

  - Dedicated beamline for radioactive samples
    - MARS at Soleil
    - ROBL / ID26 at ESRF
    - ANKA at KIT
    - …

Examples of actinide studies

Journal of Nuclear Materials 489 (2017) 9–21

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Charge compensation mechanisms in $U_{1-x}Gd_xO_2$ and $Th_{1-x}Gd_xO_{2-x/2}$ studied by X-ray Absorption Spectroscopy

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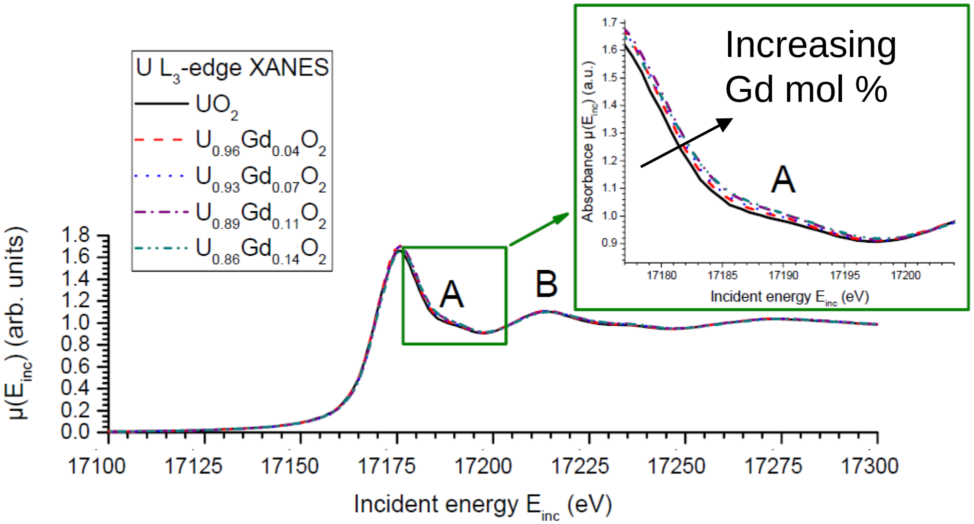
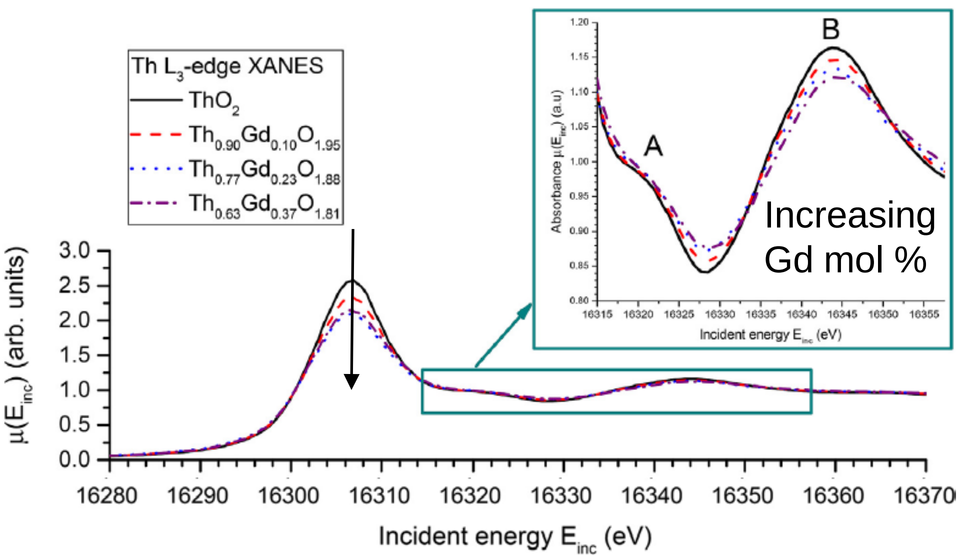
- Practical interest: Gd has large neutron cross-section - used as a burnable neutron absorber in the fresh reactor core
- Challenge: Gd^{3+} substitution to the position of U^{4+} or Th^{4+}
- U can be (3+), 4+, 5+, and 6+, Th is always 4+
- Mechanism for charge compensation?
- XANES and EXAFS @ MARS (Soleil, France)

Examples of actinide studies

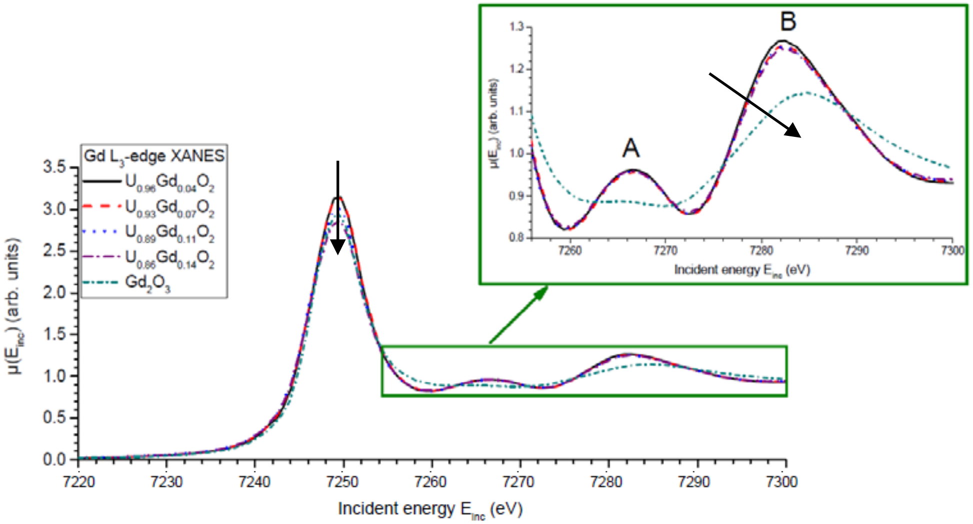


- XANES for U L_3 edge
  - Intensity increases on the high-energy side:
    - Fingerprint for U^{5+}formation
    - Linear combination fitting using reference spectra indicated this being the case

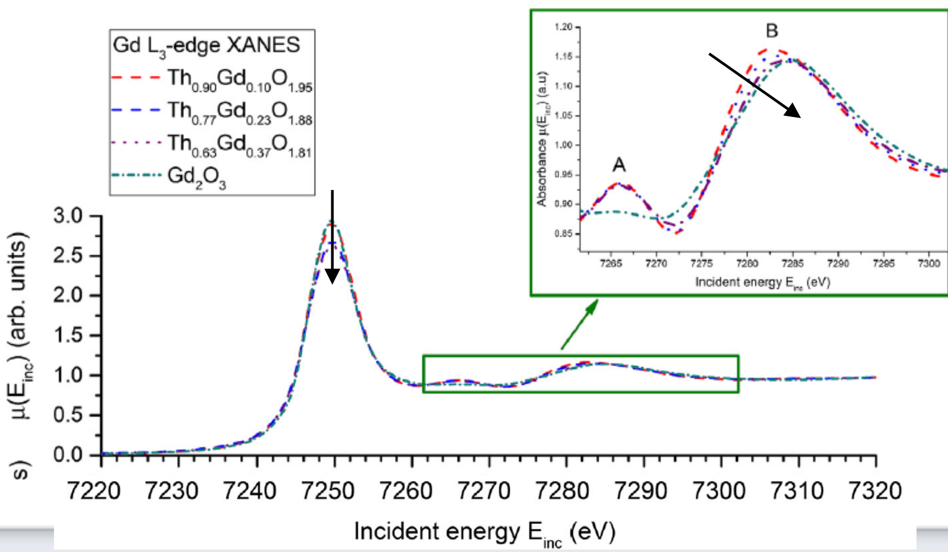


- XANES for Th L_3 edge
  - Features remain at fixed positions:
    - Th^{4+} is stable (as should be)
    - Uniform reduction is observed, charge is compensated by O vacancies which induce to local lattice disorder and reduced coordination number?

Examples of actinide studies



- XANES for Gd L_3 edge in UO_2
  - White line at fixed position:
    - Gd^{3+} is stable
    - Reduction in intensity: disorder
  - Comparison to Gd_2O_3
    - Same resonances, A – B difference approaches Gd_2O_3



- XANES for Gd L_3 edge in ThO_2
  - White line at fixed position:
    - Gd^{3+} is stable
    - Reduction in intensity: disorder
  - Comparison to Gd_2O_3
    - Same resonances, A – B difference approaches Gd_2O_3

Examples of actinide studies

+ full EXAFS analysis for U L_3, Th L_3, and Gd L_3

Conclusion:

- Charge compensation in Gd-doped UO_2 proceeds via disorder and formation of U^{5+}
- Charge compensation in Gd-doped ThO_2 proceeds via disorder and formation of O vacancies
- Thus: $U_{1-x}Gd_xO_2$ vs $Th_{1-x}Gd_xO_{2-x/2}$

Examples of actinide studies

Inorganic Chemistry

Inorganic Chemistry 56 (2017) 6784

Communication

pubs.acs.org/IC

Evolution of the Uranium Chemical State in Mixed-Valence Oxides

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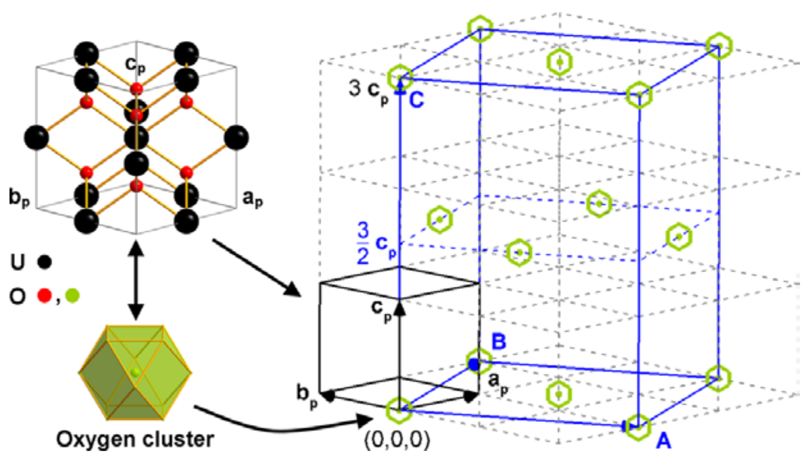
[∥]Helmholtz Zentrum Dresden-Rossendorf (HZDR), Institute of Resource Ecology, P.O. Box 510119, 01314 Dresden, Germany

- Main motivation: breakthrough in solving the crystal structure of U_3O_7
- Does chemical state of U match the proposed structure?
- HERFD-XANES @ ID26 (ESRF)

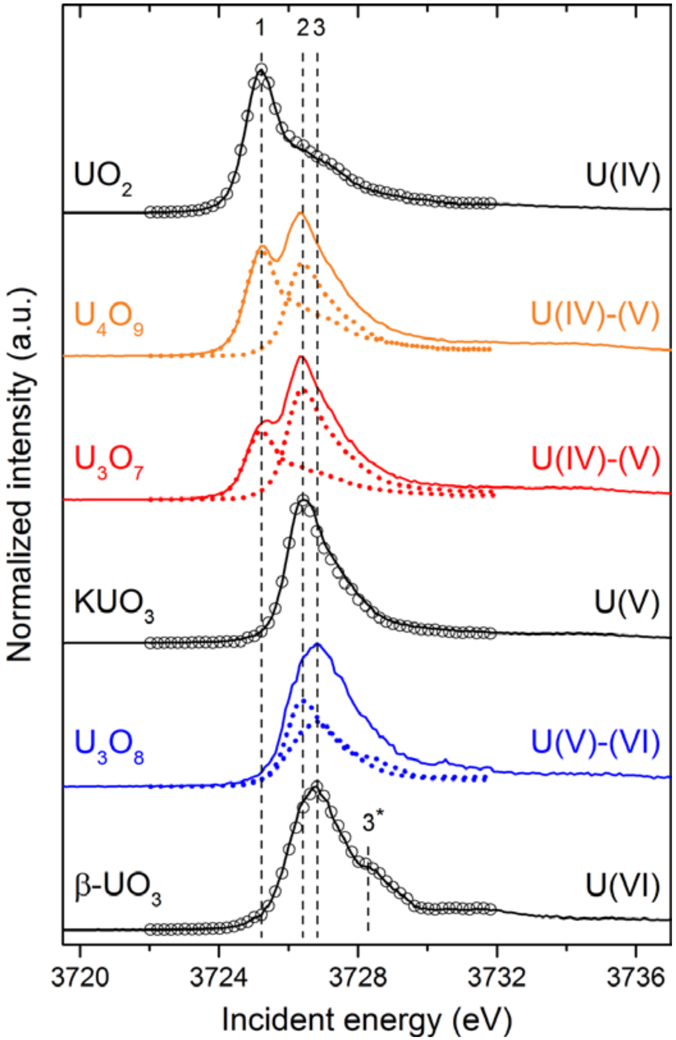


G. Leinders et al., Inorganic Chemistry 55 (2016) 9923

Examples of actinide studies

- "Typical" approach:
  - Well known references and fitting for the unknown
- Excellent agreement with the theory
  - U_3O_7 matches perfectly
  - world's best U_4O_9
- EXAFS was done @ ROBL (ESRF)
  - Analysis ongoing

	relative abundance of valence states (%), ±3%			average U valence, ±0.03	
	U(IV)	U(V)	U(VI)	exptl.	theor.
U_4O_9	51	49	0	4.49	4.50
U_3O_7	36	64	0	4.64	4.67
U_3O_8	0	65	35	5.35	5.33



Inorganic Chemistry 56 (2017) 6784

Examples of actinide studies

Journal of Nuclear Materials 507 (2018) 50–53

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Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Laboratory-scale X-ray absorption spectroscopy approach for actinide research: Experiment at the uranium L_3-edge

Check for updates

R. Bès [a, *], T. Ahopelto [b], A.-P. Honkanen [b], S. Huotari [b], G. Leinders [c], J. Pakarinen [c], K. Kvashnina [d, e]

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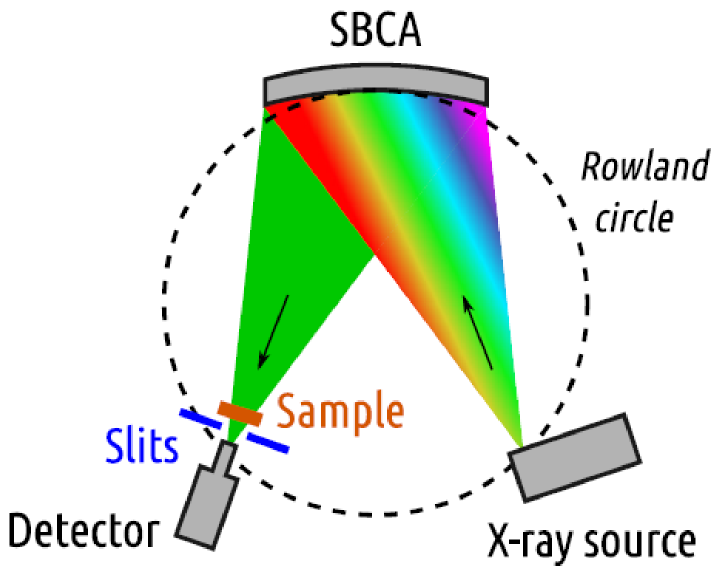
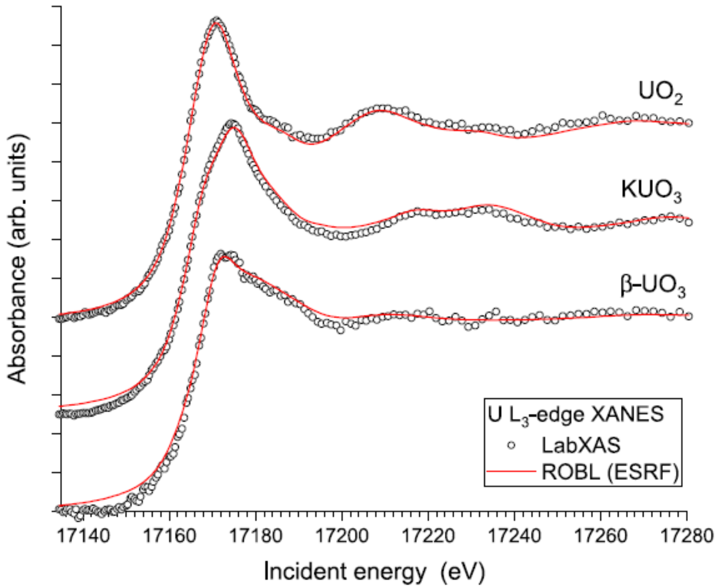
- Demonstration of lab-XAS @ University of Helsinki
- XANES measurement at U L3 edge – comparison to measurement @ ROBL (ESRF)

Examples of actinide studies





- Lab-XAS: Time consuming compared to synchrotron (24h vs 2h) but all XANES features were reproduced!
- Set-up in the lab offers possibilities: screening of samples before beam time, in-situ development, instrument time availability,…

Outline

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- **Fuel lab introduction**
- Collaboration possibilities

Fuel fabrication: from powder to pellet

Powder(s) As-received
↓
MILLING/ HOMOGENEISATION
↓
Milled Homogeneous Powder
↓
PRESSING
↓
Green Pellets
↓
SINTERING
↓
Sintered Pellets
↓
GRINDING
↓
Finished Pellets
↓
Clad filling & welding under pressure

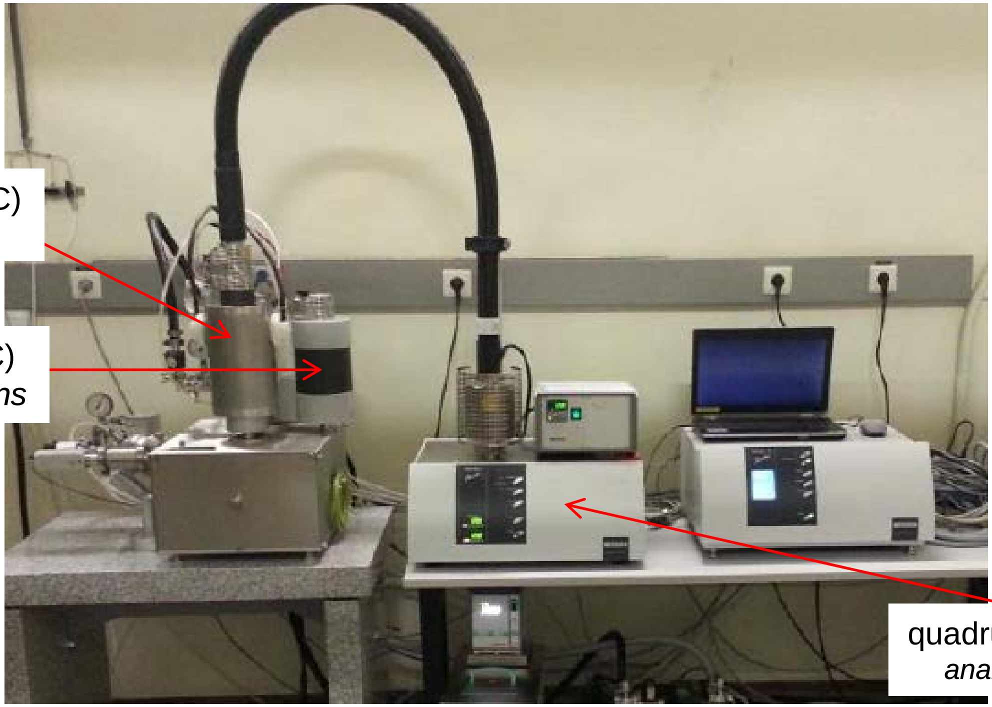
Fuel lab introduction

- **Silmutaneous Thermal Analyser (STA)** *Netzsch Jupiter 449 F1*

  → **Thermogravimetry** (TGA): precise measure of sample mass change in function of time/temp in a controlled atmosphere
  → **Differential Scanning Calorimetry** (DSC): precise measure of heat fluxes from sample in function of time/temp in a control. atm.
  → **Mass Spectrometry** (MS): analyse the chemical composition of the evolved gases during test

Graphite furnace (25-2000°C)
Reducing conditions only

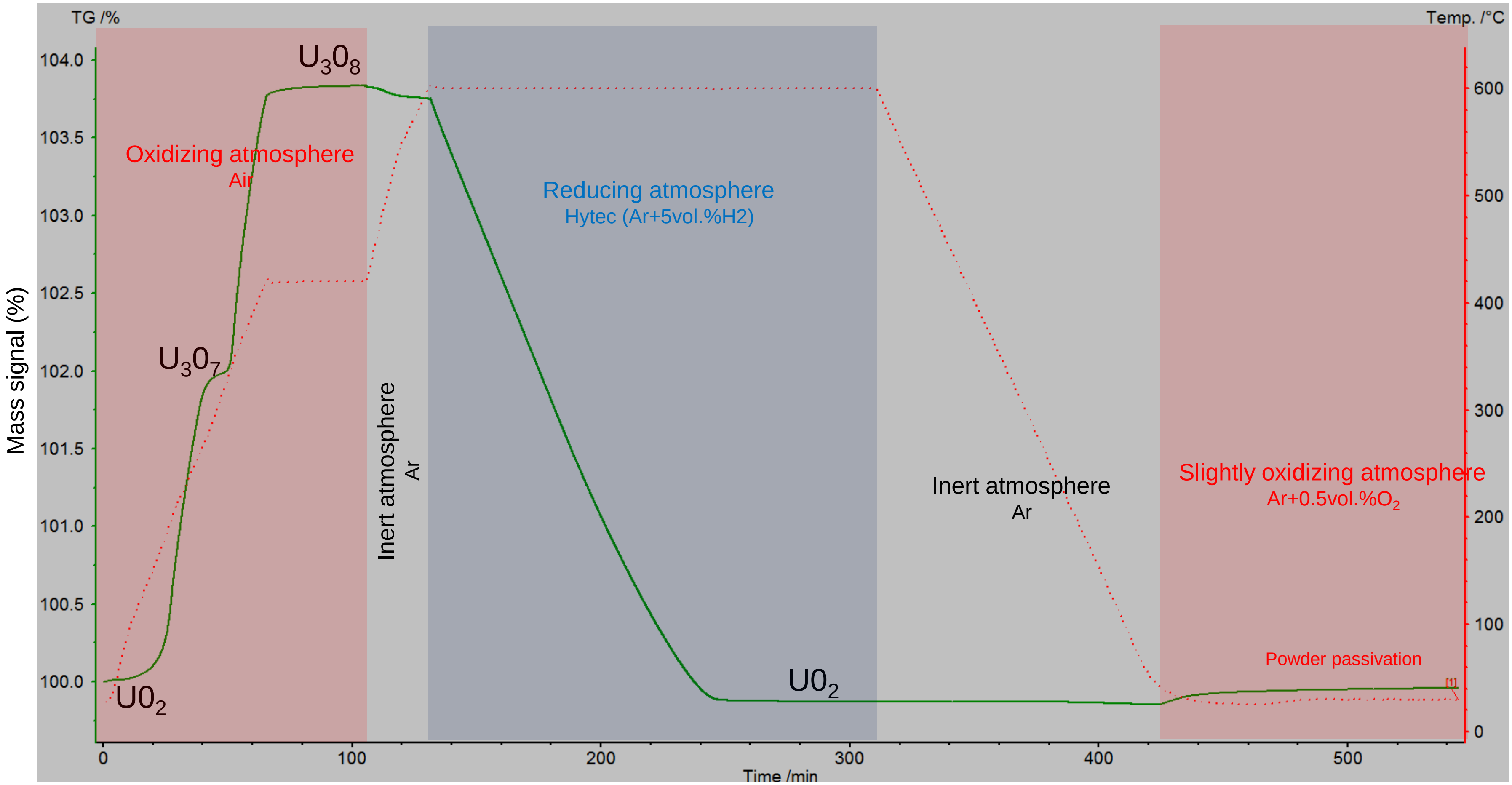
Rodium furnace (25-1680°C)
Reducing/oxidizing conditions



quadrupole Mass Spectrometer (MS)
analyzes evolved gases composition

Fuel lab introduction

U02 → U3O8 → UO2 transformation followed by TG



Fuel lab introduction

- Complete laboratory for fuel pellet fabrication from powder to pellet (U and Th)

- Coming: new laboratory for MOX fuel processing (everything in glove boxes).

- Complimented by capabilities for full post-processing characterization
  - XAS through collaboration
  - In-house: SEM, FIB, TEM, XRD, Raman (coming),…

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Collaboration possibilities

- We're always looking for bright students!
- Internships, MSc, and PhD program through SCK•CEN Academy: http://academy.sckcen.be/
- Internships and MSc can be tailored (in case of interest – contact directly by email).
- Possibility for a small financial support + affordable housing during your stay.
- For PhDs, there's a yearly competition (deadline for applications ~ end of March).
  - University promotor is always needed
  - Possibility for full SCK•CEN funding

- Thank you for your attention!