Karlsruhe Institute of Technology

U redox state and speciation of U in contact with magnetite nanoparticles: high-resolution XANES, EXAFS, XPS and TEM study

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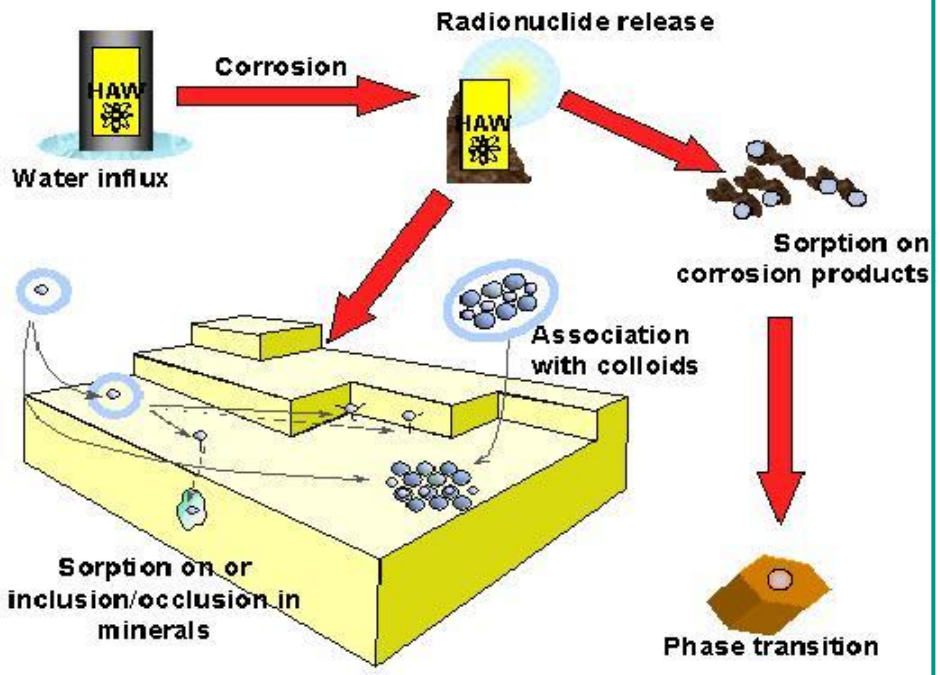
Advanced synchrotron-based systematic investigations of actinide (An) and lanthanide (Ln) systems to understand and predict their reactivity

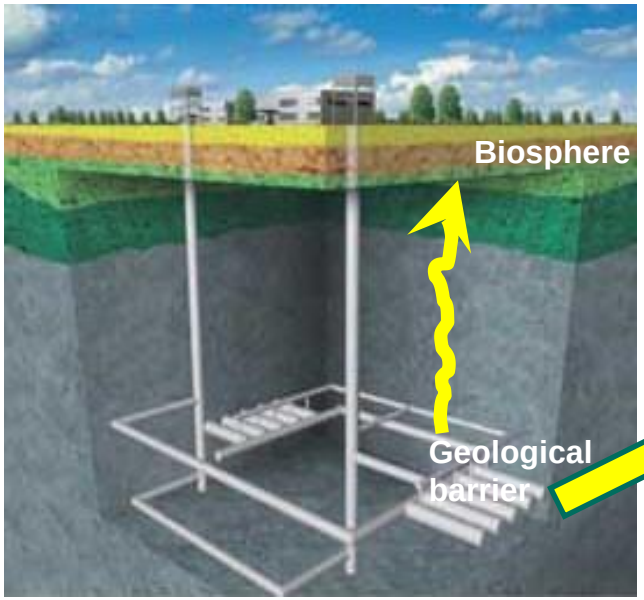
An geochemistry

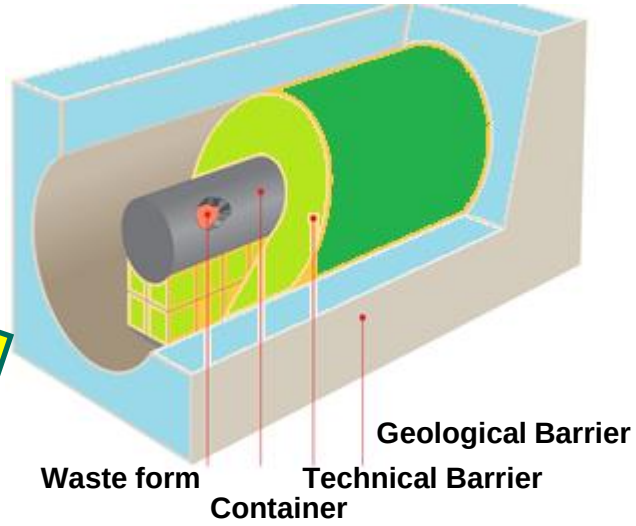


What is the U/Pu redox state and speciation after contact with magnetite?

Helmholtz-Young Investigators Group VH-NG-734
Institute for Nuclear Waste Disposal (KIT)

MOTIVATION





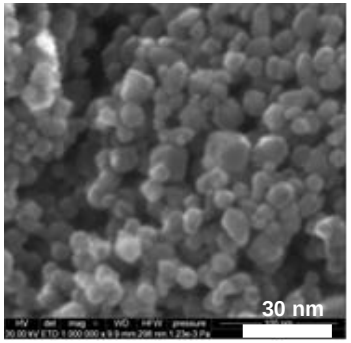
Anaerobic corrosion >1000 years

Fe canister Corrosion Studies (INE)

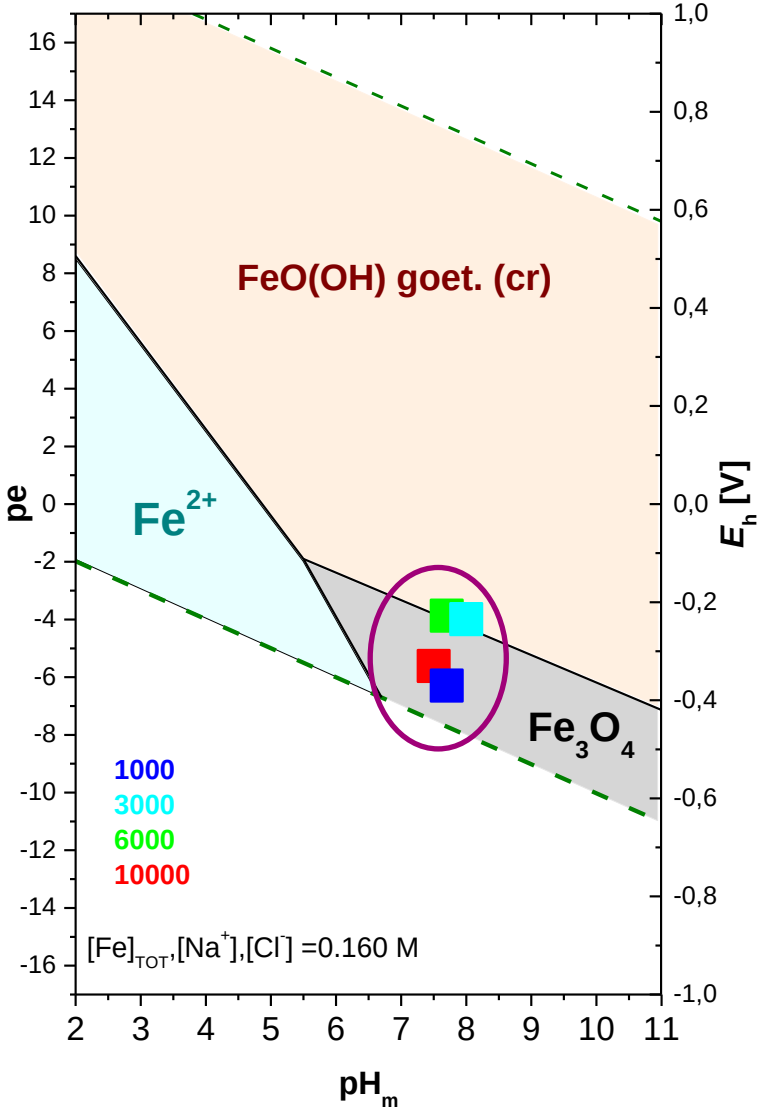
U^{6+} co-precipitation with magnetite

- ❑ **U INCORPORATION INTO MAGNETITE ?**
- ❑ **IS U^{5+} POSSIBLE / STABLE ?**
- ❑ **WHAT IS U^{6+} REDOX KINETICS DURING MAGNETITE FORMATION ?**

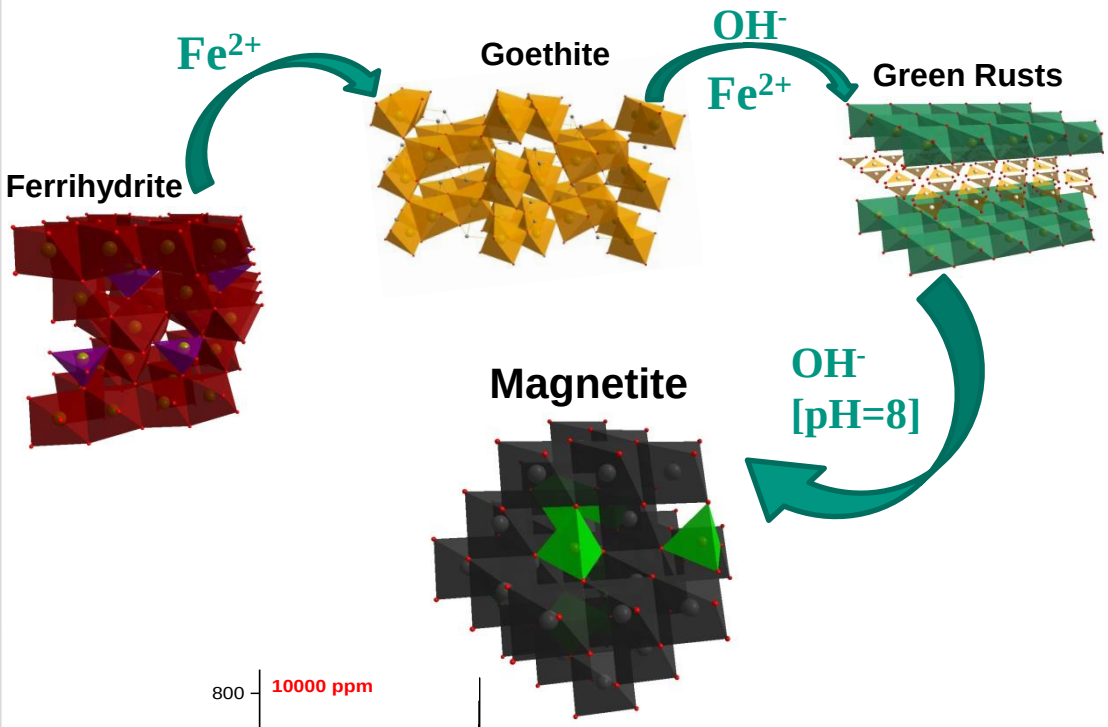
- ➢ **$FeCl_2$ / $FeCl_3$** (1:2)
- ➢ **NaOH** (1 hour titration)
- ➢ **1 wt % NaCl** (final)
- ➢ **U 1000-10000 ppm**
- ➢ **4 samples**



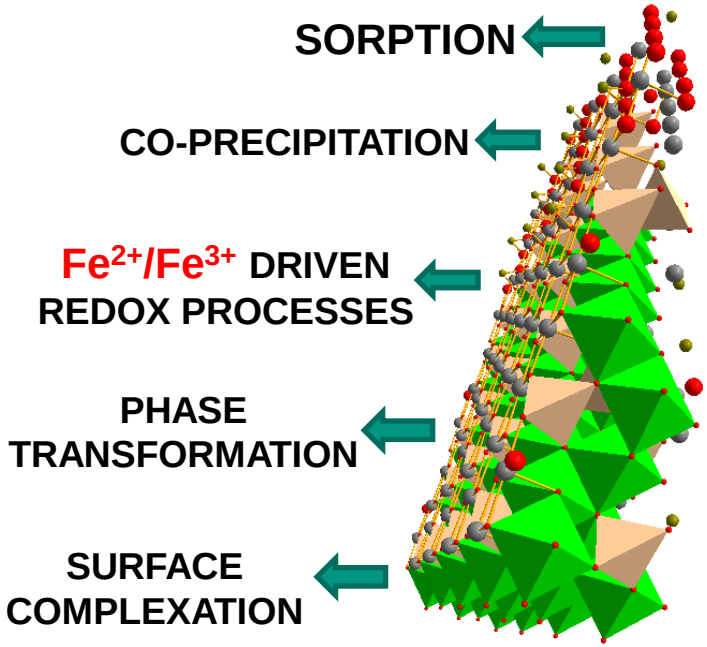
pH 2.5 → ~ 8.0
E_h 750 mV → – 370 mV

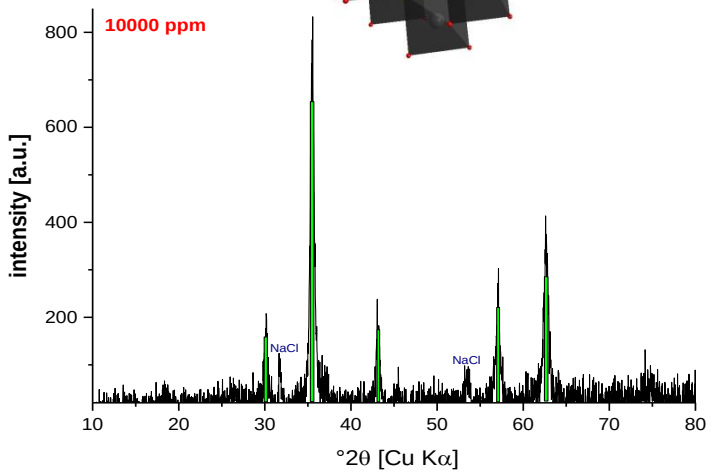


U^{6+} co-precipitation with magnetite



What happens to U?

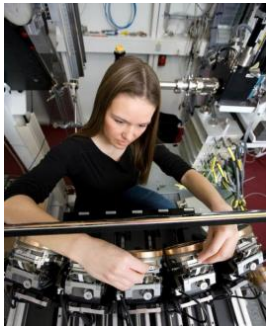


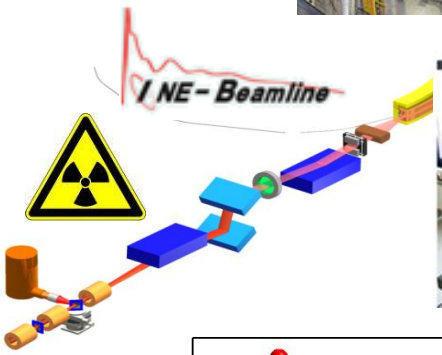


Jolivet et al, ChemCom, 2004
Massey et al, GCA, 2014

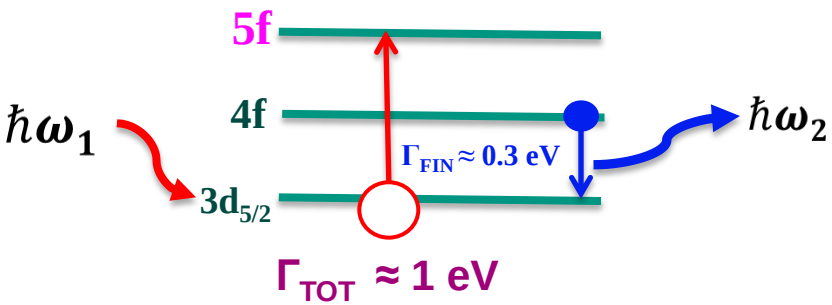
U M_4 HR-XANES / U L_3 EXAFS

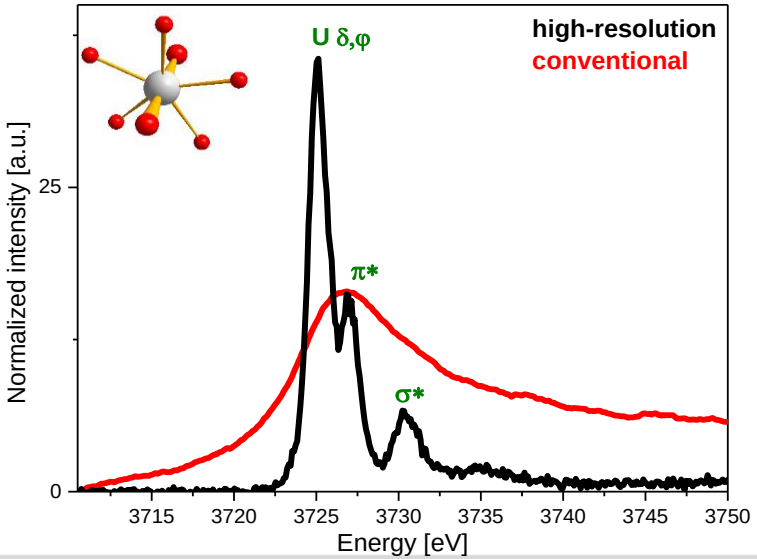
ID26 - High-Brilliance X-ray Spectroscopy





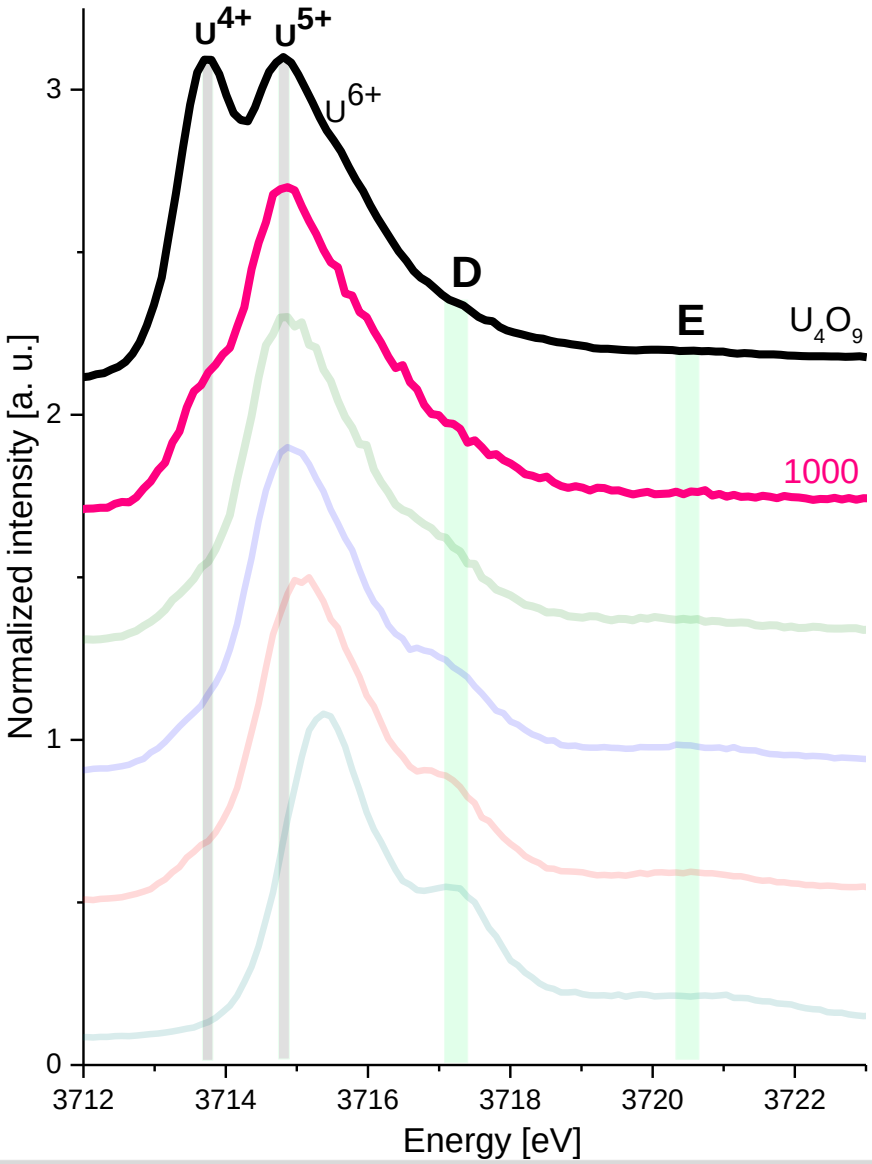
U M_4 XES/XAS principle

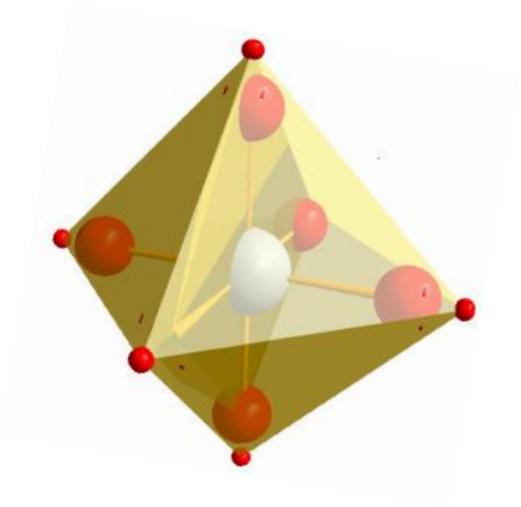




Kvashnina et al., PRL, 2013

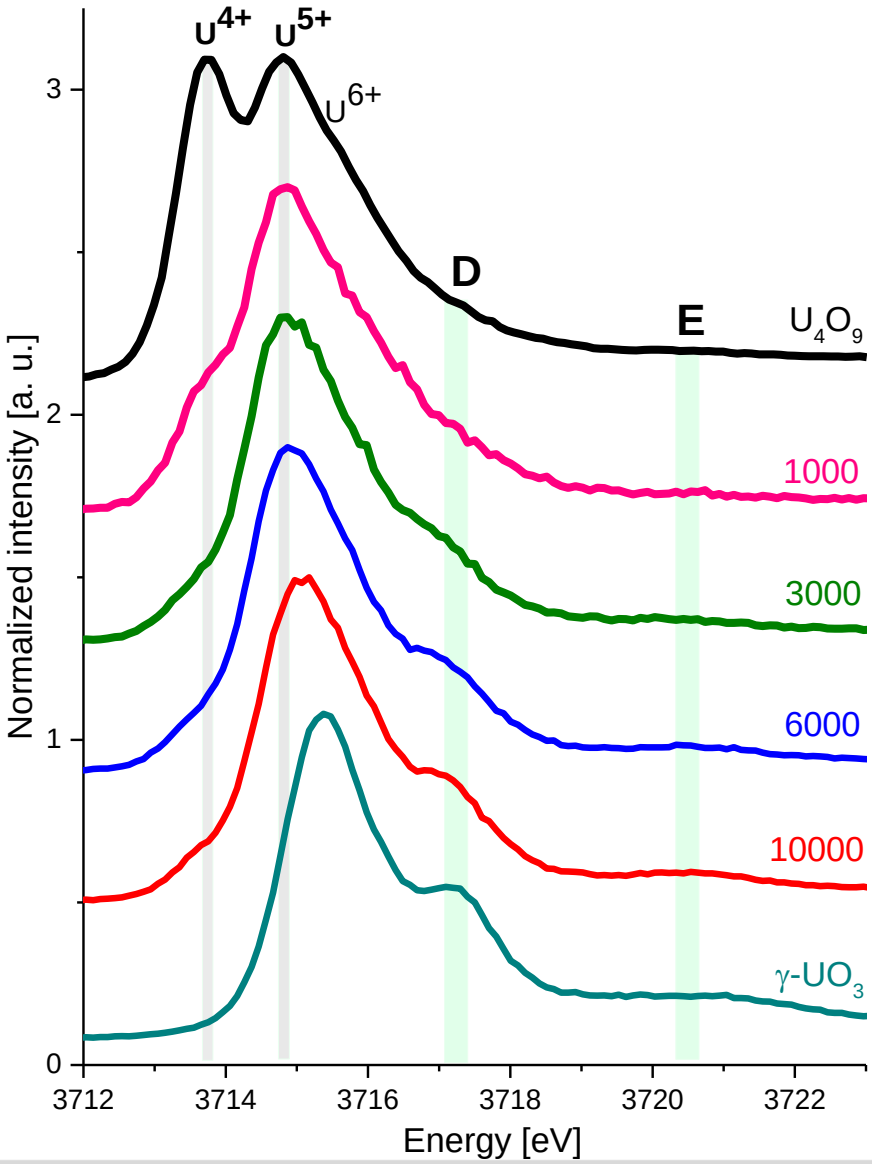
U M_4 HR-XANES / 15 days

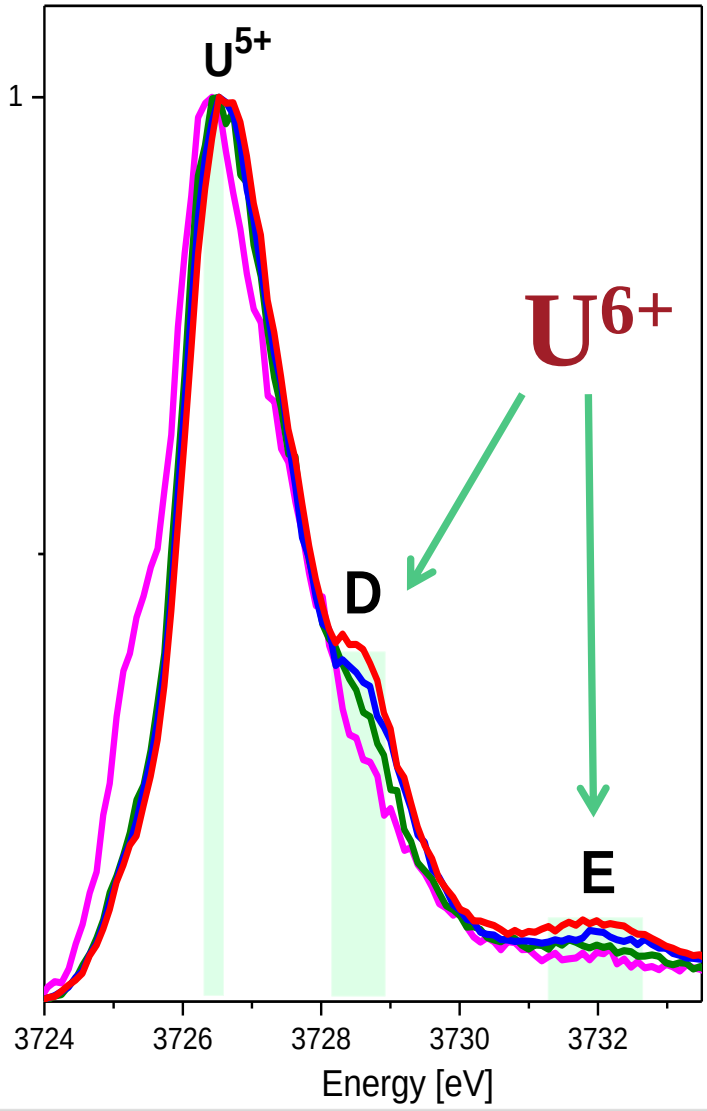




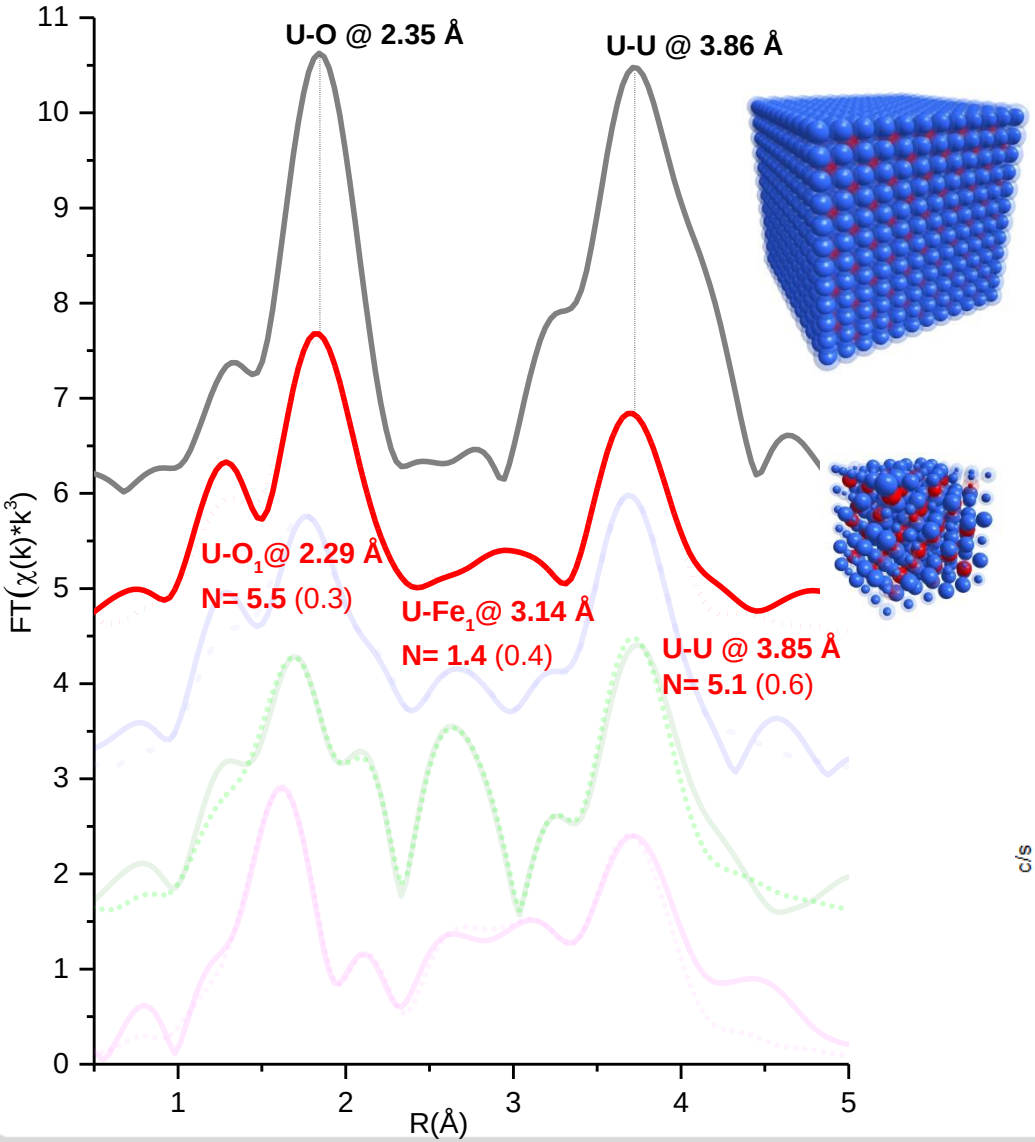
Kvashnina et al., PRL, 2013

U M_4 HR-XANES / 15 days

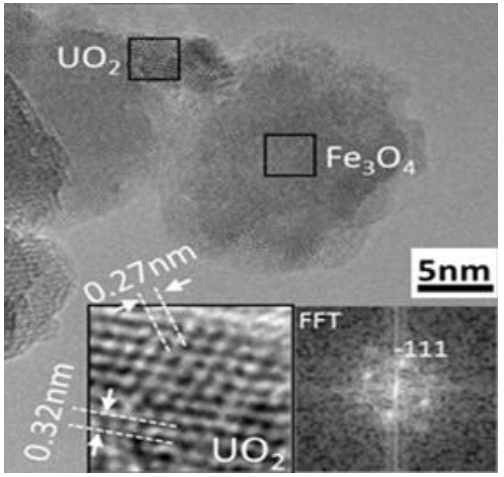


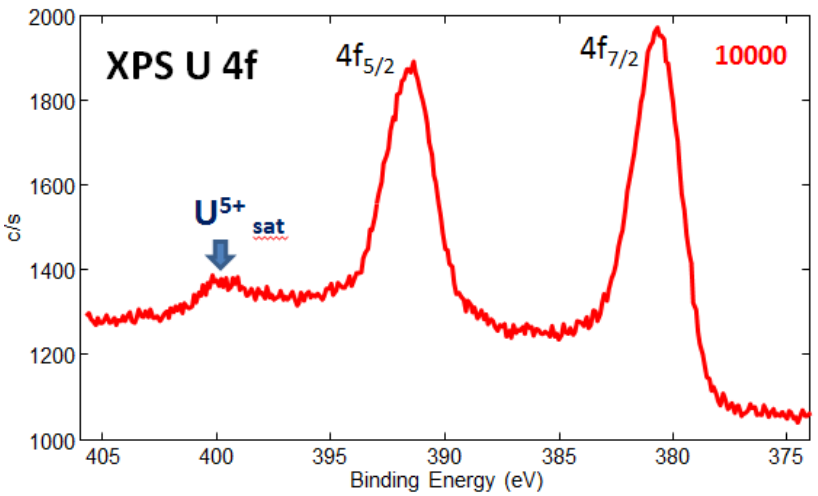


U L_3 XAFS/ ~200 days

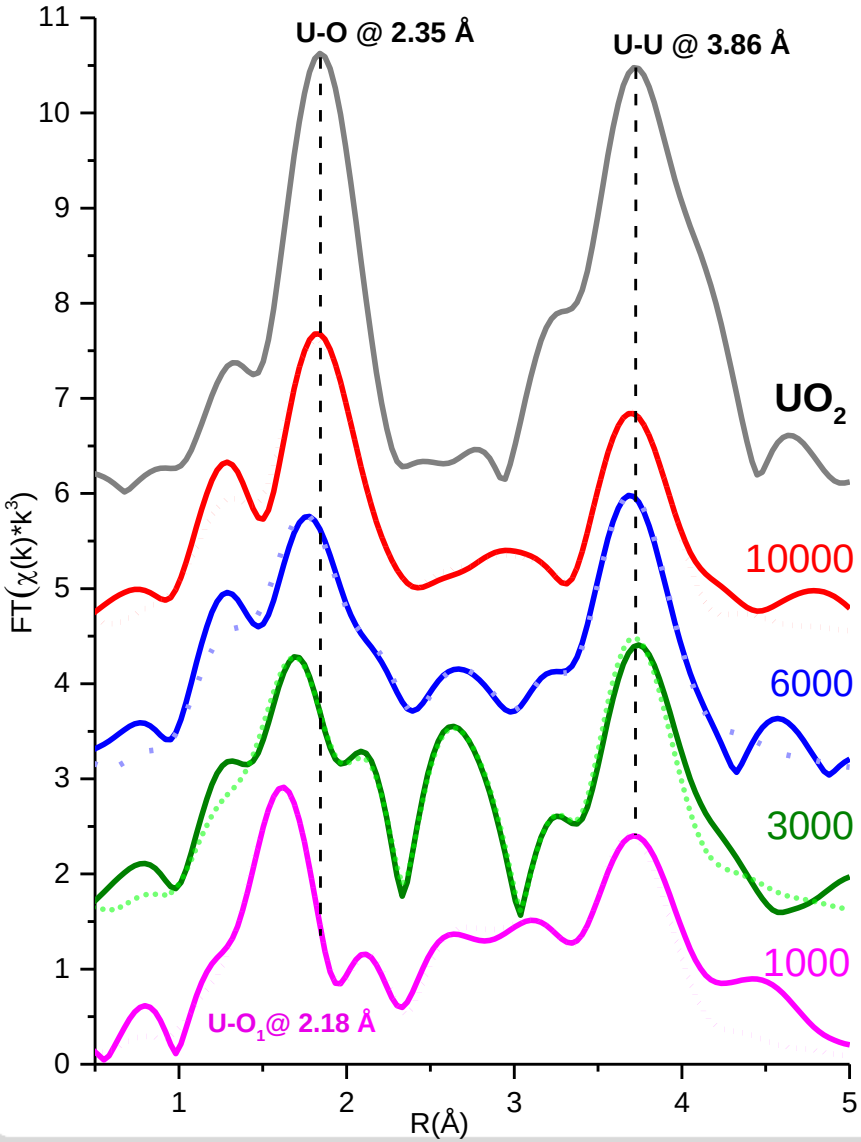


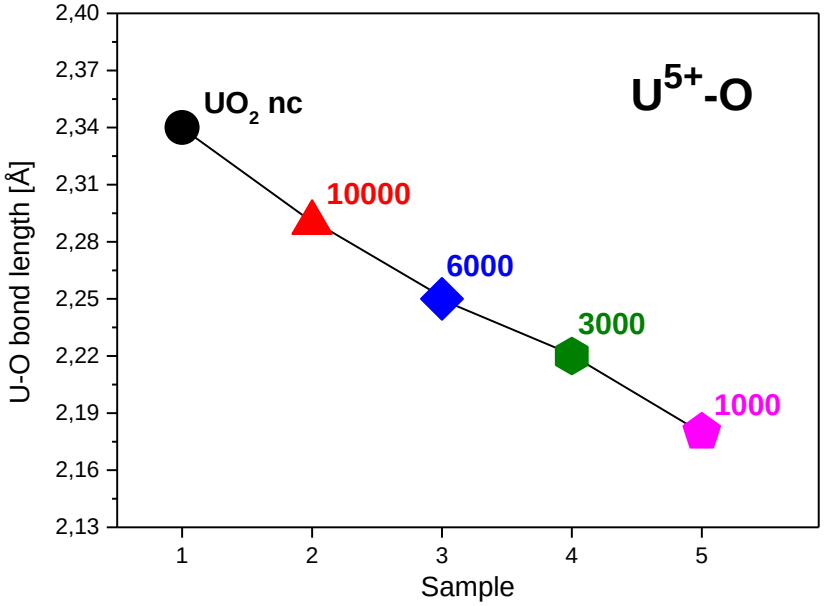
HR-TEM on 10000 (UO_{2+x})

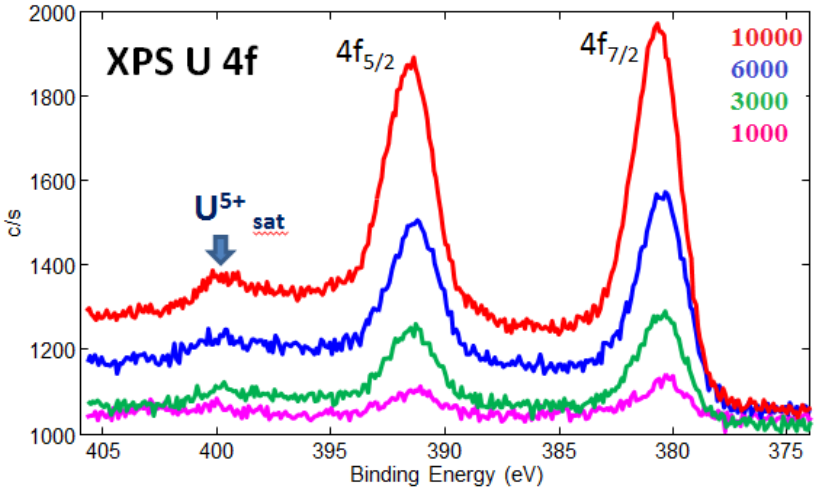




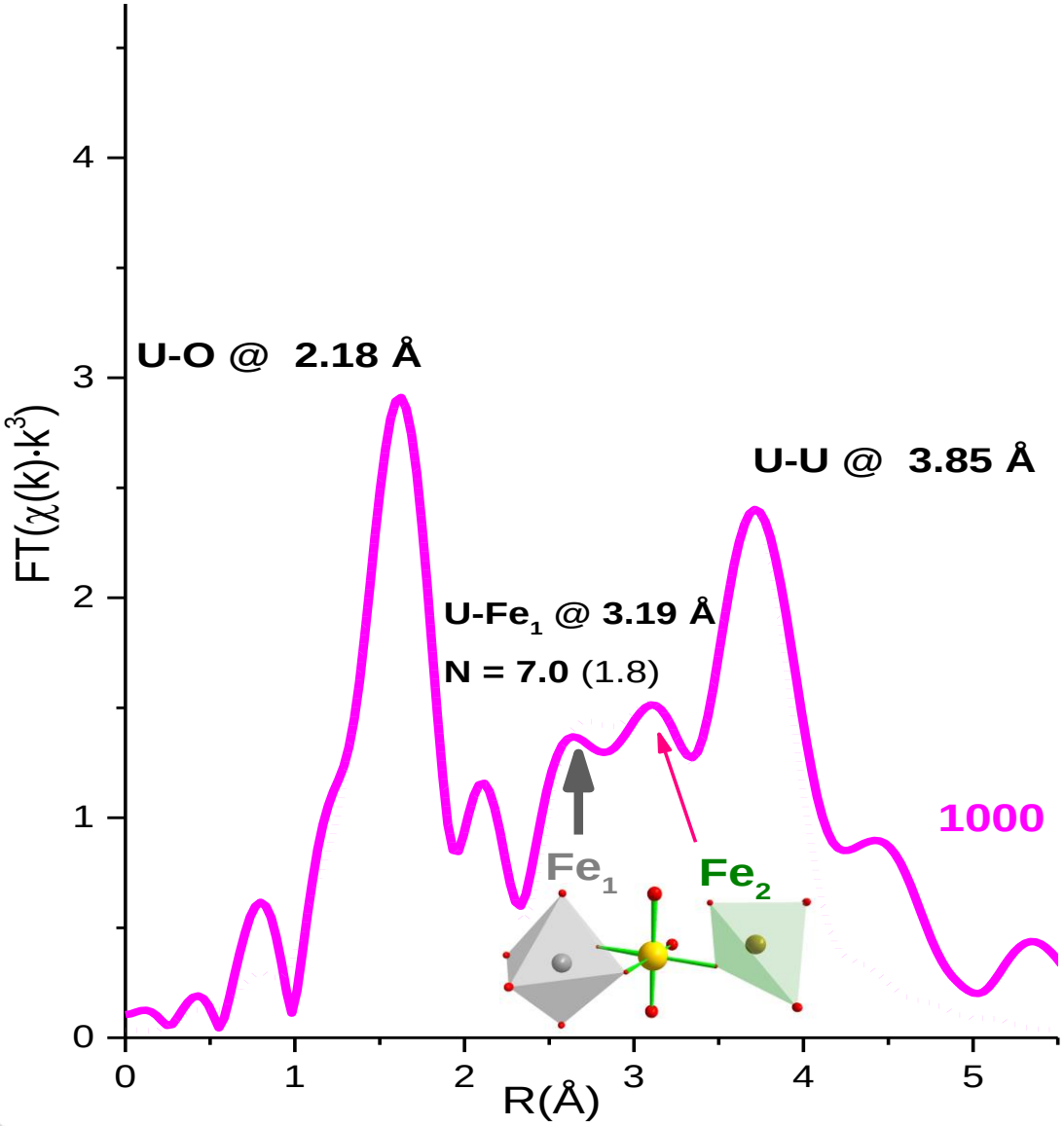
U L_3 XAFS/ ~200 days



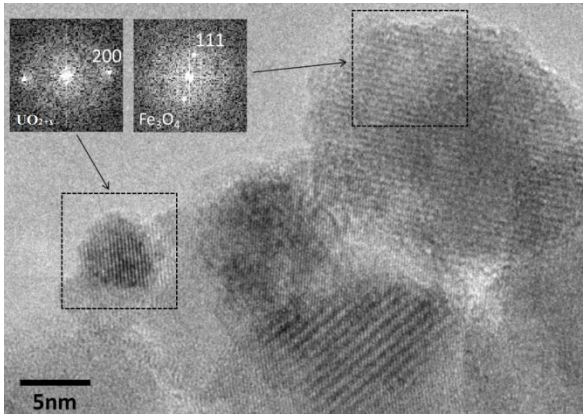


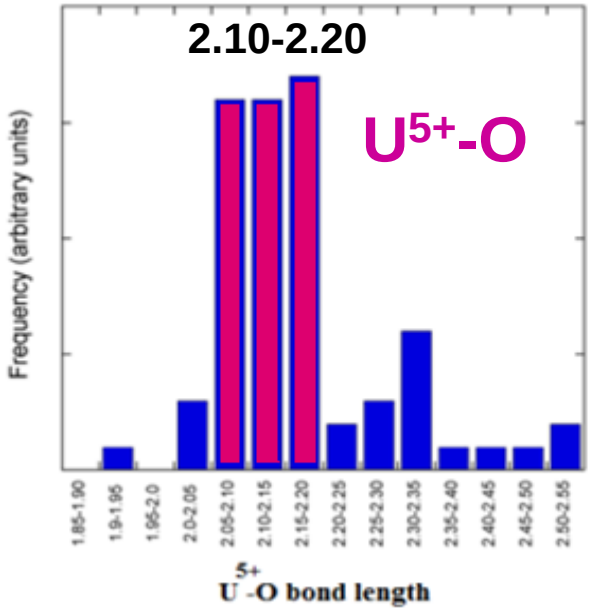


U L_3 XAFS/ ~200 days



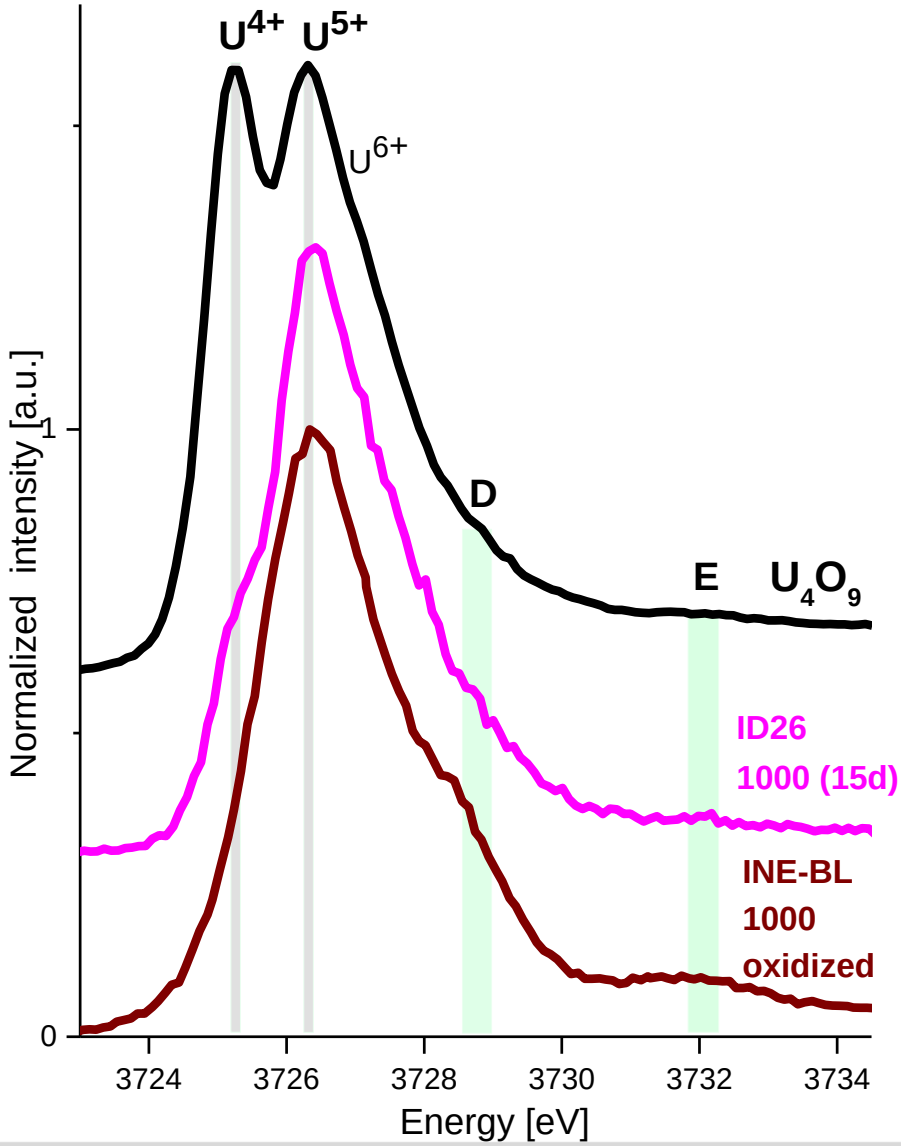
HR-TEM 1000 (UO_{2+x})

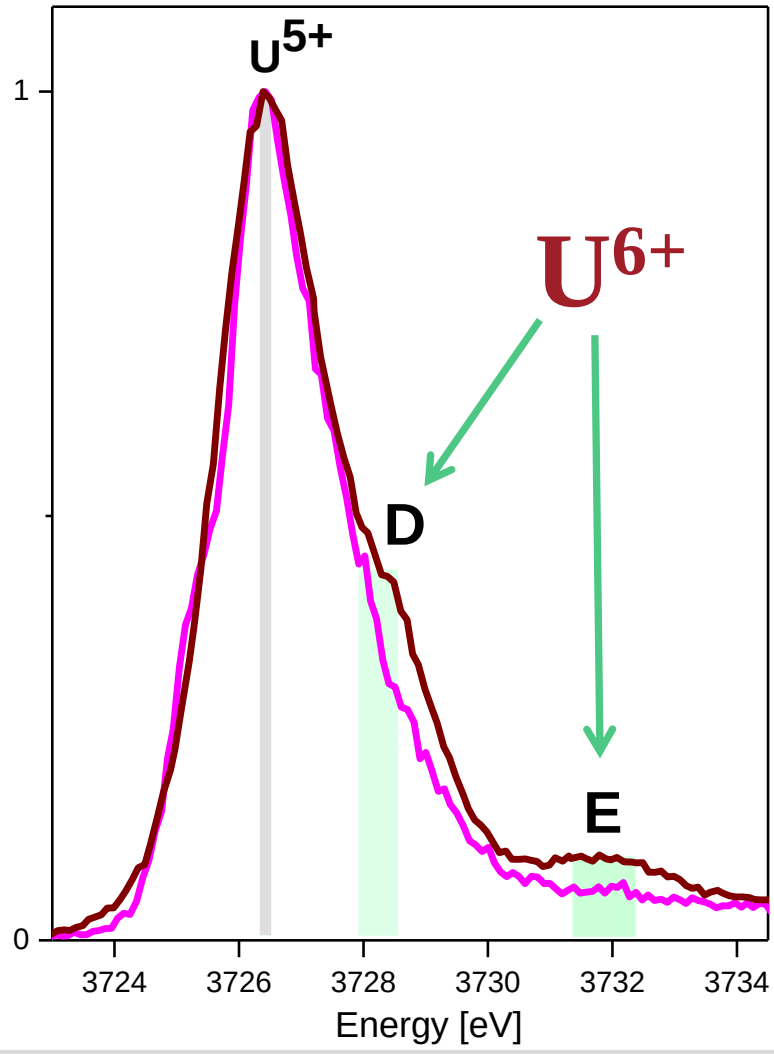




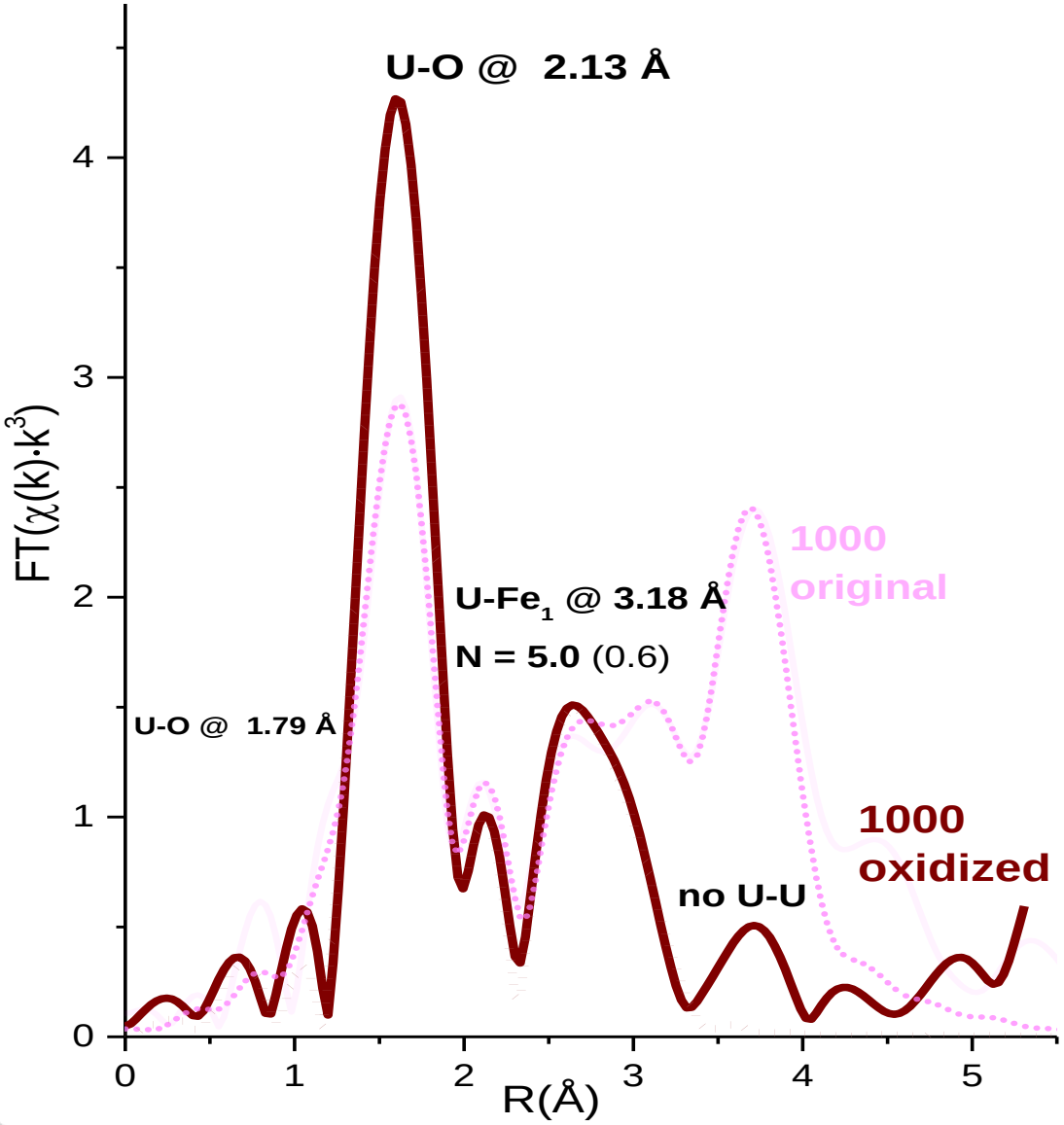
Ilton et al, EnvSci Tech 2010

U M_4 HR-XANES / ~150 days on air

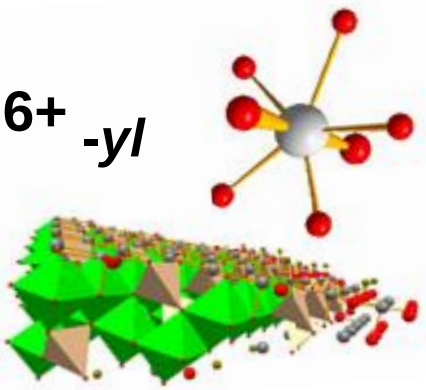


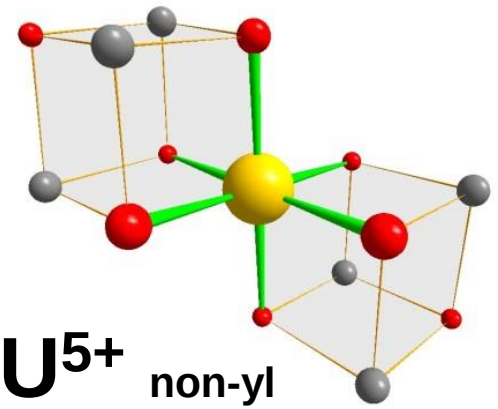


U L_3 XAFS/ ~250 days on air



~ 40% U^{6+} *-yl*





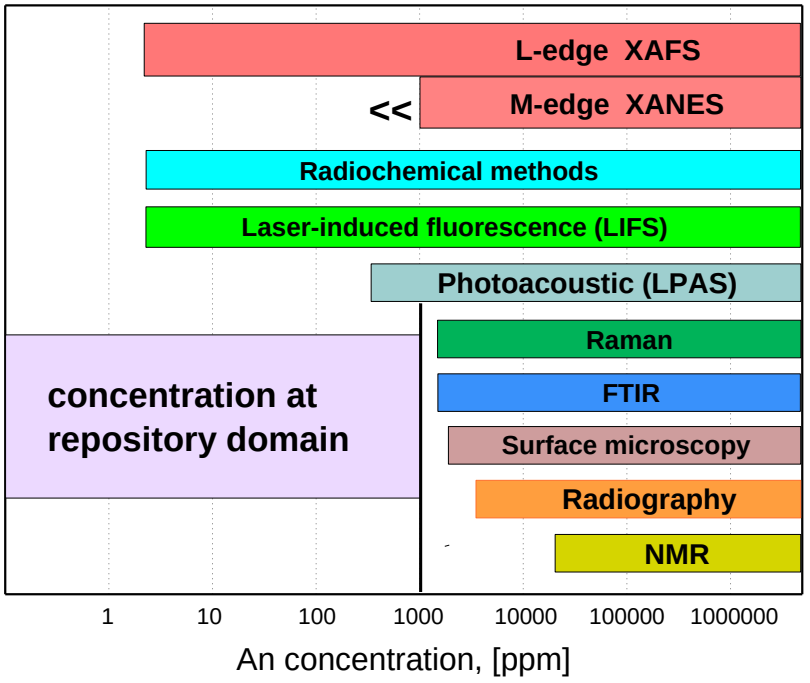
~ 60% U^{5+} non-yl

incorporated

octahedral site of Fe_3O_4

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**
- **U^{6+} kinetics can be studied provided that the experimental conditions are the same**
- **Pentavalent U is stable on to air when incorporated into the structure of magnetite**



Readopted from W. Runde LA Science

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Jörg Rothe
Kathy Dardenne…

Radiation protection team

THANK YOU !

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André Rossberg

Yulia Podkovyrina

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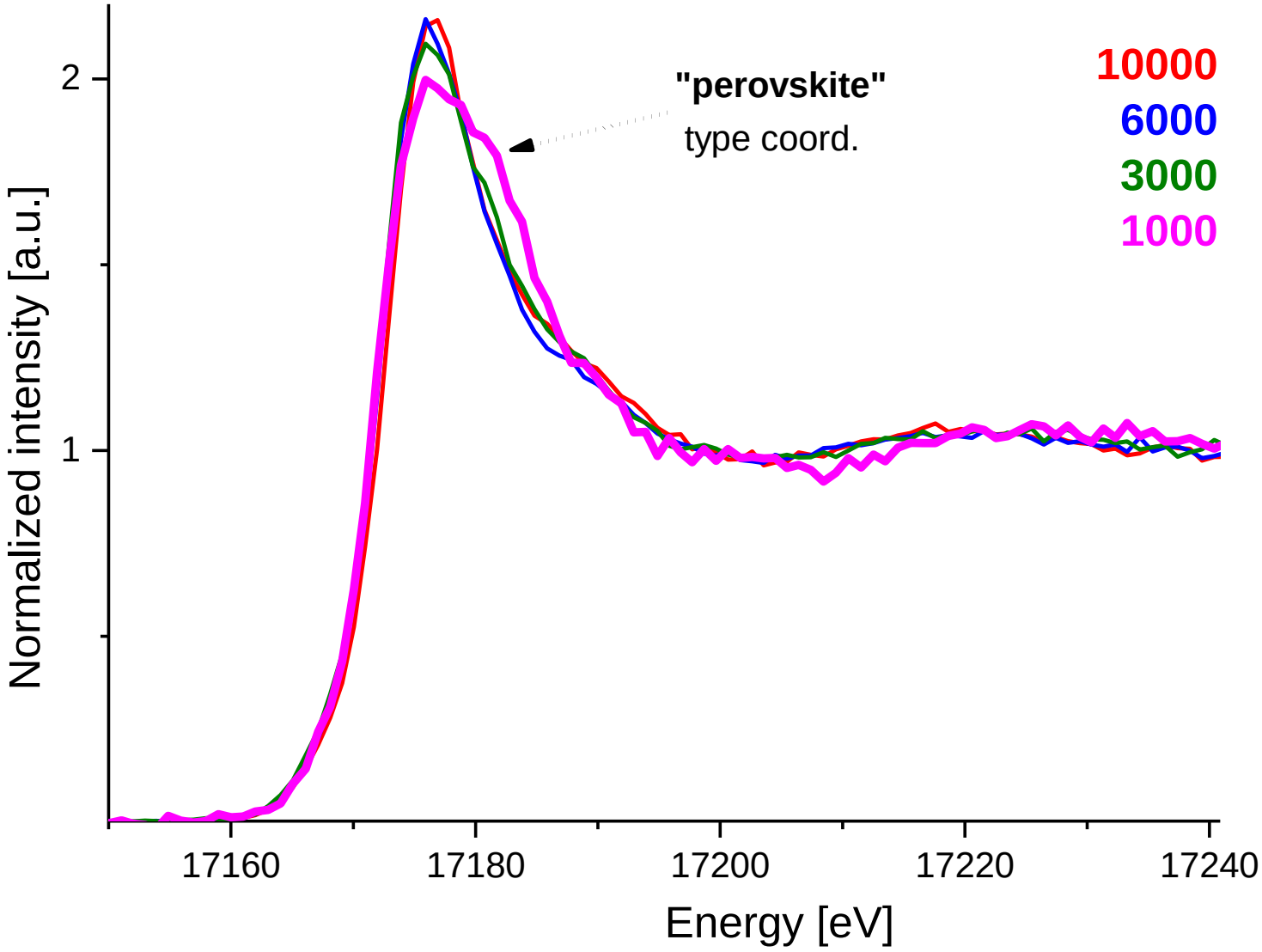
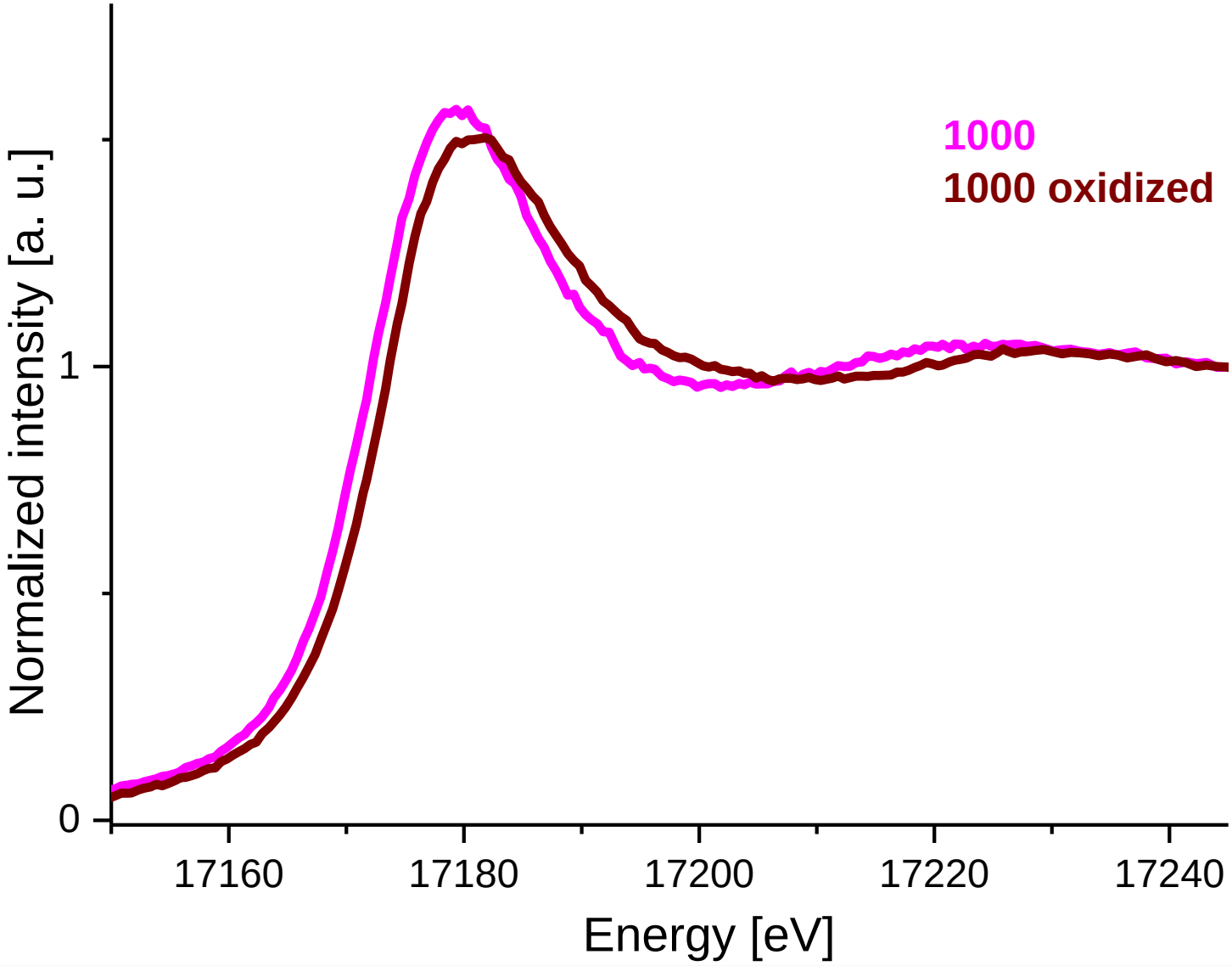
Supporting information

U L_3 HR-XANES / 15 days

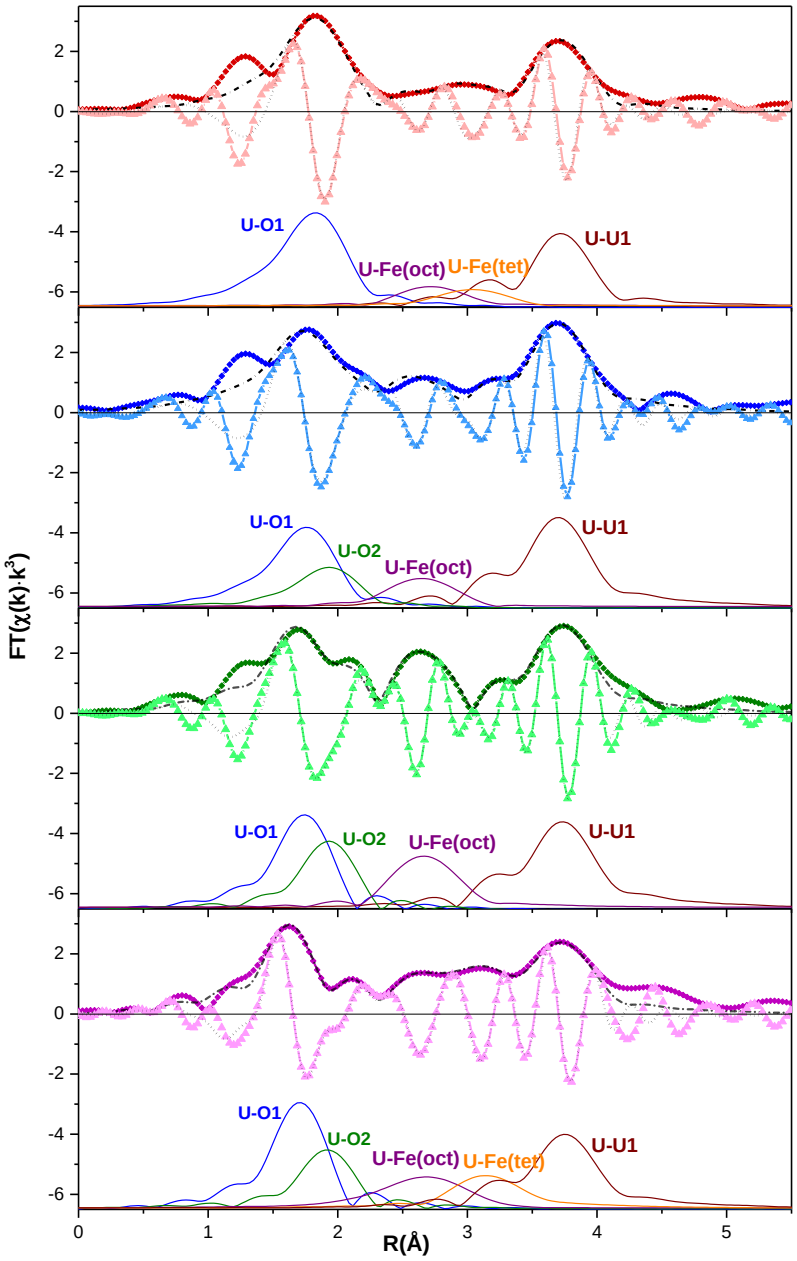


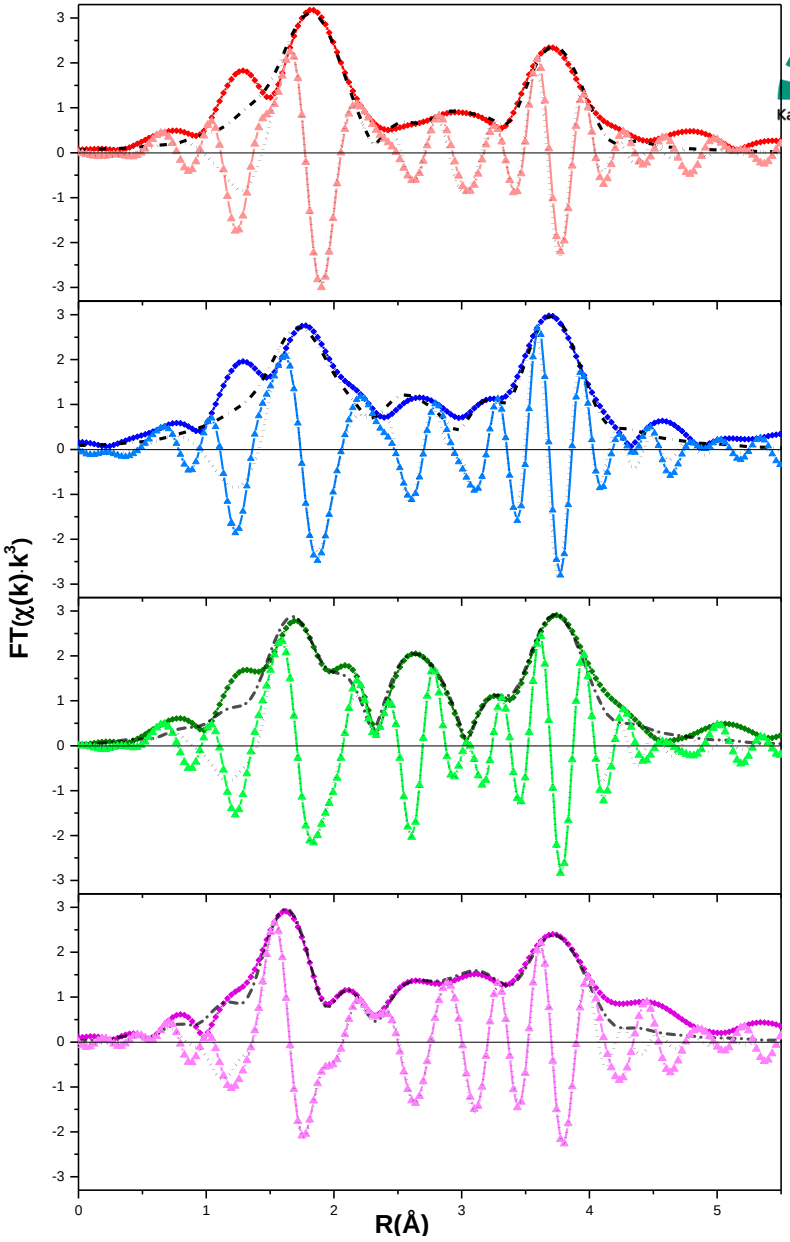
U L_3 XANES / 200 days + oxidized



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)			





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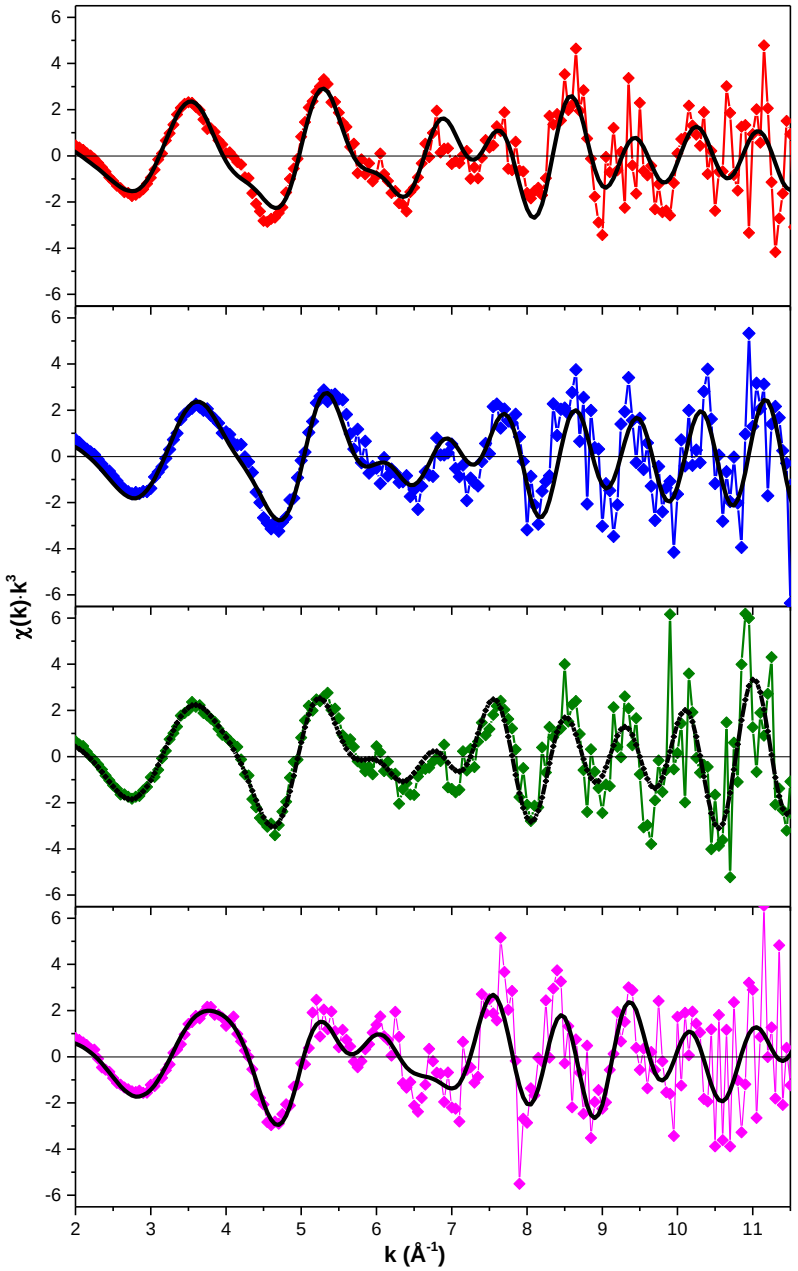
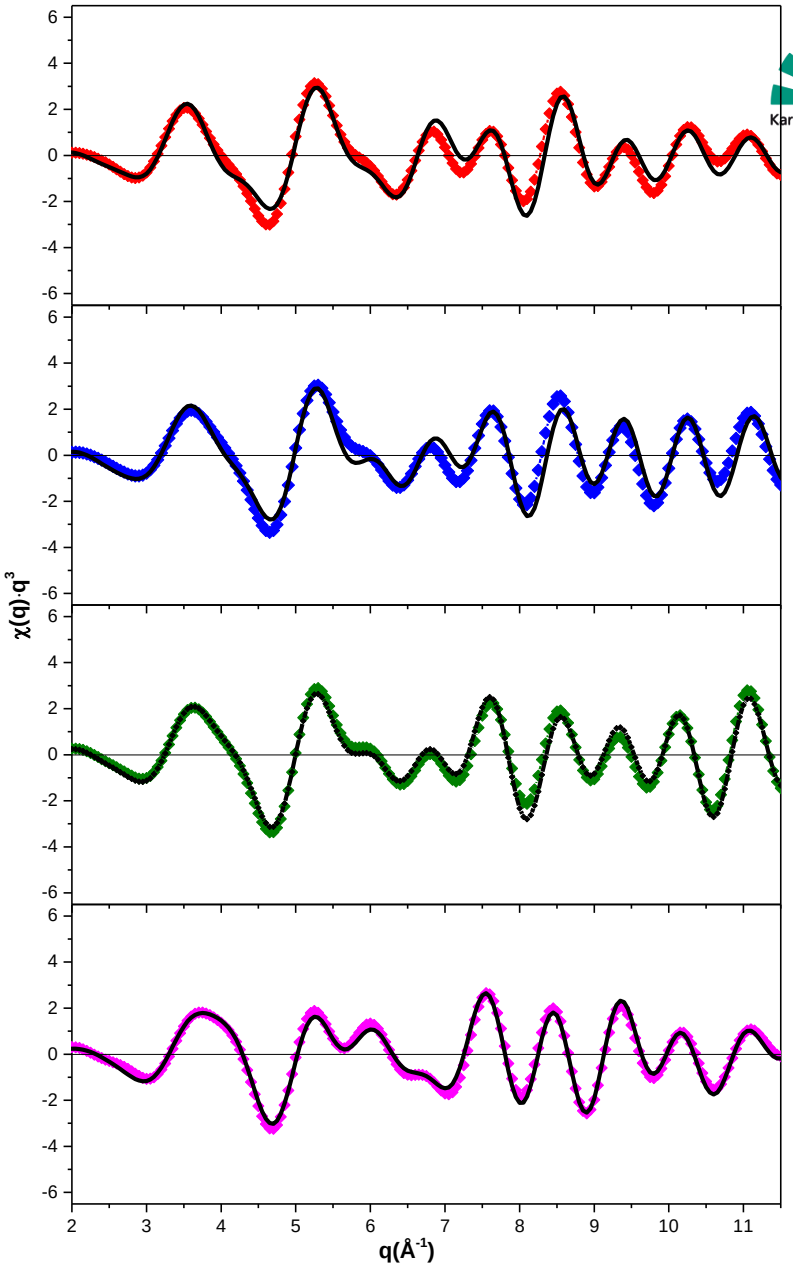

χ(k)·k³
k (Å⁻¹)


χ(q)·q³
q(Å⁻¹)