Plutonium speciation during sorption on natural clay

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Outline

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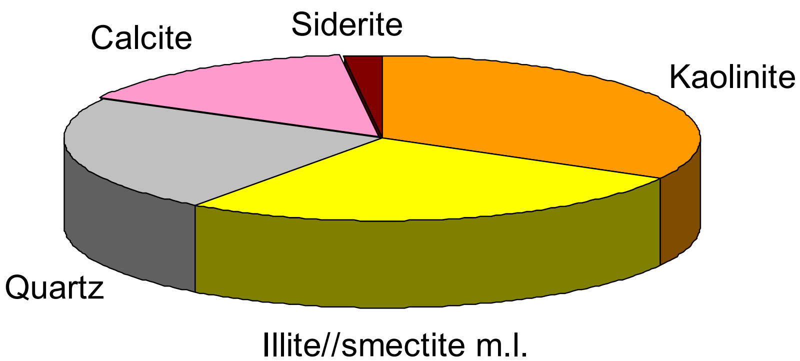
- Characteristics of Opalinus Clay (OPA) and pore water
- Sorption of Pu on OPA
  - Results of batch experiments
  - Synchrotron radiation based speciation
- Conclusions

Motivation

- Plutonium is a major contributor to the radiotoxicity of spent nuclear fuel after a storage time of more than 1,000 years.
- Argillaceous rocks are considered as potential host rocks for the construction of high-level nuclear waste repositories.
- Opalinus Clay (OPA) from the Underground Laboratory Mont Terri, Switzerland, was selected as a reference for a natural clay rock.
- Detailed sorption studies of Pu are needed to predict its migration behaviour in the geological barrier after a leakage of Pu from the repository.
- Our sorption studies are aimed at the determination of
  - K_d values
  - Chemical information about Pu (speciation)

Characteristics of Opalinus Clay (OPA) and pore water

Average mineralogy of OPA [1]



- CEC: 9 ± 2 meq/100 g
- spec. surf. area: 38.0 m^2/g
- TOC: ≤ 1%

Pore water composition [2]

Component	mol/L
Na^+	0.2404
K^+	0.0016
Mg^{2+}	0.0169
Ca^{2+}	0.0258
Sr^{2+}	0.0005
Cl^-	0.2998
SO_4^{2-}	0.0141
HCO_3^-	0.0005
I.S.	0.39
Eh (SHE)	+ 200 mV
pH	7.6

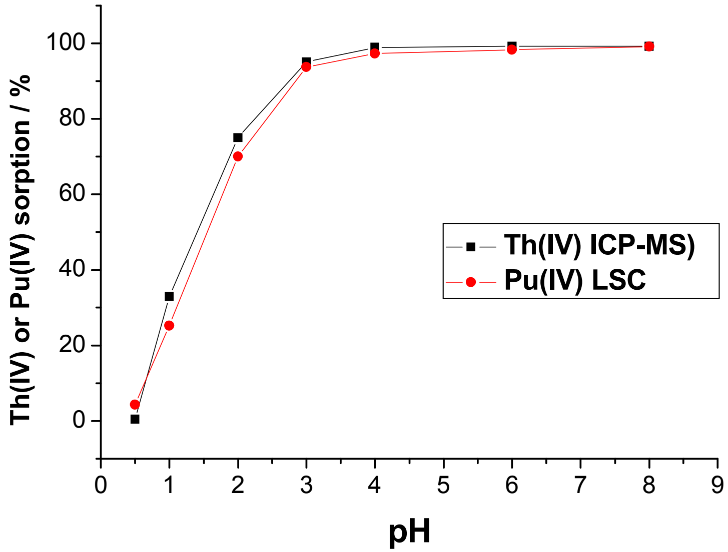
[1] Nagra (2002), NTB 02-03

[2] Pearson (1998), PSI Technical Report TM-44-98-07

Sorption of Pu on OPA – Results of batch experiments

[An(IV)] = 4×10^{-7} M, S/L = 1 g/L,
0.1 M $NaClO_4$

Influence of pH



Distribution coefficients K_d for the sorption of Th, U, Np, Pu, Am on OPA in PW (pH = 7.6)

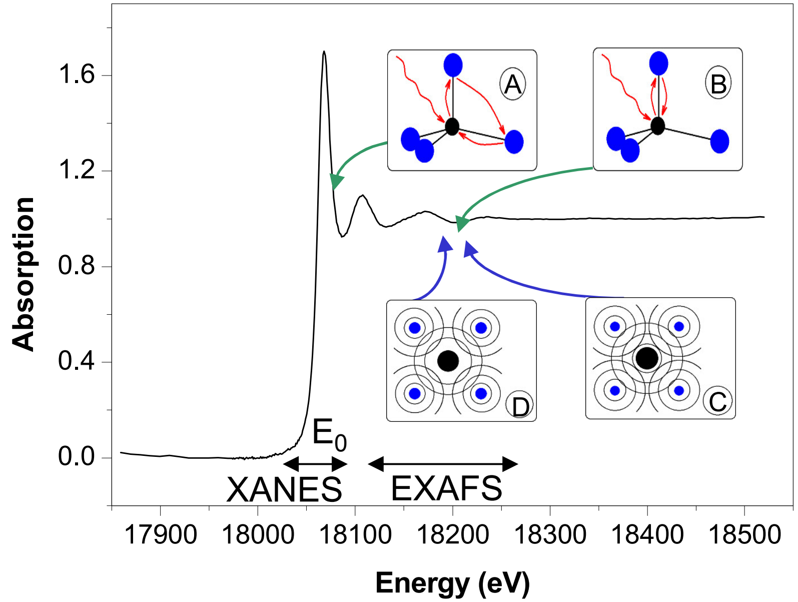
K_d values in m^3/kg [1]

Pu	K_d	K_d	Element
III	159 ± 37	30 ± 2	Am(III)
IV	83 ± 34	29 ± 16	Th(IV)
V	-	0.03 ± 0.01	Np(V)
VI	13 ± 3	0.03 ± 0.01	U(VI)

[1] Amayri et al. (in preparation)

Synchrotron radiation based techniques

XAFS (X-ray Absorption Fine Structure)



ESRF, ROBL BM 20

µ-XAFS

- Actinide speciation

µ-XRF (X-ray fluorescence)

- Elemental distributions

µ-XRD (X-ray diffraction)

- Crystalline phases

PSI, SLS, microXAS

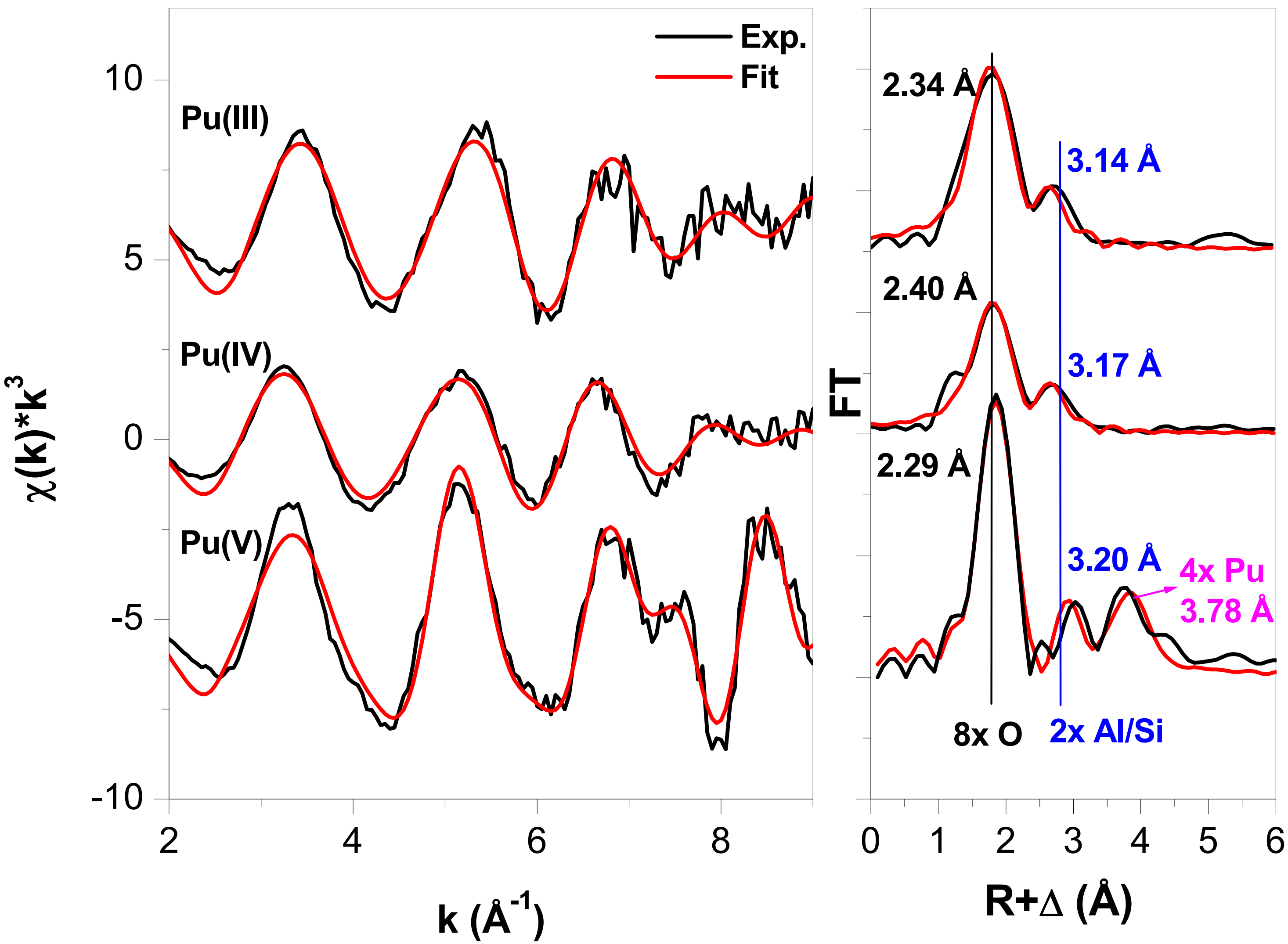
Samples for XAFS, XRF and XRD measurements

Sample	Pu oxidation state	$[Pu]_{tot}$ mol/L	pH	Atmosphere	Eh (SHE) mV
Powder	III	1×10^{-5}	7.6	Argon	- 58
Powder	IV	1×10^{-5}	7.6	Argon	- 59
Powder	V	1×10^{-5}	7.6	Argon	- 40
Thin section	VI	2×10^{-5}	7.6	Air	+ 236

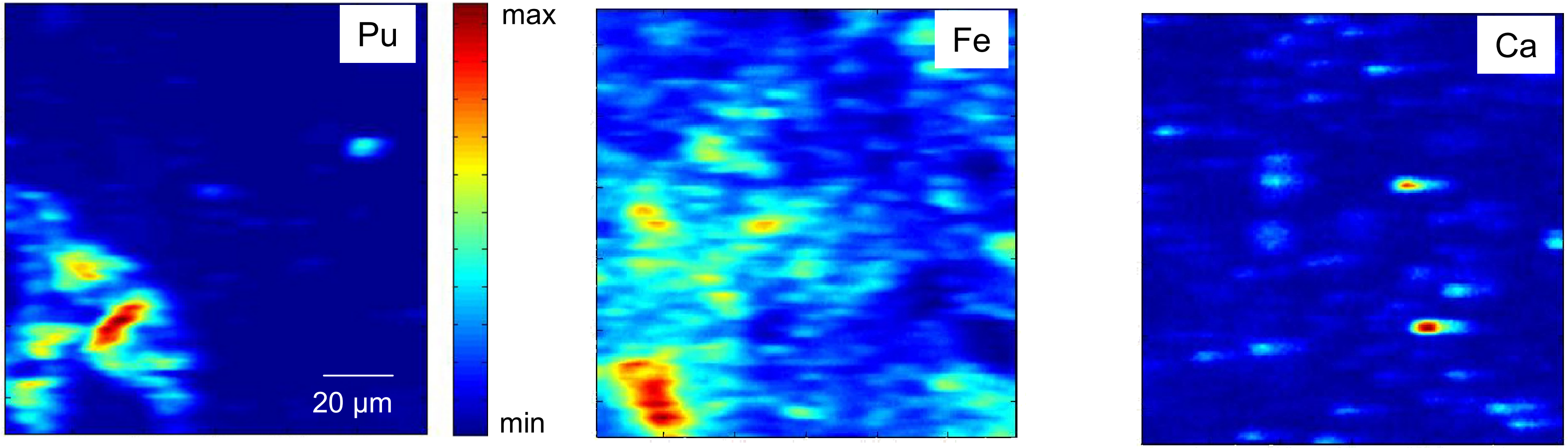
Pu L_{III}-edge EXAFS spectra and corresponding FT

JG|U

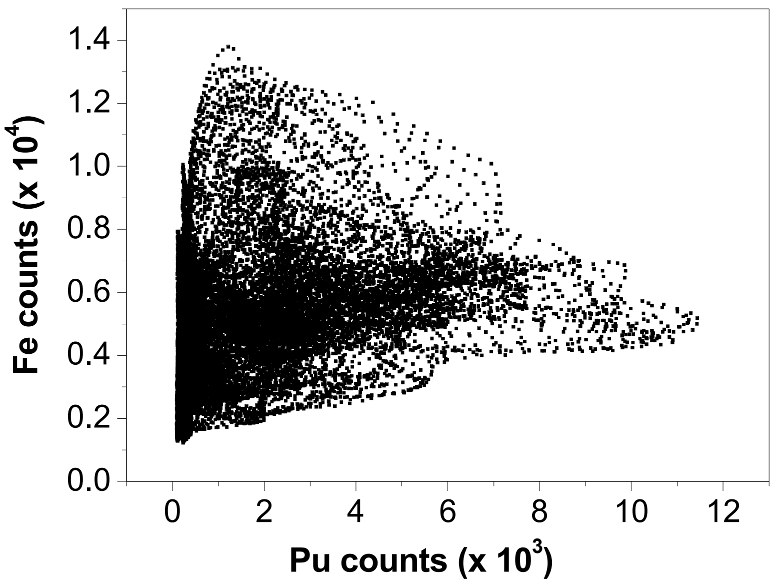
400 ppm Pu sorbed onto OPA at pH 7.6 under Ar atmosphere



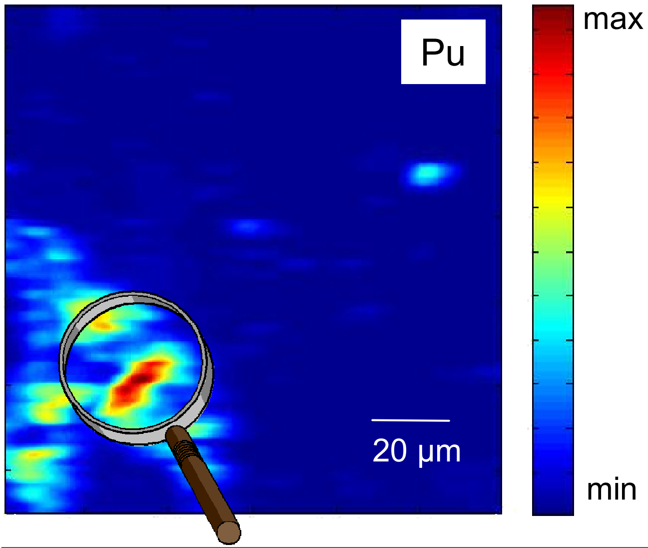
µ-XRF mapping of OPA thin section

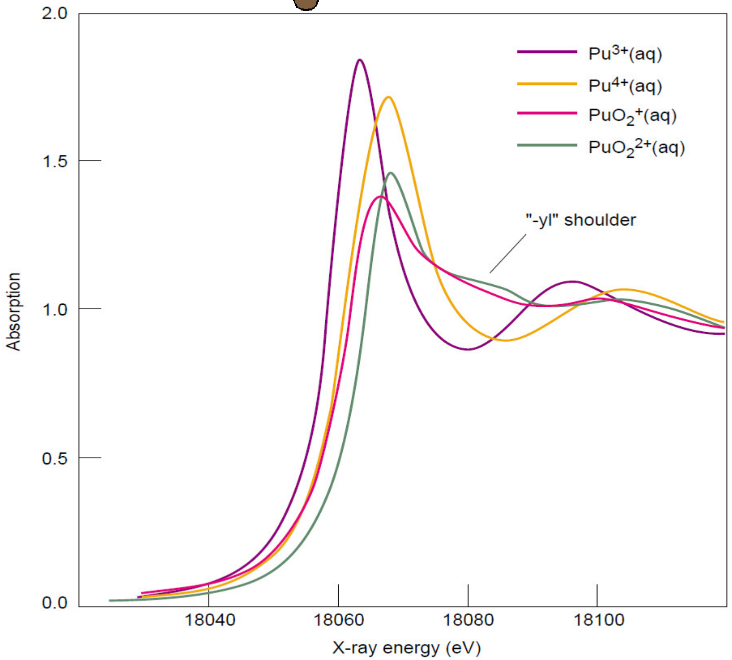


Fe vs. Pu scatterplot

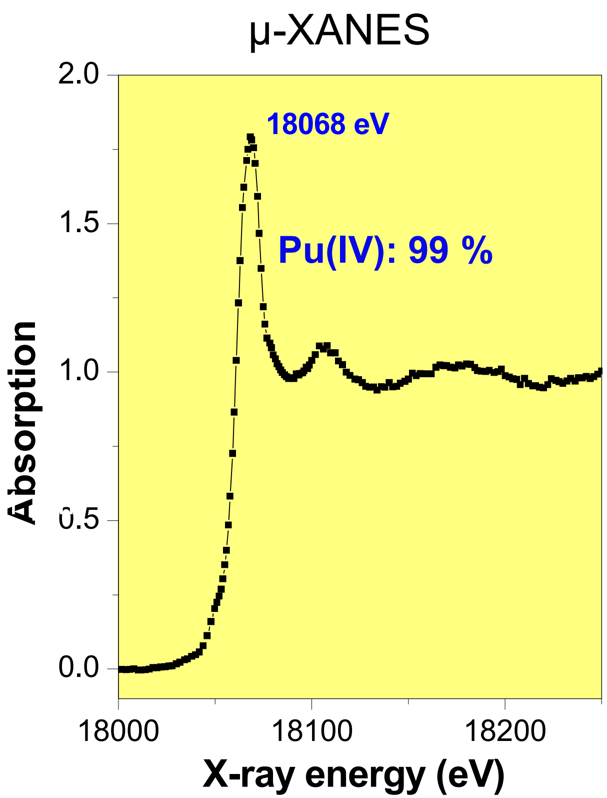


Pu L_{III}-edge μ-XANES of OPA thin section





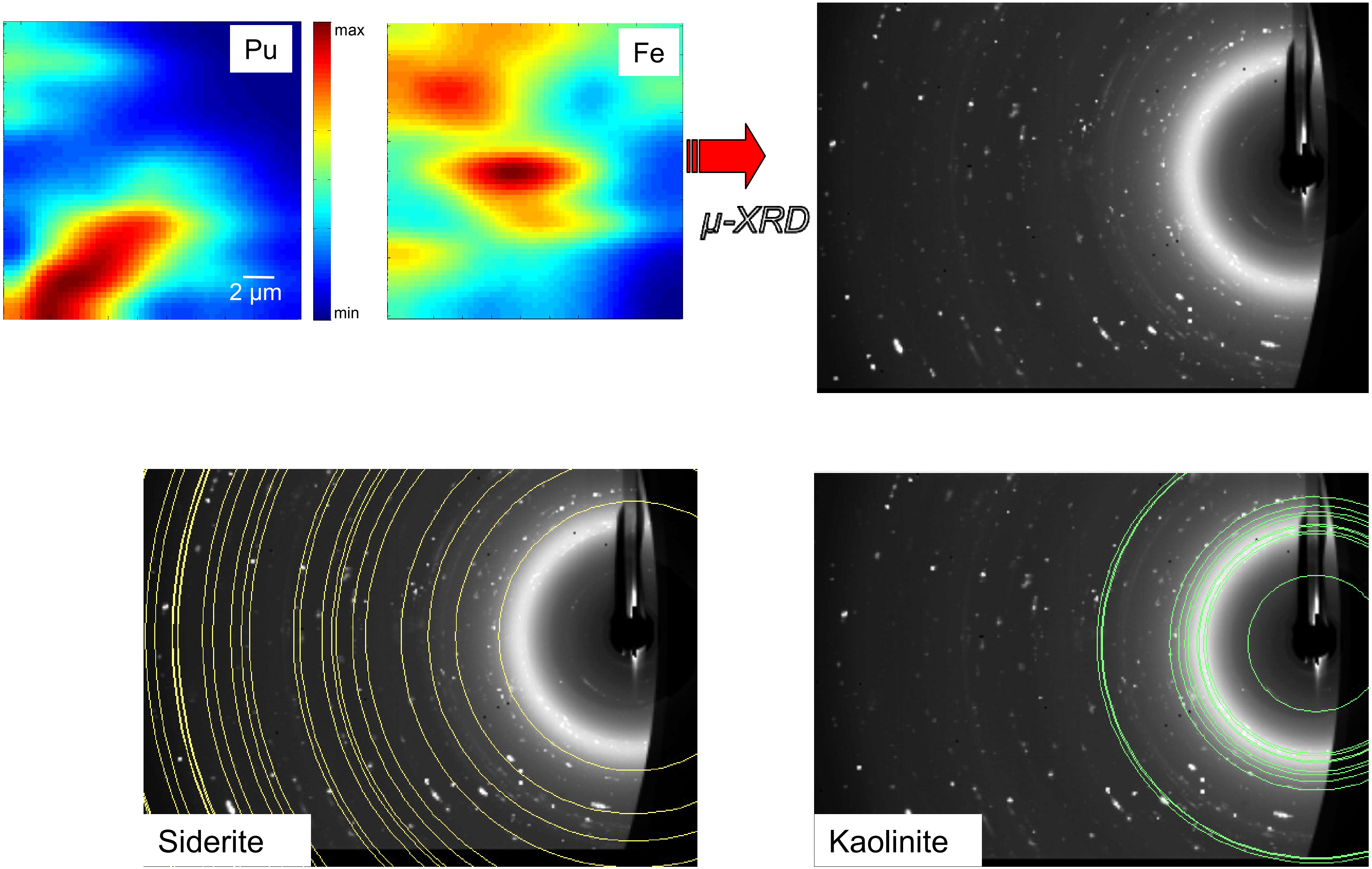
Conradson et al., Polyhedron 17, 599 (1998)



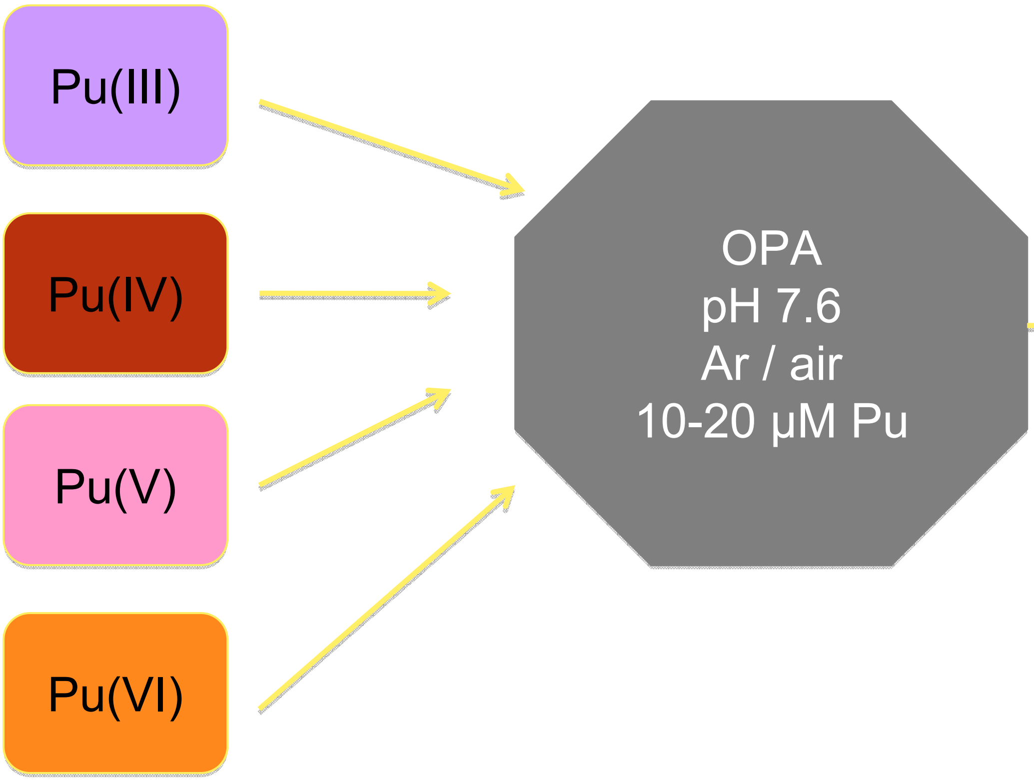
μ-EXAFS

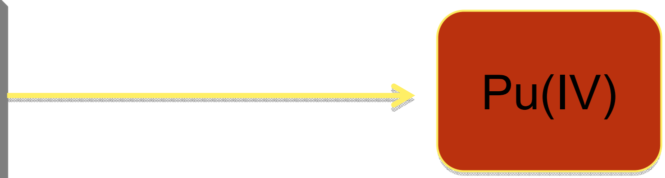
	N	R/Å	σ^2/Å^2
Pu-O	8	2.38	0.009

µ-XRD of OPA thin section (preliminary result)



Conclusions





Pu is retained by OPA in the reduced and less mobile tetravalent oxidation state of Pu

Pu is localized on or in close vicinity of the Fe(II) mineral siderite and the clay mineral kaolinite

Chemical information on trace elements in heterogeneous media can be obtained with high spatial resolution using synchrotron radiation based μ-XAFS, μ-XRF and μ-XRD.

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