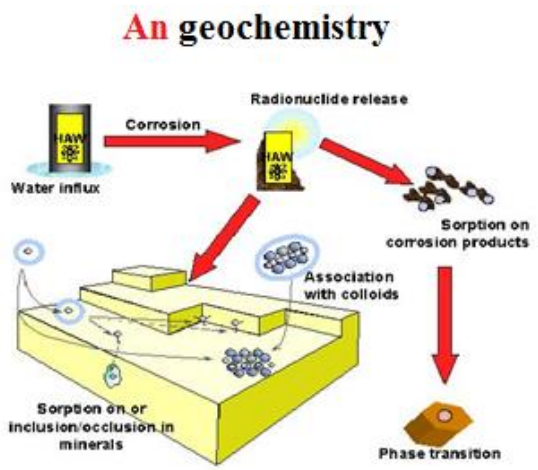
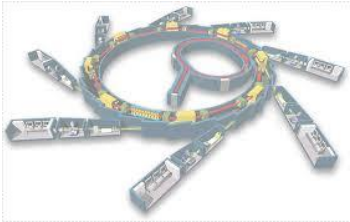
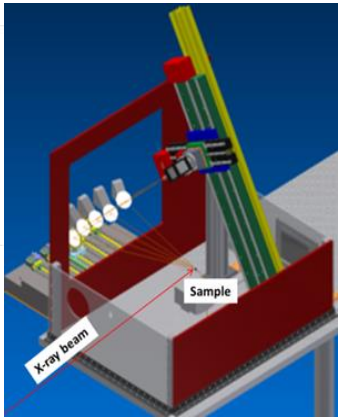
U Redox State and Speciation of U Co-precipitated with Magnetite Nanoparticles: High-Resolution XANES, EXAFS, XPS and TEM Study

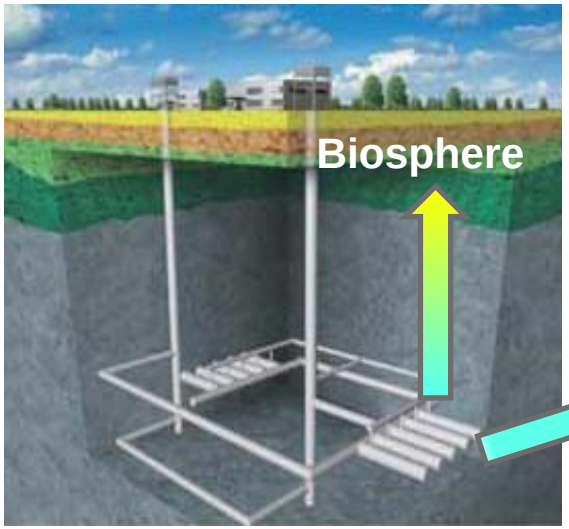
I. Pidchenko, D. Schild, T. Yokosawa, K. Kvashnina, J. Rothe, K. Dardenne, T. Schäfer, H. Geckeis, T. Vitova

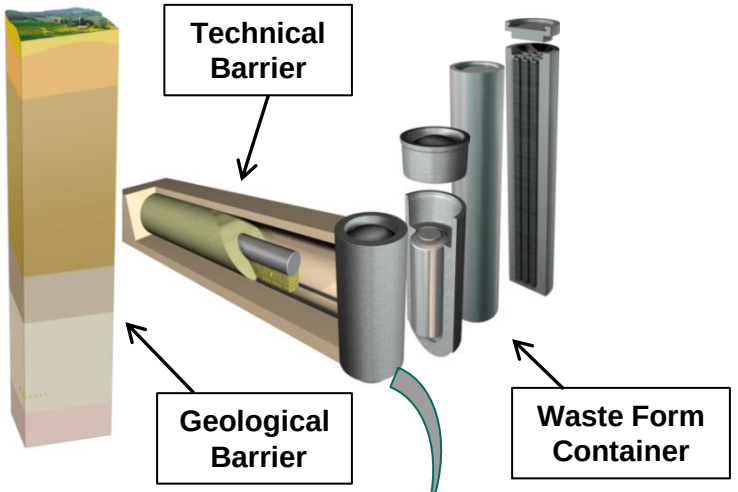
Institute for Nuclear Disposal (INE), KARLSRUHE INSTITUTE FOR TECHNOLOGY (KIT)





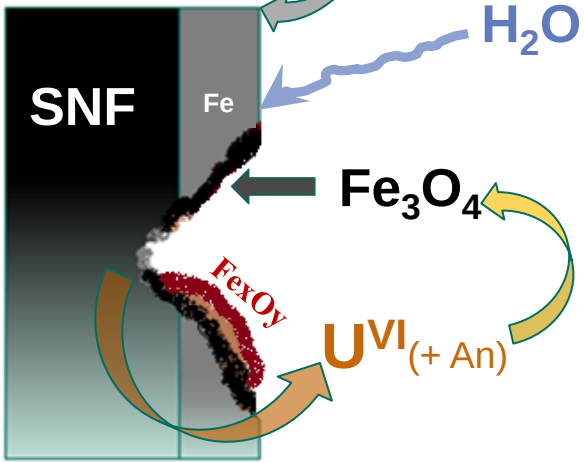






High Level Waste – final disposal in deep geological formations

- *granite / granitoides* (Sweden, Finland, Russia)
- *salt* (Germany, USA)
- *clay rock*, plastic/solidified (Germany, Belgium, Switzerland)



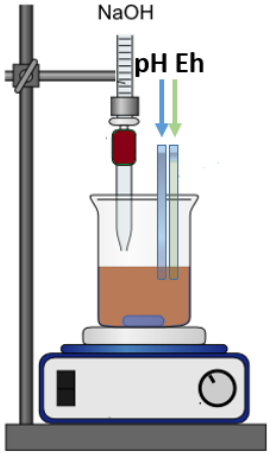
Sources: Nagra Info, March 2010; July 2014 ; Bel et al. (2004)

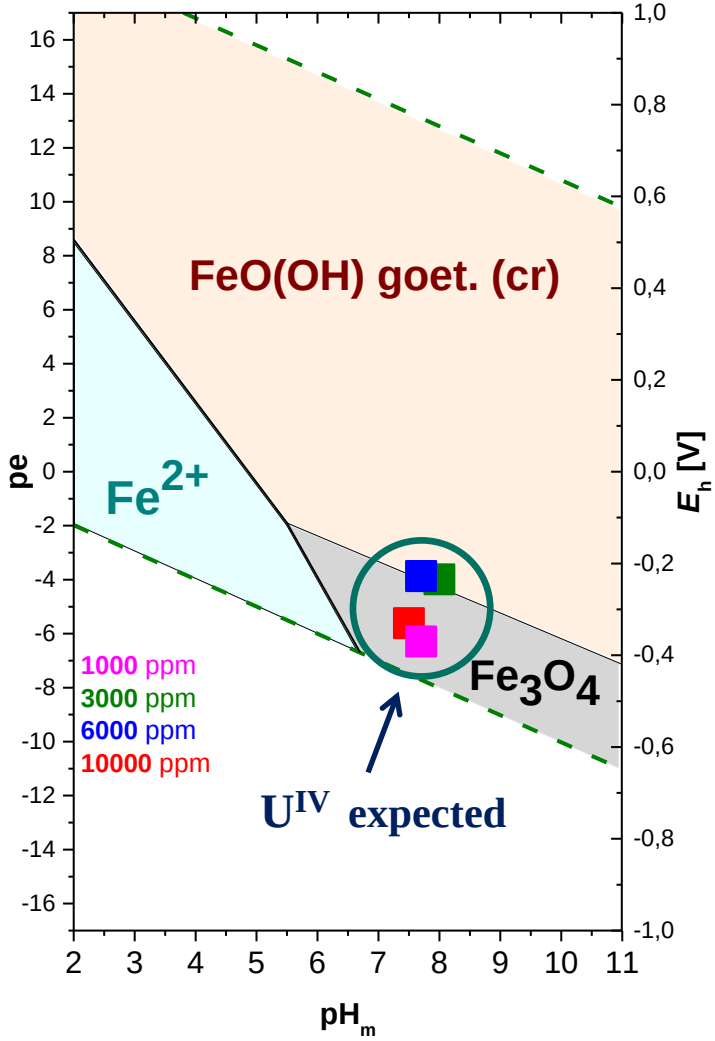
U^{VI} co-precipitation with magnetite

- **U** Incorporation into Magnetite ?
- Is $\mathbf{U^{V}}$ Possible ? How Stable ?
- What is **U** Redox Kinetics ?

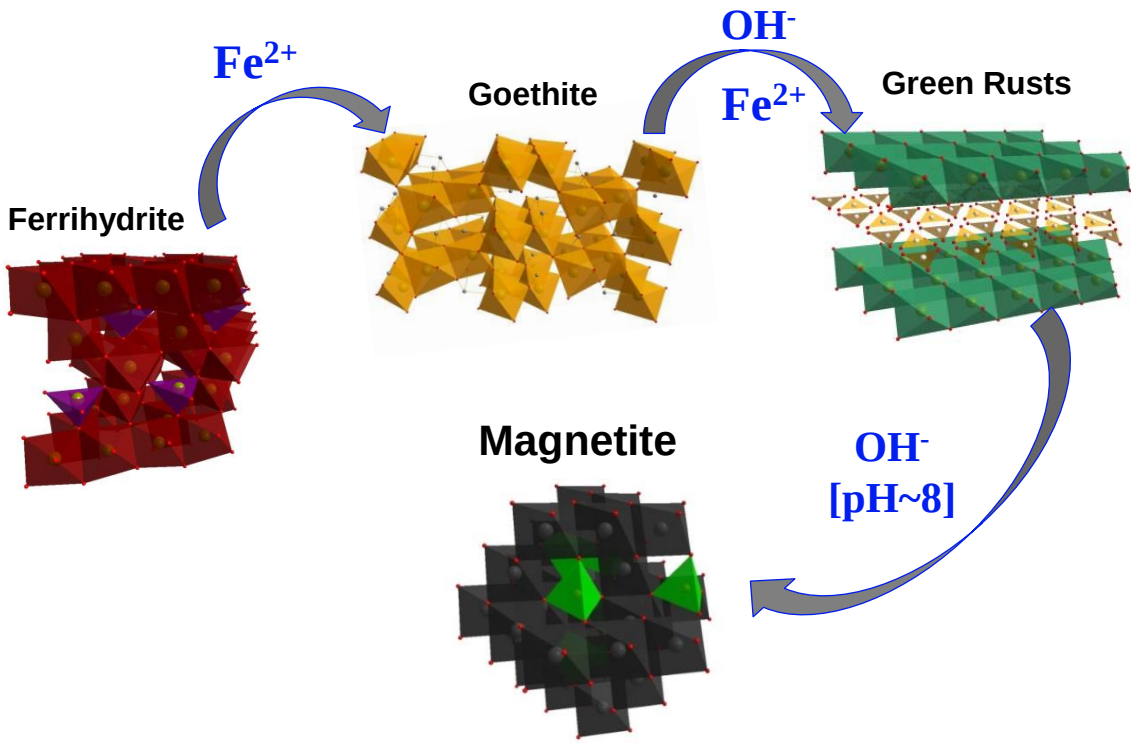
U^{VI} co-precipitation with magnetite

- **$FeCl_2$ / $FeCl_3$** (1:2)
- **NaOH** (0.5 M)
- **NaCl** (1 wt %)
- **CO_2 free, Ar atm.**
- **U 1000-10000 ppm**
- **4 samples**

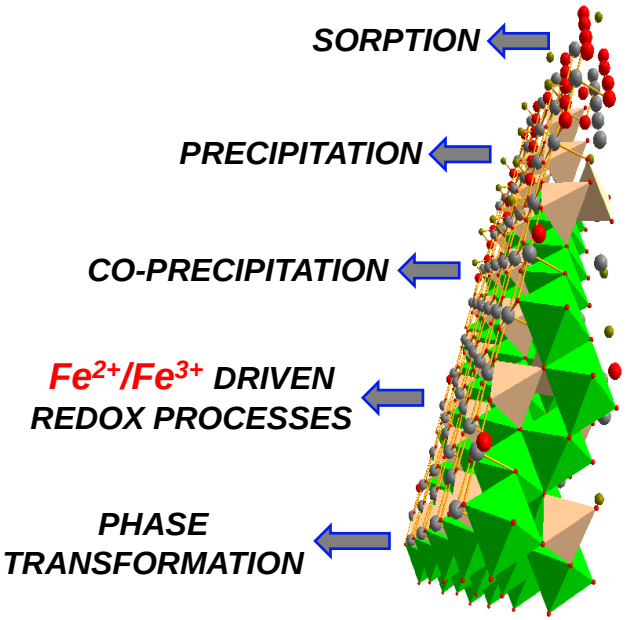


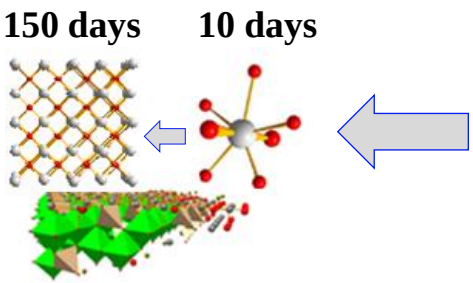


X. Gaona, INE


Fe2+
Goethite
OH-
Fe2+
Green Rusts
Ferrihydrite
Magnetite
OH-
[pH~8]

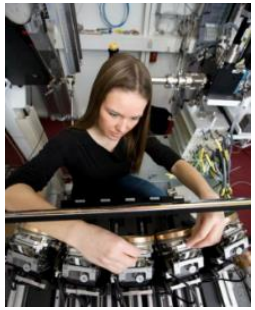
U behavior

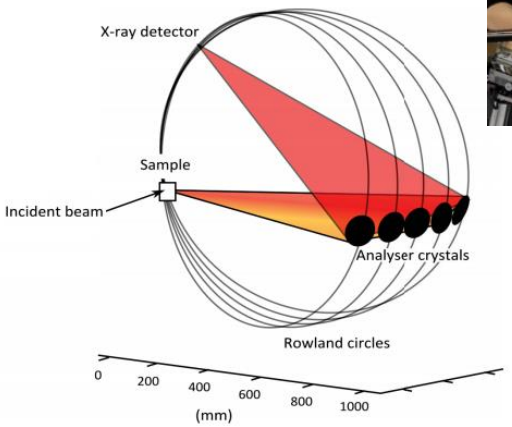

SORPTION
PRECIPITATION
CO-PRECIPITATION
Fe2+/Fe3+ DRIVEN
REDOX PROCESSES
PHASE
TRANSFORMATION

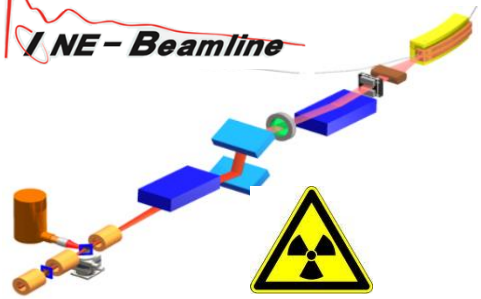

150 days
10 days

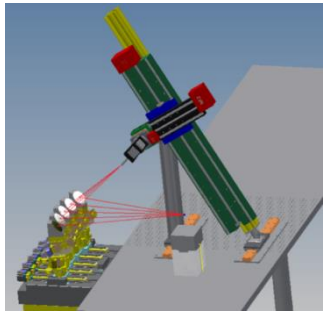
High-Resolution XANES

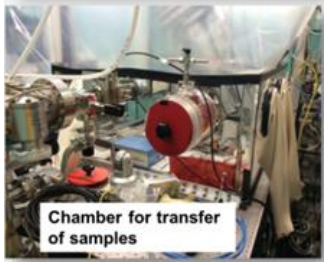
ID26 - High-Brilliance X-ray Spectroscopy



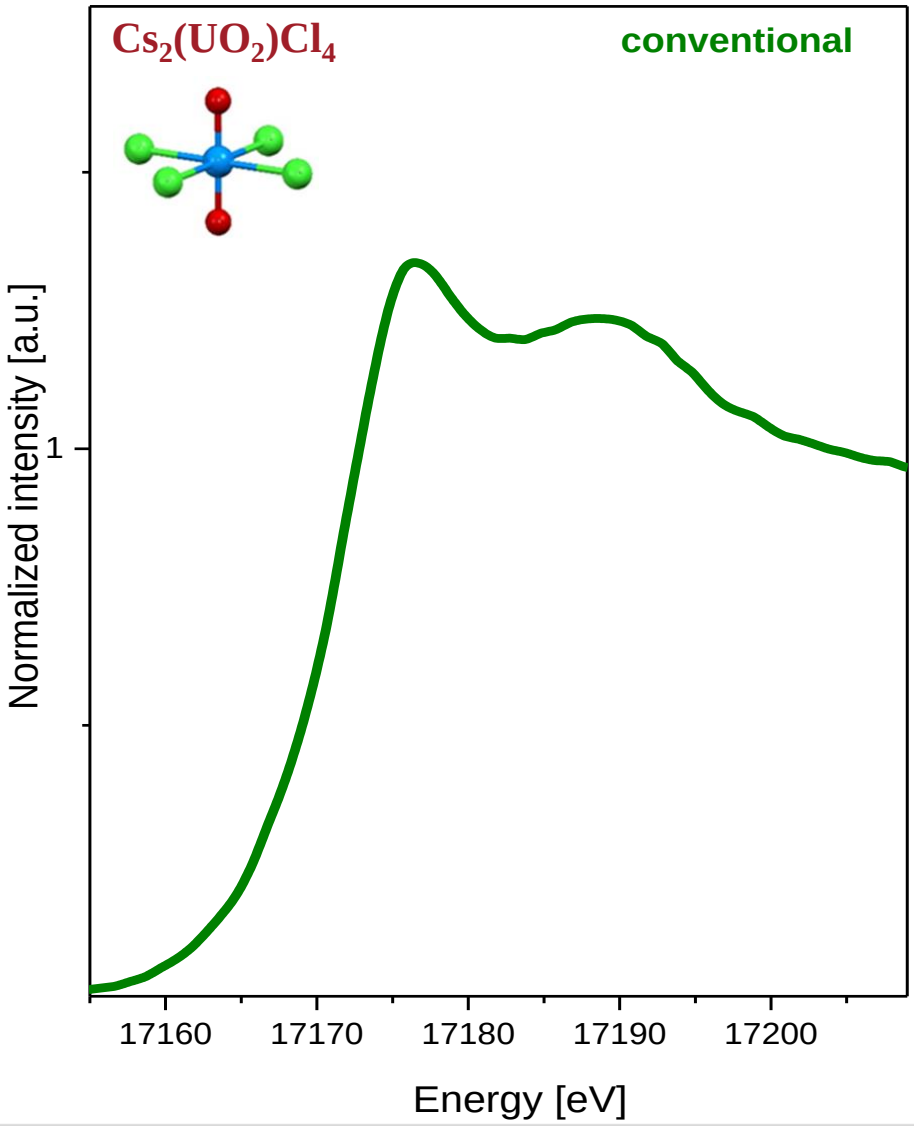


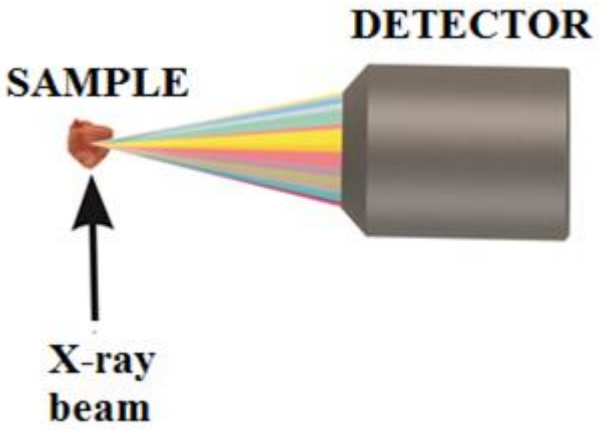






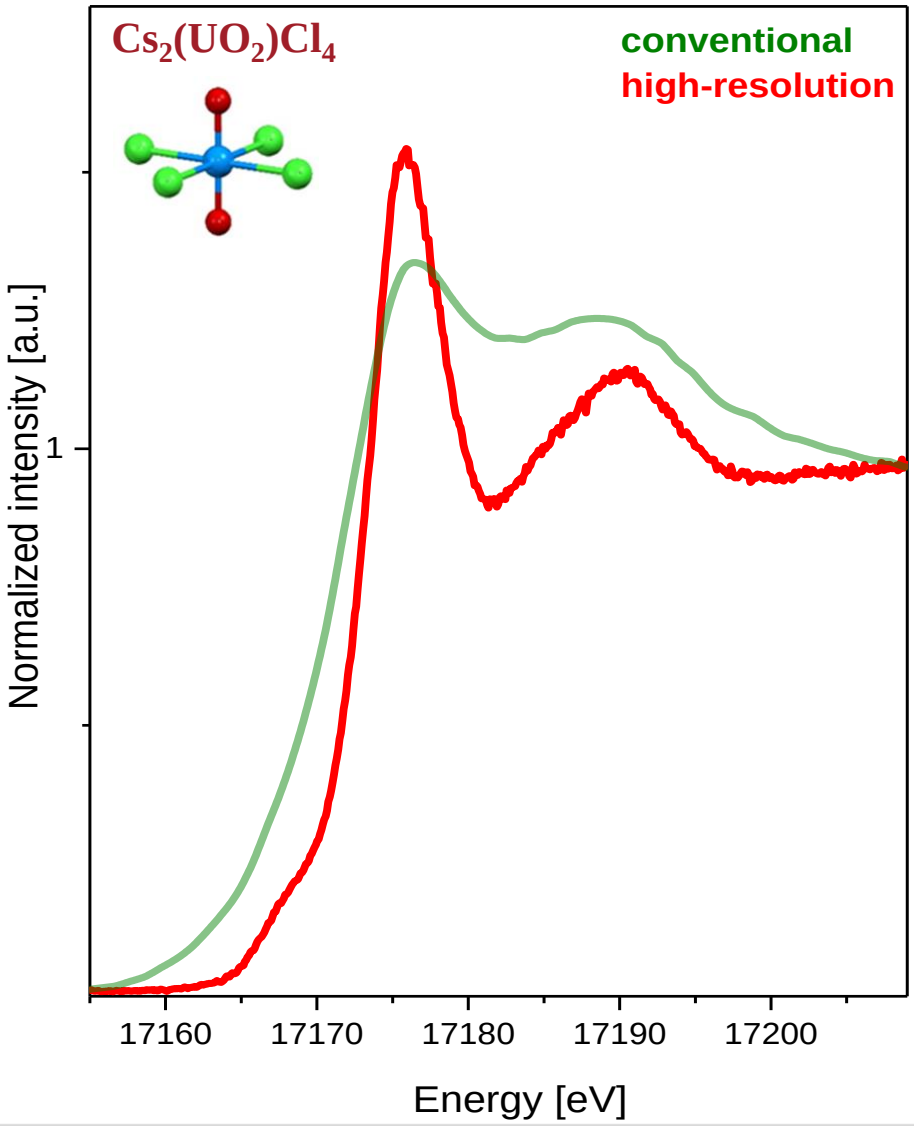
U L_3 conventional XANES

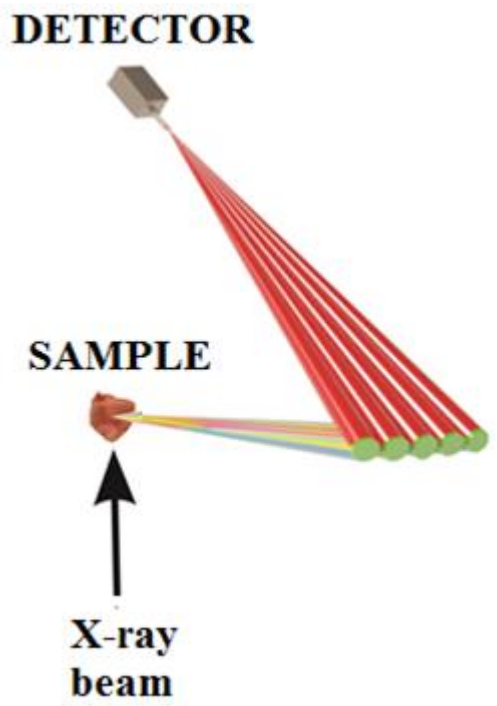




Detector's energy resolution >100 eV

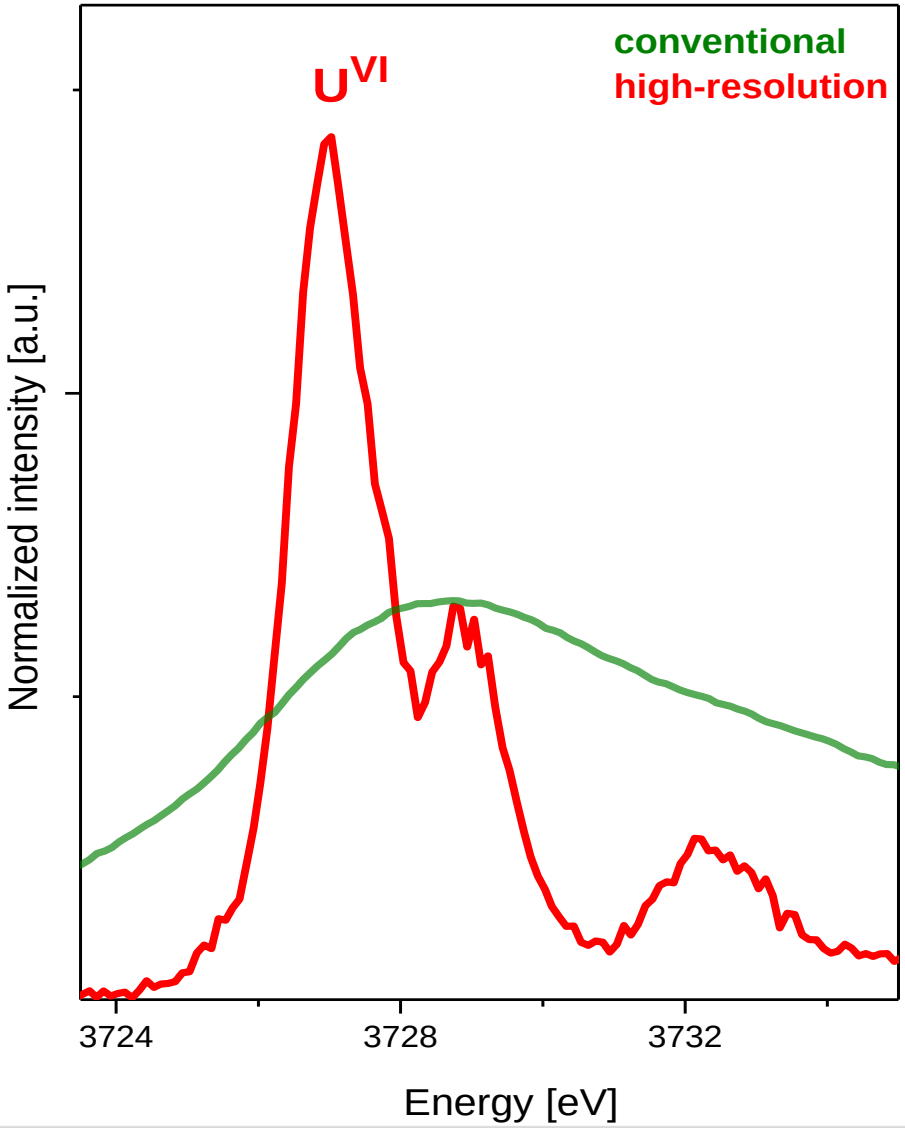
U L_3 HR-XANES



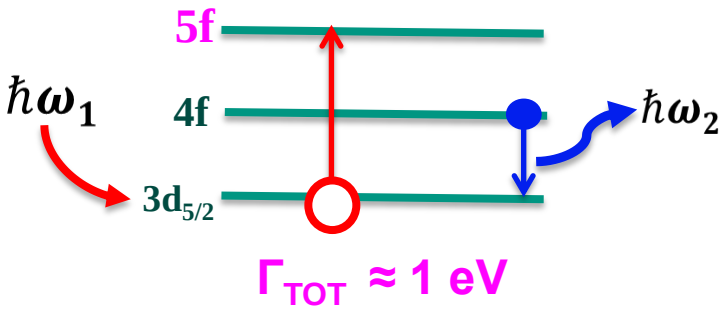


Spectrometer's energy resolution 0.5-2 eV

U M_4 HR-XANES

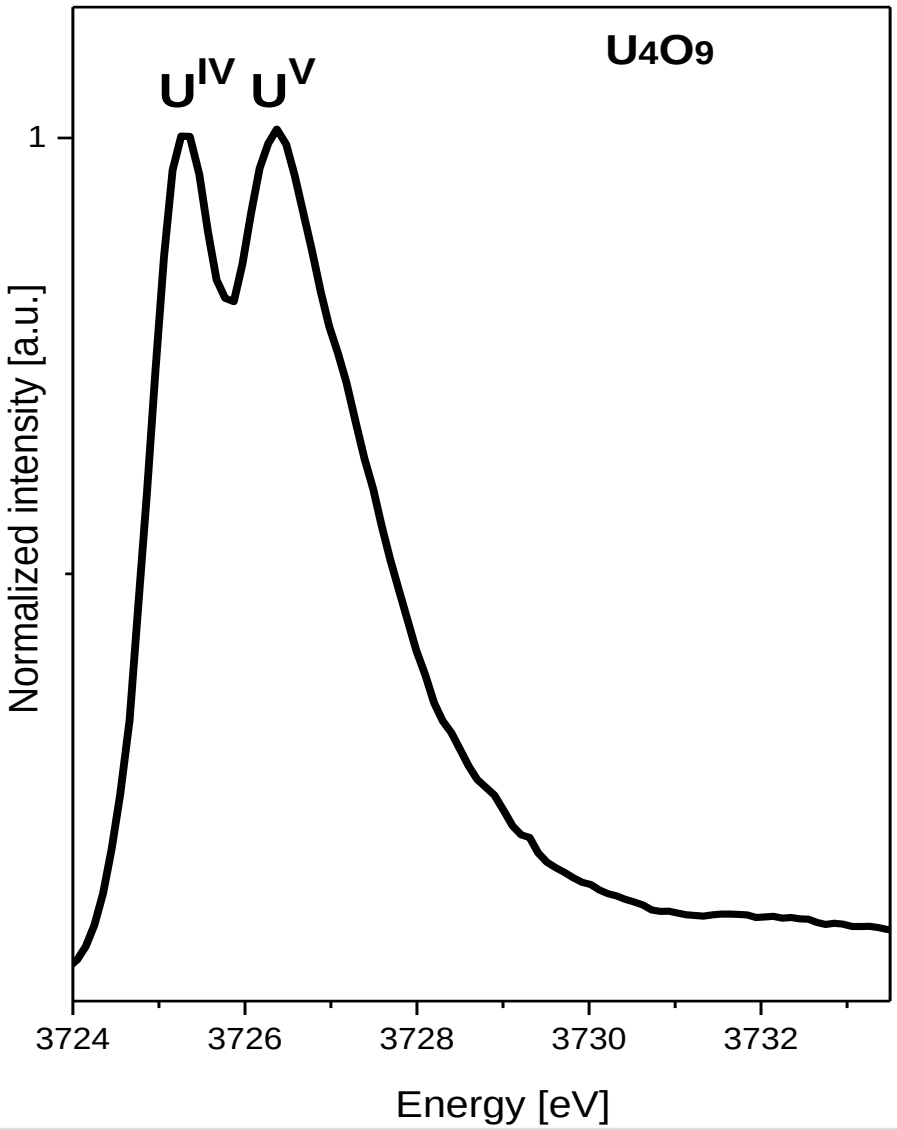


An M edge XES/XAS



- probes An 5f states
- better resolution than for L_3 edge

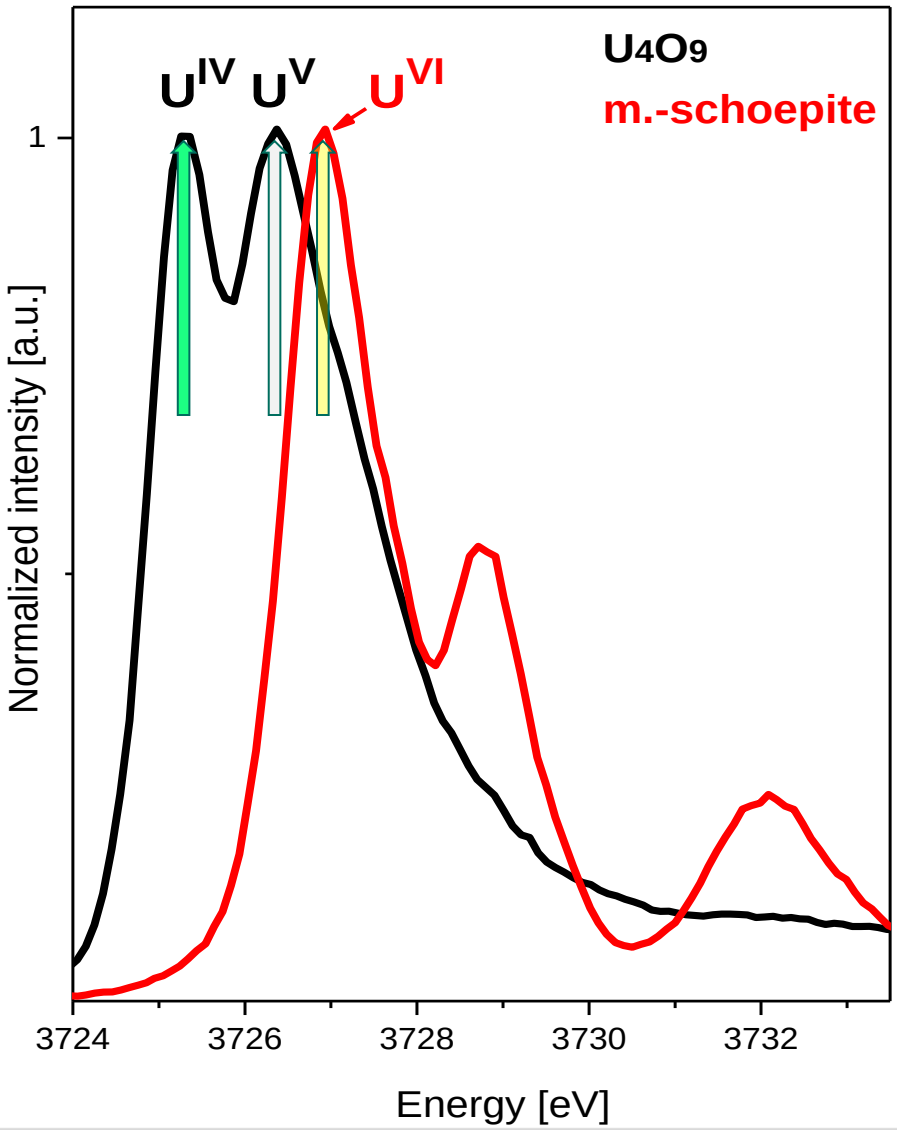
U M_4 HR-XANES



Reference for U^V studies

Kvashnina et al., PRL, 2013

U M_4 HR-XANES

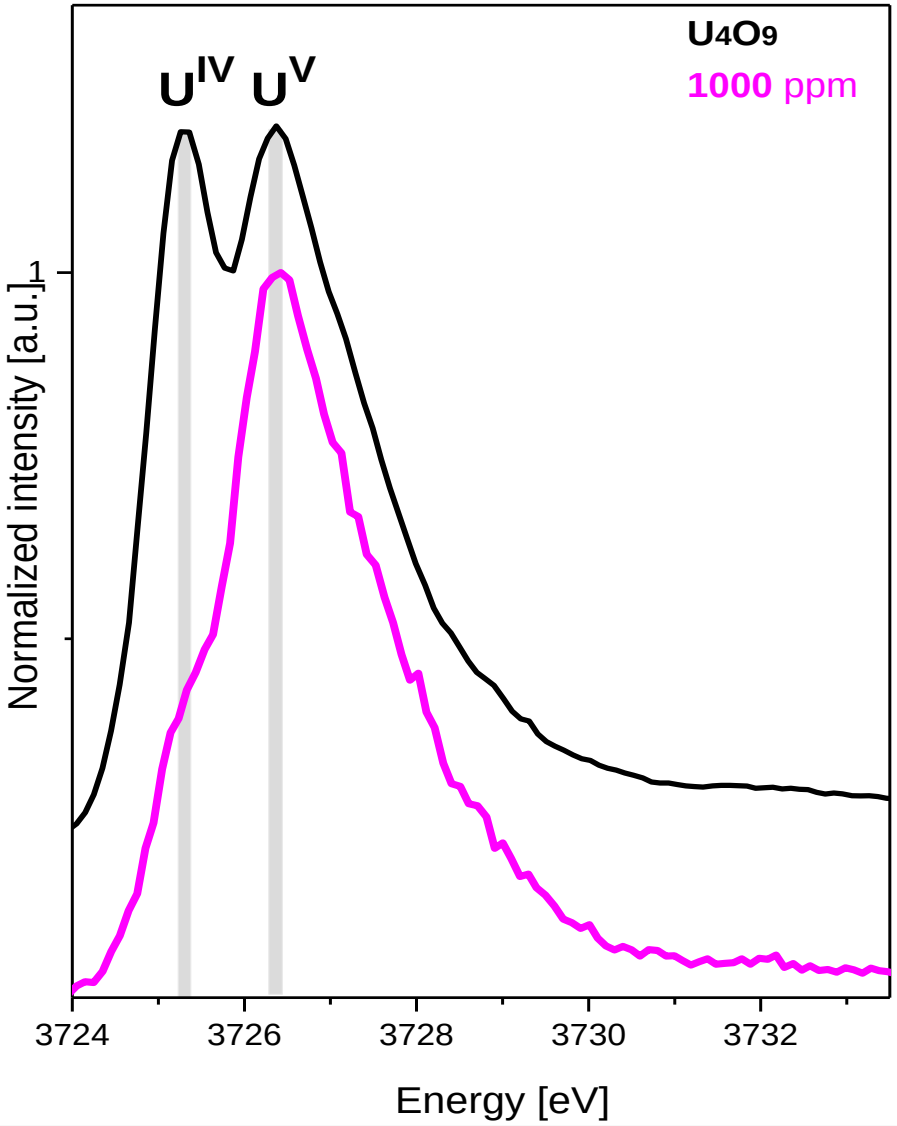


U oxidation states in mixtures

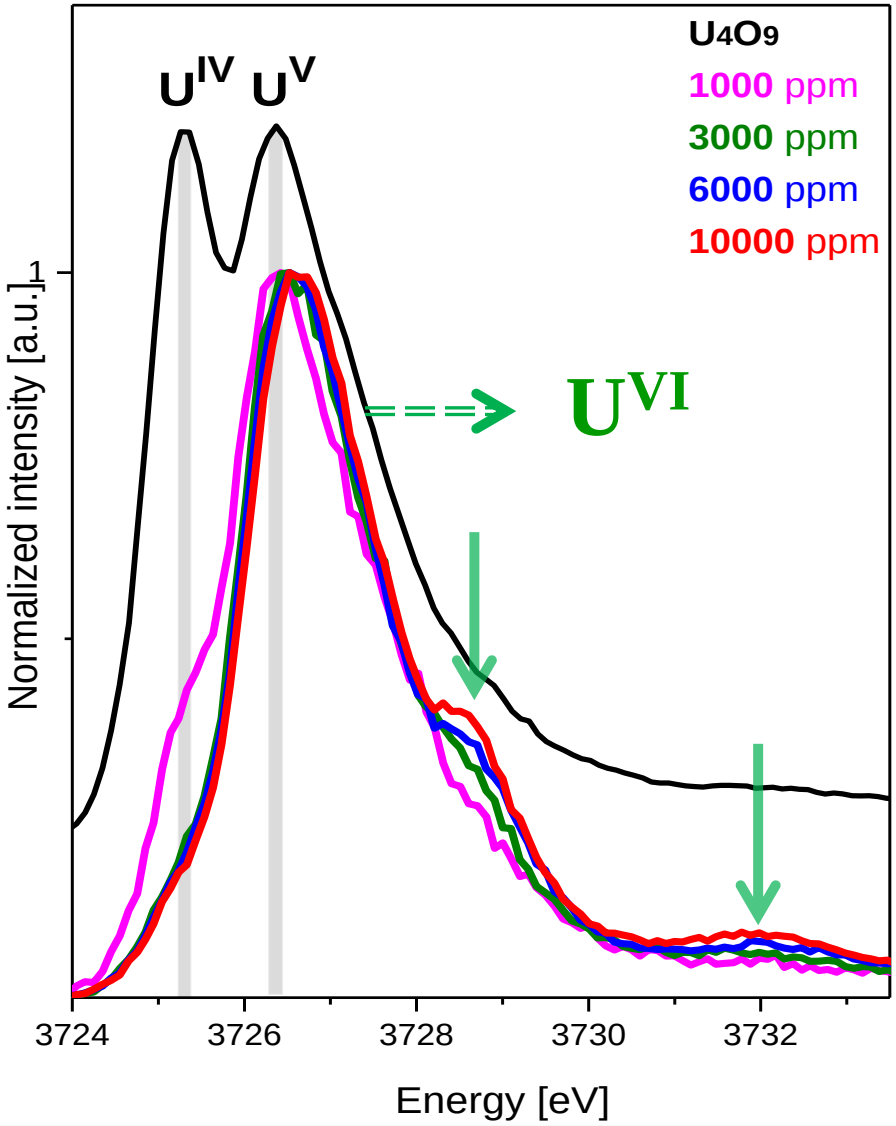
$5f^2$ **U^{IV}**	$5f^1$ **U^{V}**	$5f^0$ **U^{VI}**

Kvashnina et al., PRL, 2013

U M_4 HR-XANES 15 days



U M_4 HR-XANES 15 days

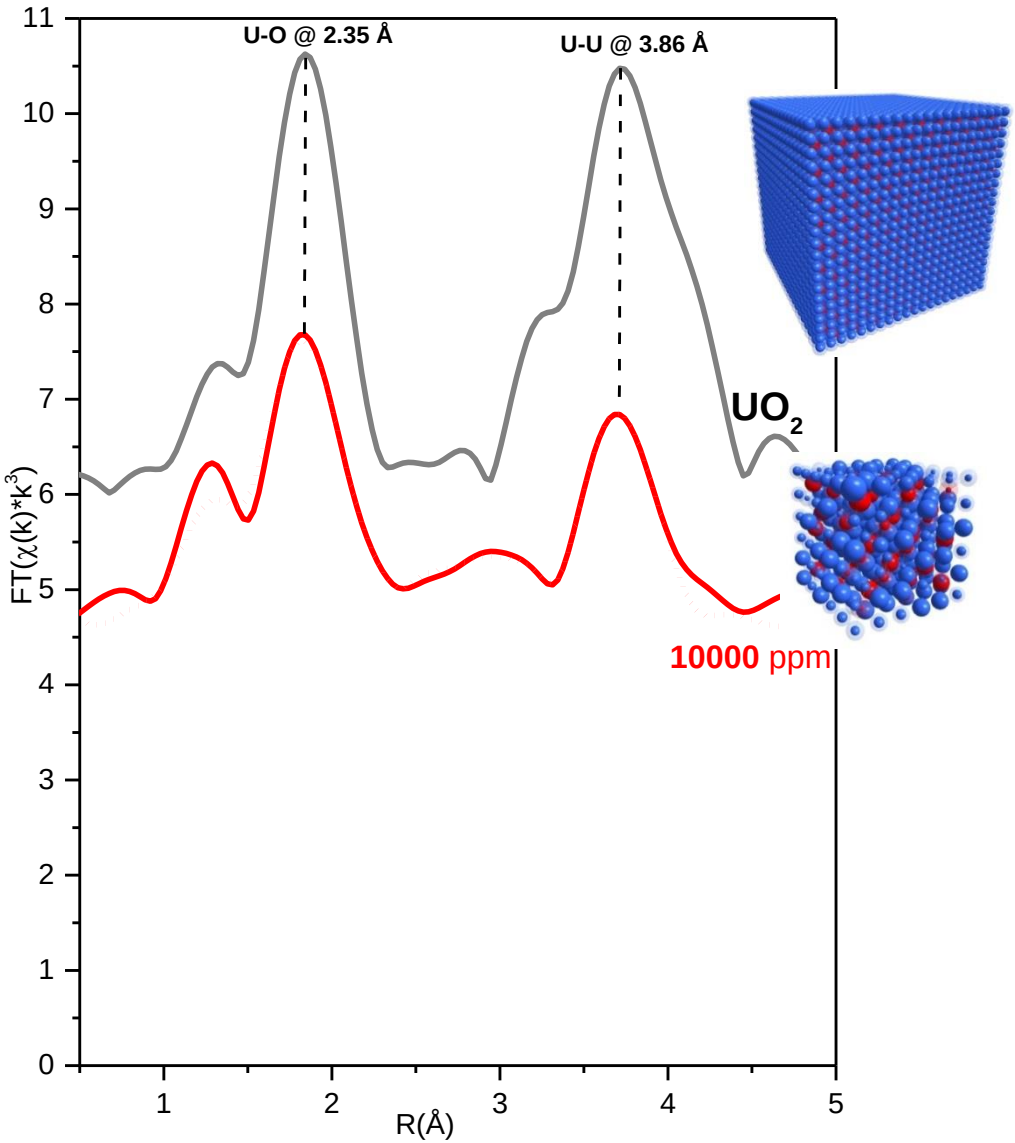


1000 ppm

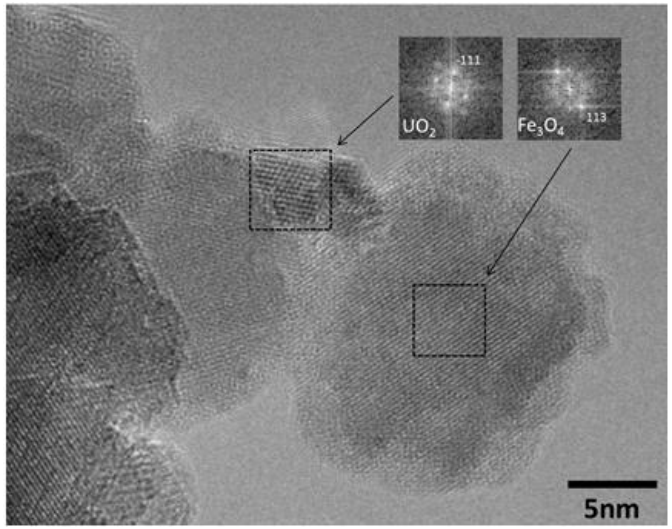
U^V *non-yl*

UO_{2+x} ?

U L_3 EXAFS 200 days



HR-TEM on 10000 ppm (UO_{2+x})



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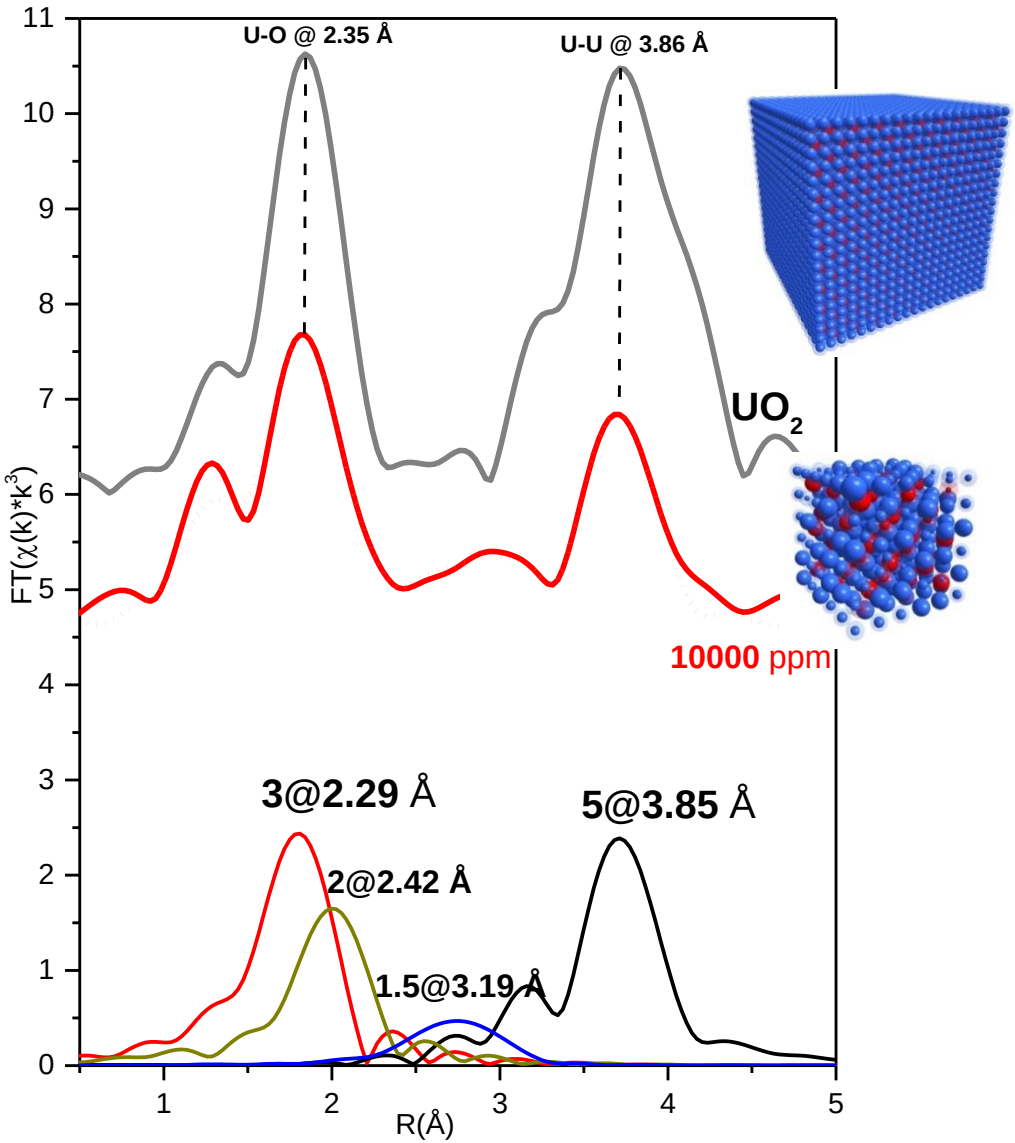
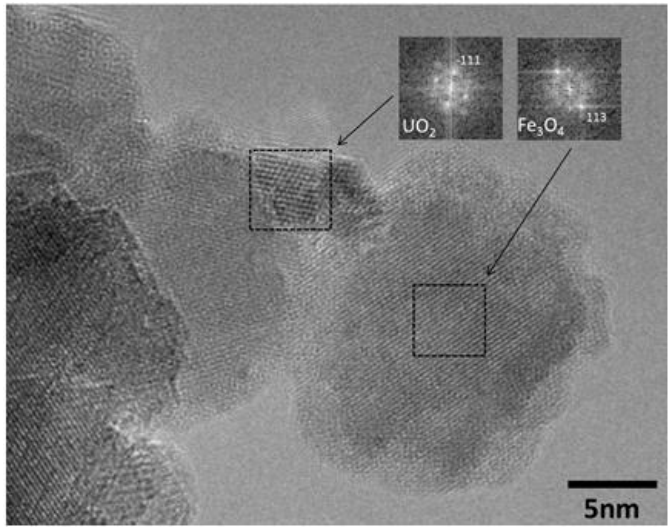
U L_3 EXAFS 200 days



HR-TEM on 10000 ppm (UO_{2+x})



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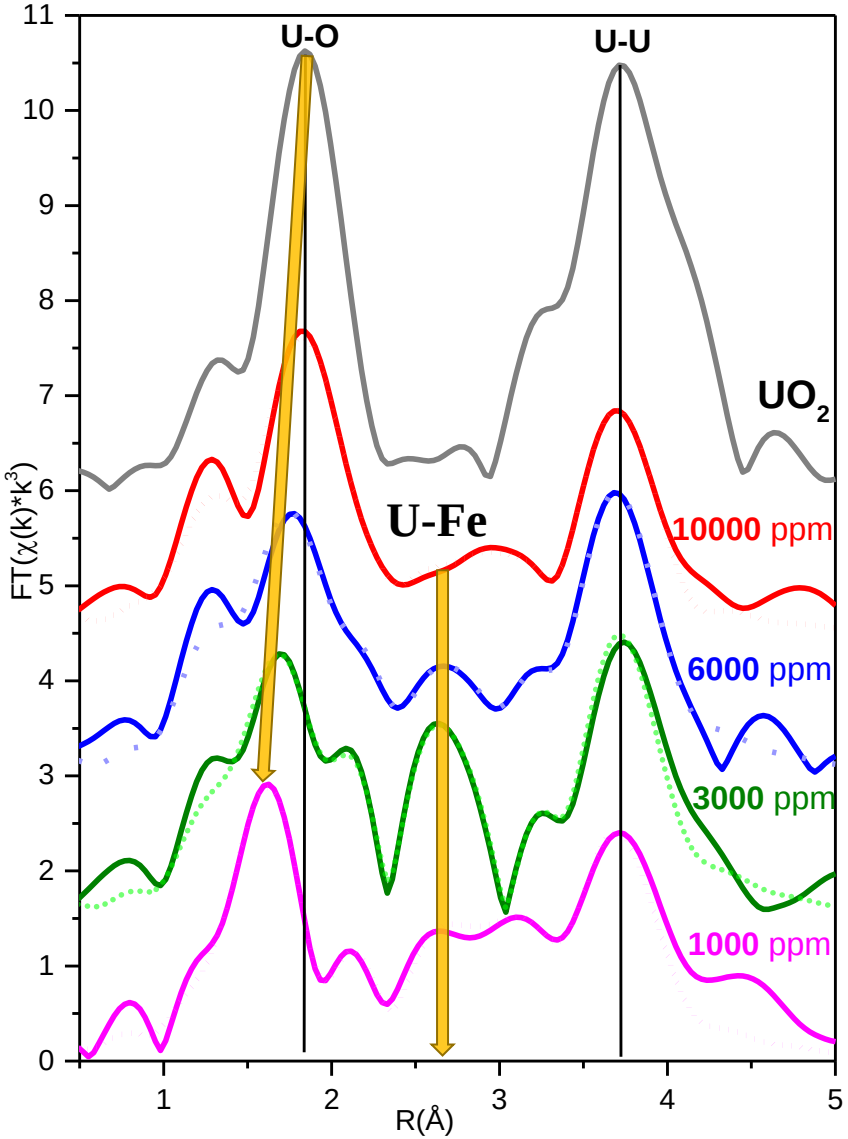
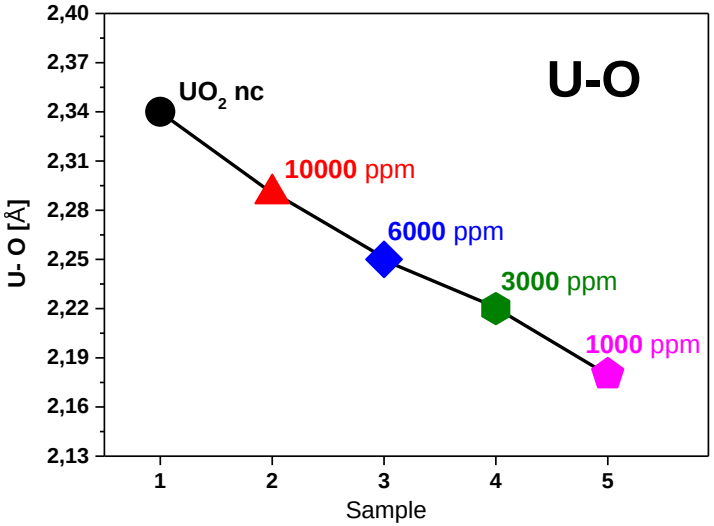
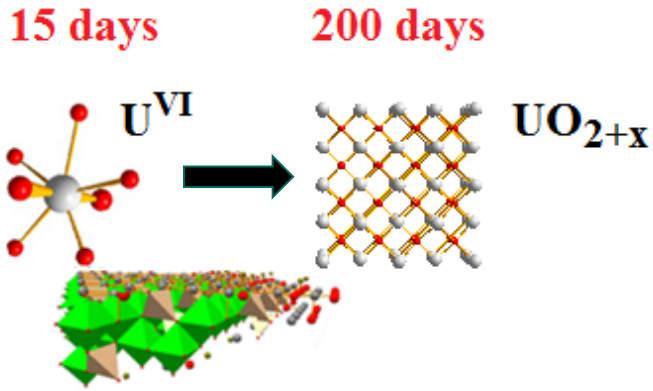
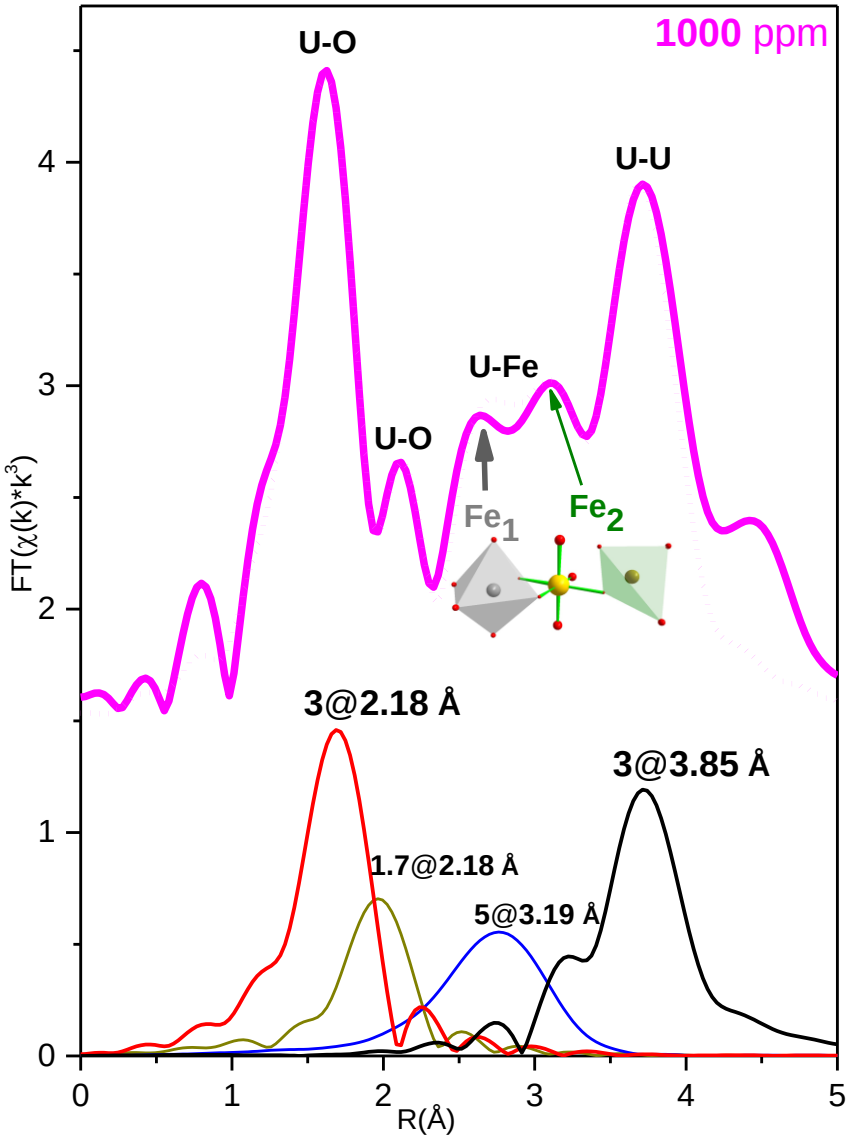
U L_3 EXAFS 200 days



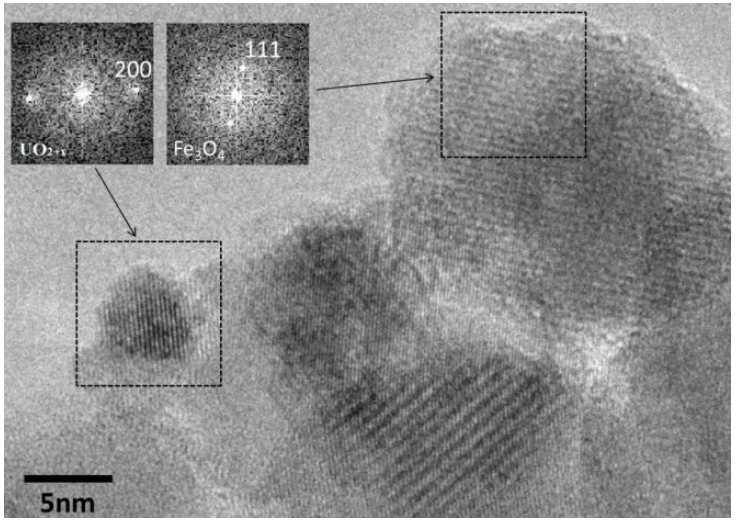




U L_3 EXAFS 200 days



HR-TEM 1000 ppm (UO_{2+x})



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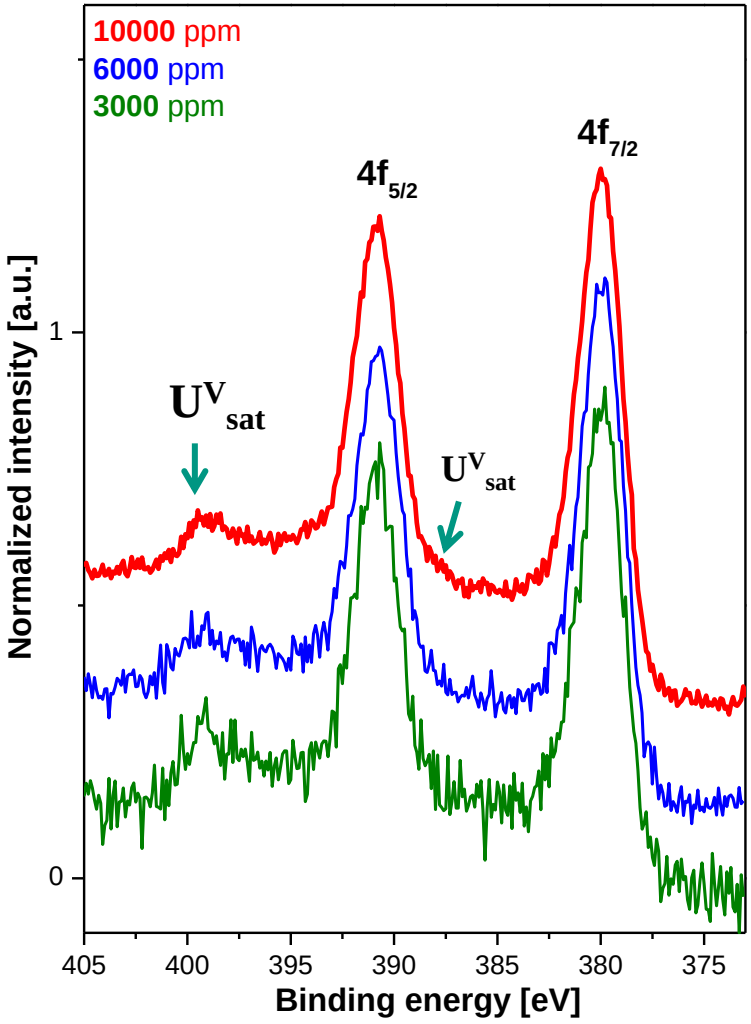
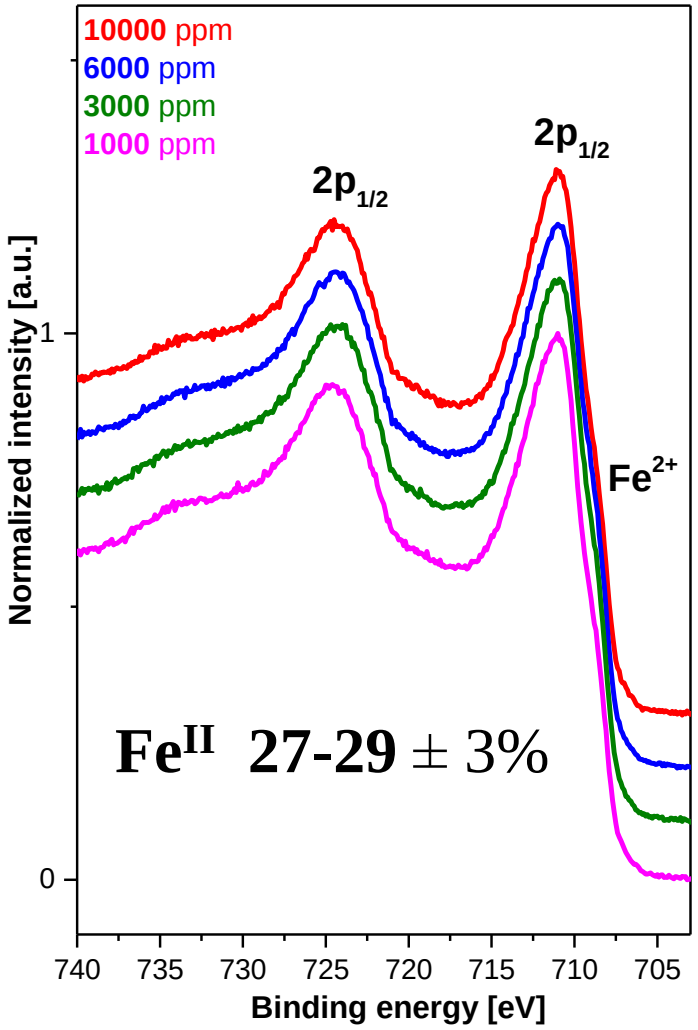
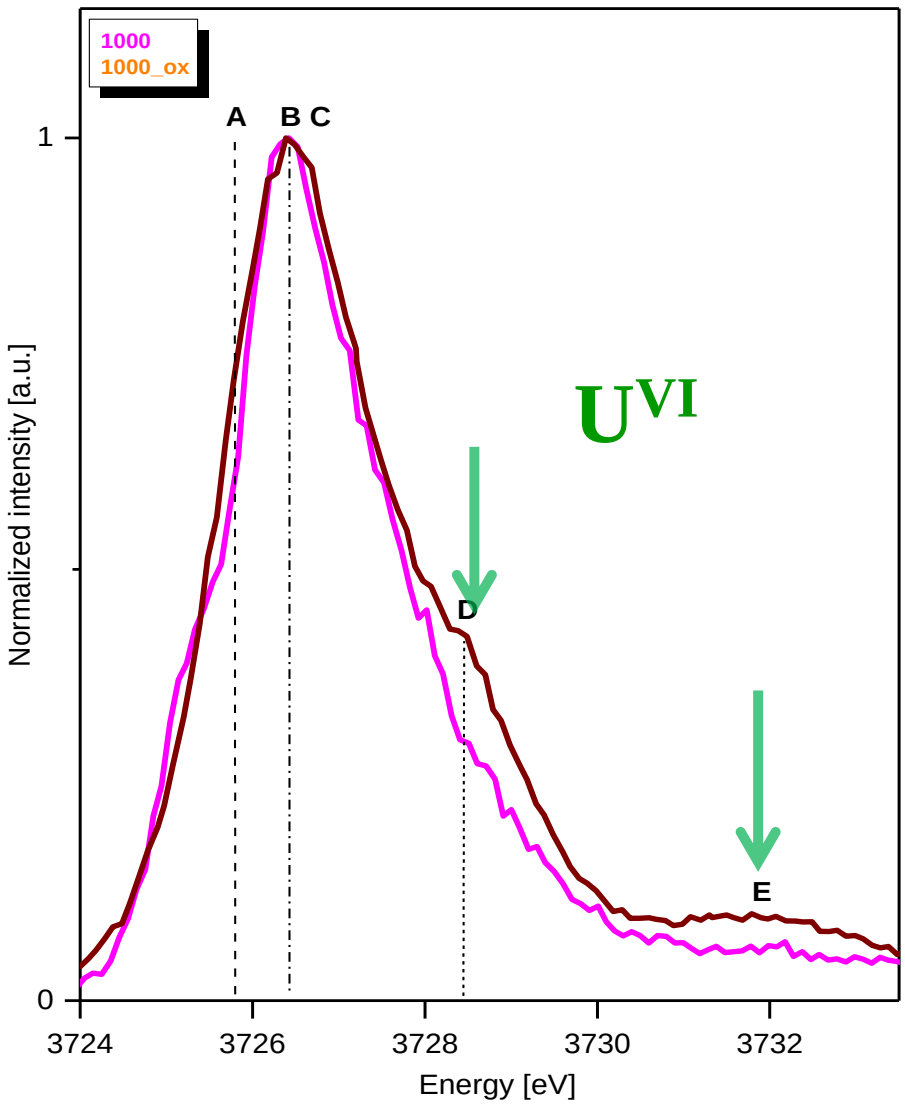
U 4f XPS 200 days





D. Schild (INE)

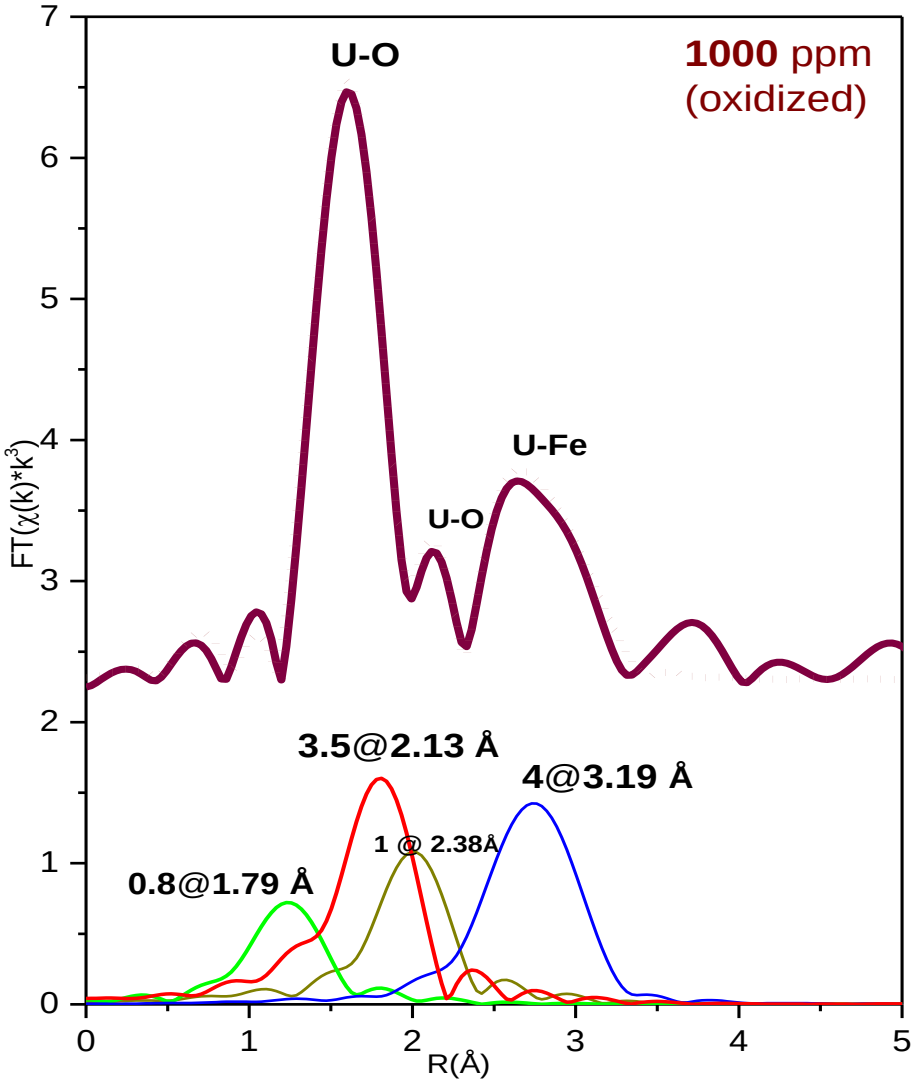
U M_4 HR-XANES 150 days on air



Ambient conditions:

$$UO_{2+x} \rightarrow U^{VI}$$

U L_3 EXAFS 250 days on air



U speciation:

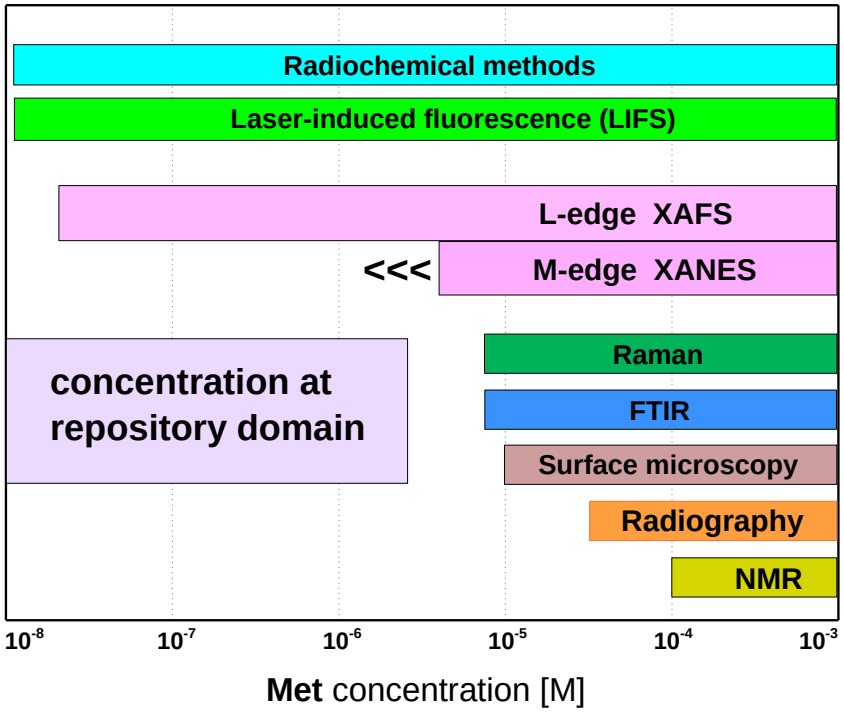
~ 40% U^{VI} *-yl*

???

~ 60% U^{V} *non-yl*

CONCLUSIONS

- **HR-XANES is an emerging tool for speciation studies of An with concentrations relevant to HLW repository**
- **The HR-XANES allows to resolve several U oxidation states in mixtures**
- **Pentavalent U is stable to air when coordinated to Fe in the structure of magnetite**
- **U kinetics can be studied provided that the experimental conditions are the same**



Adopted from W. Runde, LA Science

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Jörg Rothe
Kathy Dardenne…

INE Workshop

ESRF

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Atsushi Ikeda

THANK YOU !

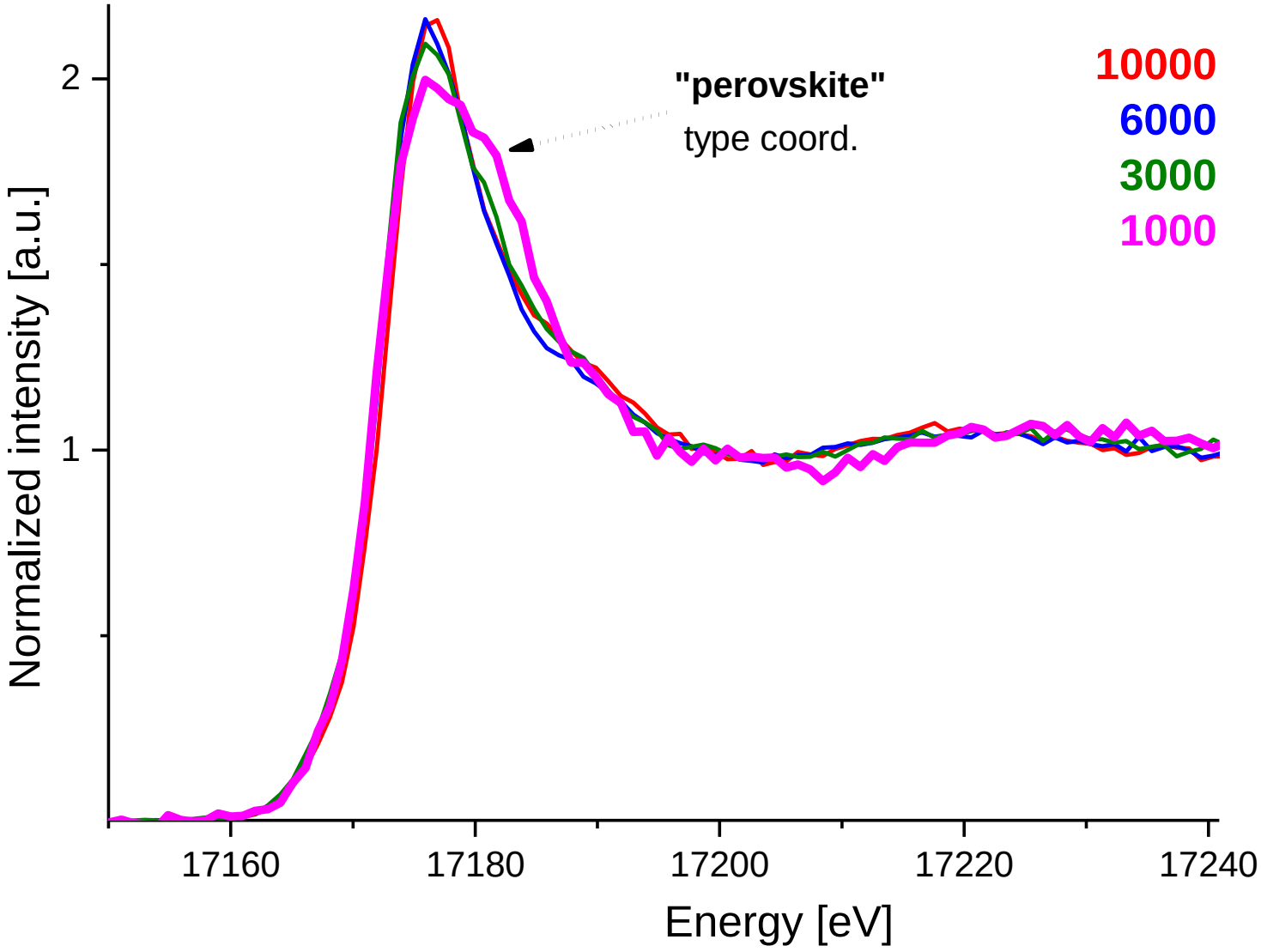
HELMHOLTZ GEMEINSCHAFT

Supporting information

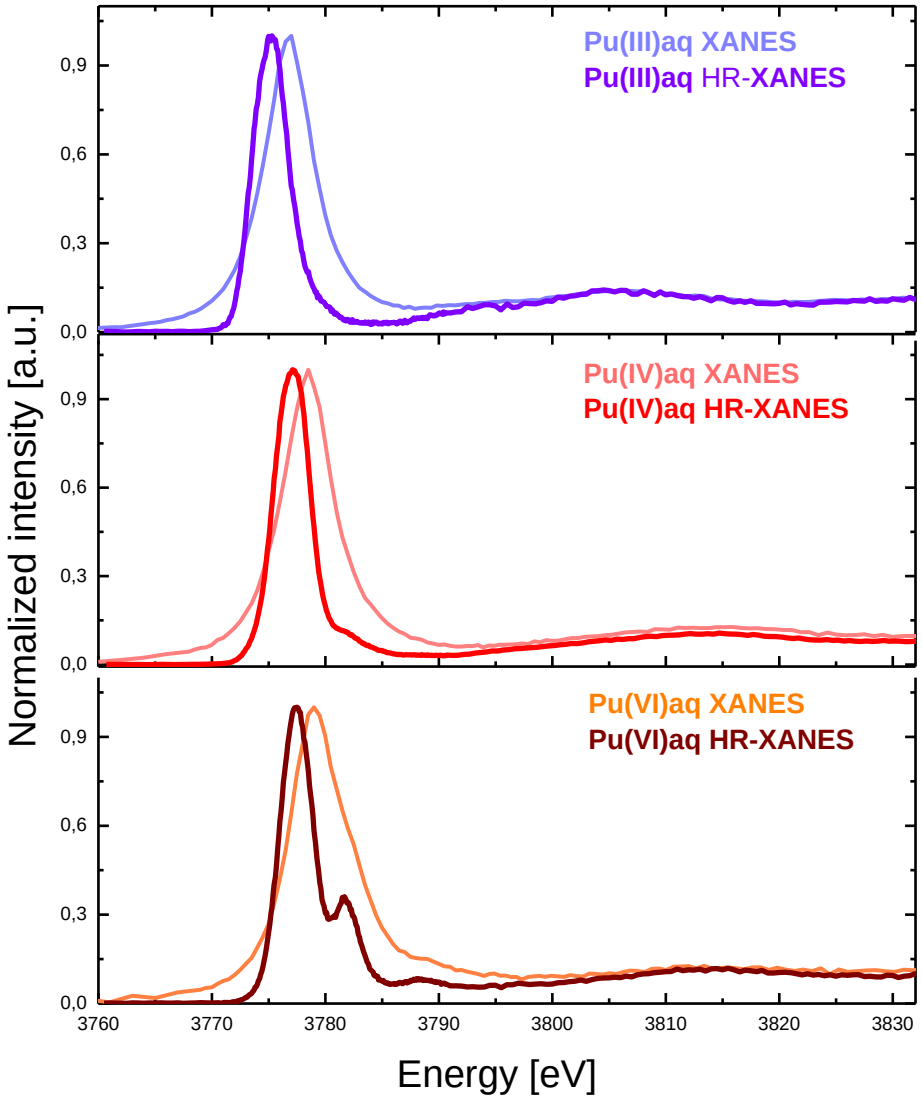
EXAFS fit results for 1000-10000 XAFS

sample	Scater Path	N	R (Å)	DW (Å^2)	ΔE_0 (eV)	S_0^2 (aver. from 4 UO2 fits)	r, (chi^2)
1000	U-O3	0.2 ± 0.1	1.73 (3)	0.006 (1)	6.6 (5)	0.77	0.008
	U-O1	3.0 ± 0.3	2.17 (1)	0.006 (1)			
	U-O2	1.7 ± 0.1	2.38 (2)	0.006 (1)			
	U-Fe_{oct}	7.0 ± 1.8	3.18 (2)	0.020 (2)			
	U-Fe_{tet}	0.6 ± 0.3	3.55 (3)	0.001 (1)			
	U-U1	2.9 ± 0.7	3.85 (2)	0.002 (1)			
1000 on air	U-O3	0.8 ± 0.2	1.79 (2)	0.004 (1)	5.0 (8)	0.77	0.008
	U-O1	3.5 ± 0.2	2.13 (1)	0.004 (1)			
	U-O2	0.8 ± 0.1	2.41 (1)	0.004 (1)			
	U-Fe_{oct}	5.0 ± 0.6	3.19 (1)	0.016 (2)			
3000	U-O3	0.3 ± 0.2	1.70 (1)	0.006 (1)	7.4 (3)	0.77	0.003
	U-O1	2.8 ± 0.3	2.22 (1)	0.006 (1)			
	U-O2	2.4 ± 0.2	2.43 (1)	0.006 (1)			
	U-Fe_{oct}	1.9 ± 0.4	3.11 (1)	0.006 (1)			
	U-Fe_{tet}	0.6 ± 0.3	3.34 (2)	0.006 (4)			
	U-U1	3.2 ± 0.7	3.84 (3)	0.002 (1)			
6000	U-O3	0.4 ± 0.2	1.69 (2)	0.006 (1)	7.0 (4)	0.77	0.003
	U-O1	2.7 ± 0.3	2.25 (1)	0.006 (1)			
	U-O2	2.1 ± 0.2	2.43 (1)	0.006 (1)			
	U-Fe_{oct}	4.8 ± 1.6	3.14 (2)	0.023 (2)			
	U-Fe_{tet}	0.6 ± 0.3	3.50 (2)	0.005 (3)			
	U-U1	3.4 ± 0.7	3.83 (3)	0.002 (1)			
10000	U-O3	0.4 ± 0.2	1.68 (2)	0.006 (1)	7.3 (3)	0.77	0.003
	U-O1	2.9 ± 0.2	2.29 (1)	0.006 (1)			
	U-O2	2.1 ± 0.2	2.44 (1)	0.006 (1)			
	U-Fe_{oct}	1.2 ± 0.4	3.14 (2)	0.013 (4)			
	U-Fe_{tet}	0.6 ± 0.2	3.50 (2)	0.004 (3)			
	U-U1	5.2 ± 0.8	3.83 (3)	0.006 (1)			

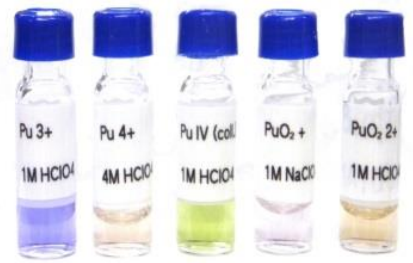
U L_3 HR-XANES / 15 days



Pu M_5 HR-XANES in aqueous solution

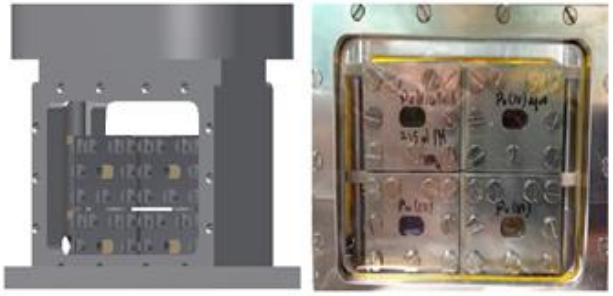


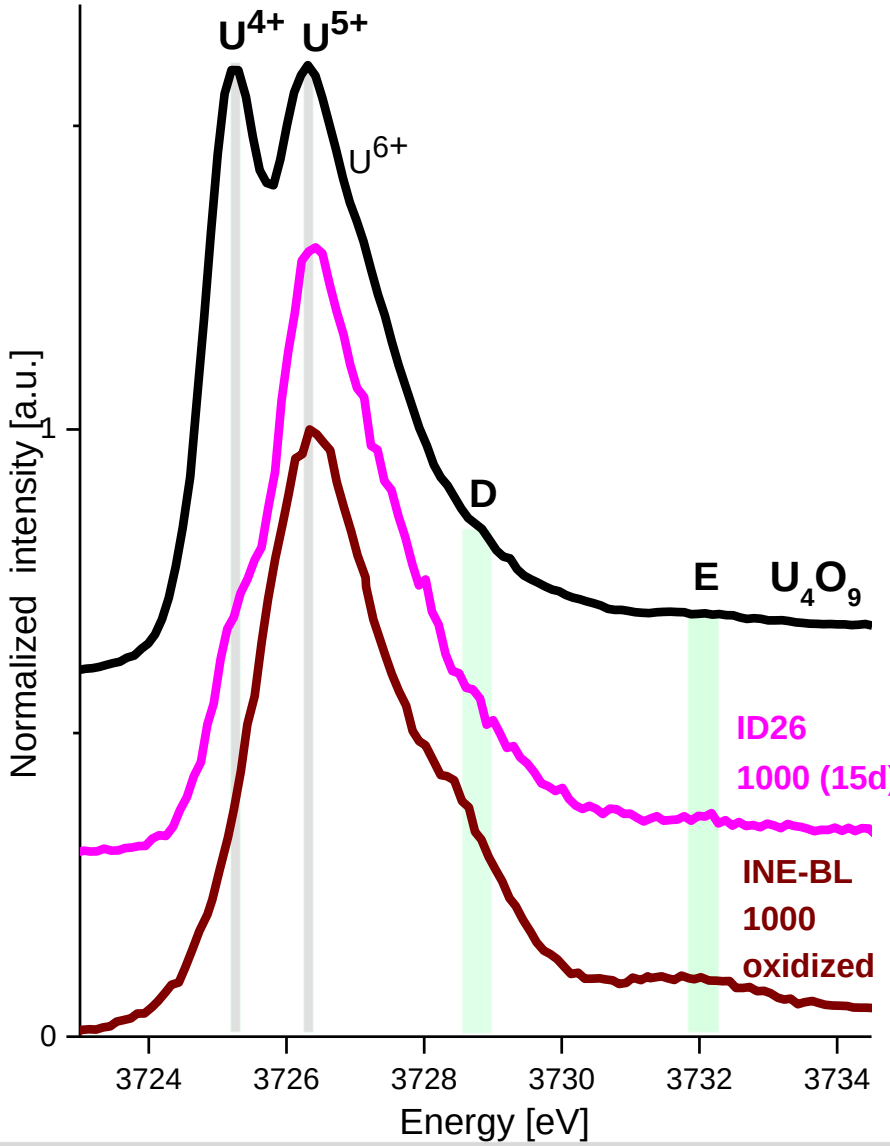
Pu oxidation states

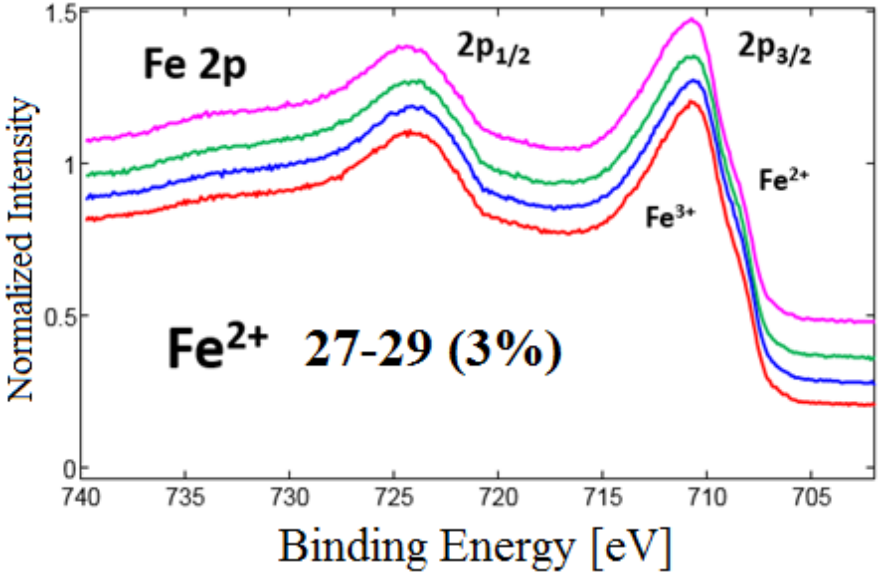


D. Fellhauer (INE)

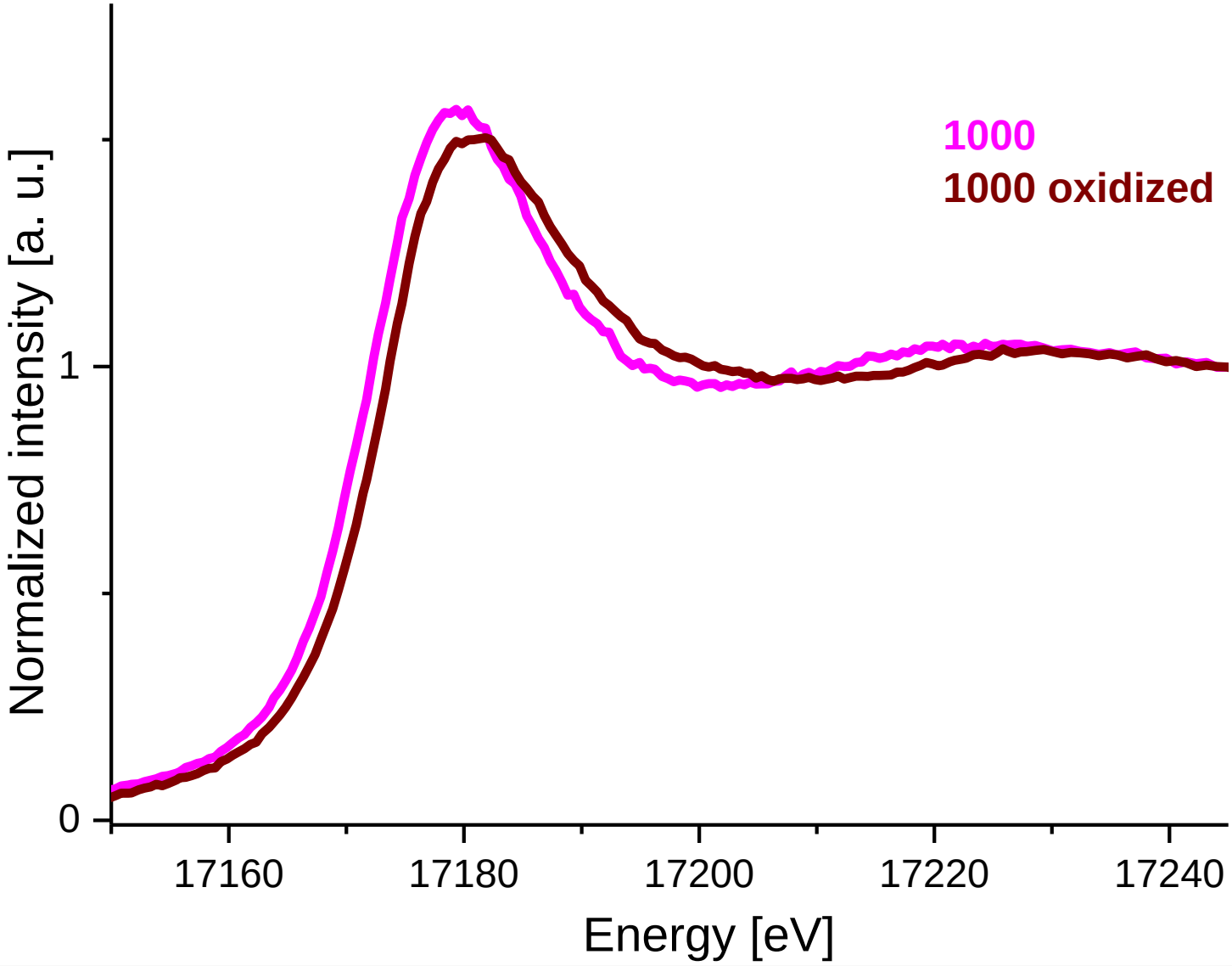
An liquid cell

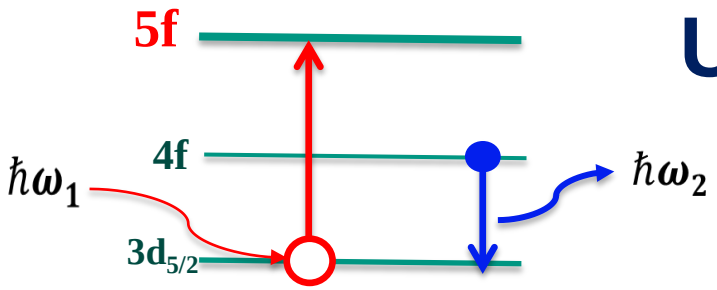



U4+
U5+
U6+
D
E
U4O9
ID26
1000 (15d)
INE-BL
1000
oxidized
Normalized intensity [a.u.]
0
1
3724
3726
3728
3730
3732
3734
Energy [eV]


Fe 2p
2p1/2
2p3/2
Fe2+
Fe3+
Fe2+ 27-29 (3%)
Normalized Intensity
1.5
1
0.5
0
740
735
730
725
720
715
710
705
Binding Energy [eV]

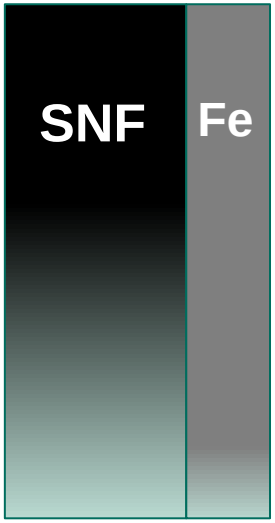
U L_3 XANES / 200 days + oxidized

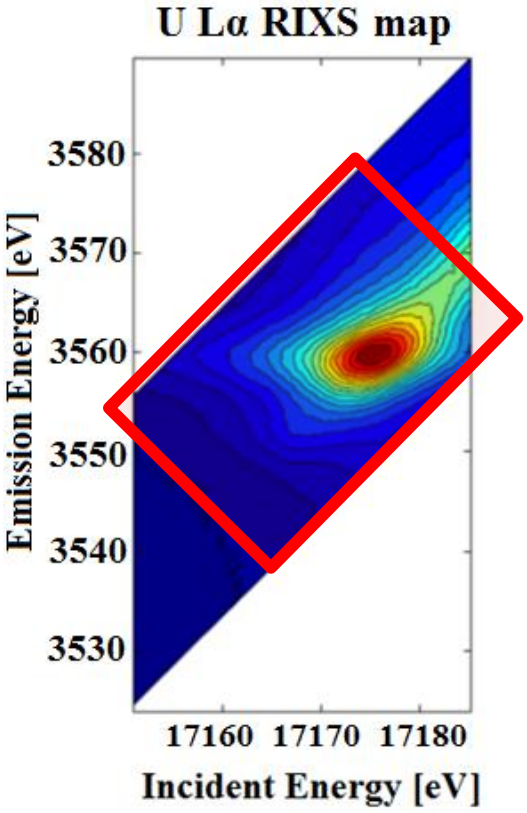


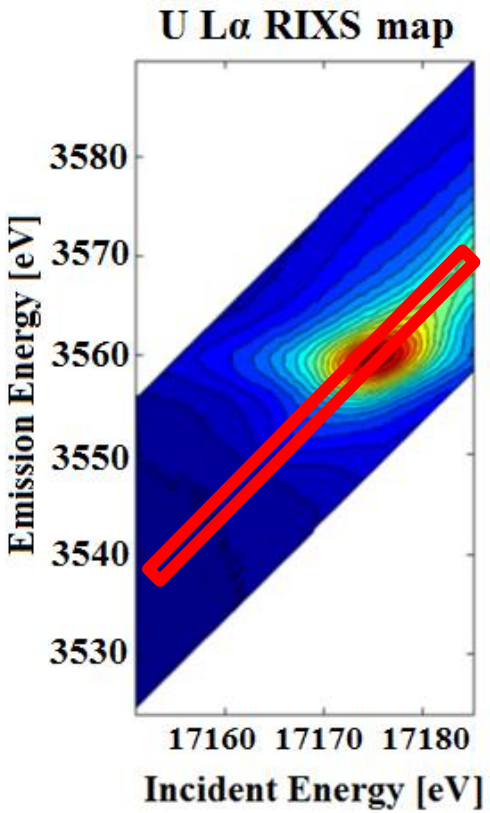


$\Gamma_{TOT} \approx 1$ eV

$UO_{2.00} \rightarrow UO_{2+x}$


SNF
Fe


U Lα RIXS map
Emission Energy [eV]
3580
3570
3560
3550
3540
3530
17160
17170
17180
Incident Energy [eV]


U Lα RIXS map
Emission Energy [eV]
3580
3570
3560
3550
3540
3530
17160
17170
17180
Incident Energy [eV]

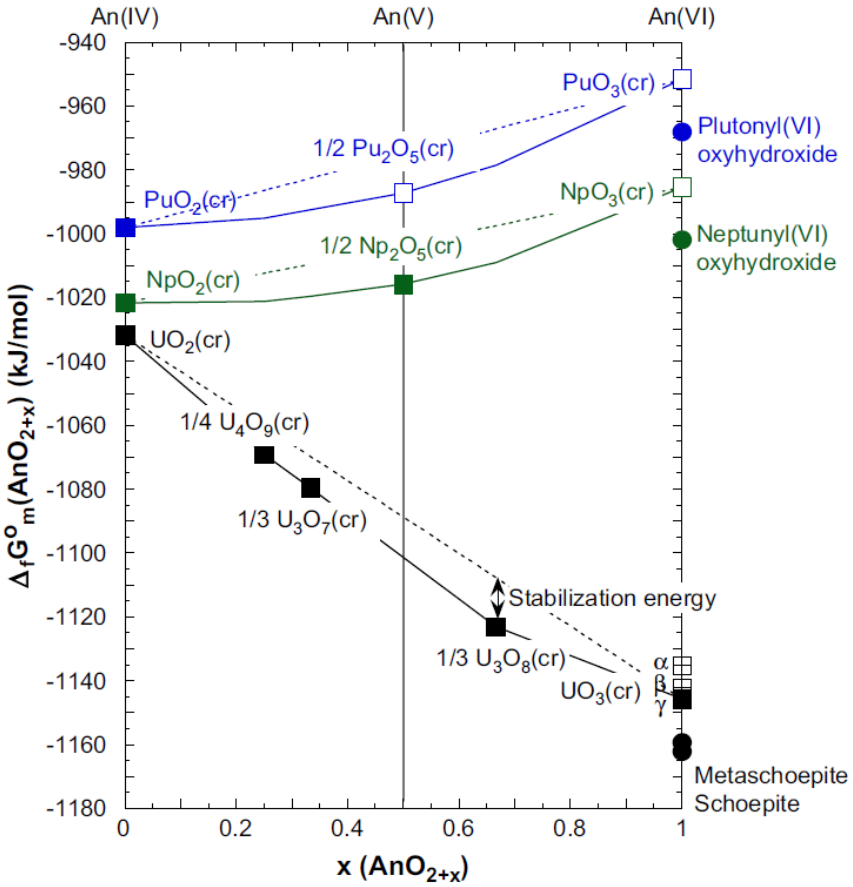


Fig. 8. Normalized standard molar Gibbs energies of formation of crystalline An(IV, V, VI) oxides AnO_{2+x}(cr) and actinyl(VI) oxyhydroxides AnO_3(cr,hyd) as a function of x; known data (filled symbols) selected in the NEA-TDB [1,2] and estimated values for unknown Np and Pu oxides (open symbols).