Spent Fuel Worshop 2019

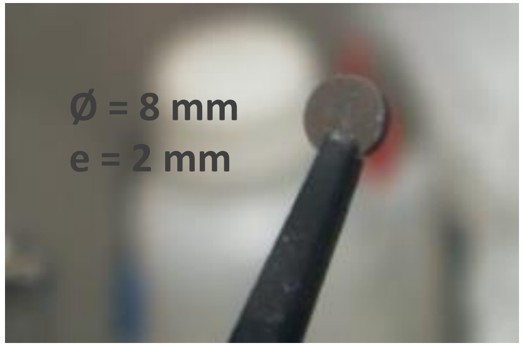
DE LA RECHERCHE À L'INDUSTRIE

EFFECT OF CLAYSTONE ON THE OXIDATIVE DISSOLUTION OF UO_2 DOPED WITH A RADIOACTIVE ALPHA EMITTER IN SYNTHETIC CLAYEY GROUNDWATER

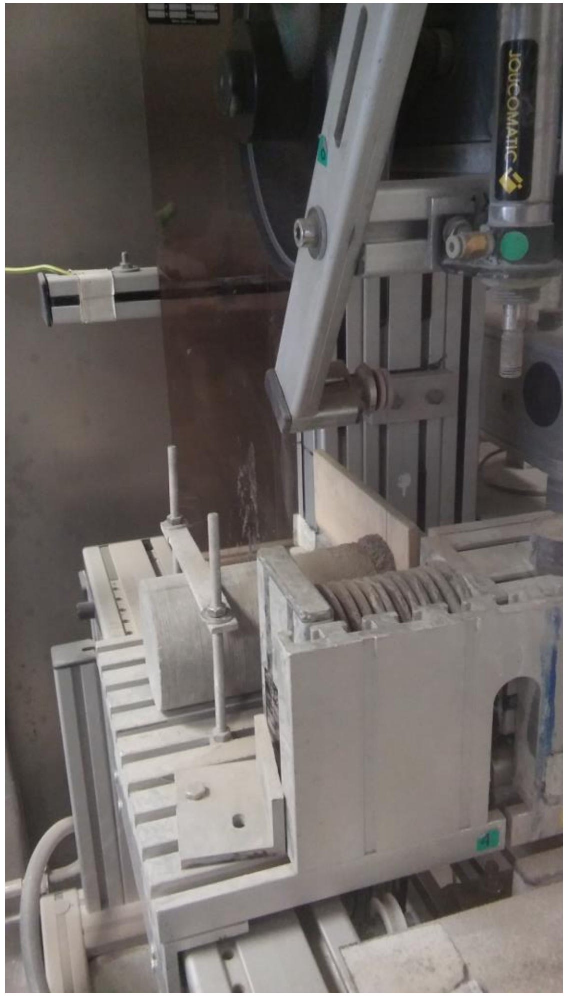
18th of September

V. KERLEGUER, C. JEGOU, L. DE WINDT, V. BROUDIC, C. MARQUES, C. MARTIN, F. TOCINO

- Introduction
- Experimental and analytical developments
- Leaching experiments on alpha-doped UO_2 pellets in synthetic COx water with and without a solid claystone disc
- Conclusions and outlooks



α-emitters doped UO_2 pellet



Solid claystone disc

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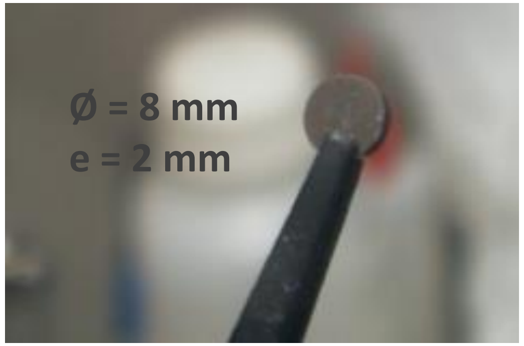

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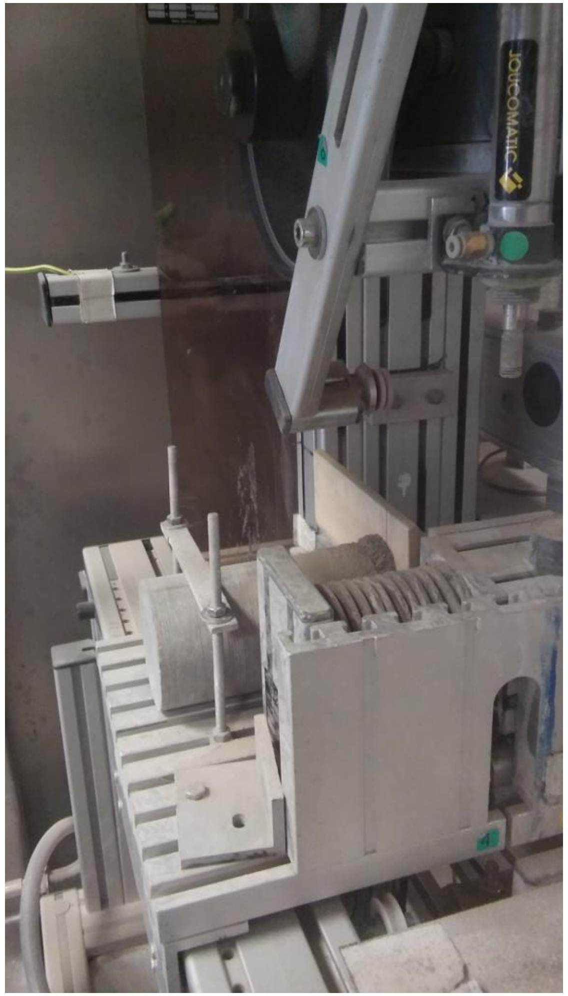


Solid claystone disc

Nuclear fuel cycle in France

Electricity production
Light water reactor (4y)

1200 t.y^{-1}

Interim pool storage
(few years to decades)

850 t.y^{-1}

UOx/MOx Fuel

Direct disposal of spent fuel: alternative way

Geological disposal
(> 10^5 y)

Iron canister

Callovo – Oxfordian
(COx) claystone
-500 m

The French National Radioactive Waste Management Agency (Andra) has selected a Callovo-Oxfordian (COx) clay formation for repository

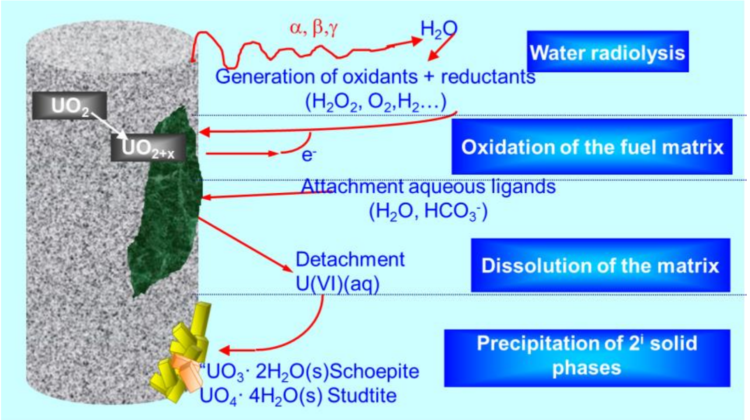
MOx fuel fabrication

Nuclear fuel reprocessing
and U-Pu recycling

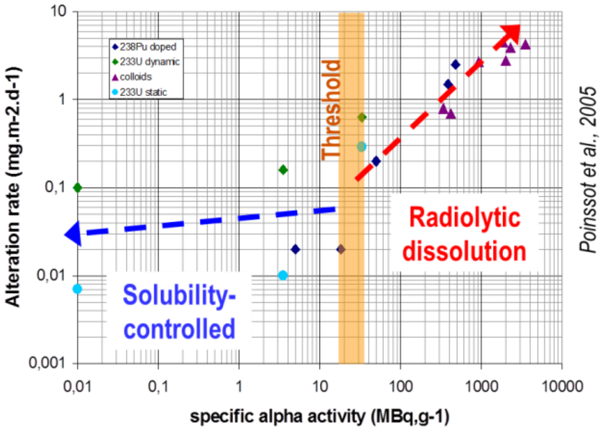
Nuclear
glass

Nuclear glasses disposal: reference way

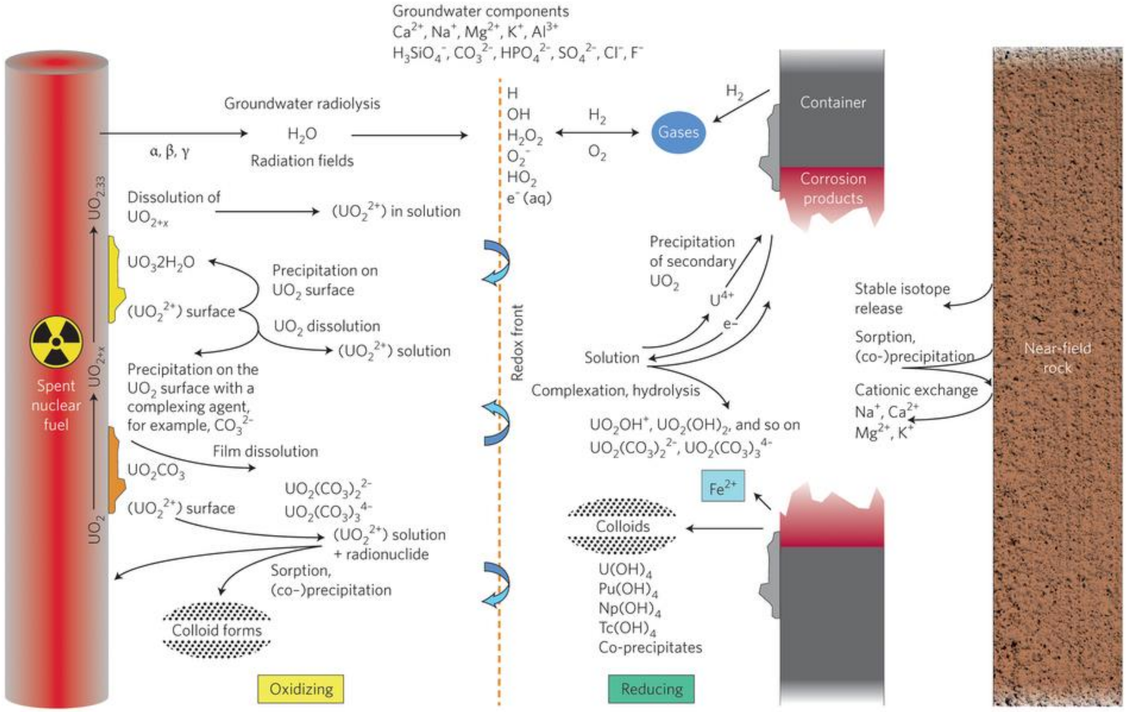
The mechanisms of alteration of UOx spent fuel



European Project SFS - 2005



•Rodney C. Ewing
Nature Materials
2015

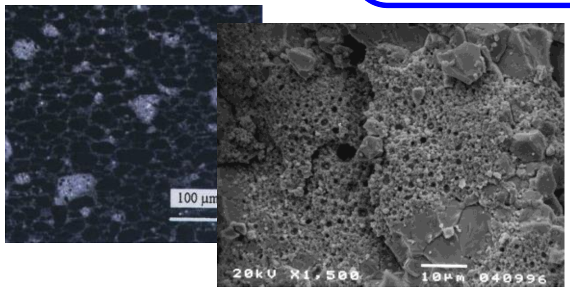


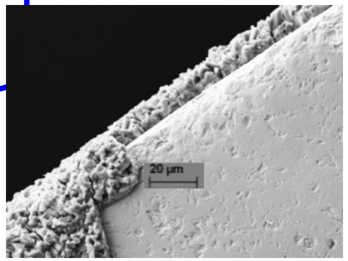
Can we really extend these mechanisms to the case of the selected Callovo-Oxfordian (COx) clay formation ?

Experiments

A step by step approach integrating the environmental constraints is implemented on UOX and MOX fuels (unirradiated and irradiated materials)

Carbonated water → COX water → COX water + iron and corrosion products / COX water + claystone → COX water + iron and corrosion products + claystone

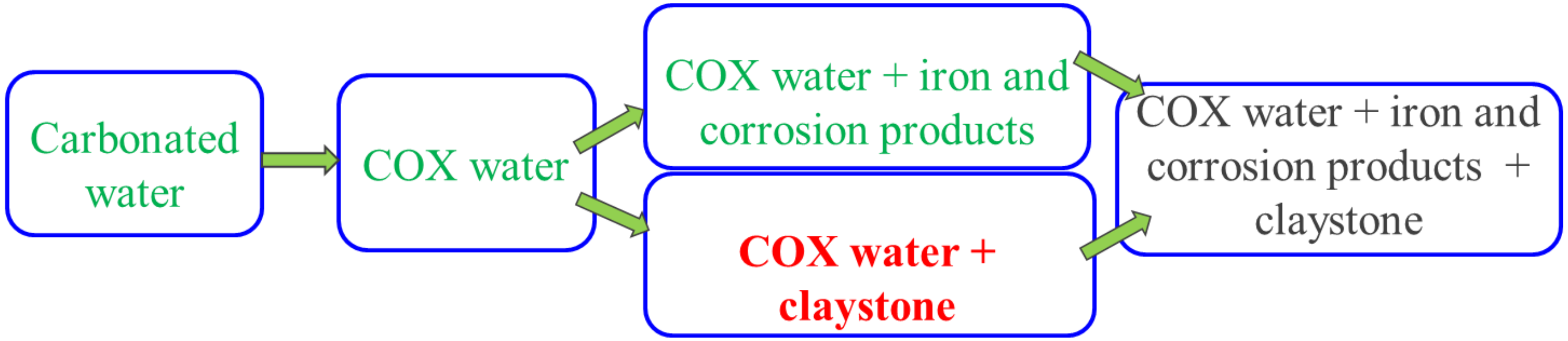


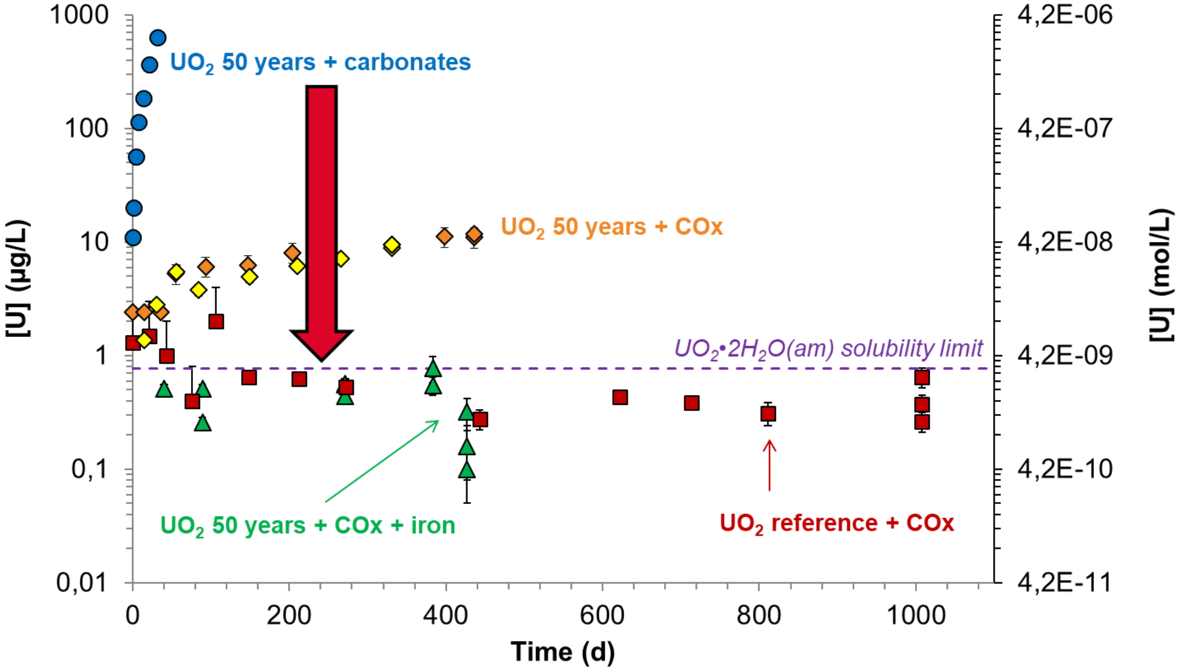


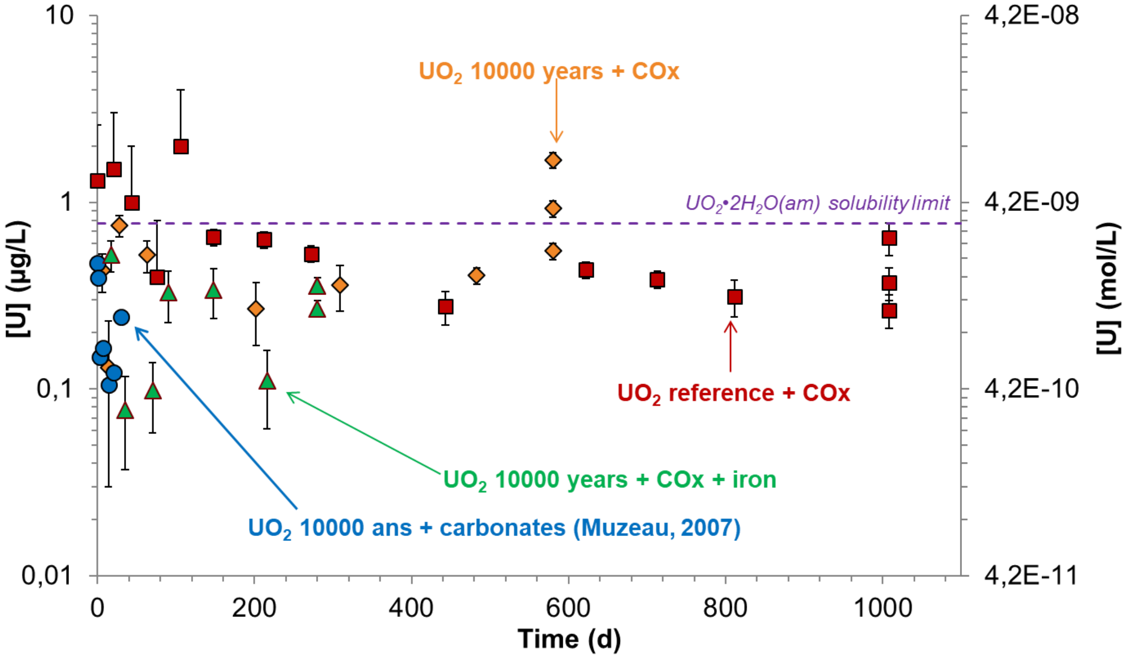
Modeling tool

- CHESS (geochemical) and HYTEC (reactive transport) codes
- EQ3/6 + NEA database, ThermoChimie database

The UOx Spent Fuel matrix alteration under geological disposal







Odorowski 2015

Outlines

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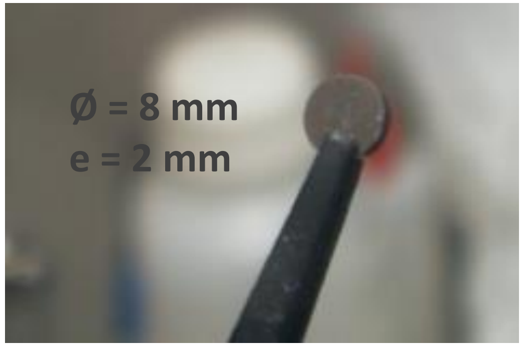

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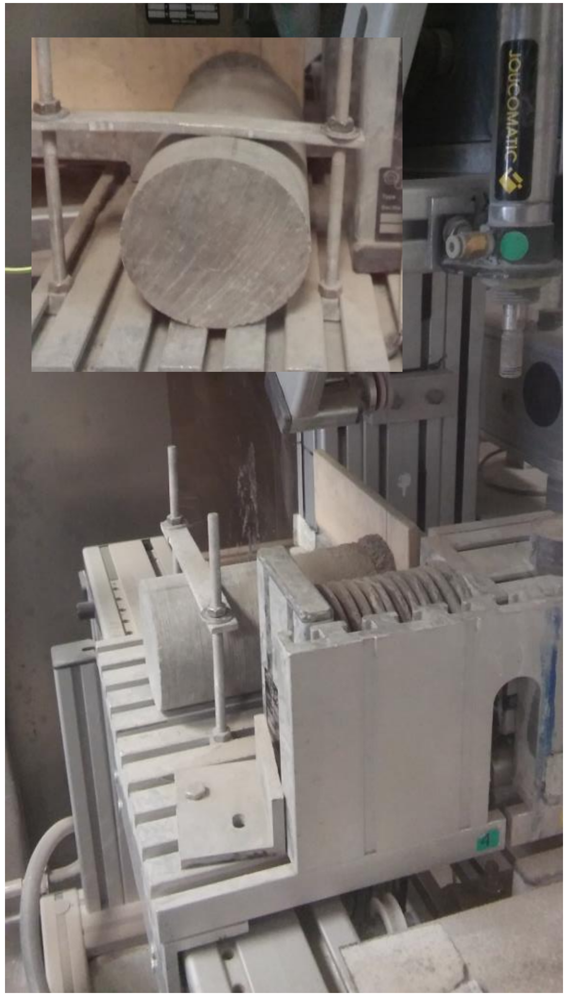
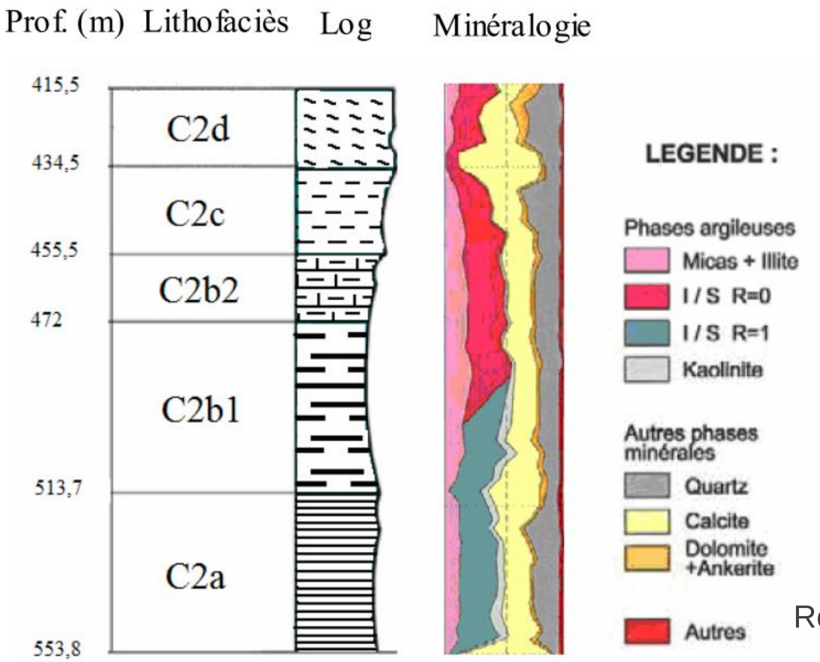


Solid claystone disc

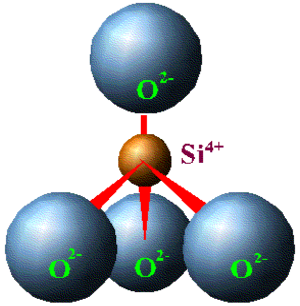
Mineralogy of the CLAYSTONE

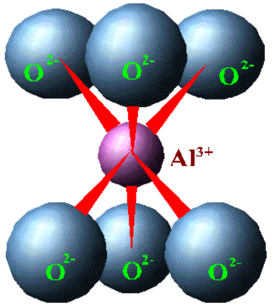
Samples	K100	K119	R_0	R_1
Borehole	EST205	EST205	EST322	EST212
Depth (m)	424.48 – 425.18	477.37 – 477.69	528.42 – 528.72	534.35 – 534.51
Mica, illite, I/S 90% illite, glauconite	2 – 11	5 – 20	14 – 20	17 – 21
Kaolinite	0	0 – 3	0	2 – 7
Chlorite	> 0 – 2	> 0 – 5	0 – 3	> 0.5
I/S r=0 (50% illite and 50% montmorillonite)	14 – 25	25 – 35	12 – 20	–
I/S r=1 (50% illite and 50% montmorillonite)	–	–	–	17 – 23
Quartz	25 – 35	25 – 35	24 – 28	25 – 29
K-Feldspar	> 0 – 2	> 0 – 4	0 – 3	0 – 3
Plagioclase	> 0 – 2	> 0 – 3	0 – 2	0
Calcite	17 – 25	15 – 22	33 – 41	23 – 28
Dolomite or ankerite	8 – 13	2 – 7	3 – 10	1 – 8
Pyrite	> 0 – 2	> 0 – 2	0 – 1	0 – 2
TiO_2	> 0 – 0.5	> 0 – 1	< 0.5	0 – 1
Calcium phosphate	> 0 – 0.5	> 0 – 0.5	< 0.5	< 0.5
Siderite	> 0 – 2	> 0 – 2	0 – 3	0 – 3

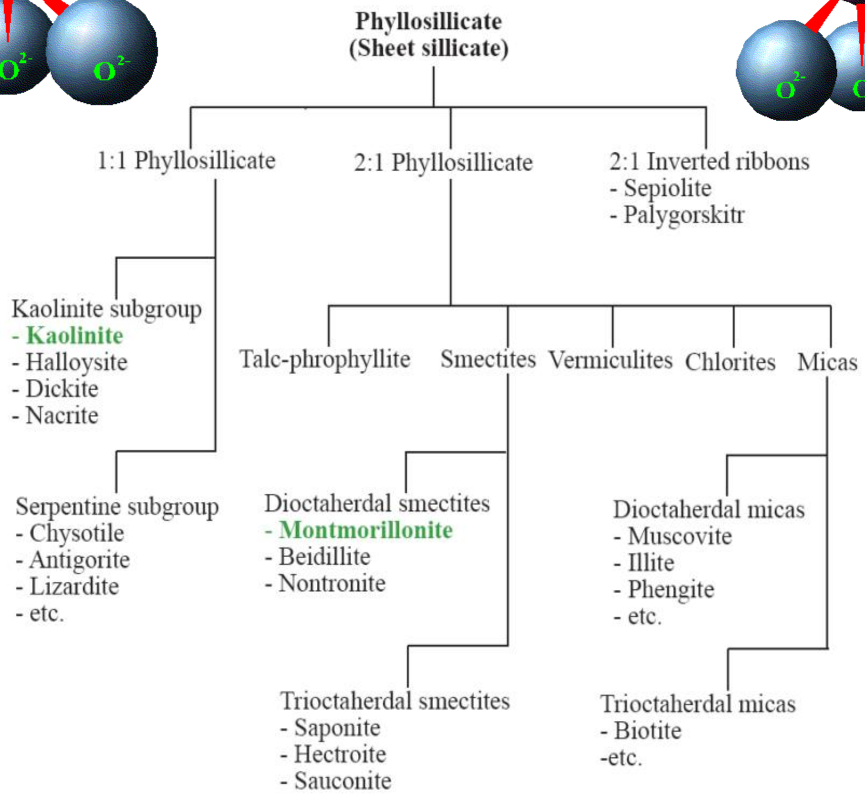
Gaucher et al., 2009, 2006, 2004



Robinet, 2008







Rieder et al., 1998

Synthetic COX water stability in the presence of the claystone and mechanical behavior of the disc

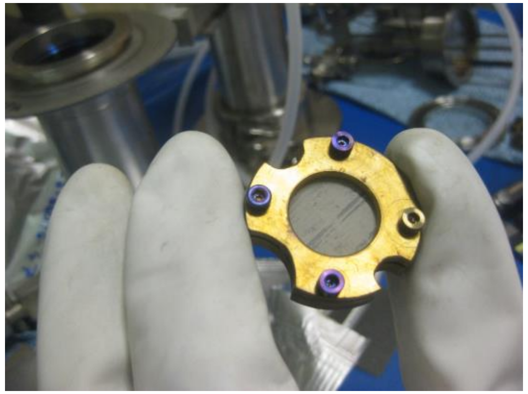
Synthetic COX water - Chemical composition (25°C)

pH = 7,2
3 bars Ar/3000 ppm CO_2

	$[Na^+]$	$[K^+]$	$[Ca^{2+}]$	$[Mg^{2+}]$	$[Sr^{2+}]$	$[Cl^-]$	$[SO_4^{2-}]$	$[HCO_3^-]$	[Si]
$mg.L^{-1}$	993	39,1	341	131	17,5	1454	1412	146	5,62
$mol.L^{-1}$	0,0432	0,0010	0,0085	0,0054	0,0002	0,0410	0,0147	0,0024	0,0002

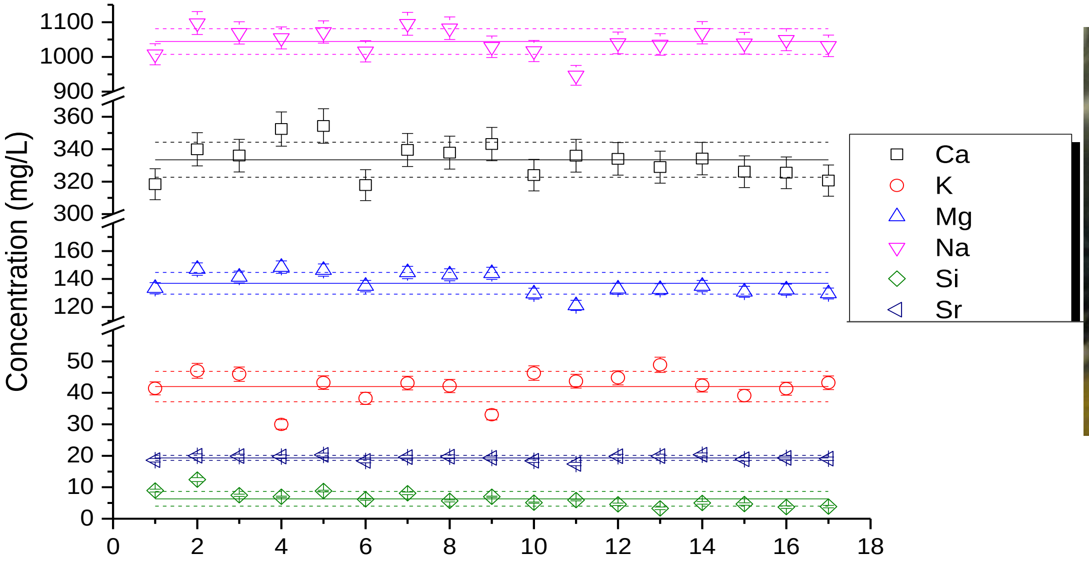
+

A solid claystone disc

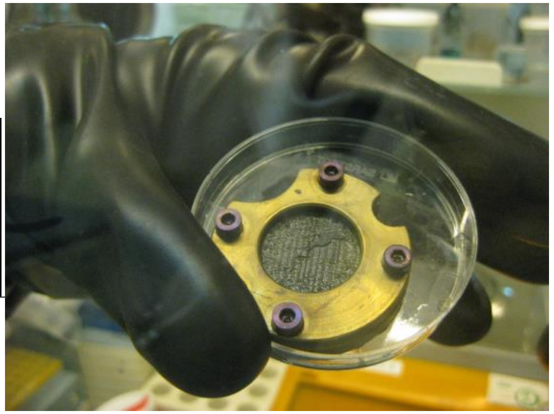


Initial disc

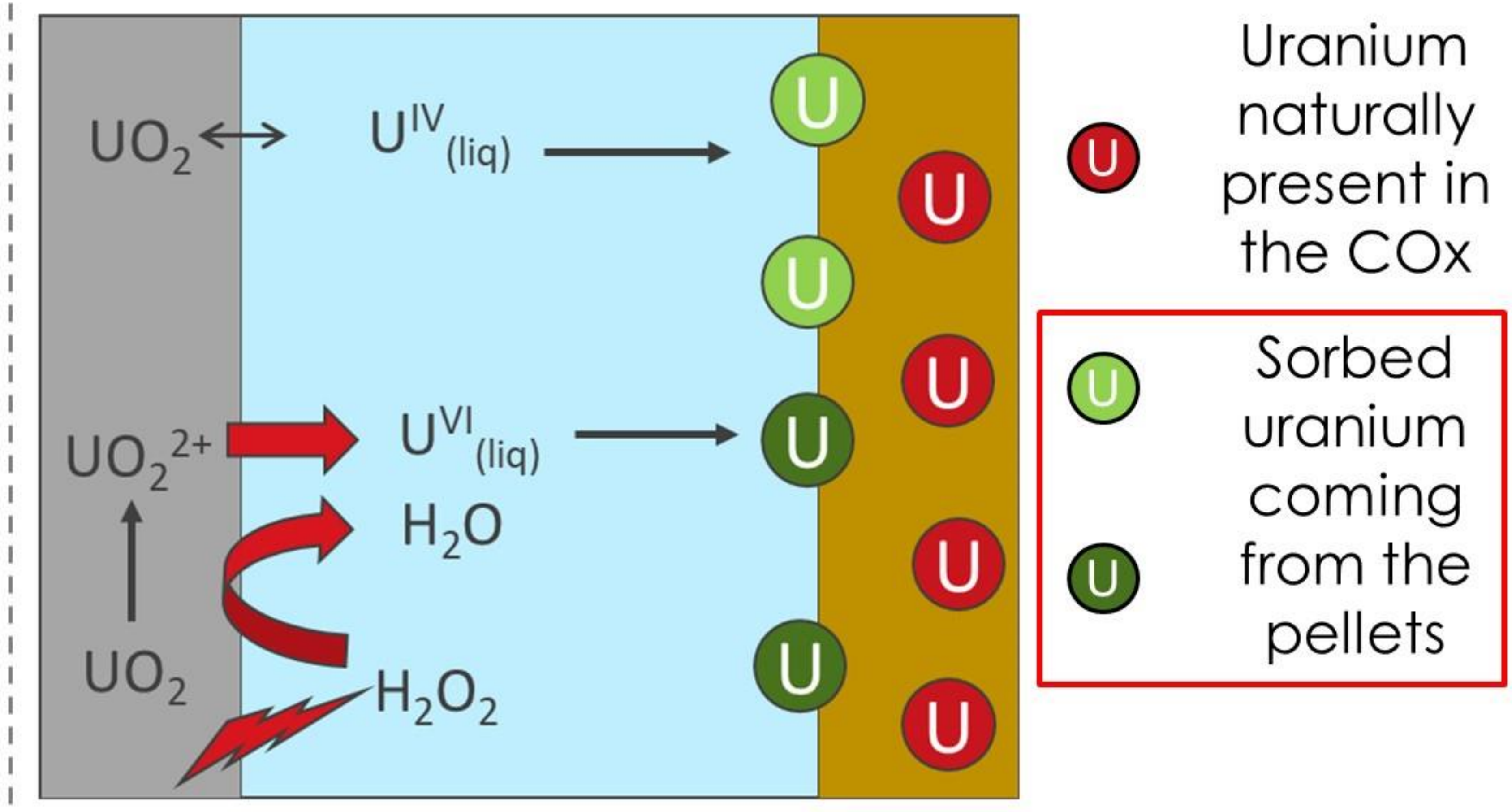
No evolution of water chemistry



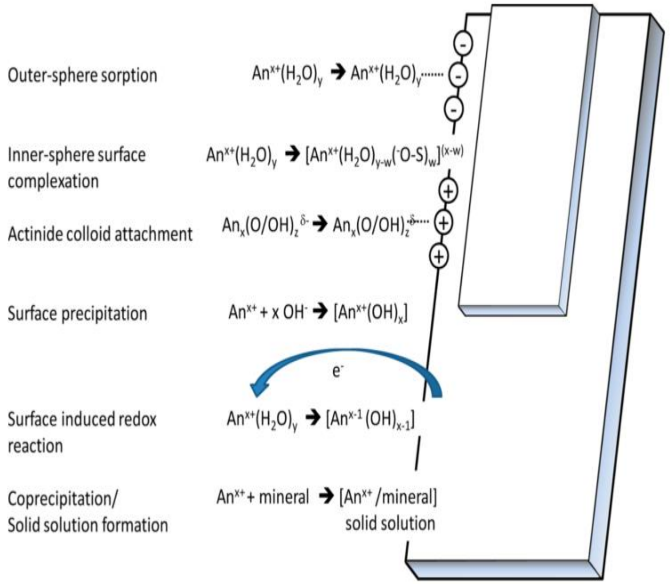
Samplings over few months



Hydrated disc
Good mechanical stability



$[U]_{solid}$ 2,25 ± 0,15 ppm
Average value



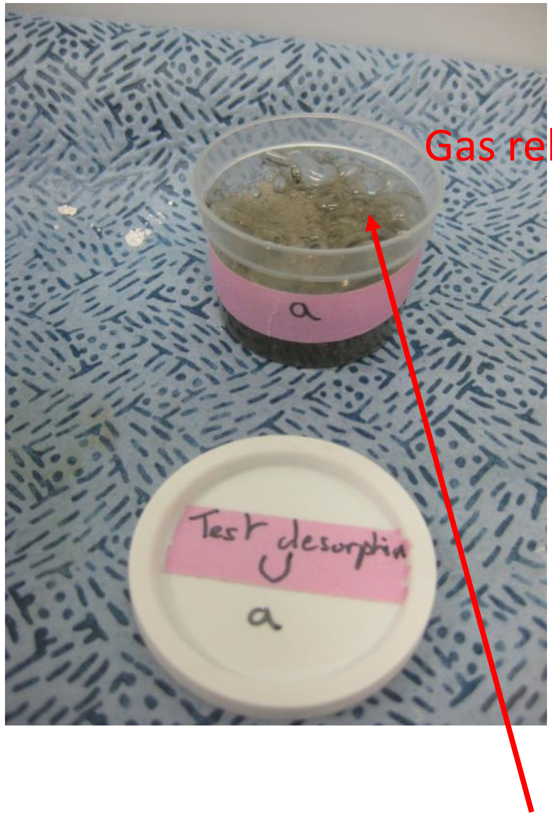
Geckeis et al., 2013

Kd ($L.Kg^{-1}$) ➔ According to different studies (Lab, In-situ) : 1 to 10 or 100 to 300
(F Maia 2018, Dagneli R 2014…)

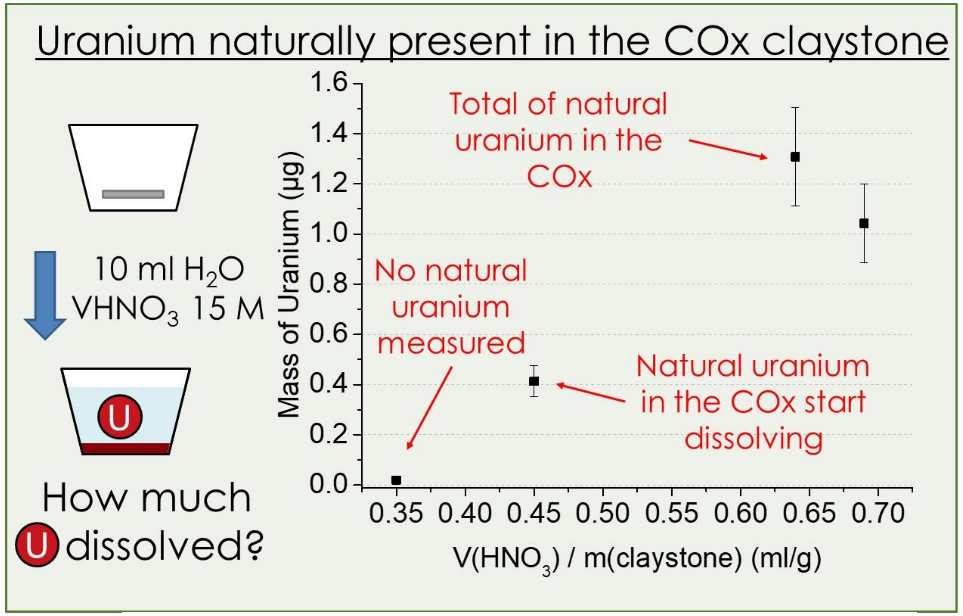
Natural Uranium located into the claystone discs

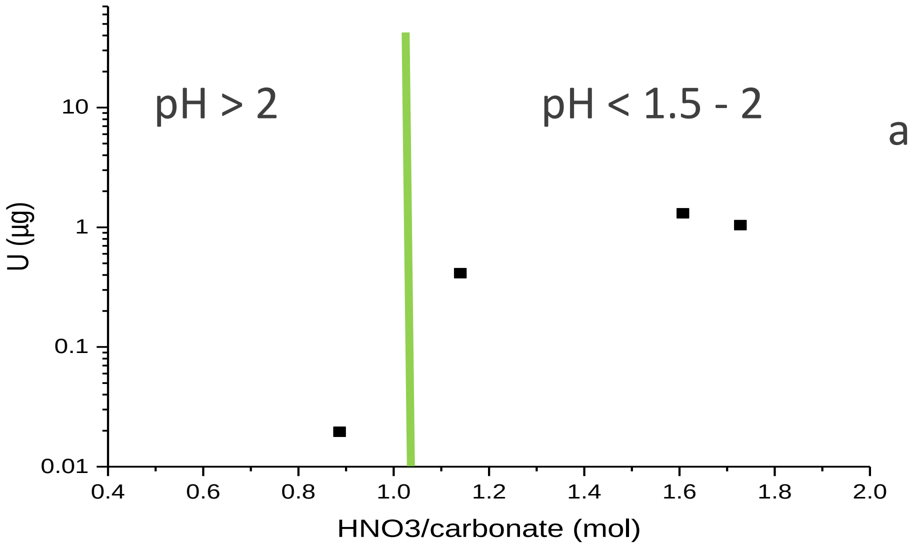
Dissolution of a claystone disc (~ 3 g) under acidic conditions

Dagnelie et al (2014) protocol



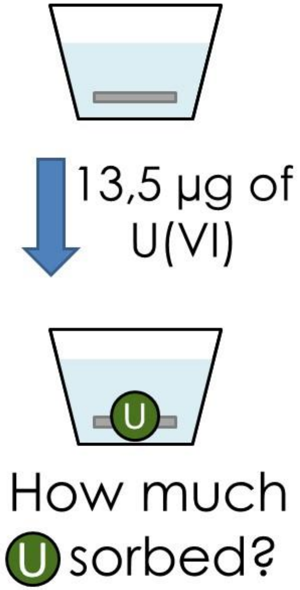
$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O$



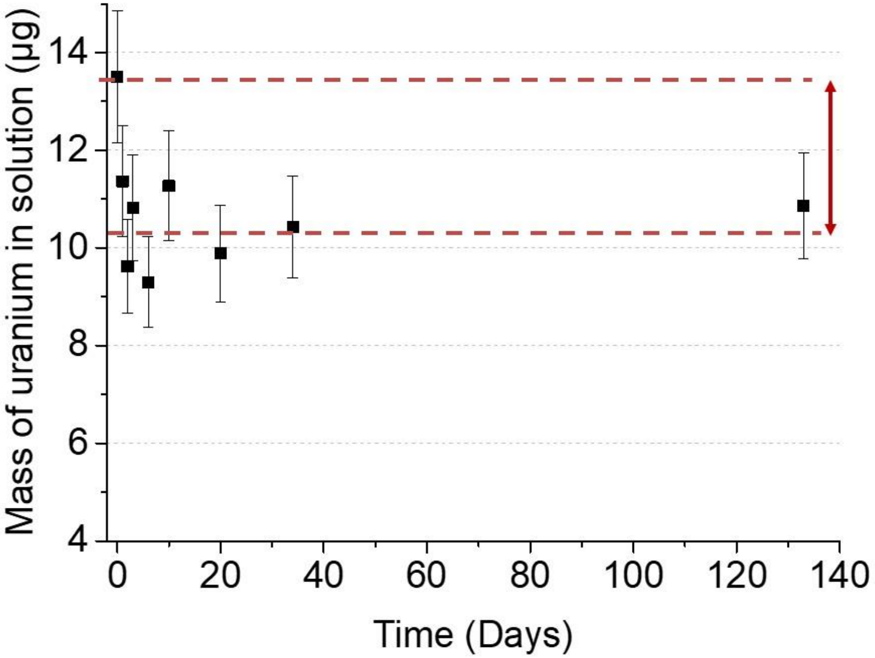


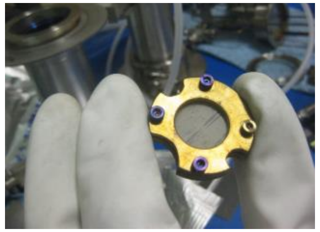
Expected values around 6-7 µg / disc

Recovery of uranium sorbed on claystone disc and coming from the UO_2 pellets



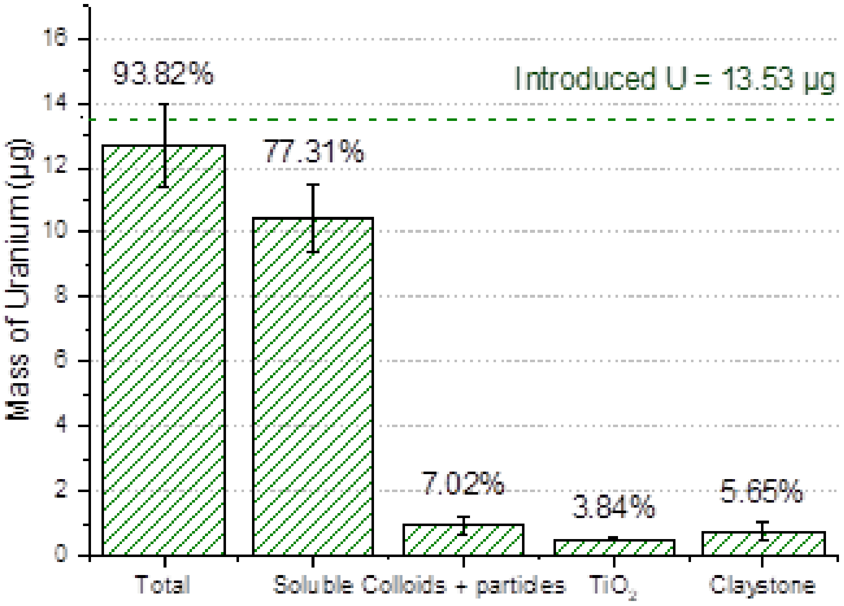
Uranium sorption





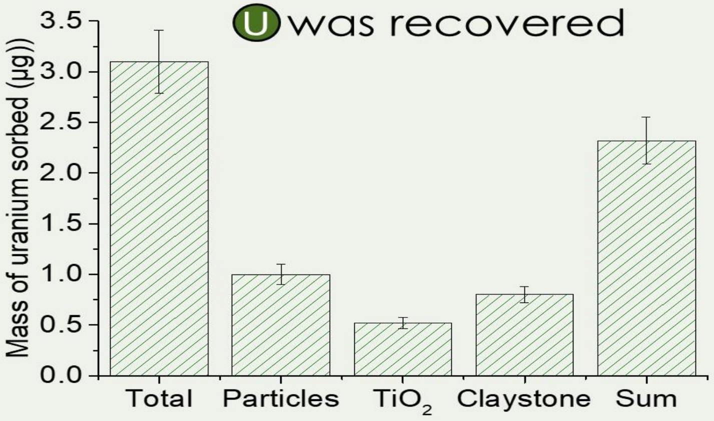
On particles and the disc

Kd = 2 to 4 $L.Kg^{-1}$

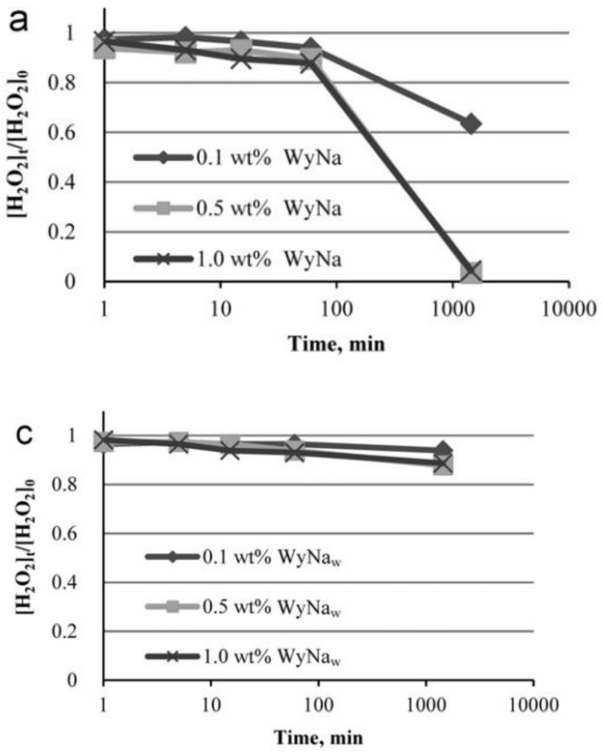


Uranium desorption

80% of the sorbed U was recovered

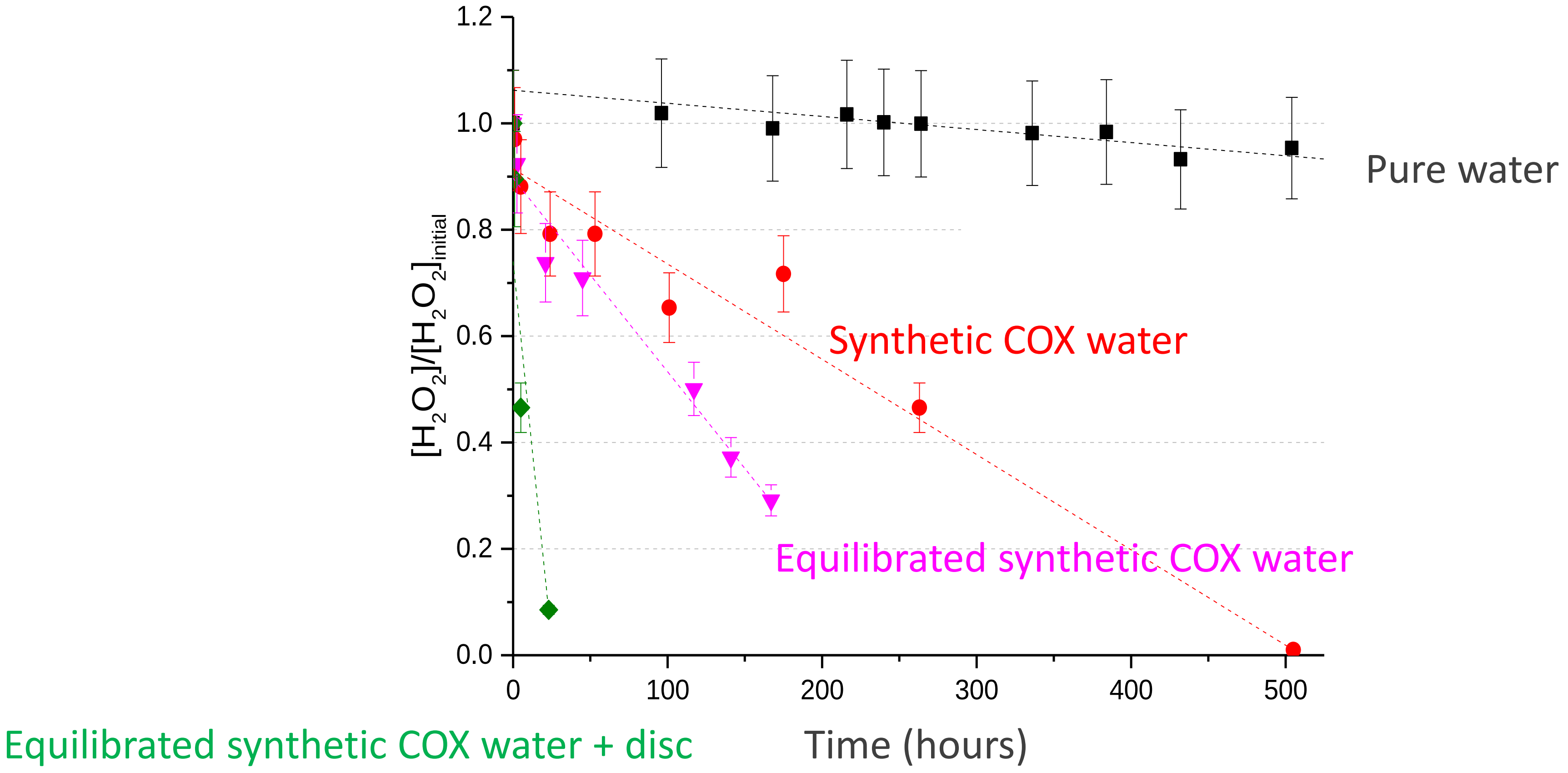


Hydrogen peroxide stability



Holmboe et al., 2011

The presence of clay rock and equilibrated water lead to an acceleration of the hydrogen peroxide consumption



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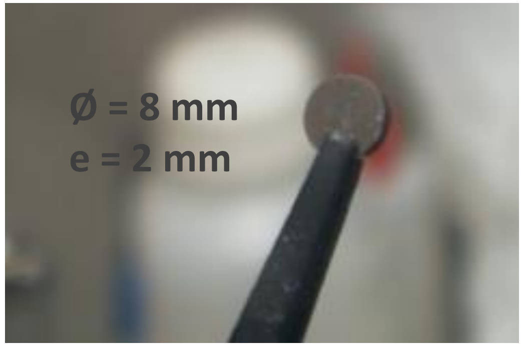

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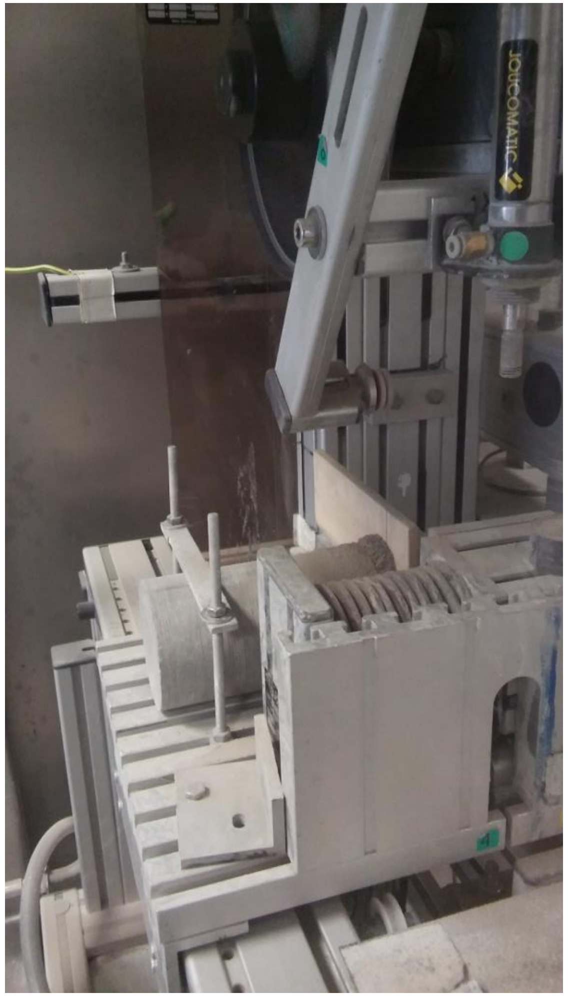
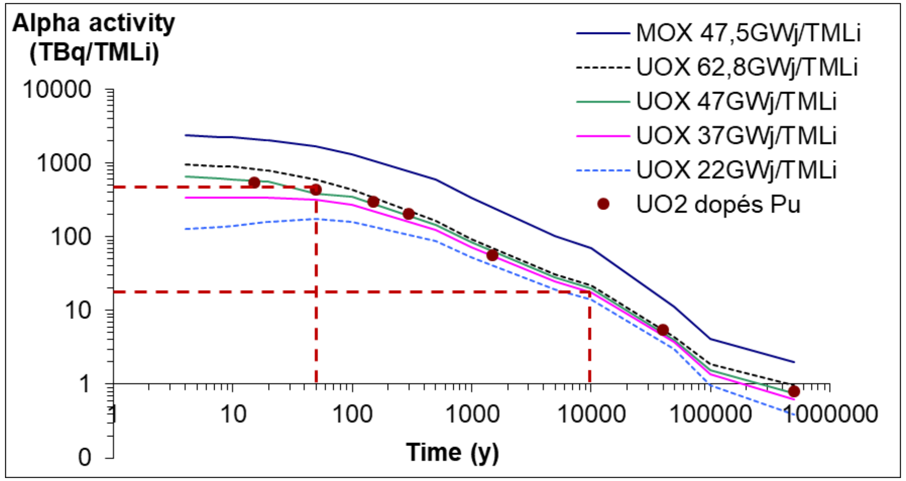
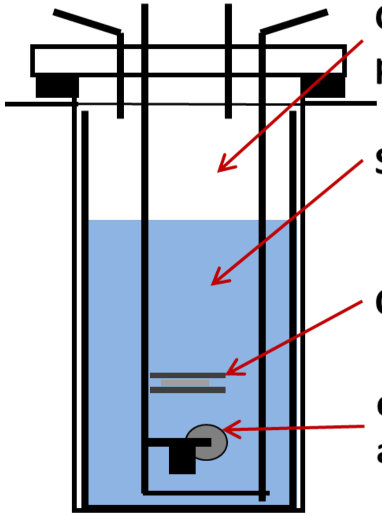


Solid claystone disc

Effect of CLAYSTONE on the dissolution of UO_2 doped with a radioactive alpha emitter



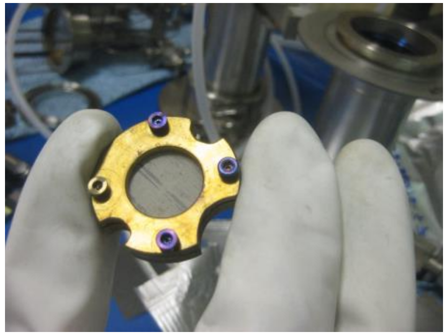


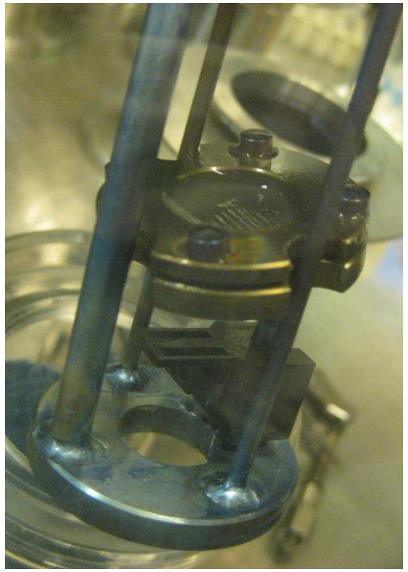
Gaseous phase Ar/CO_2 3000 ppm (P=3.5 bars)
↳ **Anoxic atmosphere**

Synthetic COx water
↳ **To simulate environmental water chemistry**

COx claystone pellet (in its support)
↳ **To simulate the claystone**

α-doped UO_2 pellets with different activity
↳ **To test there reactivity**





2 months ⟷ | 1 year ⟷

EQUILIBRATION CLAYSTONE / COX WATER → LEACHING → ACID RINSES OF THE REACTOR

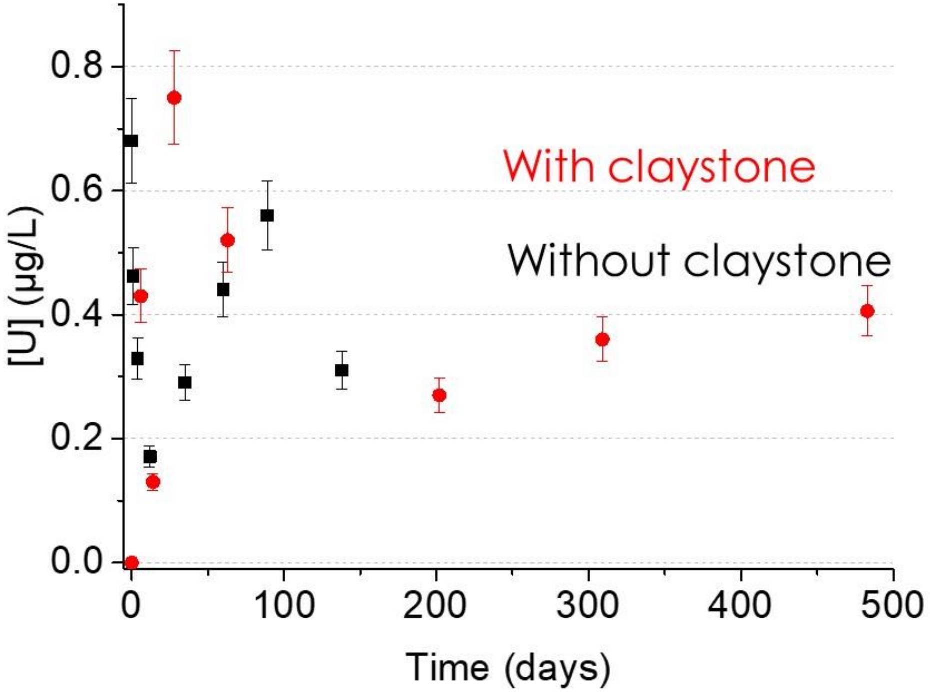
Equilibration claystone / COx water		Leaching		Acid rinses of the reactor
Solution analysis	Gas analysis	Solution analysis	Gas analysis	Solution analysis

Surface characterizations of the pellets

<u>Solution analysis :</u> pH, Eh, U, Pu, Clayey elements, Iron, H_2O_2
<u>Gas analysis :</u> O_2, H_2, N_2
<u>Surface characterizations :</u> SEM-EDS, µ-Raman

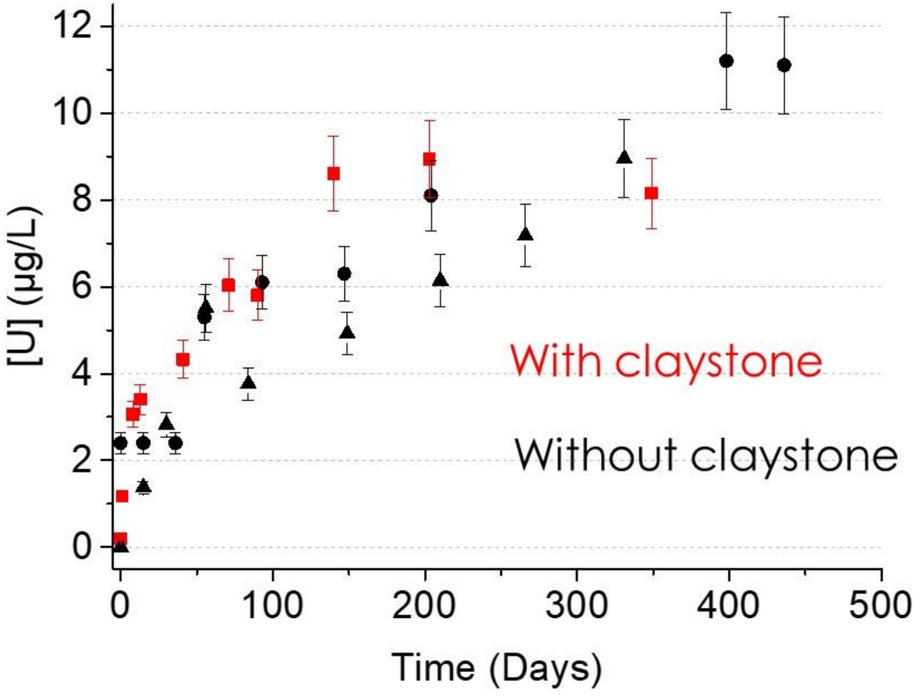
Uranium concentrations into the solution

Thermodynamic control by $UO_2x(H_2O)am$



10 000 years batch

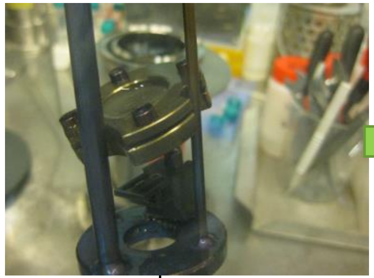
Oxidizing dissolution induced by α radiolysis

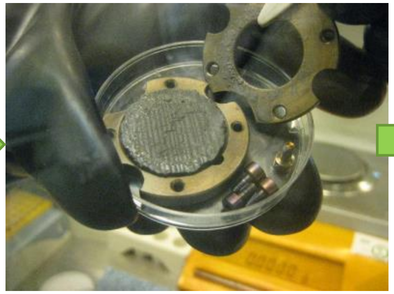


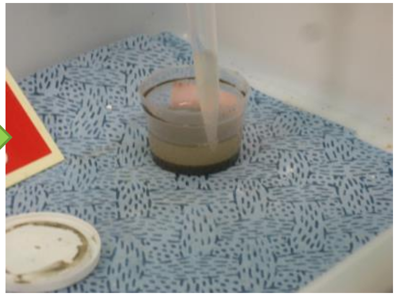
50 years batch

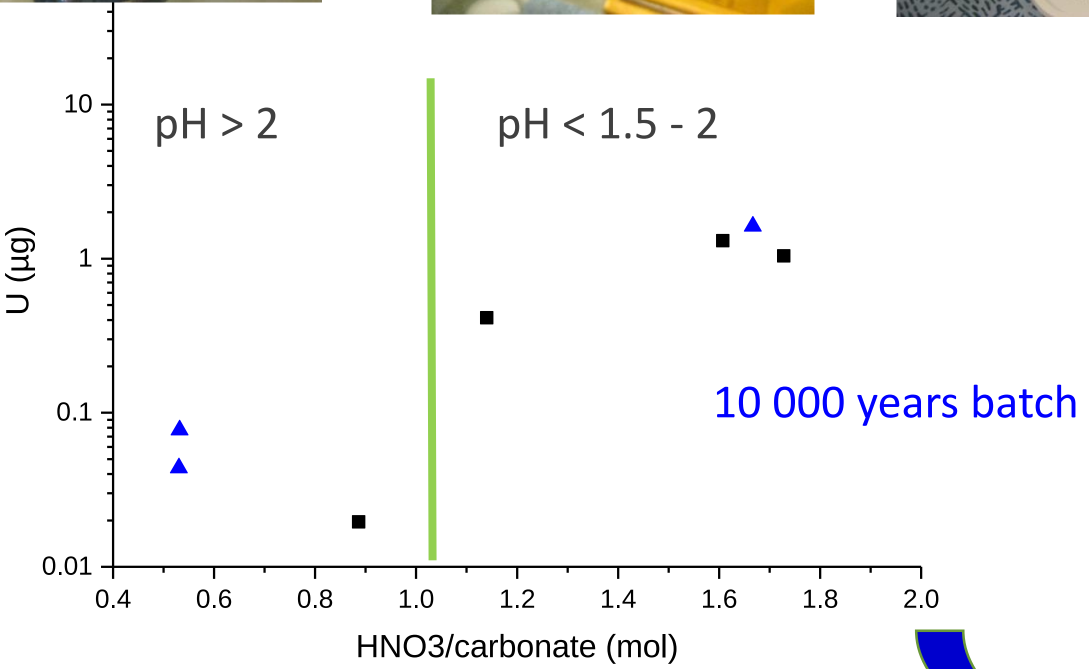
No significant effect of the COx claystone on uranium concentrations

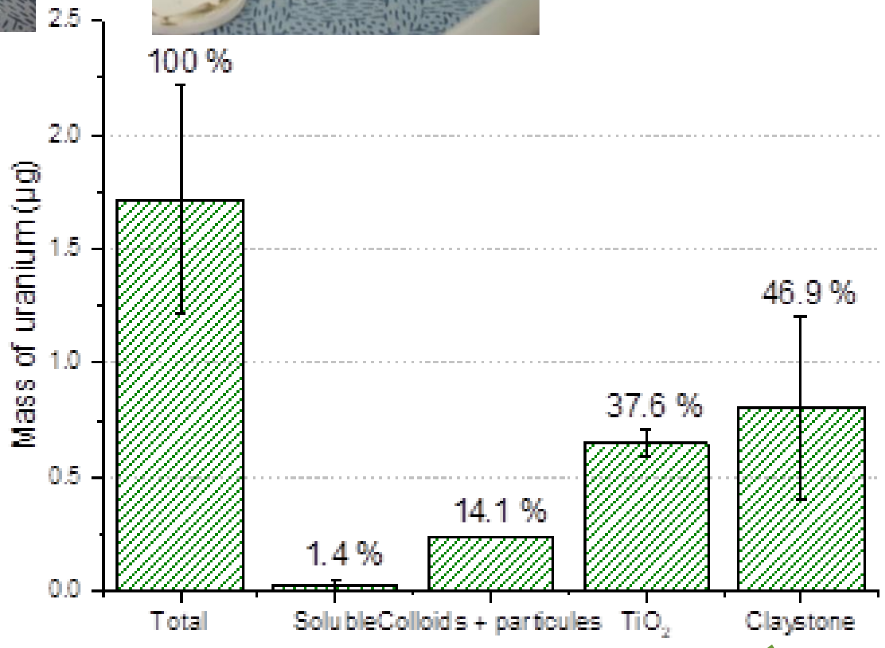
Uranium distribution between the solution and the solid phases – 10 000 years batch

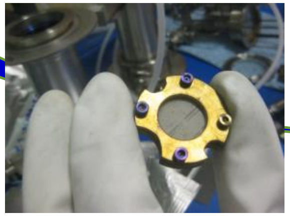






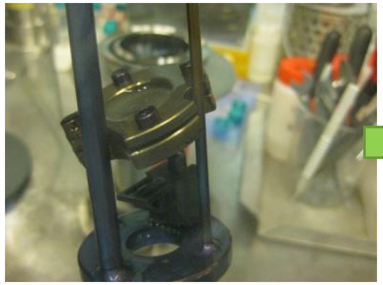


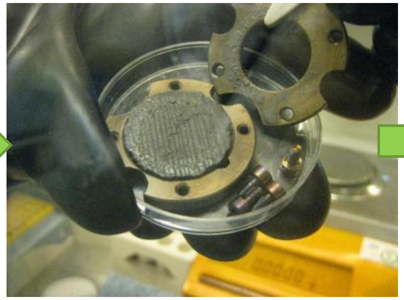


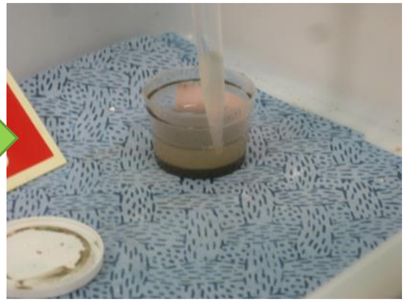


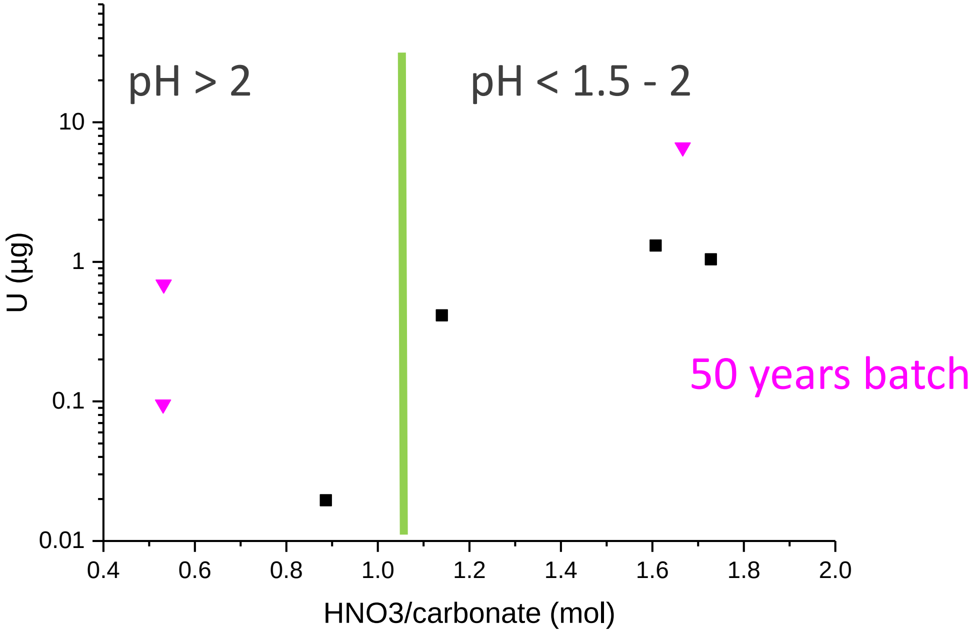
The amount of uranium sorbed does not exceed that naturally present in the clay rock

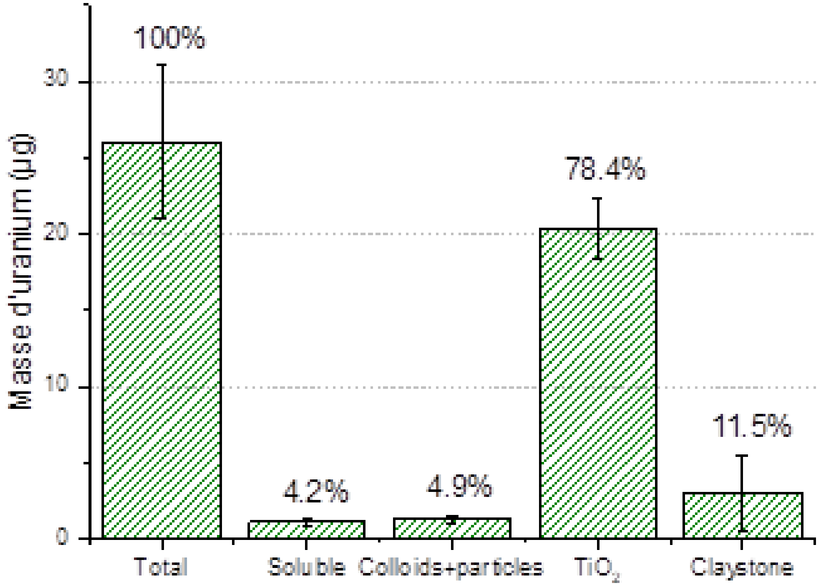
Uranium distribution between the solution and the solid phases – 50 years batch

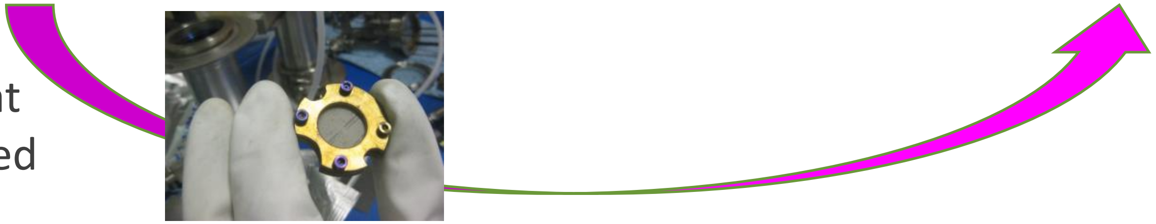






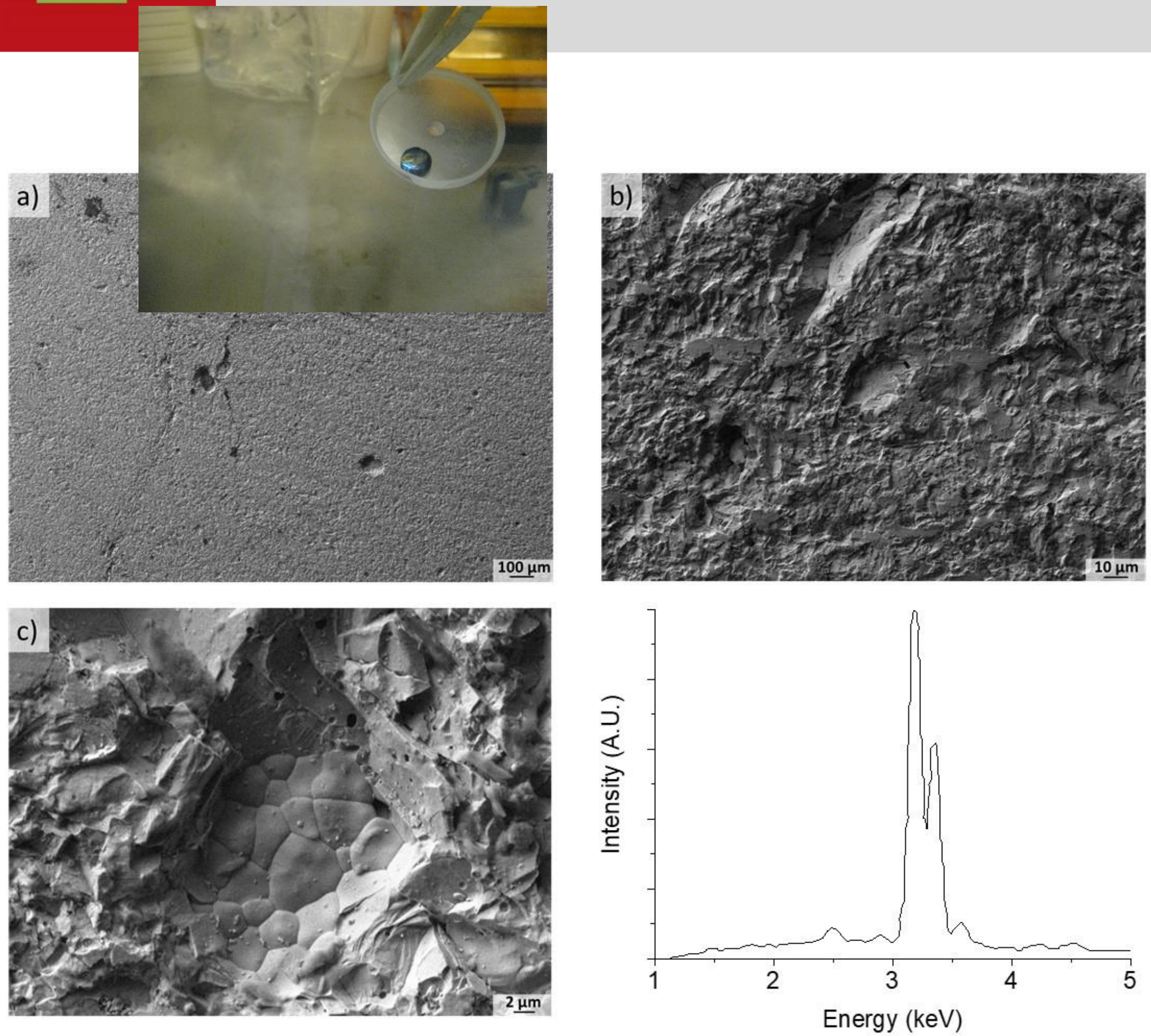




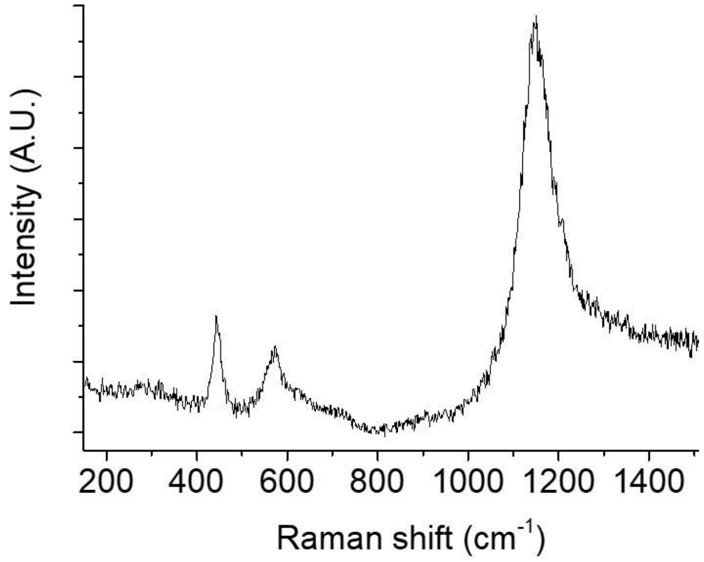


The amount of uranium sorbed exceeds that naturally present in the clay rock but is limited

Surface characterizations – 50 years batch



EDS analysis 80 spectrum	Mg	Al	Si	Ca	Ti	U
Average Wt %	0,18	0,64	0,05	0,05	1,49	97,57
Standard deviation	0,21	0,41	0,09	0,18	0,51	0,86
Max	0,68	2,02	0,42	1,41	2,93	99,35
Min	0	0	0	0	0,43	95,91



No evidence of significant corrosion or precipitated secondary phases

Conclusion and Outlooks

- **The presence of claystone does not seem to modify the concentrations of uranium in solution whatever the UO_2 batch studied (50 years or 10000 years batch).**

- **Specific experimental protocols have been developed to carry out uranium mass balances.**

- **The quantities of uranium sorbed are of the same order of magnitude as those naturally contained in the rock for these experimental conditions.**

- **In general, the presence of the rock does not induce a significantly greater alteration of the UO_2 matrix.**

- **Isotopic uranium analyzes should allow in the future to specify the quantities sorbed on the clay coming from the UO_2 matrix.**

	pH	pe	Eh (mV)	PCO_2	Concentrations (mmol/L)											
					Al	Fe	Si	Sr	K	Mg	Ca	Na	Cl	S(6)	TIC	S(-2)
EST25687	7,1	-2,85	-168	-2,0	$4{,}7.10^{-6}$	0,034	0,18	0,20	1,03	6,67	7,36	45,6	41,0	15,6	3,34	$2{,}6.10^{-7}$
EST21400H	7,2	-2,90	-171	-2,0	$4{,}4.10^{-6}$	0,029	0,18	0,18	1,52	5,80	6,28	36,2	29,0	15,1	3,33	$2{,}7.10^{-7}$