Pu-loaded glasses and crystals: evolution due to self-irradiation

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V.O. Yapaskurt and many other

Immobilisation of actinides

- High-purity Pu (weapons-grade, i.e. mostly ^{239}Pu with low amounts of $^{238, 240}$Pu) can be used in new generation of power plants in MOX (mixed oxide) fuel.
- Lower quality Pu, "scrap" etc. is <u>not</u> suitable economically for MOX => must be safely immobilised (in US ~20 metric tons…+ Russia, UK, France, China…).

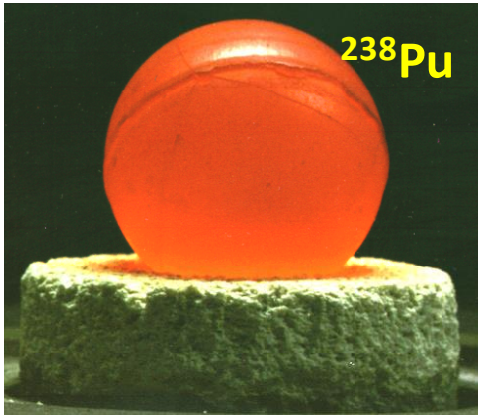
Composition of waste for immobilisation heavily depends on initial fuel chemical and isotopic composition, cladding type, burn-up degree.

<u>No universal form (matrix) for all waste types can be made!!</u>

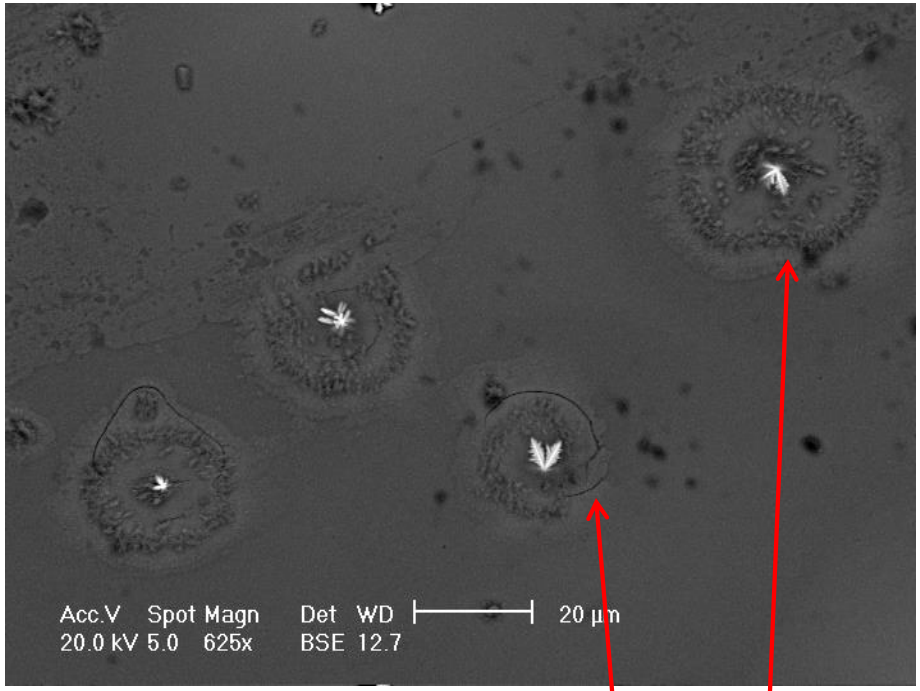
Waste separation for subsequent separate immobilisation is extremely important.

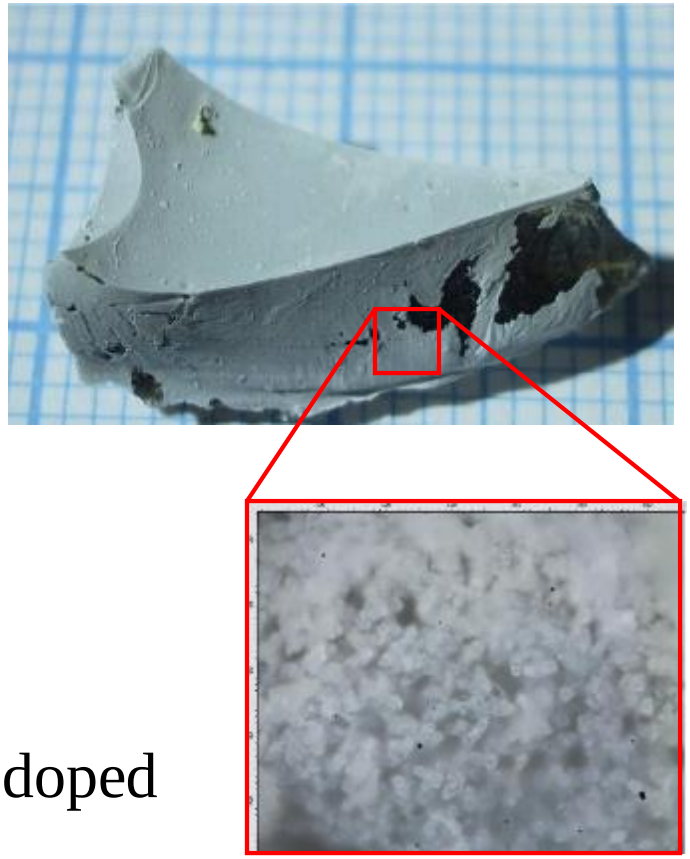
Amount of a radionuclide which does NOT require special permission to handle (Soviet Radiation safety rules from 1987)

Isotope	Activity (microCi/(microgram))
230Th	0.1/(5)
232Th	100/(900 **grams)**
233U	1/(100)
235U	1/(50000)
238U	100/(300 **grams)**
237Np	0.1/(140)
238Pu	**0.1/(0.006)**
239Pu	**0.1/(0.03)**
244Cm	0.1/(0.001)



Pu-doped glasses





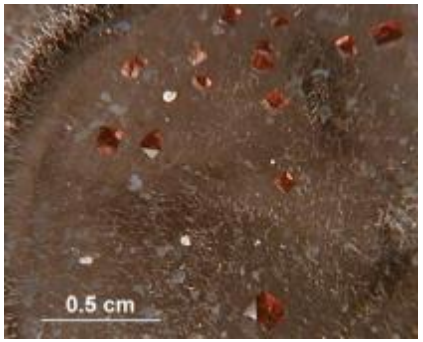
Two "complementary" mechanisms of An-doped waste forms degradation:

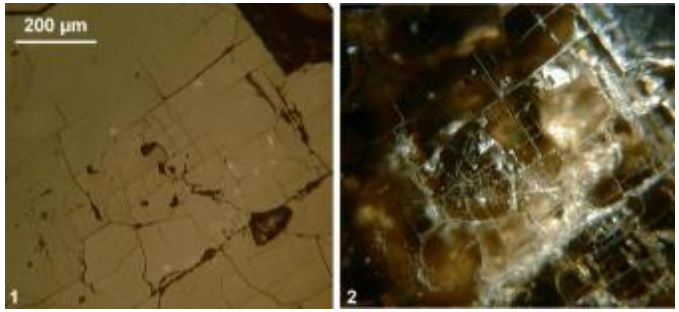
1) Thermomechanical stresses
2) Radiation damage (swelling, amorphisation/disordering….)

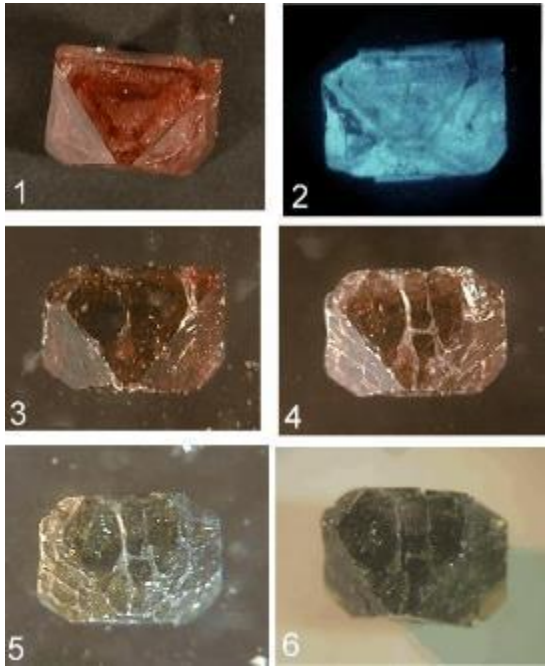
Pu-doped single crystals

Zircon doped with 2.4 wt% ^{238}Pu ($T_{1/2}$=87.7 y), grown in July 2001.

~$7x10^{17}$ decays/gram.





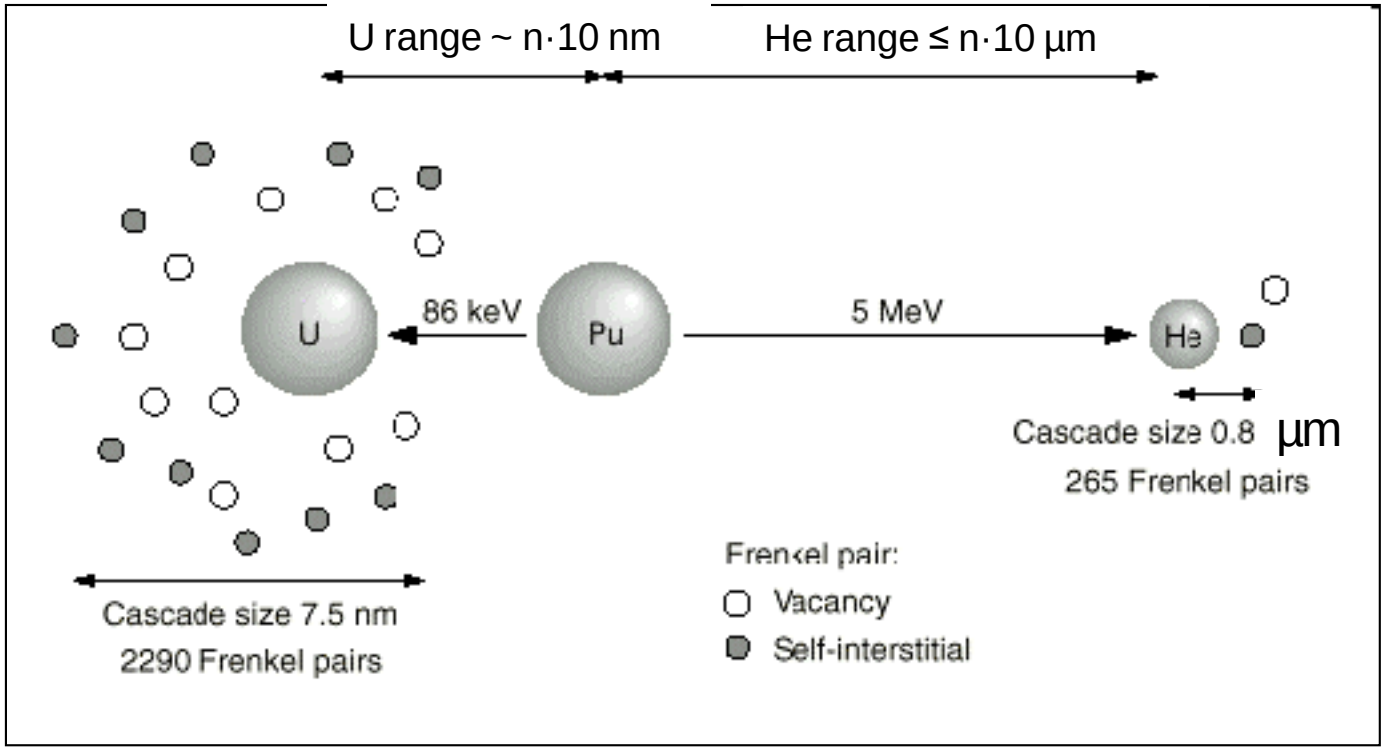


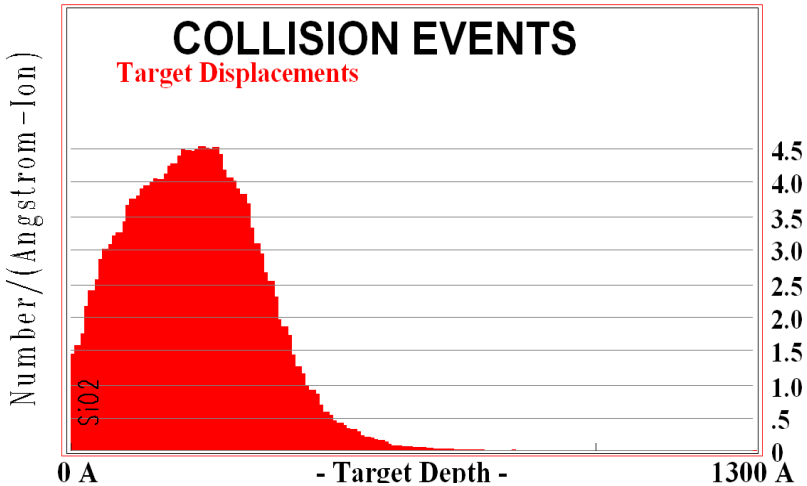
$(Eu,Pu)PO_4$ monazite doped with 4.9 wt% ^{238}Pu, grown in Dec. 2003. Now approx. ~$2x10^{19}$ decays/gram.

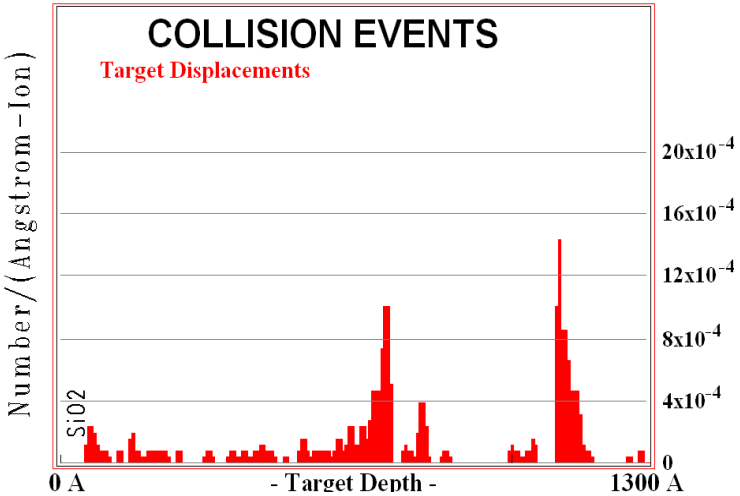
At ~$1.1x10^{18}$ decays/gram dispersed particles has appeared; at ~$5.2x10^{18}$ decays/gram "peeling" has started.

Images: B.E. Burakov

Pu decay


U range ~ n·10 nm
He range ≤ n·10 µm
U
86 keV
Pu
5 MeV
He
Cascade size 0.8 µm
265 Frenkel pairs
Cascade size 7.5 nm
2290 Frenkel pairs
Frenkel pair:
Vacancy
Self-interstitial


COLLISION EVENTS
Target Displacements
Number/(Angstrom-Ion)
SiO2
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0
0 A
- Target Depth -
1300 A


COLLISION EVENTS
Target Displacements
Number/(Angstrom-Ion)
SiO2
20x10-4
16x10-4
12x10-4
8x10-4
4x10-4
0
0 A
- Target Depth -
1300 A

Pu-loaded glasses

(Lanthanide borosilicate – LaBS
and
borosilicate SON68-like)

Lanthanide-Borosilicate glass

- Maximum PuO_2 concentration in conventional borosilicate glasses is ~3-4 wt.%. Lanthanide-Borosilicate (LaBS) glasses are potentially capable to dissolve up to ~10 wt.% PuO_2. They are much more durable in water solutions than conventional borosilicate glass (Strachan et al., 1998).
- ***Behaviour of Pu and of some other constituents in LaBS glasses is still poorly constrained.***

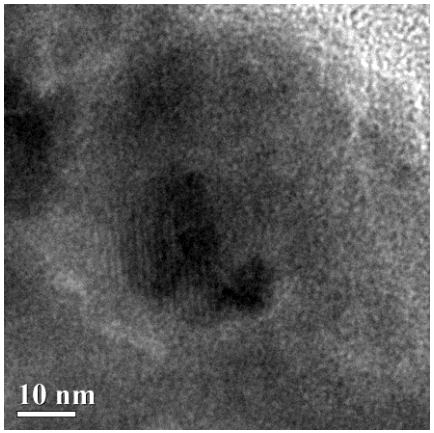
Glass preparation

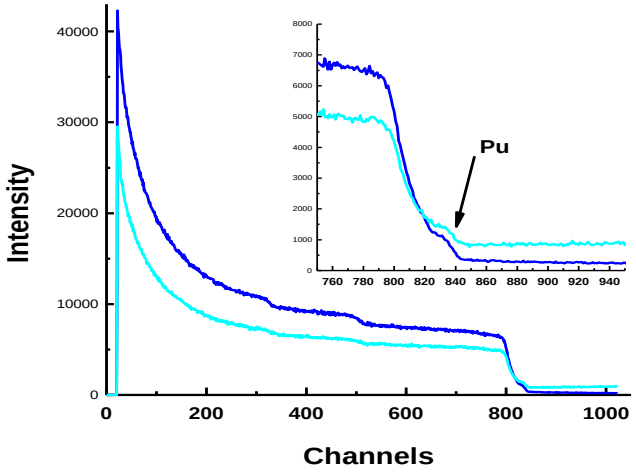
- PuO_2 powder mixed with chemicals, heated to 1500 °C at a rate of 10 °C/min, kept for 30 min and quenched.
- In contrast to Pu-free glasses of the same composition (Pu→Hf) it is very difficult to obtain homogeneous glass if high PuO_2 loads are used. In some runs the sample is clearly segregated into crystal-like and glassy parts.

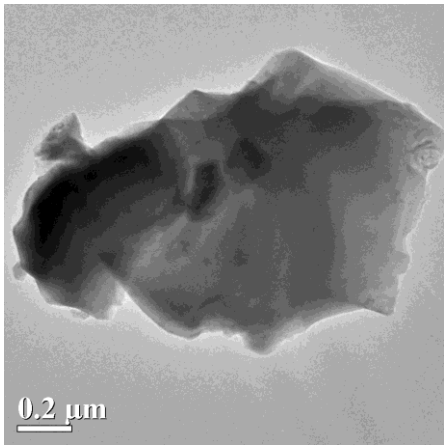
Range of target chemical compositions (wt%)

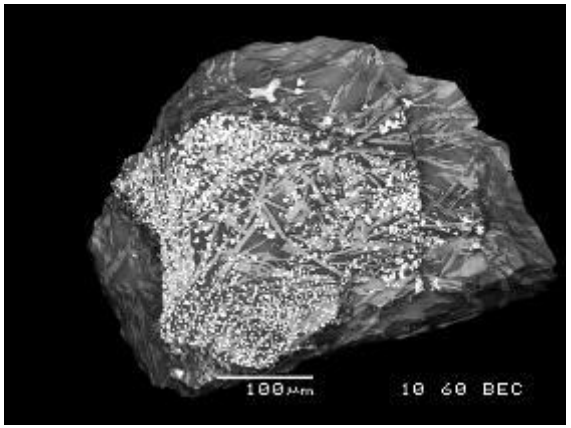
Al_2O_3	B_2O_3	Gd_2O_3	HfO_2	La_2O_3	Nd_2O_3	PuO_2	SiO_2	SrO
8-20	10-22	8-12	4-14	11-18	11-14	0-9.5	18-28	2.5

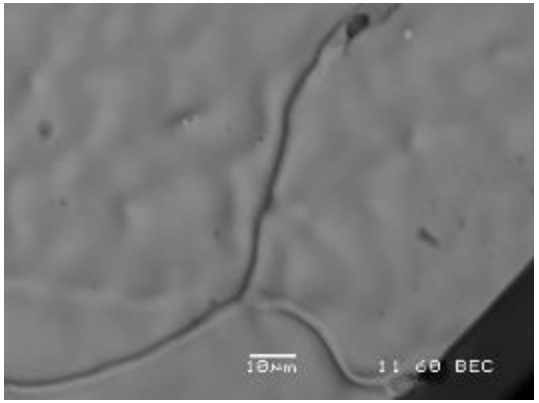
The LaBS glass seems to be homogeneous on mm-scale (RBS data), but is **markedly** heterogeneous on sub-mm scale if high PuO_2 loads (>5 mass%) are used.

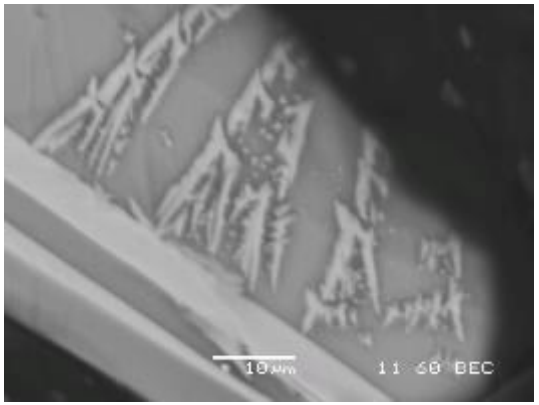






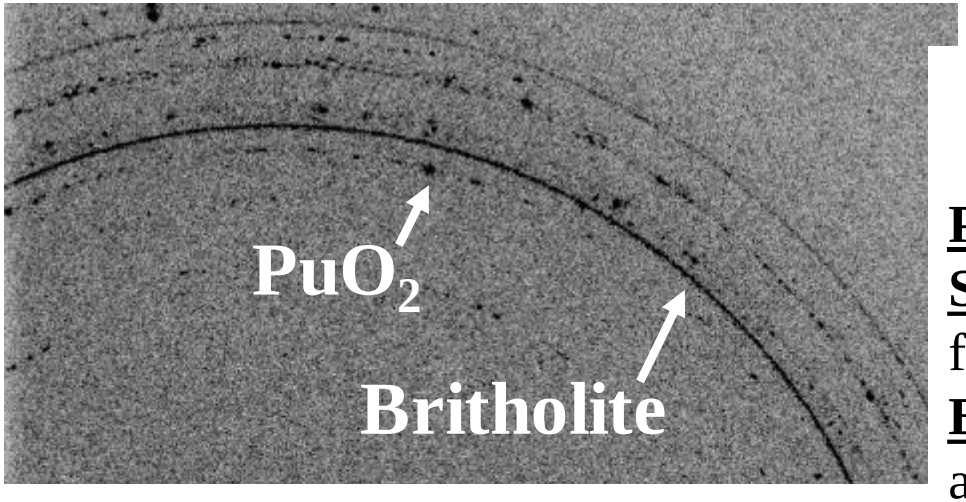






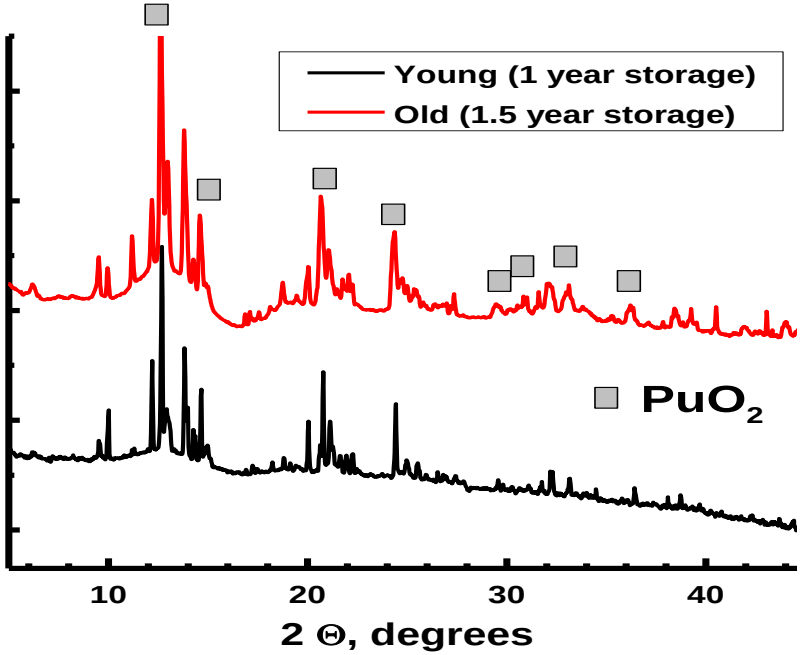
Phase composition of the LaBS glass

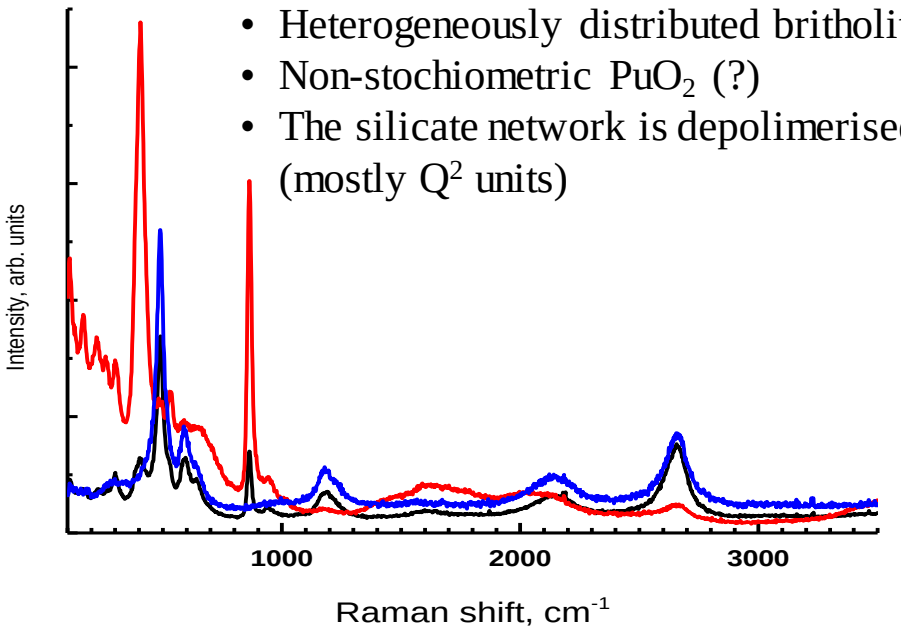
(9.5 wt% PuO_2)



Identified phases (XRD+SEM/EDX)

<u>PuO_2:</u> crystallites with sizes of >50 nm.
<u>Solid solution of $(Pu,Hf)O_2$</u> with a fluorite structure (SEM/EDX/XRD)
<u>Britholite:</u> (approx. $REE_{10}Si_6O_{24}(OH)_2$) is a "real" powder.

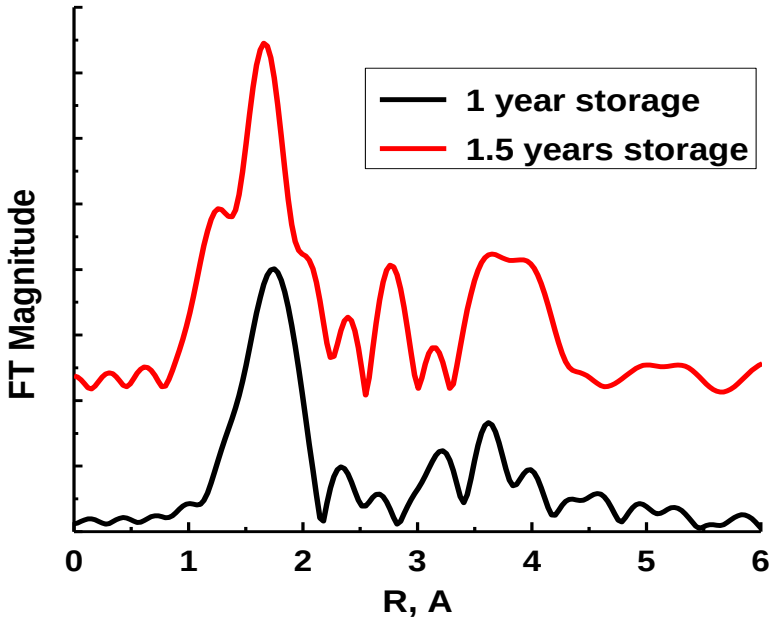




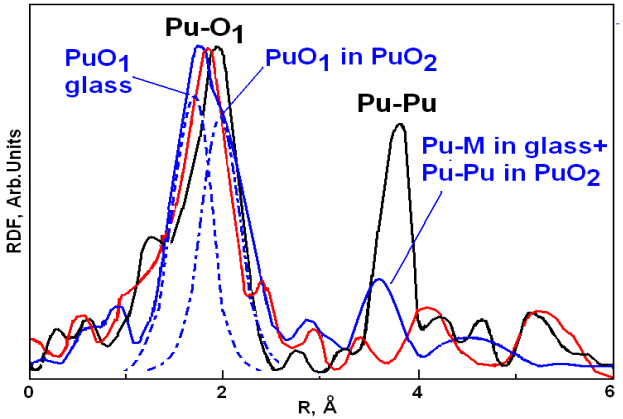
- Heterogeneously distributed britholite
- Non-stochiometric PuO_2 (?)
- The silicate network is depolimerised (mostly Q^2 units)

XAS results: Pu L_{III}-edge

- Pu is mainly tetravalent (XANES and XPS)
- First shell shows similarity to PuO_{2+x} ($PuO_{2.2}$?)
- The main fraction of Pu is in the vitreous phase.
- With increasing storage time the splitting of the first sphere becomes more pronounced. In the fresh glass it comprises two subspheres, whereas for the 2 y.o. glass – three (similar to *Conradson et al., JACS, 126, 13443, 2004*).



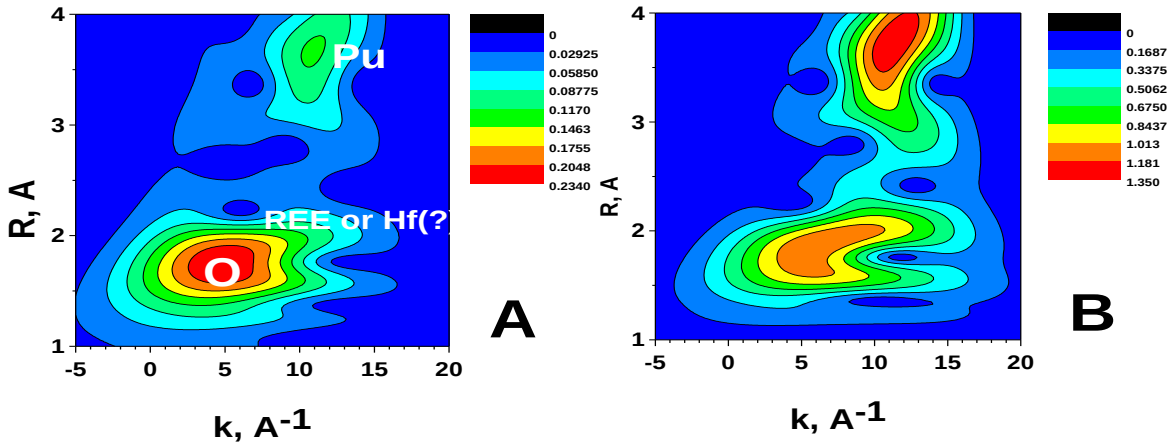
Sample	Atom	Distance, A	Occupation
2 y.o. glass	O	1.87-1.92	0.15-0.47
	O	2.09-2.12	~1.2
	O	2.20-2.27	4±1
	Pu	3.74	2±0.5
Fresh glass	O	2.13	1.3
	O	2.25-2.28	5
	Pu	3.66-3.69	2.5±0.5



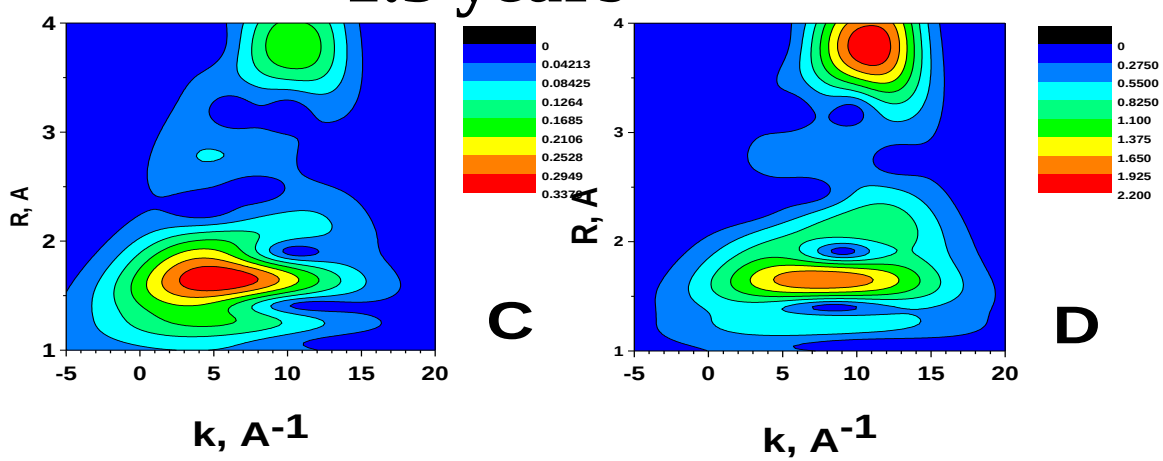
FT peak of the first coordination shell is asymmetric – superposition of contributions from various phases.

Evolution of Pu environment with glass storage time: Wavelet approach

1 year



1.5 years

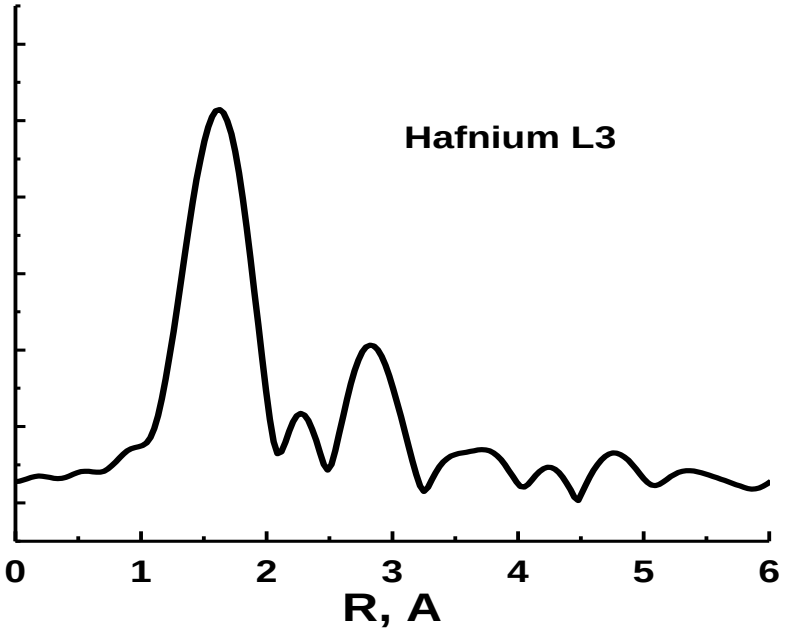


k^2-weighting **k^3-weighting**

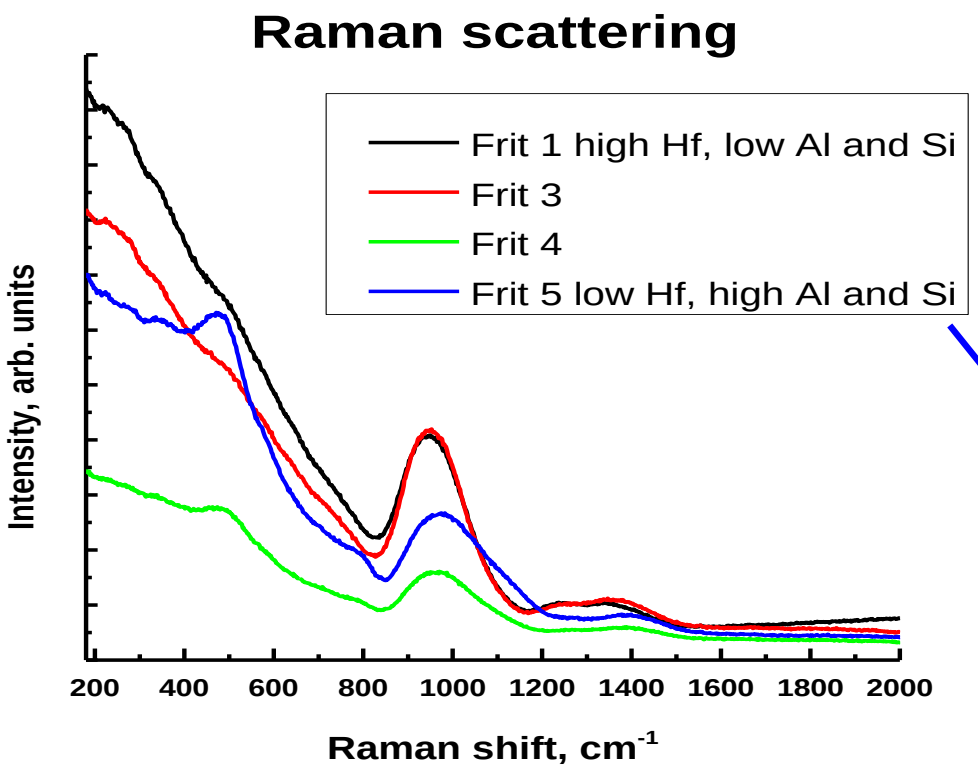
- Sharpening of the maxima in R-space indicates better separation of contributions from glassy and crystalline phases.
- PuO_2 and britholite grains are precipitated, the grain size and crystallographic perfection increases.

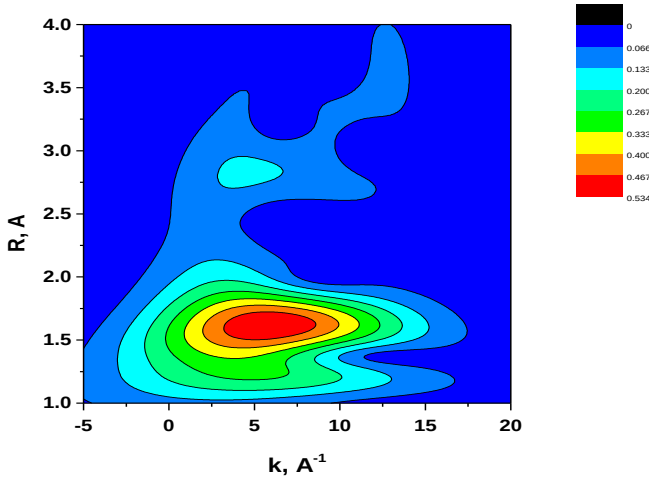
XAS results II: Hf L_{III}-edge

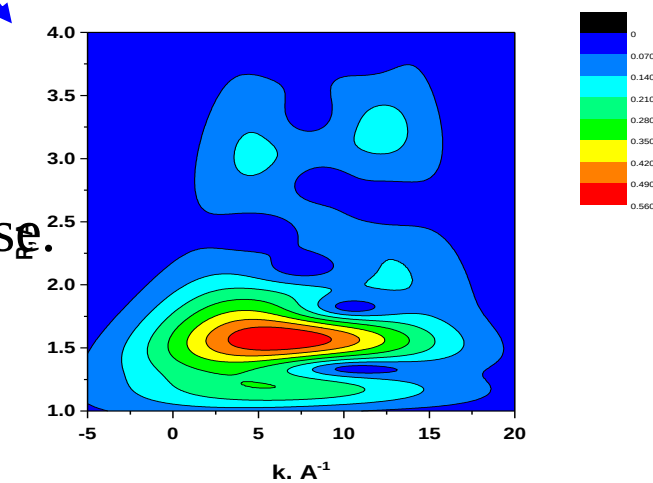
- The nearest oxygen is at 1.8 Å; small amount of a heavy element (possibly Pu) is present around 2.5 Å; at 3.6 Å minor oxygen coexists with a heavy element (most likely REE).
- The peaks due to the second coordination sphere are weak => Hf is mostly in the vitreous phase with coordination number close to 6.
- Some (minor) fraction enters the phase with approximate formula $GdHfO_{1.75}$.
- **<u>No evolution of Hf environment with time.</u>**



Hf in Pu-free glass



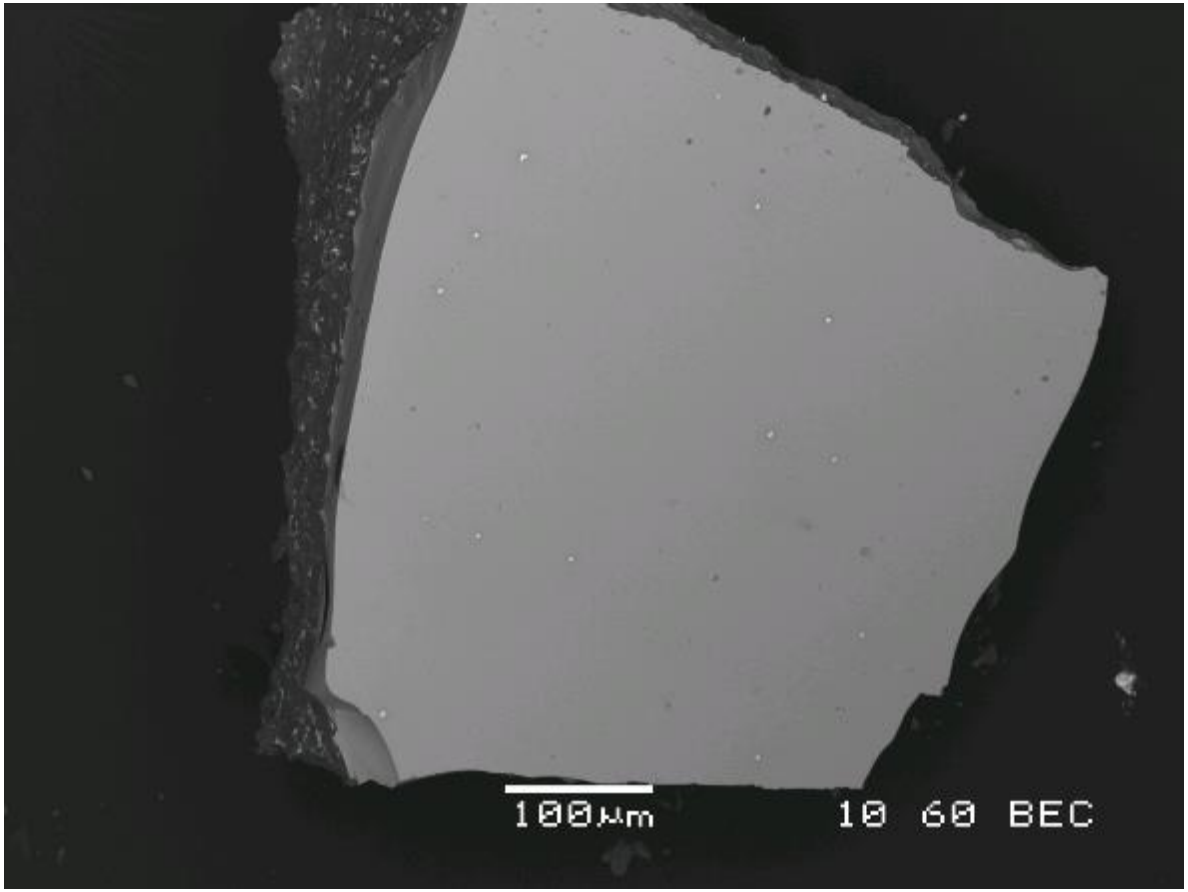




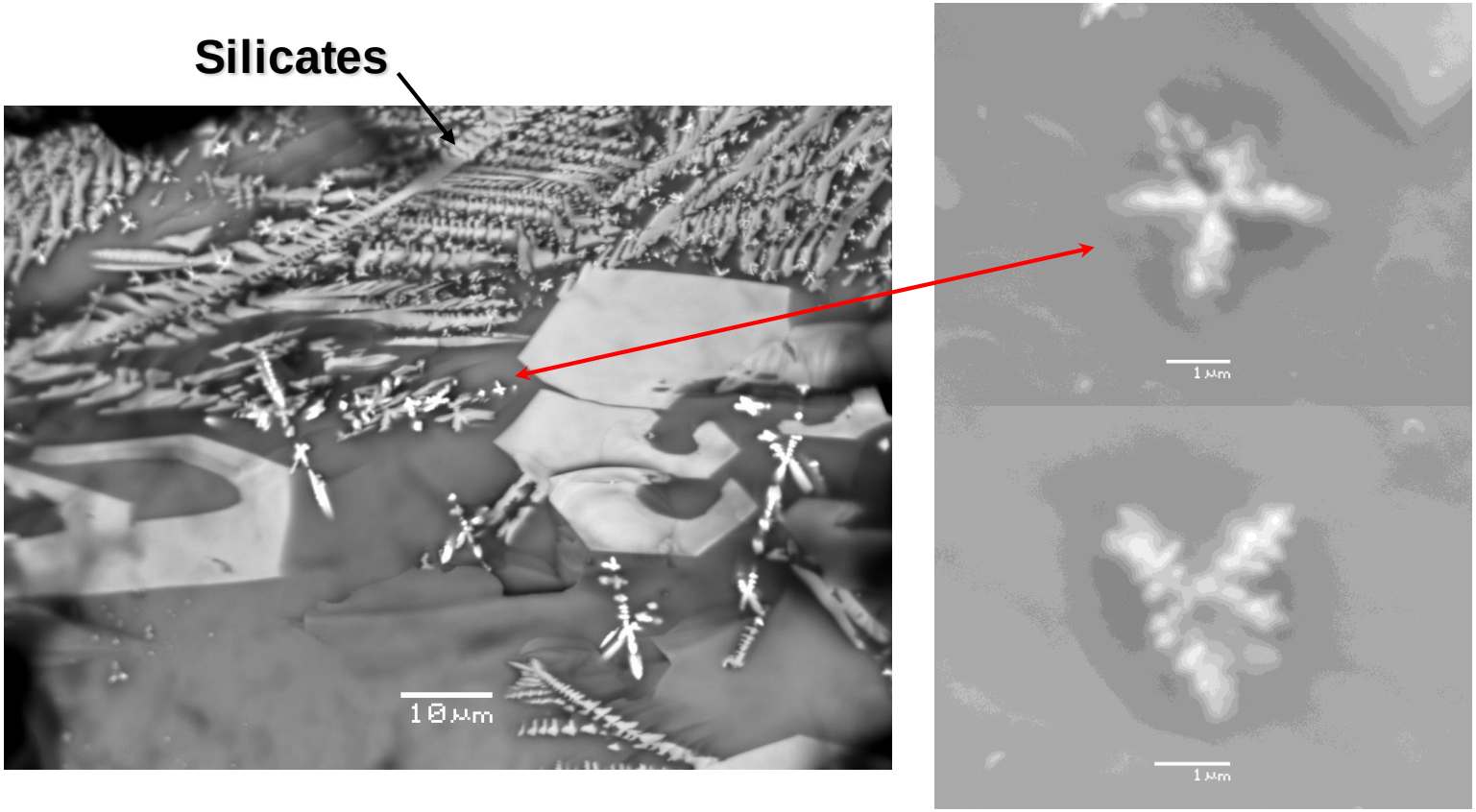
No spectral manifestations of HfO_2 as a separate phase.
Hf is mostly in vitreous environment, but weak second coordination sphere is also present.
Strong dependence on glass composition.

The “heavy spots”

Glass piece after 2 years of storage.
Many bright dots; look like some dust…

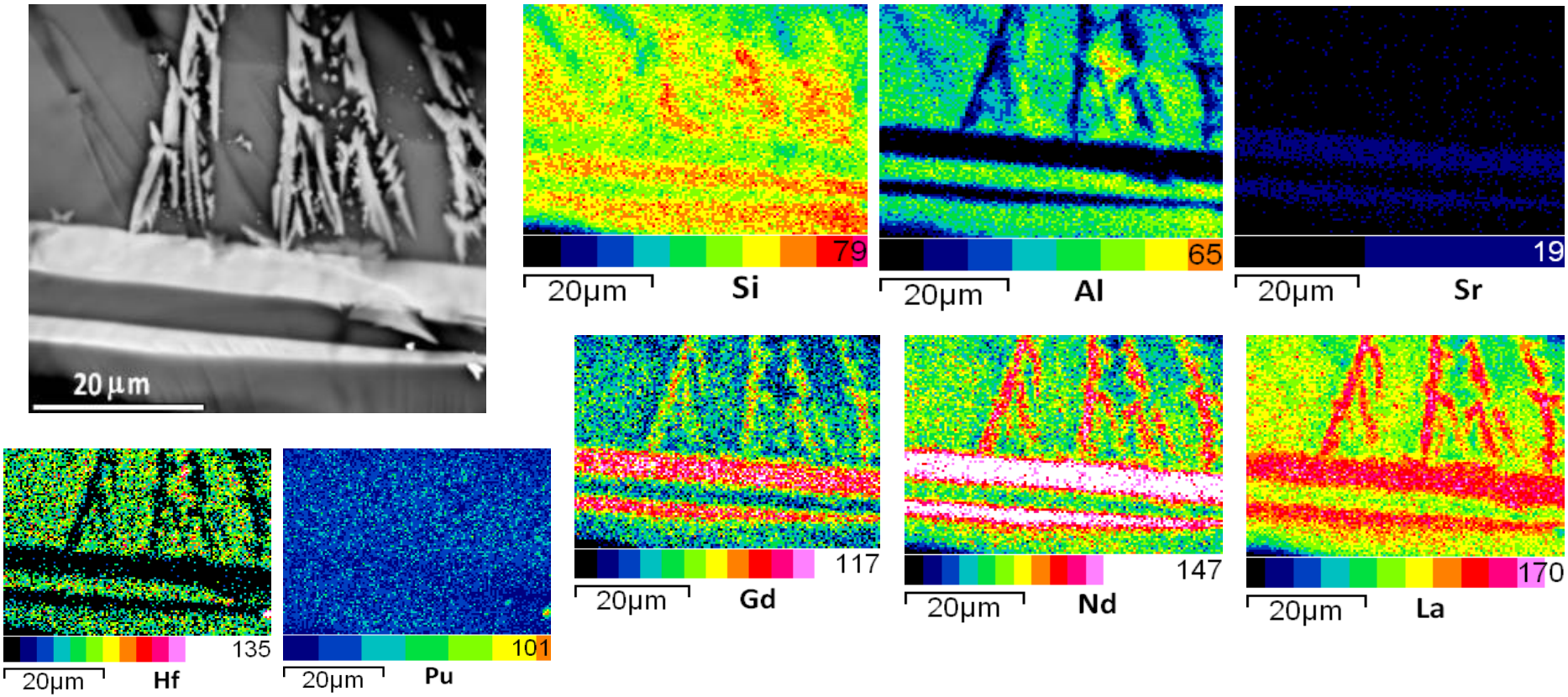


The “heavy spots”: a closer look



Precipitates of (Pu, Hf)O_2 solid solution and of REE-Al phase!!
Dendritic morphology consistent with CaF_2-structural type dendrites
Exsolution (rapid?) of excess PuO_2?

LaBS glass with 9.5 wt% PuO_2: SEM of partly crystallized sample



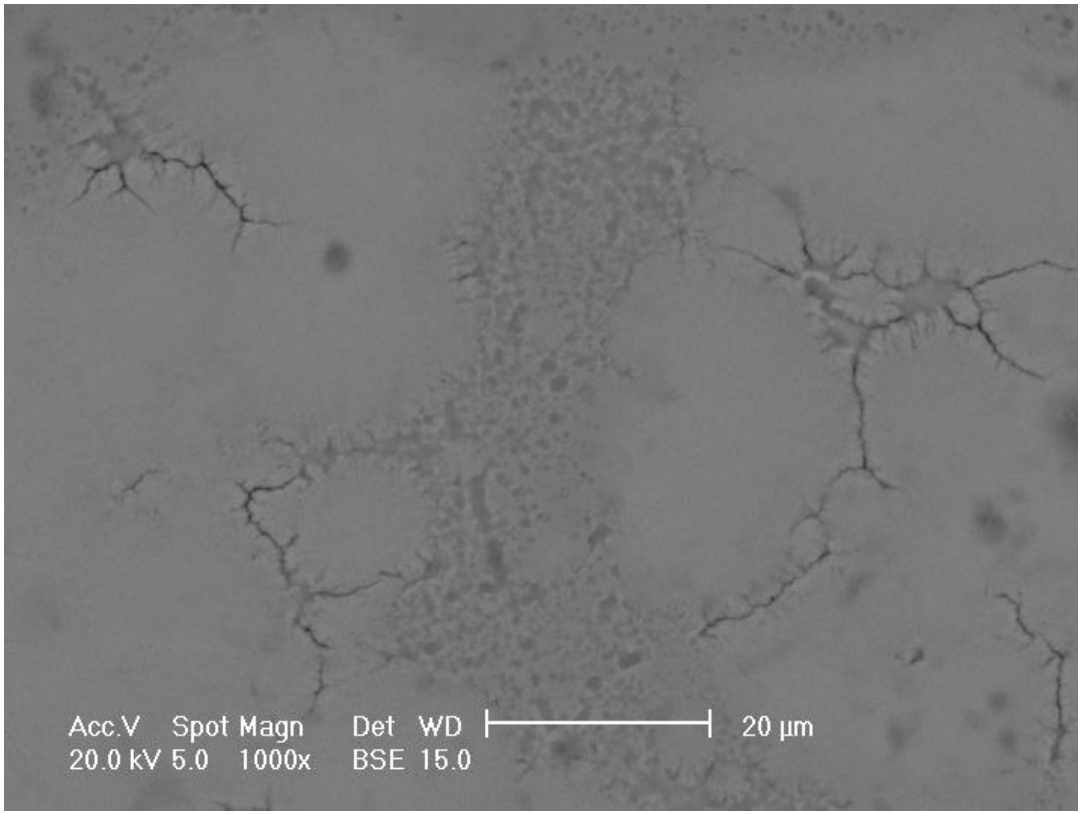
- Precipitation of britholite (?) $REE_{10}Si_6O_{24}(OH)_2$. The glass retains Al, Hf (supports XAS).
- REE, Sr and Si partition to the precipitate.
- Pu concentrations are roughly similar for the glass and the precipitate.

The Pu-rich LaBS sample is a glass-crystalline ceramics. Britholite is resistant to radiation.

But….

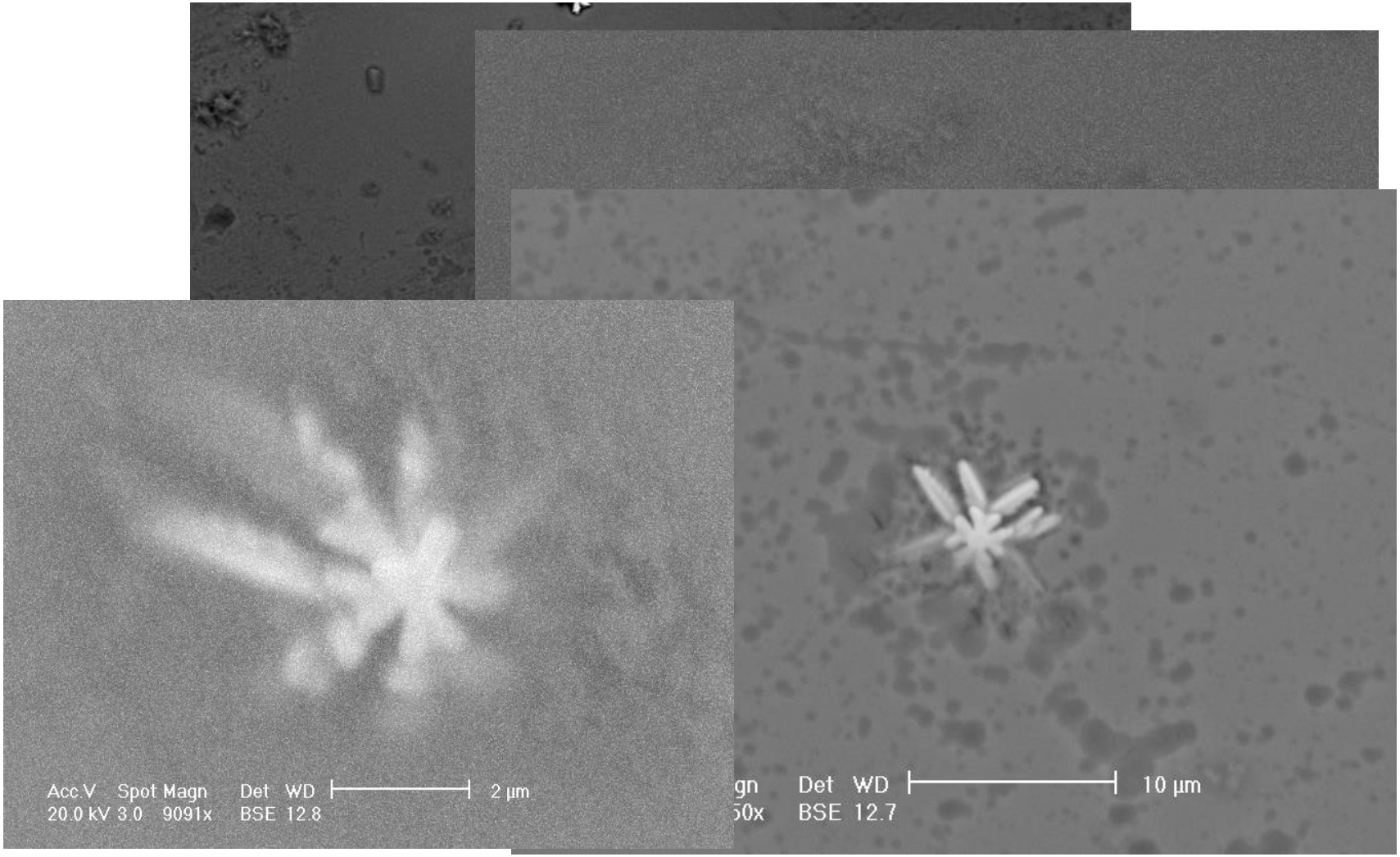
What happens if hot water contacts the glass?

Surface alteration: Pu-free glass



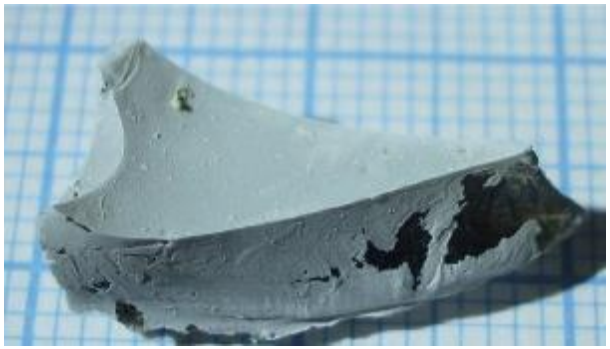
Formation of altered layer, which may crack and detach from underlying bulk
Rather uniform process on the whole glass surface

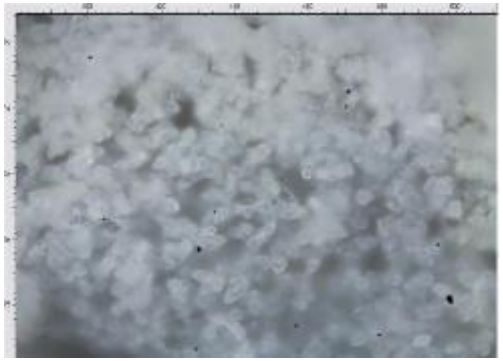
Alteration of Pu-rich glass in water

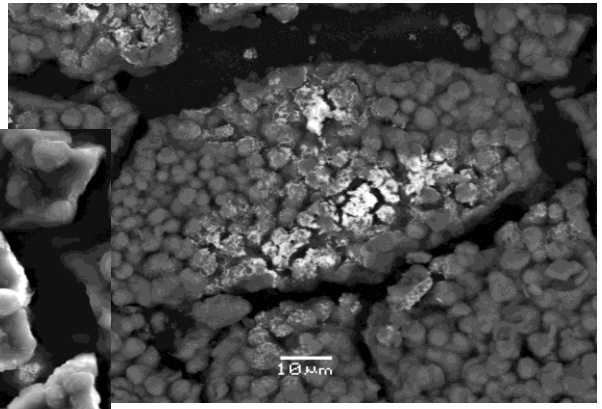


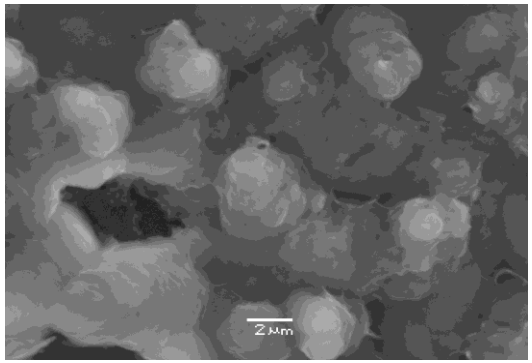
SON68-like glass with ^{238}Pu

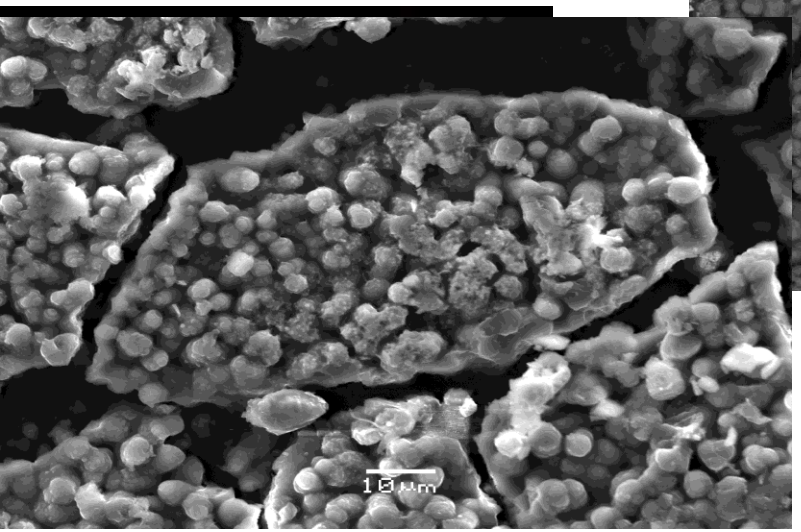
56 days at 90 °C in distilled water





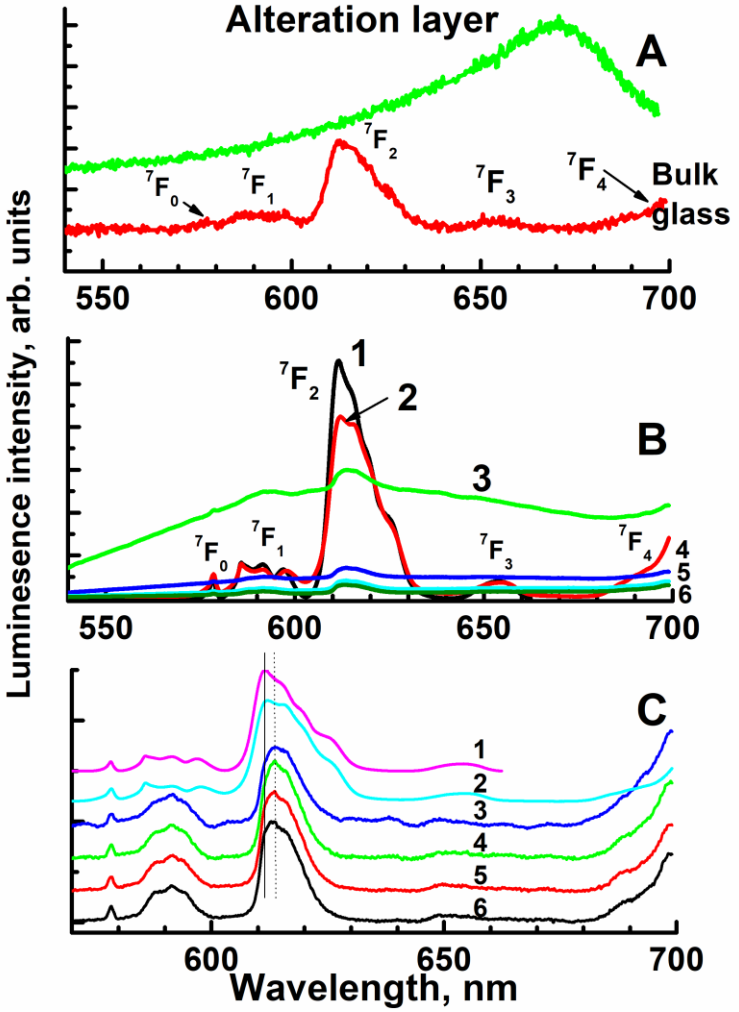






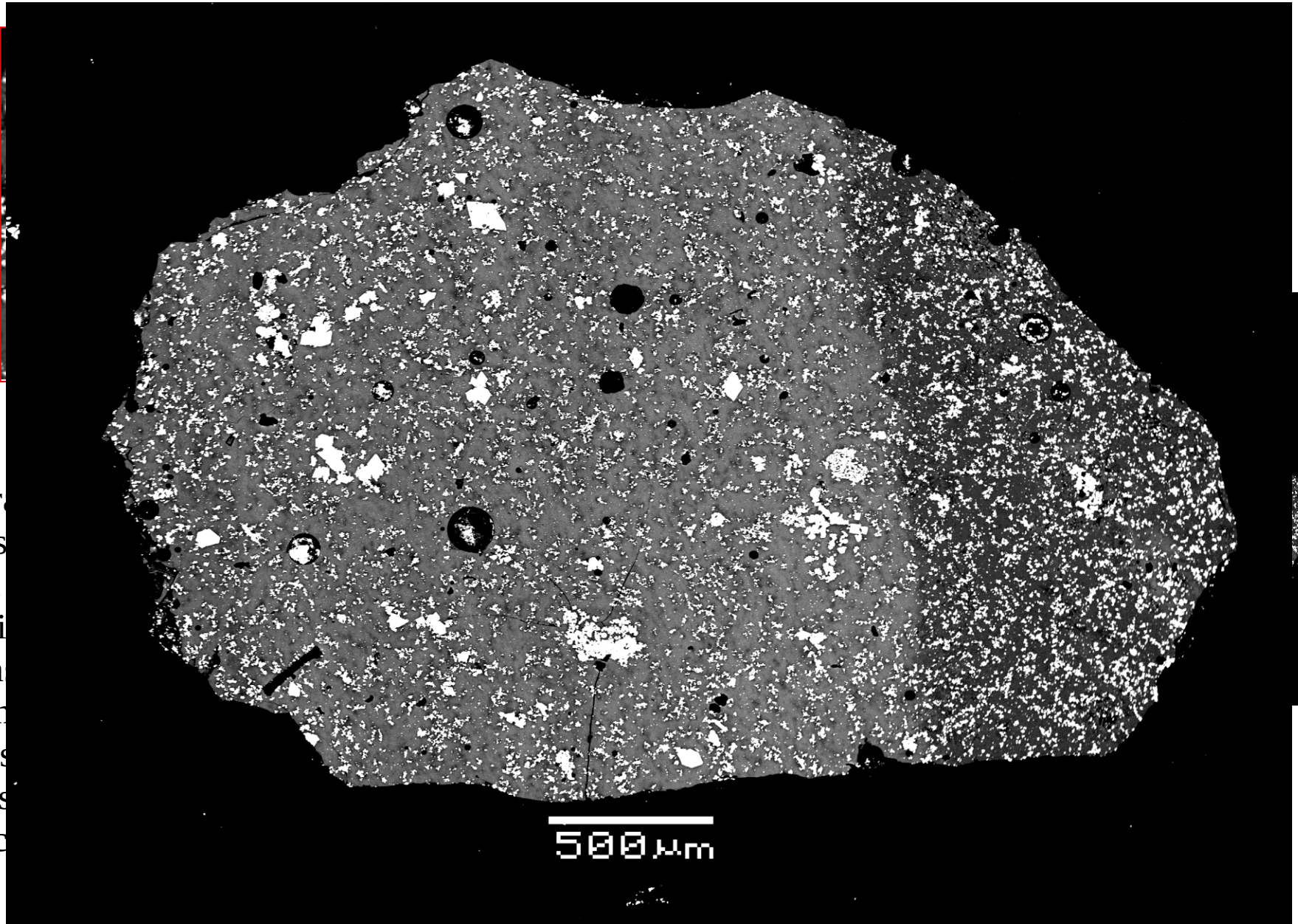
SON68 with ^{238}Pu

Changes in the photoluminescence spectra of Eu admixture indicate more ordered environment of Eu in the alteration layer in comparison with the bulk glass. Possibly this is related to higher Al/Si ratio.



Just a scientific curiosity?

Cracking of the Chernobyl lava



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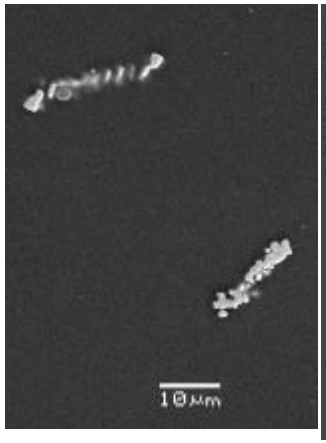
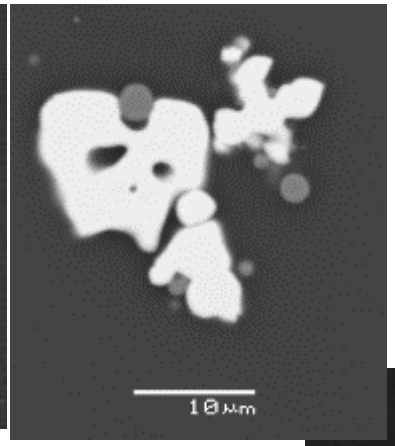
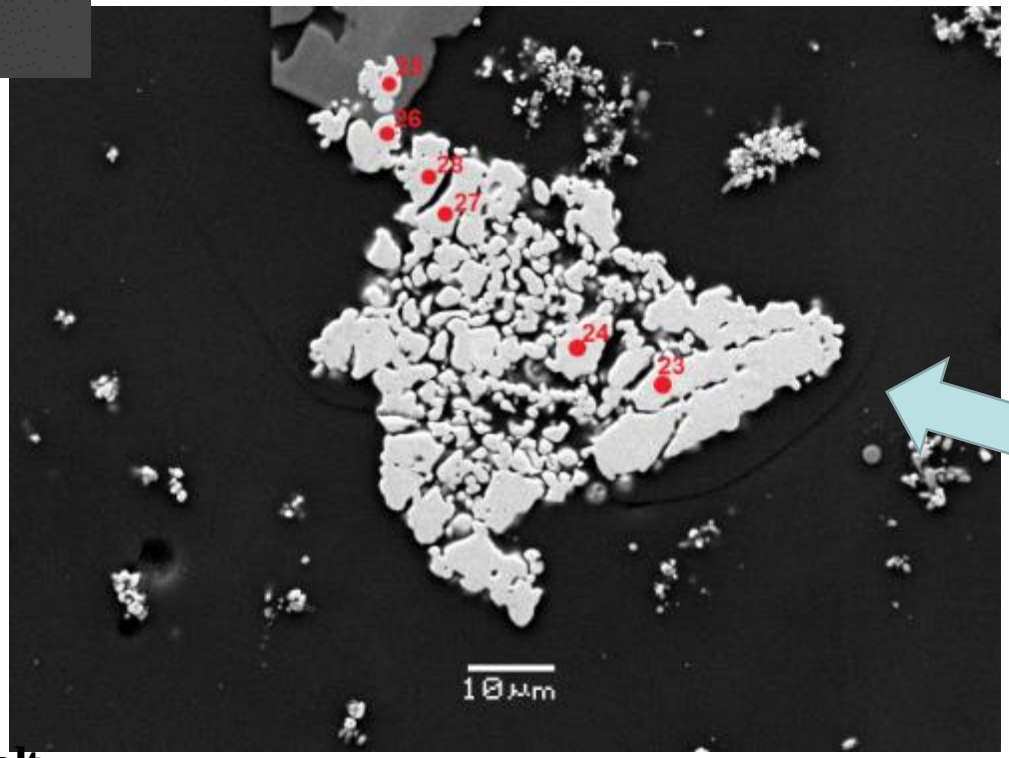
UO_{2+x} inclusions in Chernobyl lava





Variable morphology :

- **Dendrites (quenched supersaturated solution?)**
- **Rounded ("molten") pieces**

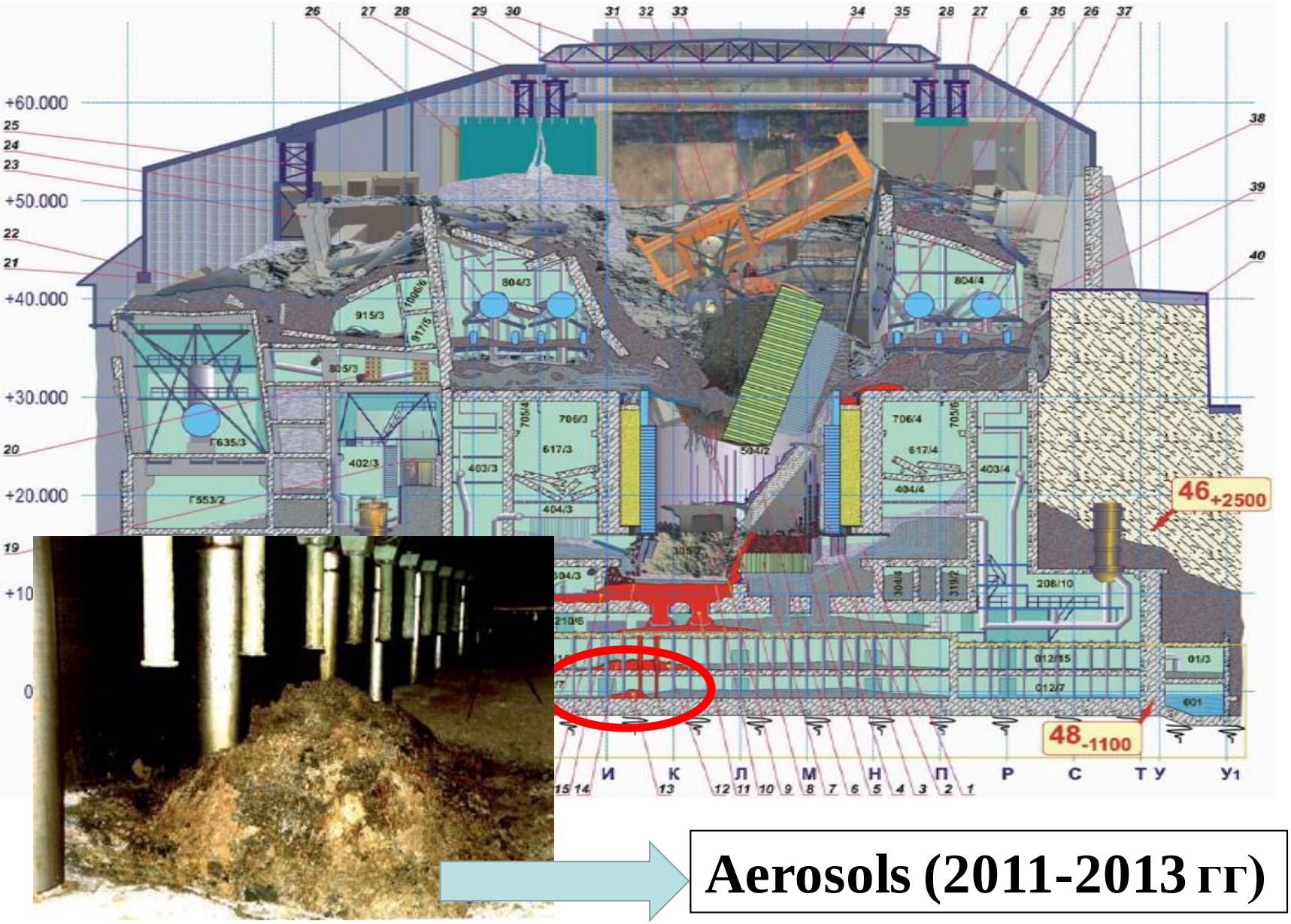


Cracks!!

Undissolved fuel pellet?

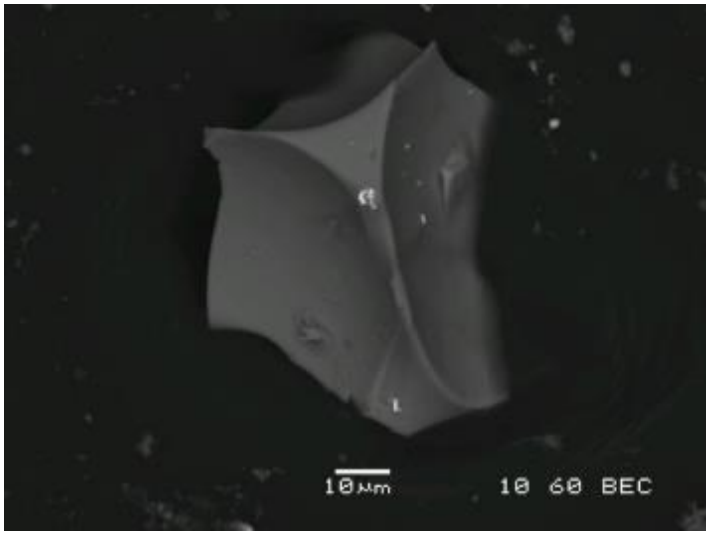
UO_2 precipitated from the melt *always* contains Zr admixture

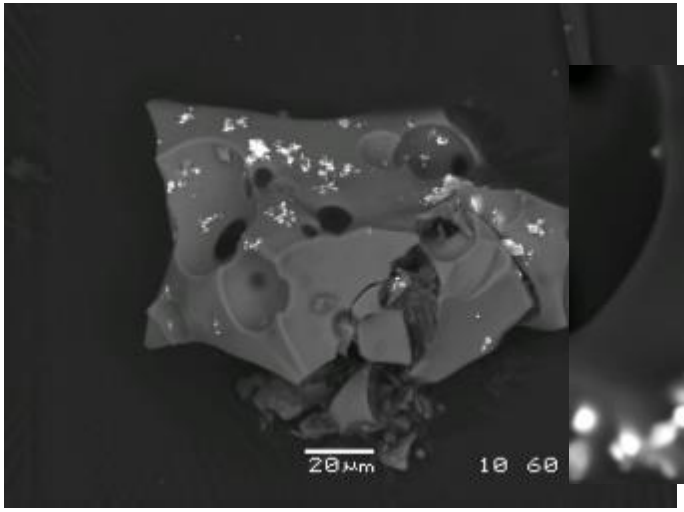
Aerosols

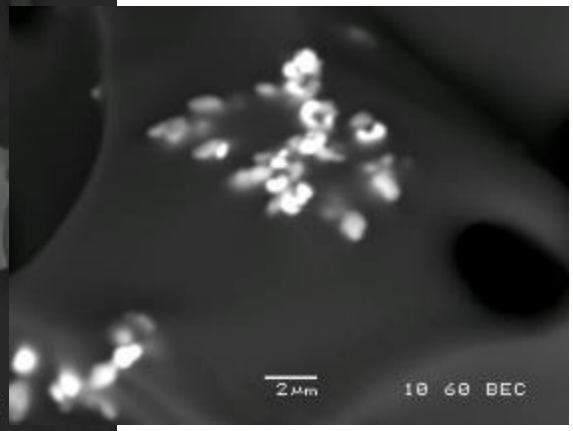


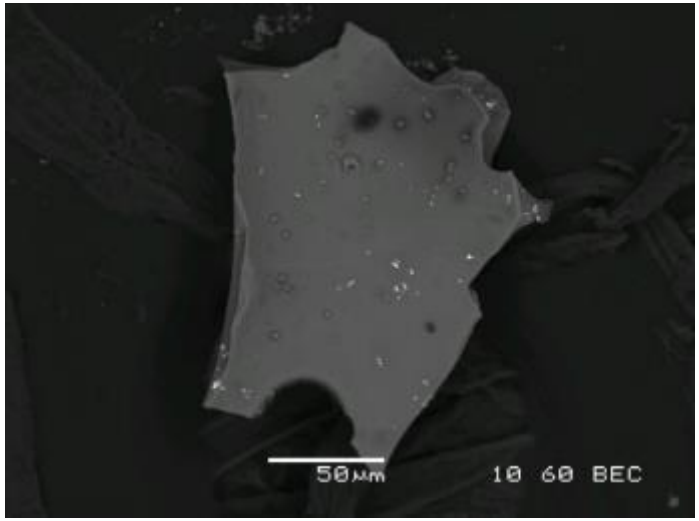
Aerosols (2011-2013 гг)

Spontaneously **detached glass particles**







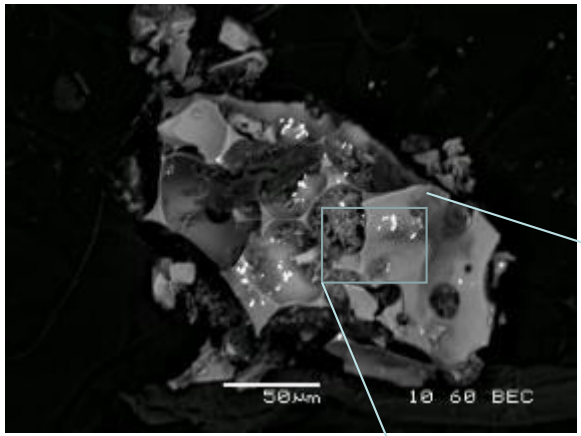


- Sizes of the glass chips reach 150x200 μm^2.
- UO_{2+x} inclusions are between ~1-2 and 5-7 μm.

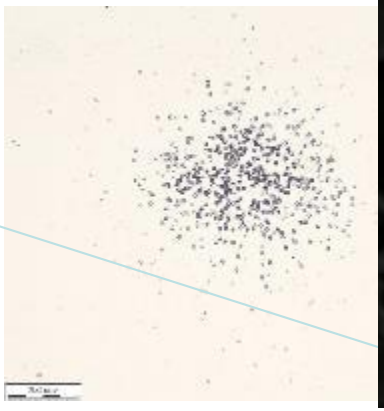
Secondary mineralisation

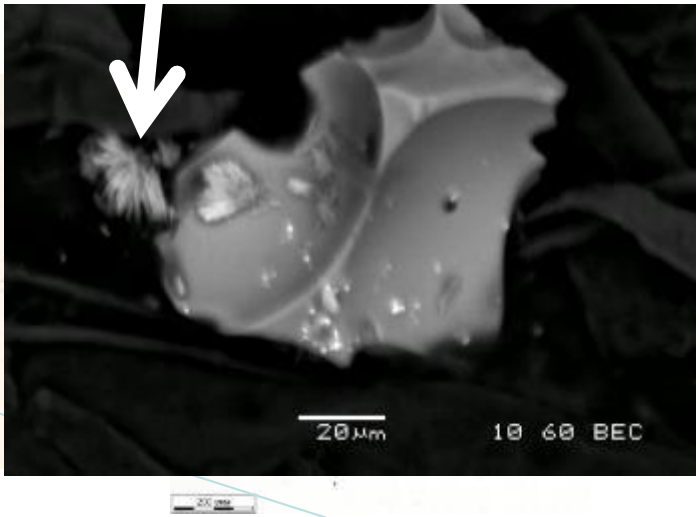
Secondary minerals are easily lost

Particle size: 200x100 µm!

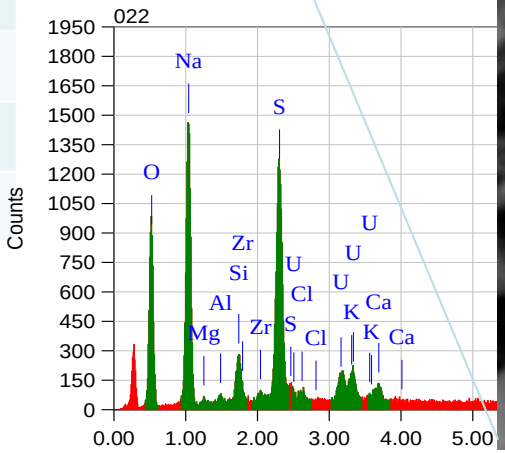


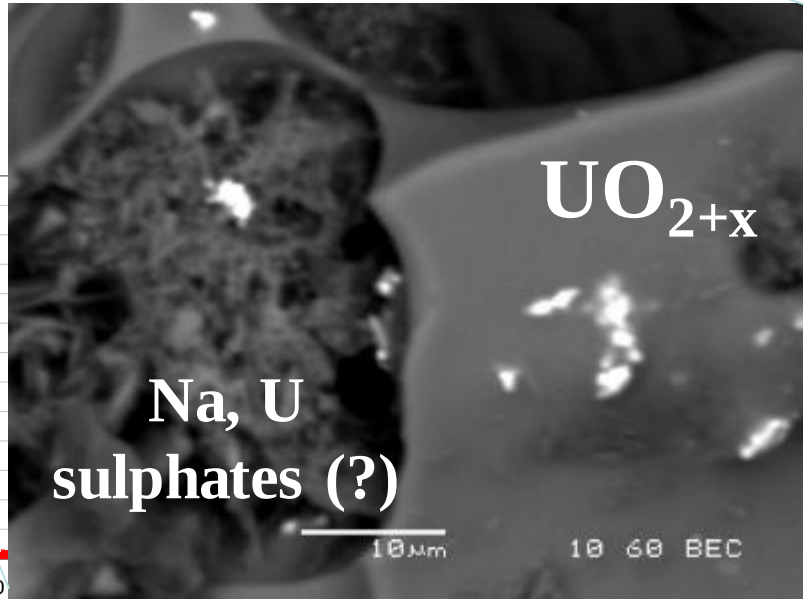
10 min





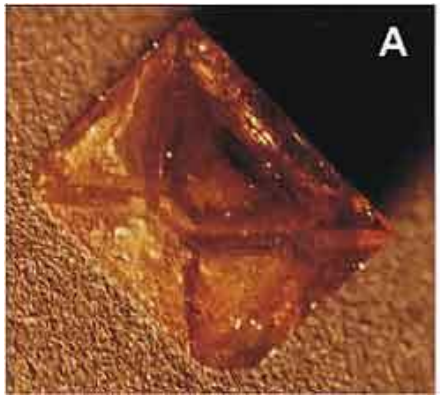
	Wt %
O	39
Na	26
S	15
U	10

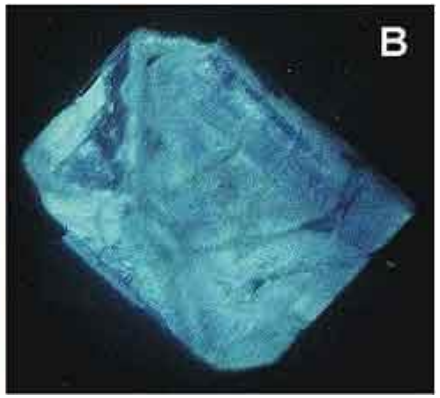




Mineral-like ceramics

Zircon as a form for actinides immobilisation

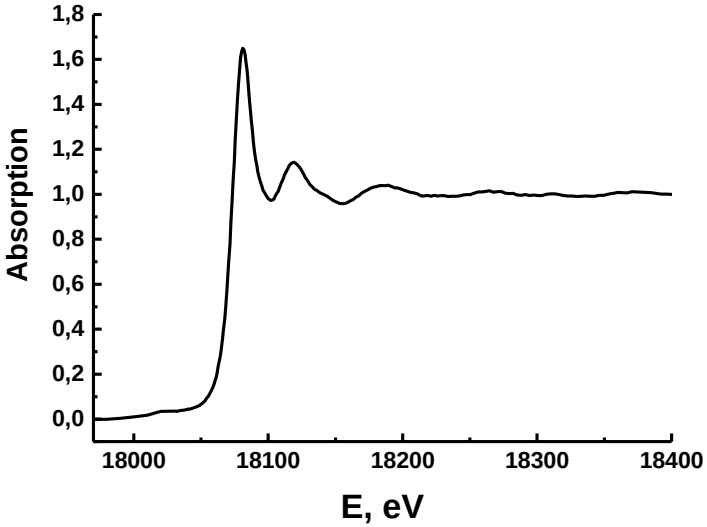


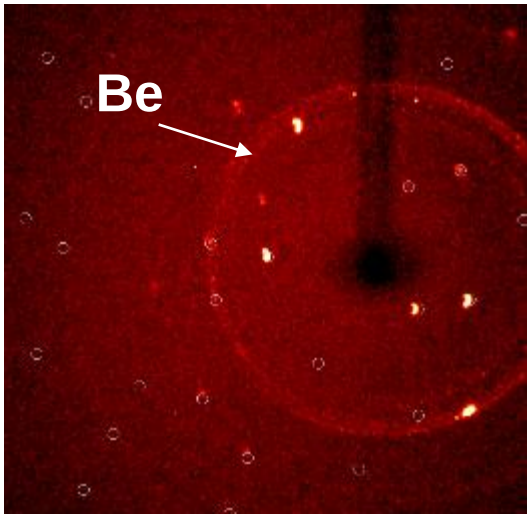


Flux-grown zircon with 2,4 wt% of ^{238}Pu

11 years after the synthesis:

- XANES confirms that Pu is tetravalent, i.e. most likely it substitutes Zr^{4+} in zircon lattice.
- SC-XRD: S.G. I 4_1/amd, a=6.52, c=5.94 Å





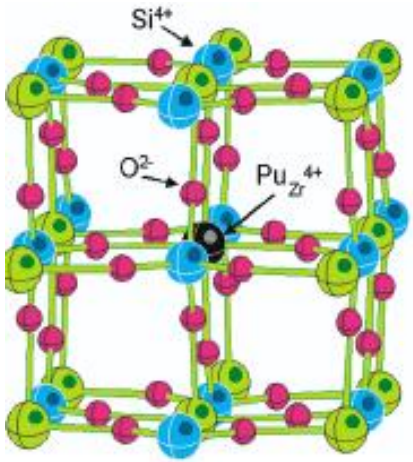


Image by R.E.Williford, PNNL

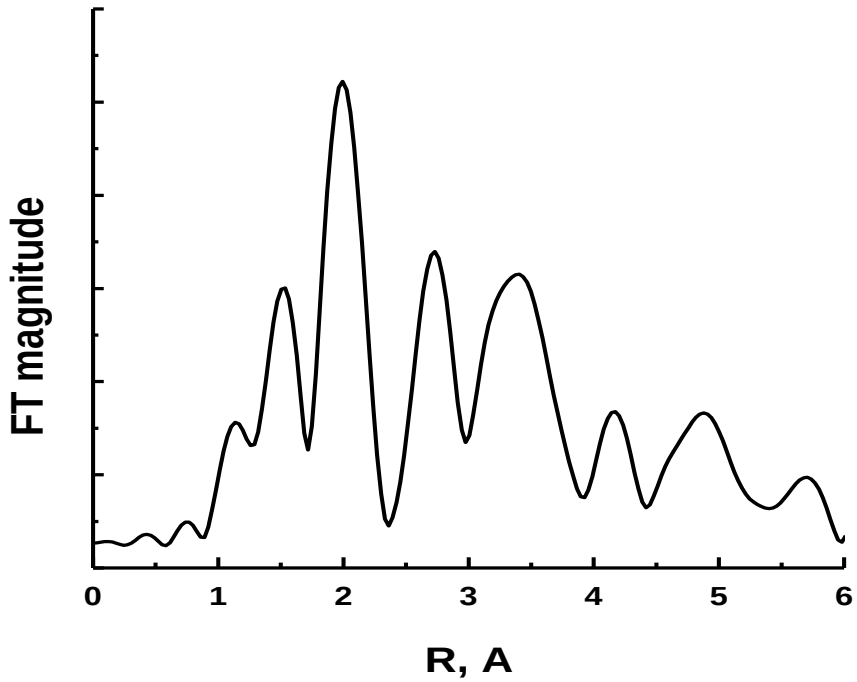
Principal problem: degradation due to self-irradiation

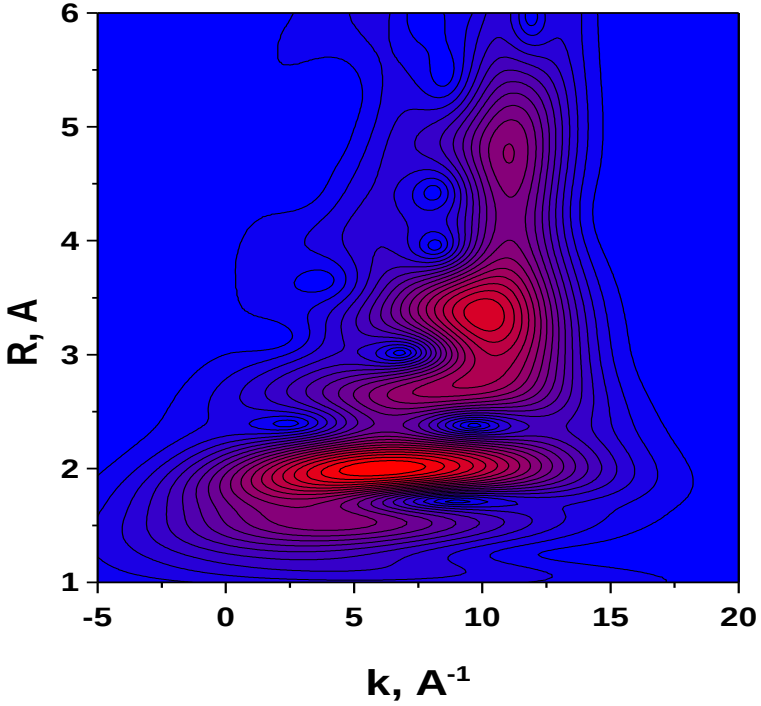
Zircon amorphises under irradiation (metamictisation). Still conflicting results on amorphisation dose and chemical resistance of metamict zircon.

Images: B.E. Burakov

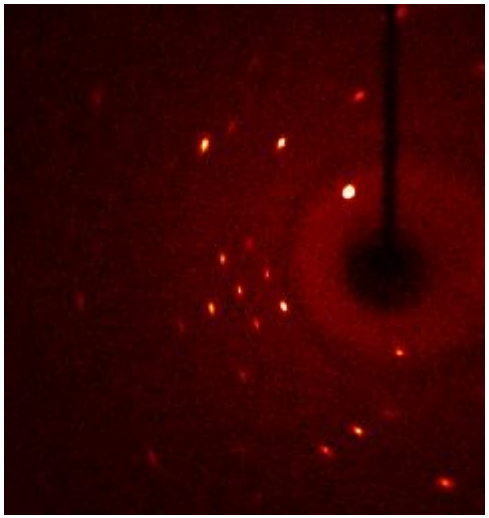
XAFS of Pu in monazite

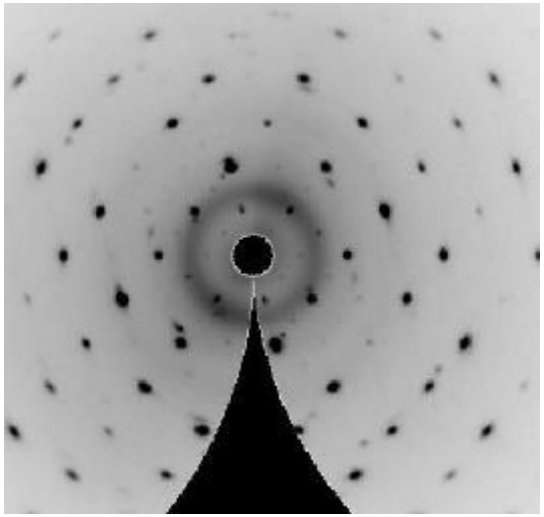
- Initially Pu(III) occupies REE sites. Self-irradiation may convert to Pu(IV).
- Complex ordered environment.





SC-XRD





(Eu, Pu)PO_4 (12 y after synthesis)

S.G. P 21/n

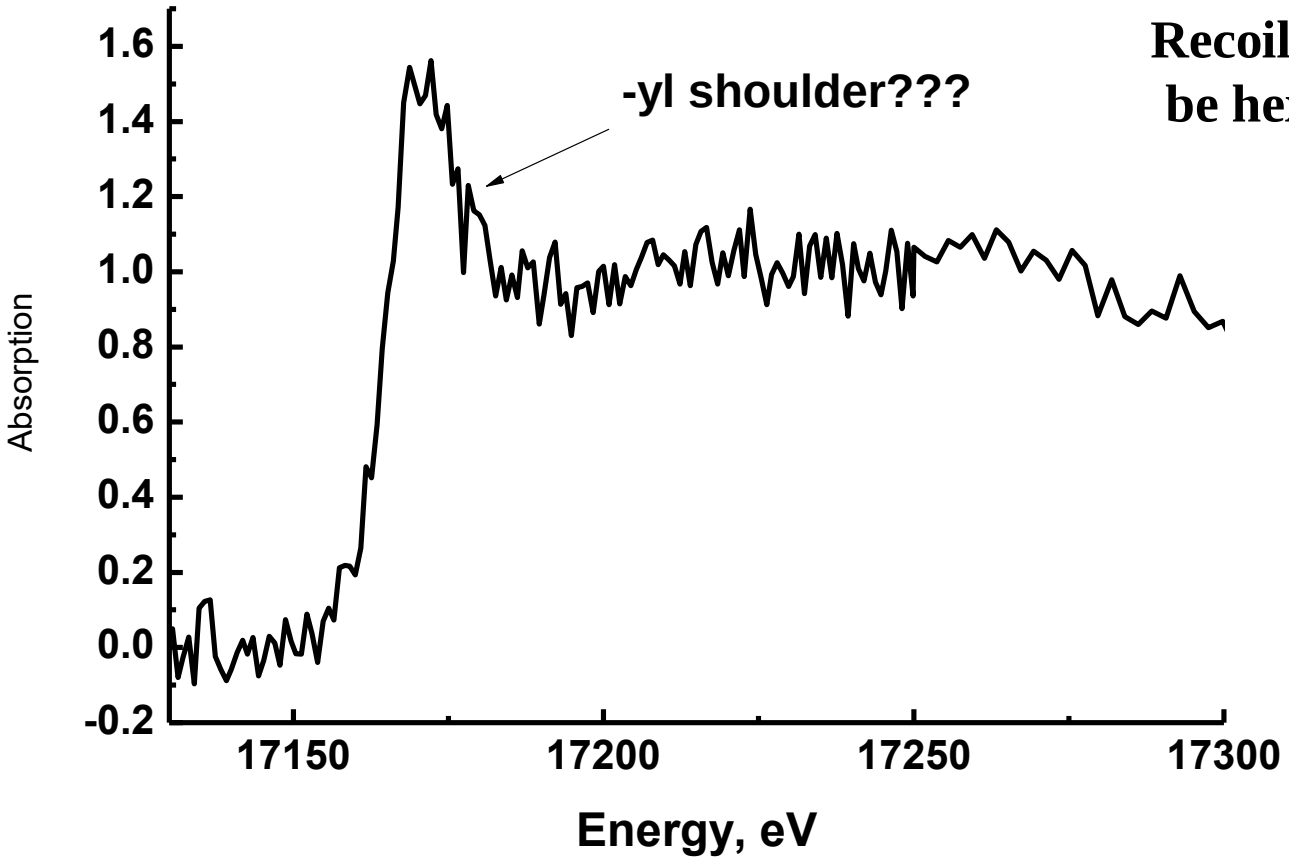
a = 6.3864(11) Å **α = γ = 90**

b = 6.8668(12) Å **β = 104.028(7)**

c = 6.6654(11) Å **V = 283.59(8)** $Å^3$

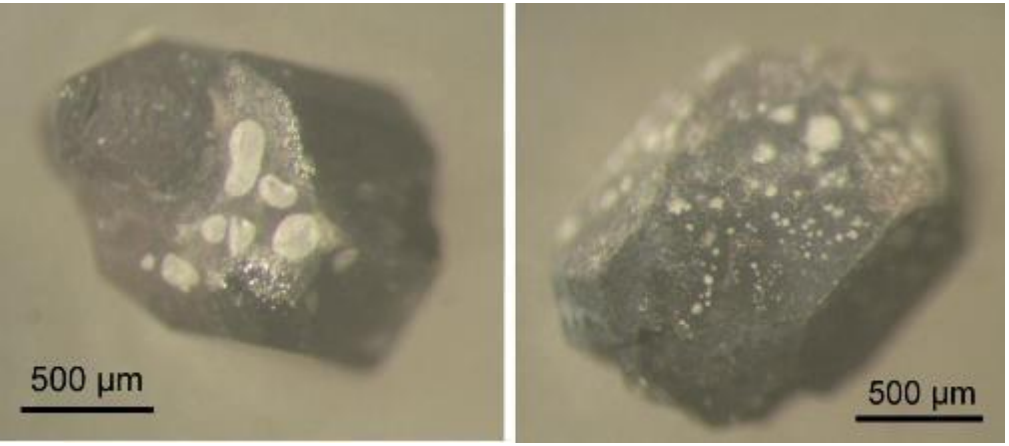
Slow swelling with accumulated dose…

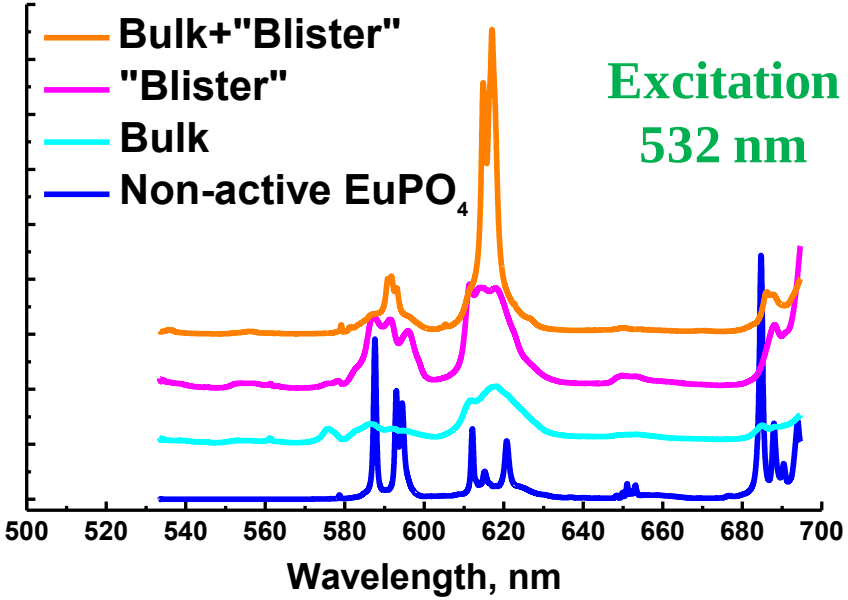
What is the fate of recoil uranium?

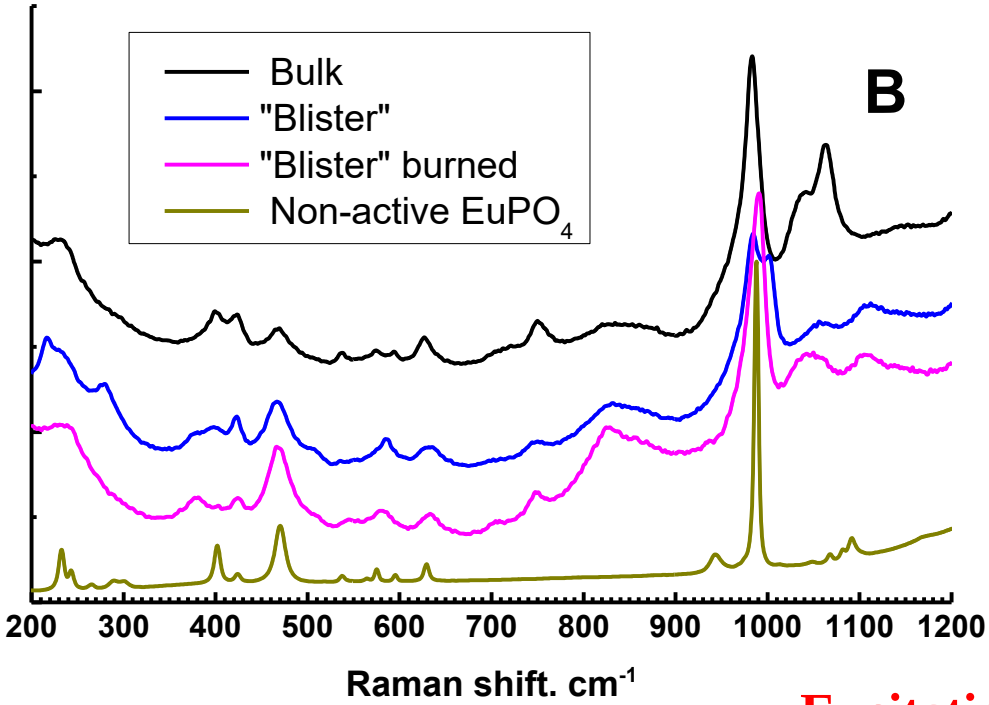


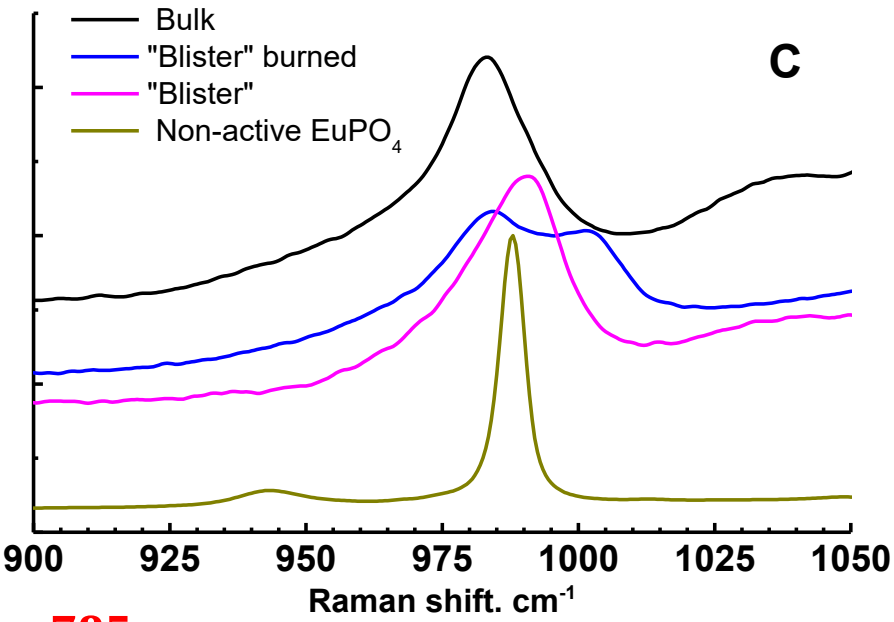
Recoil U might be hexavalent

Single crystal of $Eu_{0.937}Pu_{0.063}PO_4$



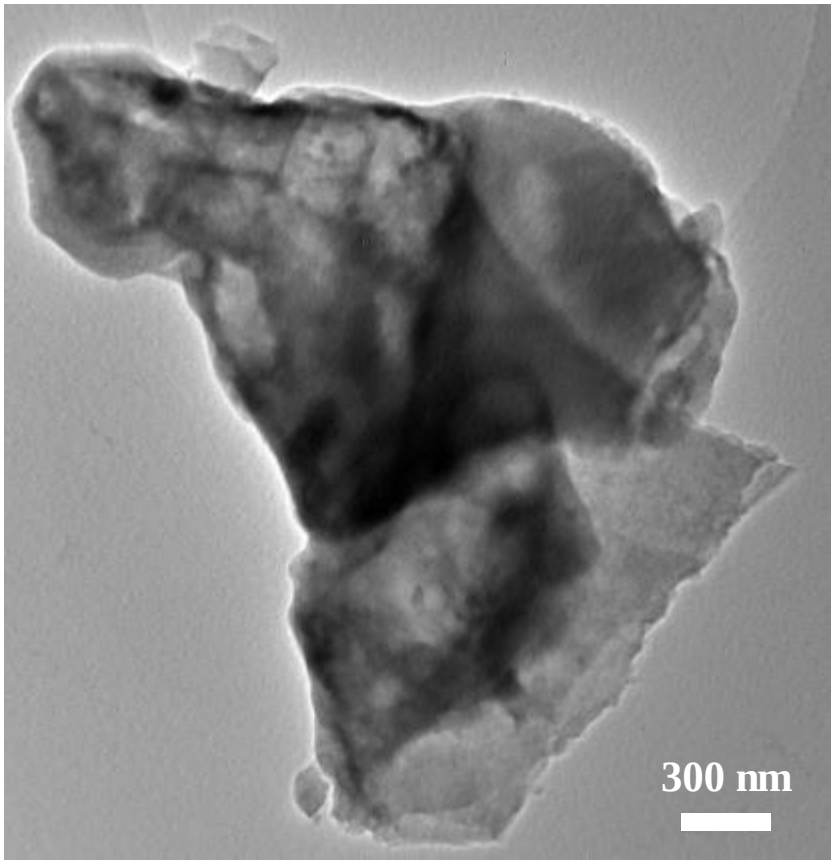


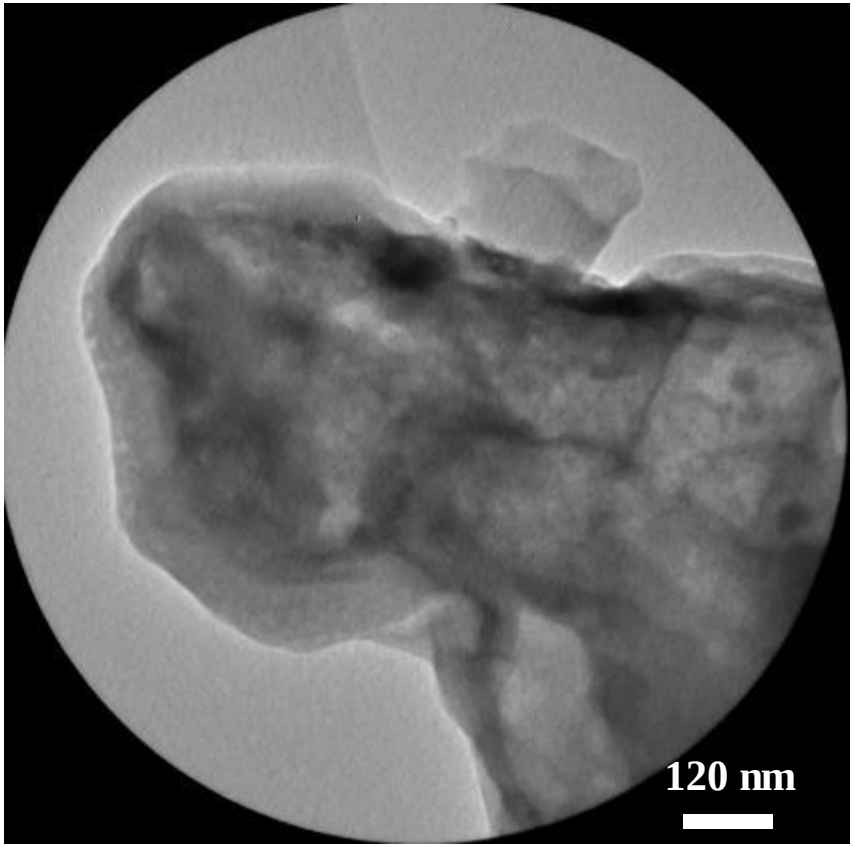




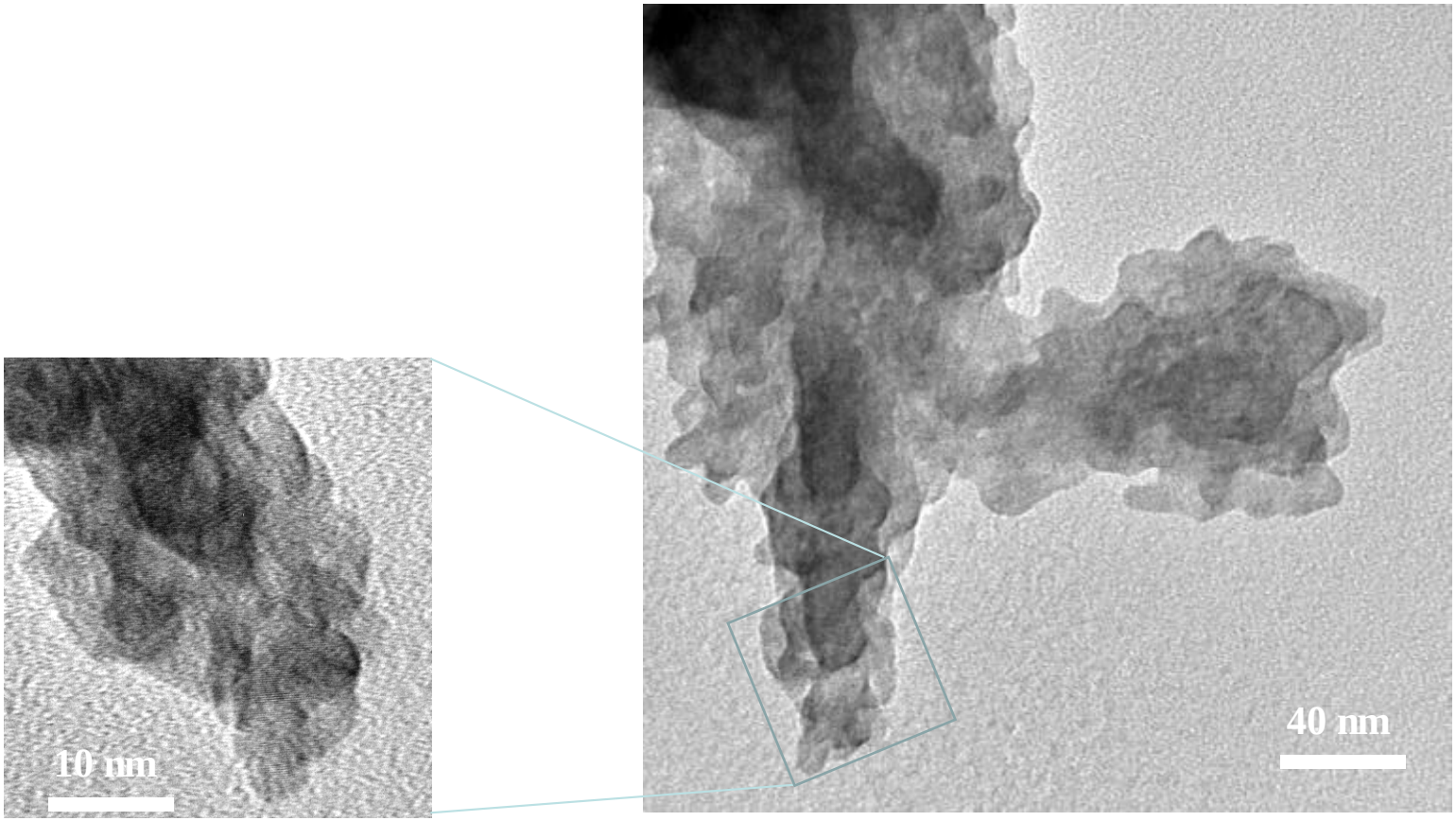
Excitation 785 nm

Single crystal of $Eu_{0.937}Pu_{0.063}PO_4$

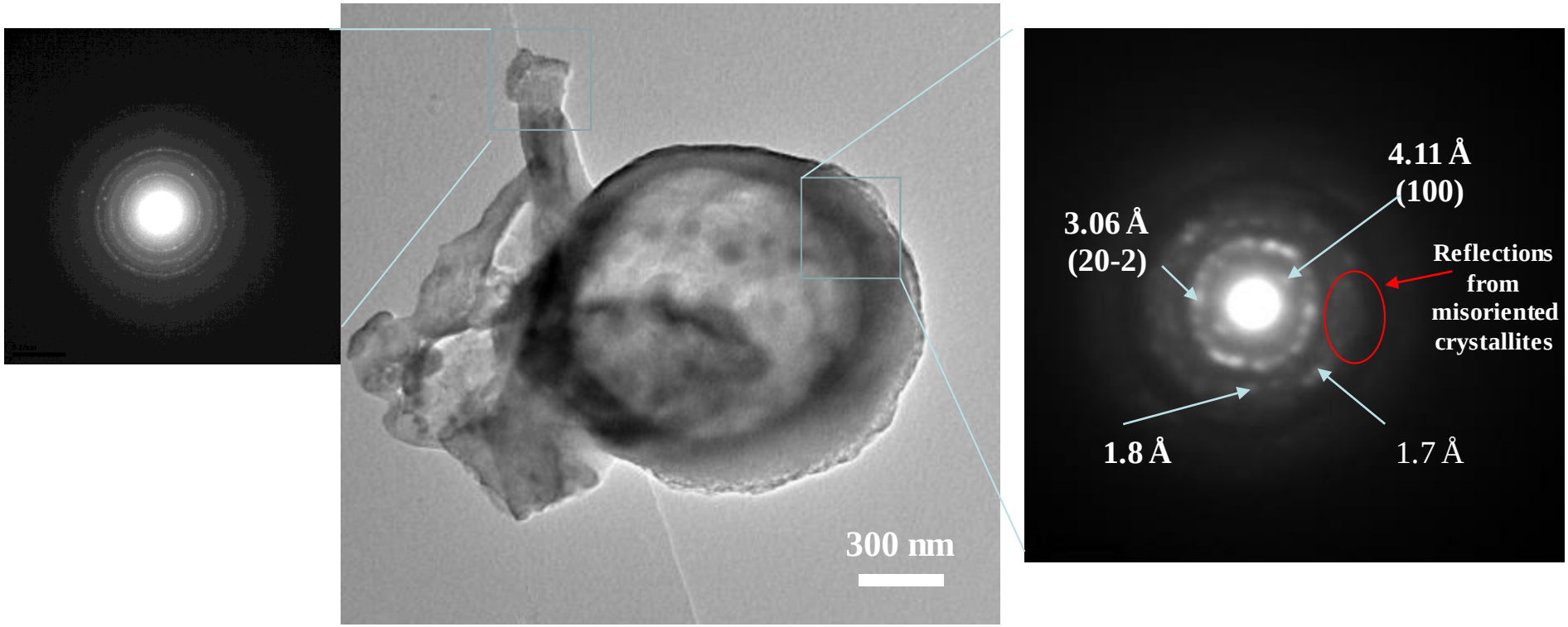




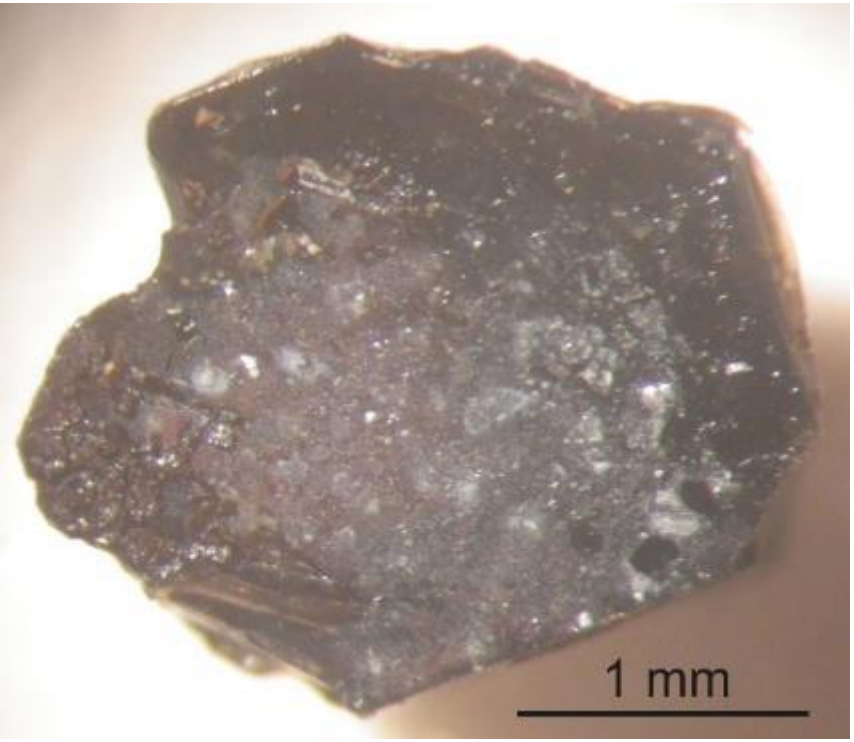
Single crystal of $Eu_{0.937}Pu_{0.063}PO_4$

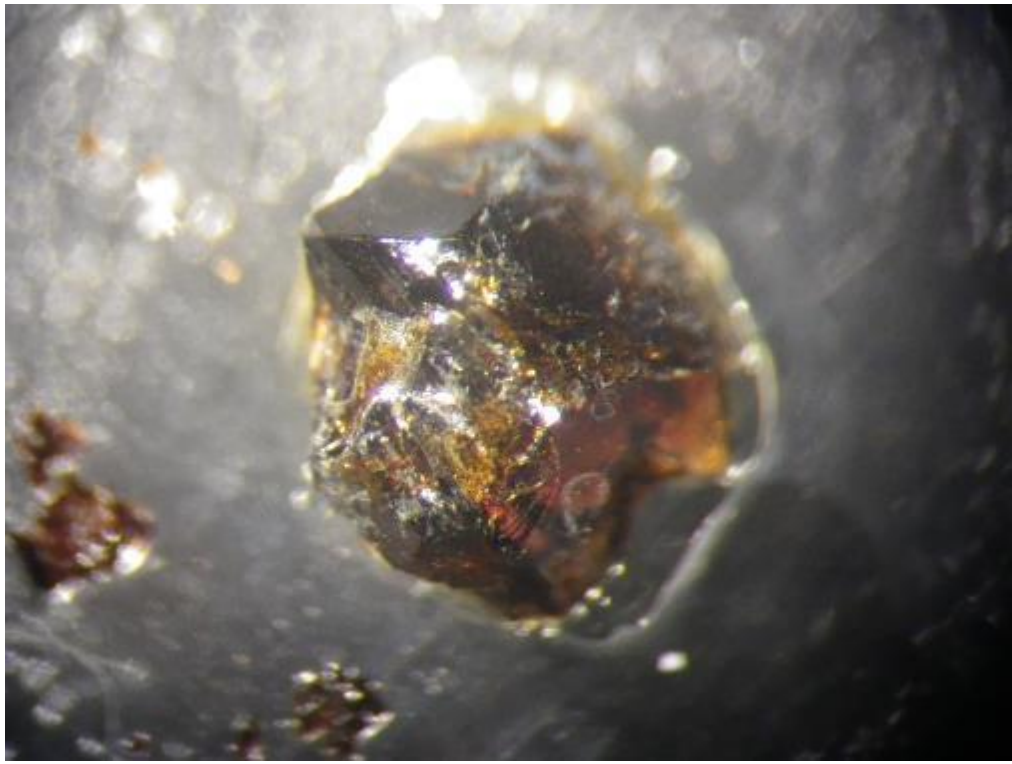


Single crystal of $Eu_{0.937}Pu_{0.063}PO_4$

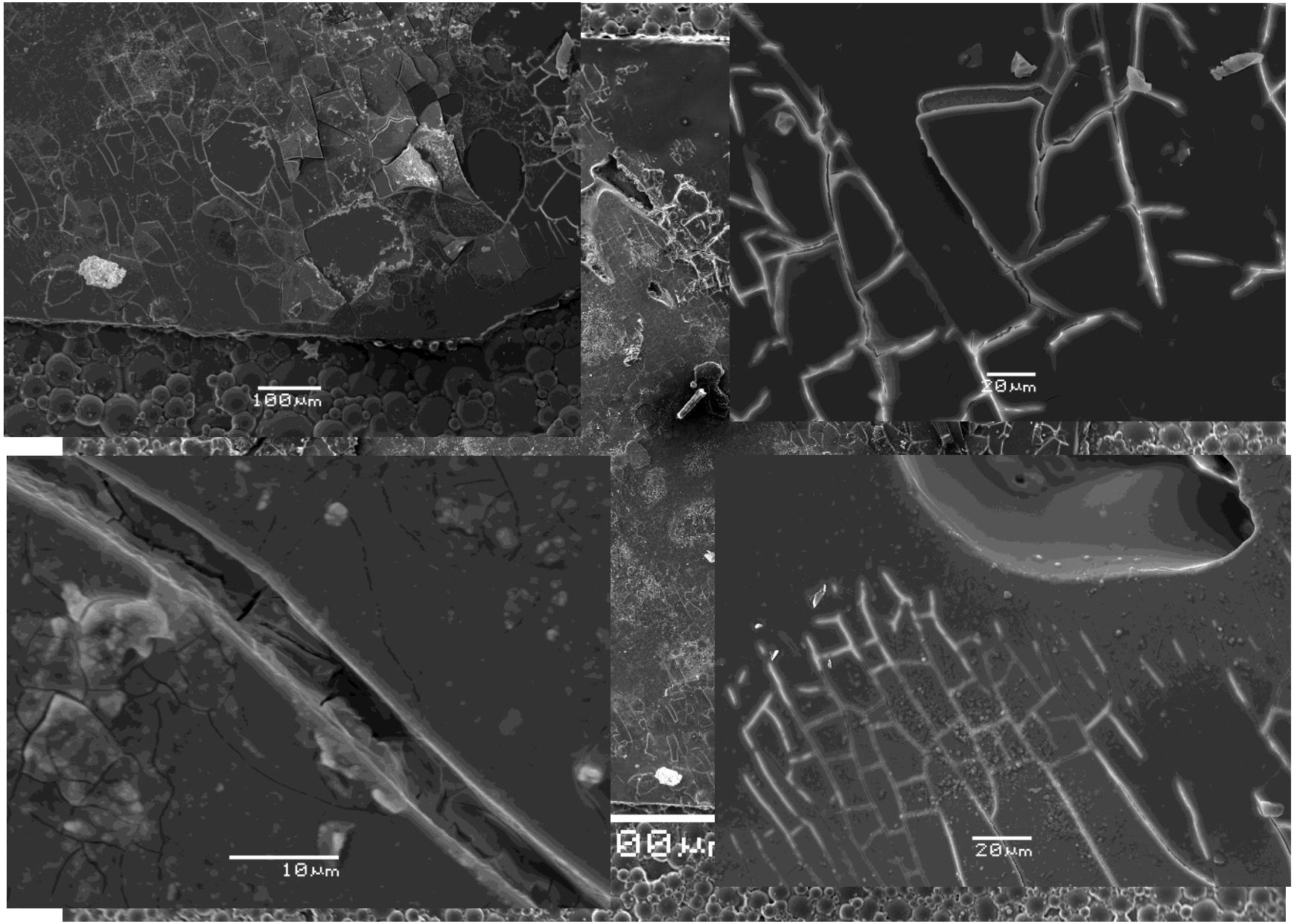


Single crystal of $Eu_{0.937}Pu_{0.063}PO_4$

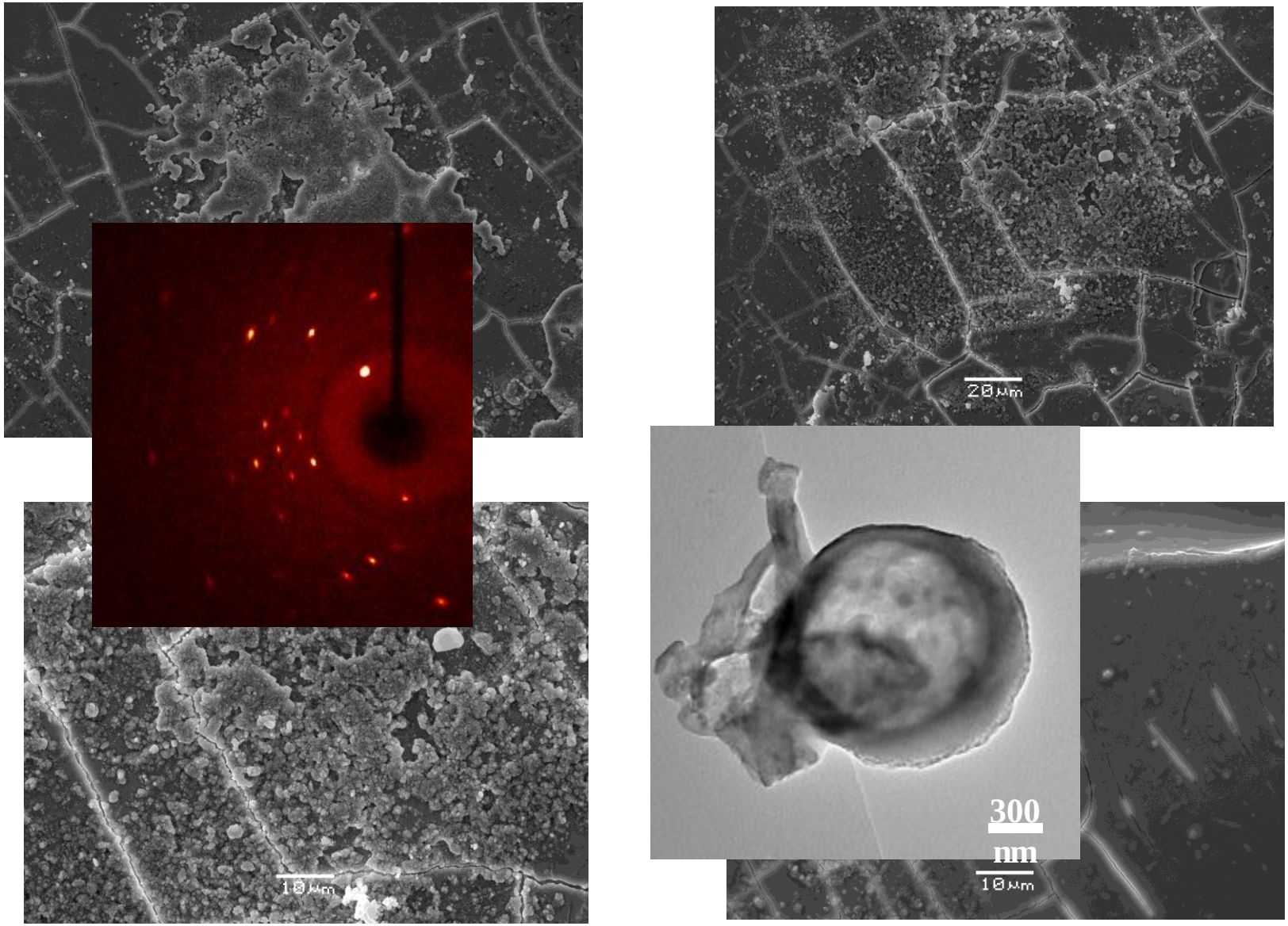




Single crystal of $Eu_{0.937}Pu_{0.063}PO_4$

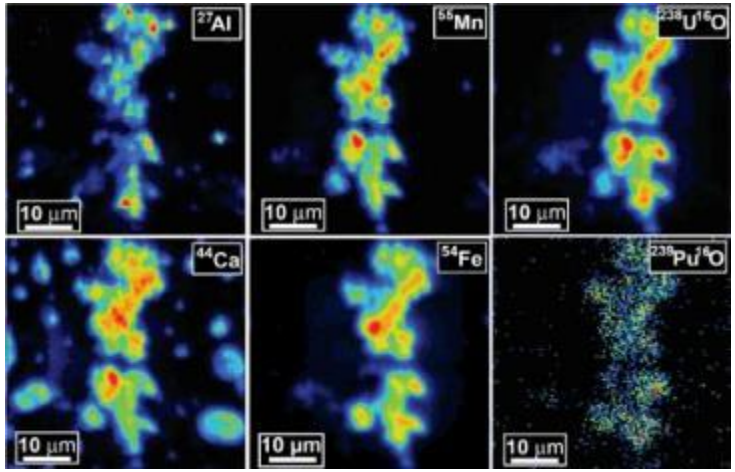


Single crystal of $Eu_{0.937}Pu_{0.063}PO_4$: “blisters”



Nanoparticles under impact

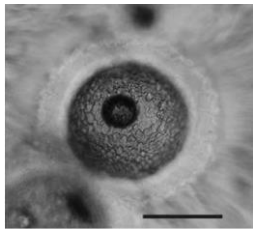
Actinides and colloids

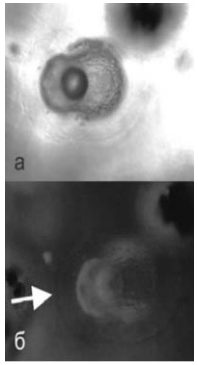


- *Novikov A.P., et al., Colloid Transport of Plutonium in the Far-Field of the Mayak Production Association, Russia. Science, 2006*
- *Kersting et al., 1999*

Silica colloids may migrate and transform to stable SiO_2 phases

Silica colloids may be exceptionally stable (time scale of ~10^7 years!)



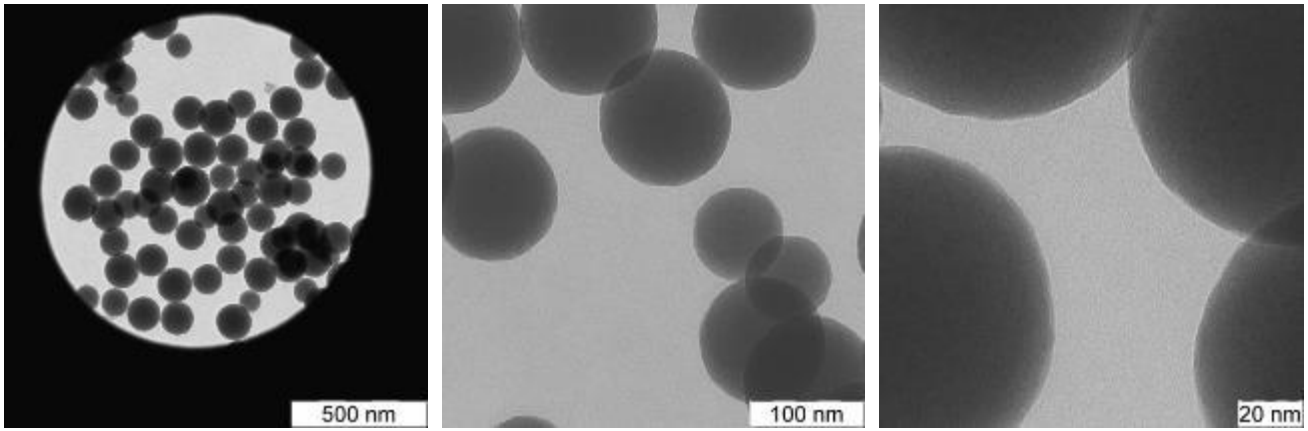


Prokofiev V.Yu., et al., Fluid inclusions with colloid solutions in chalcedony, TBG XIII Proceedings (2009)
Prokofiev V.Yu., et al., Geology, 2017

Fresh SiO_2 colloids with adsorbed Pu

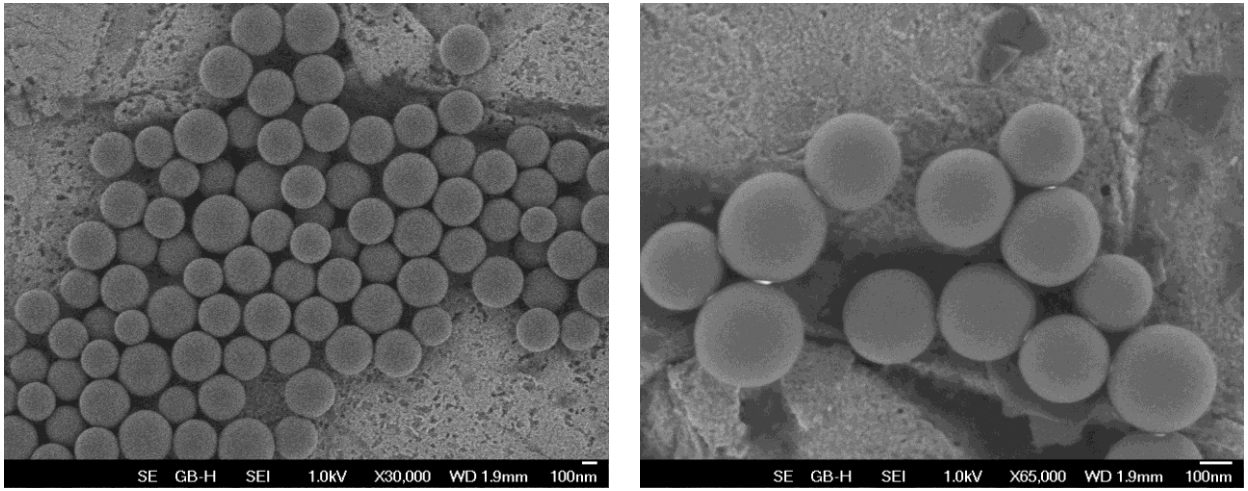
TEM

No internal structure

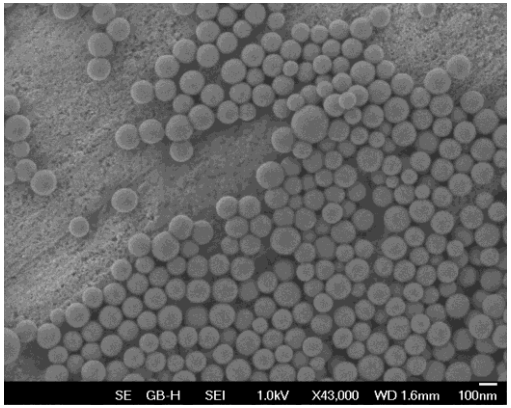


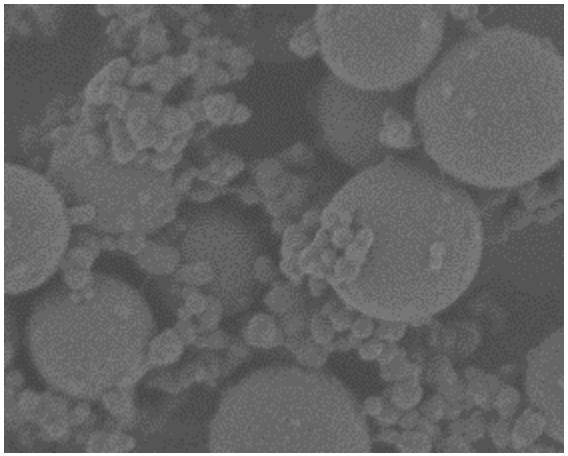
SEM

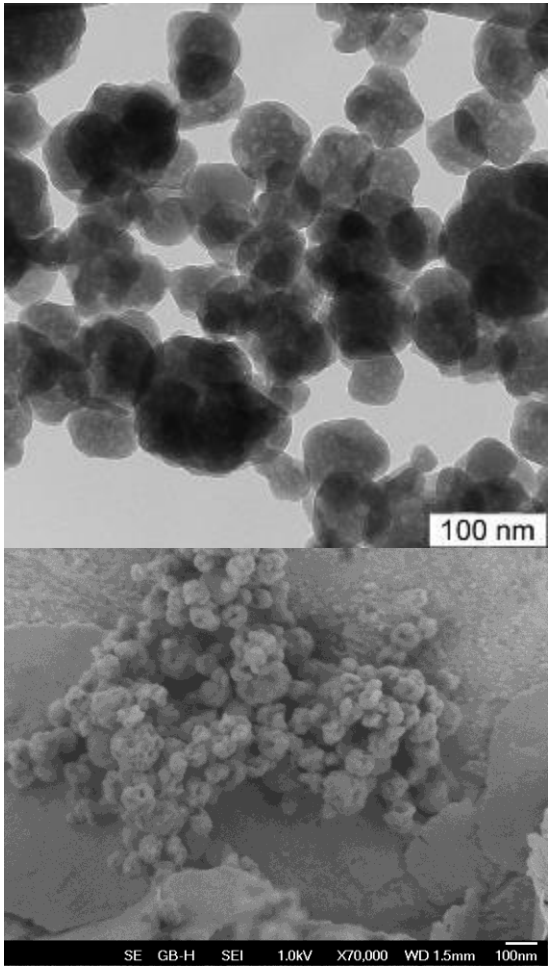
No surface features observable even in low-energy mode



Control experiment (no Pu) – high temperature



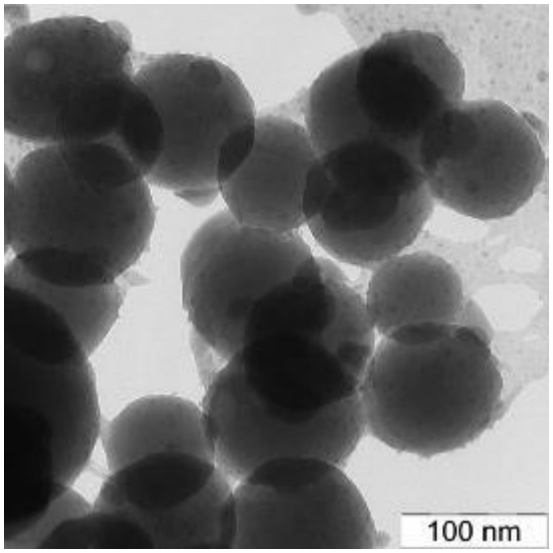


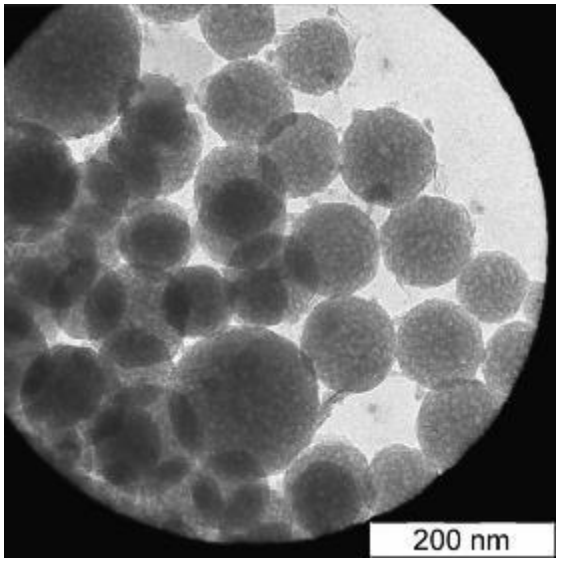


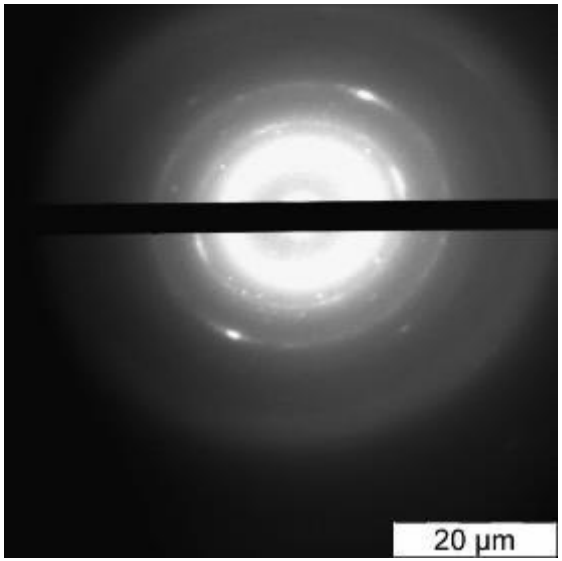
13 days at 150 °C

Colloids in solution with Pu(V)
2 days at 150 °C

TEM shows presence of three types of objects



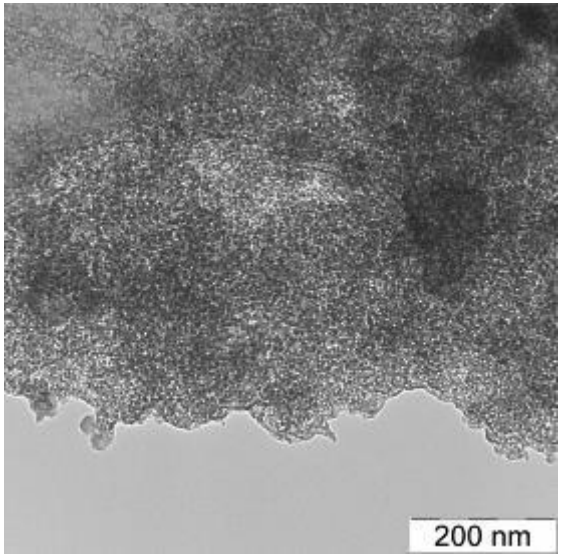


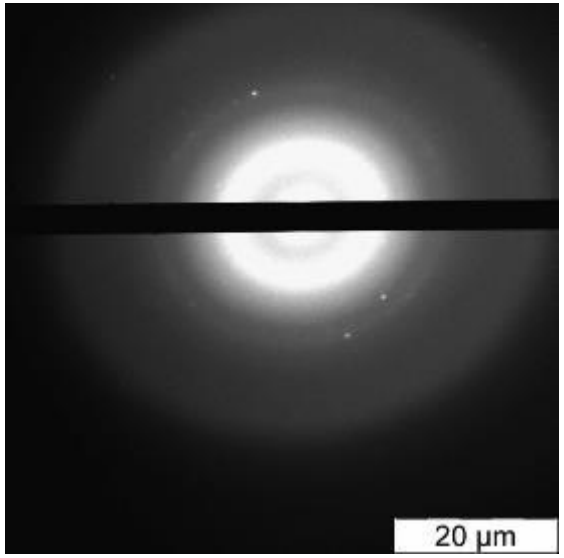


Relatively pristine nanospheres
AND
numerous nm-sized particles with
high Z-contrast –
Pu compounds?

Partly destroyed spheres. Diffraction
shows presence of crystallites
(reprecipitated SiO_2?).
Treatment at 70 °C gives similar results

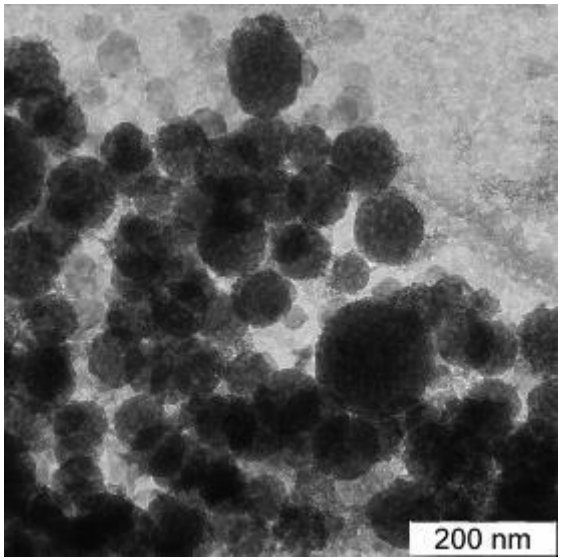
Colloids in solution with Pu(V)
12 days at 150 °C

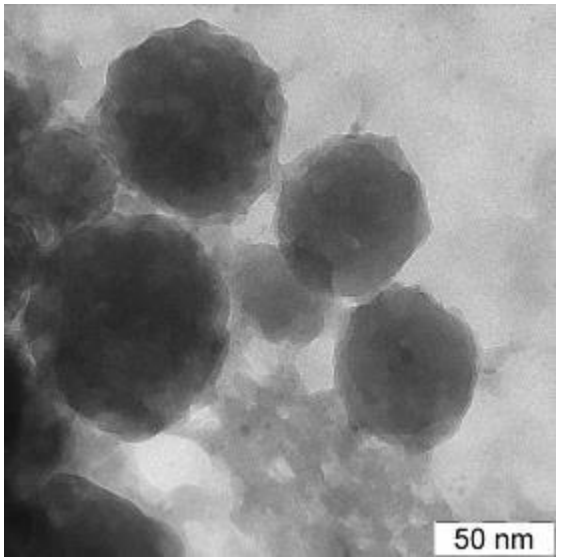




At low magnifications field of view is dominated by amorphous silica mass

Colloids in solution with Pu(V)
12 days at 150 °C



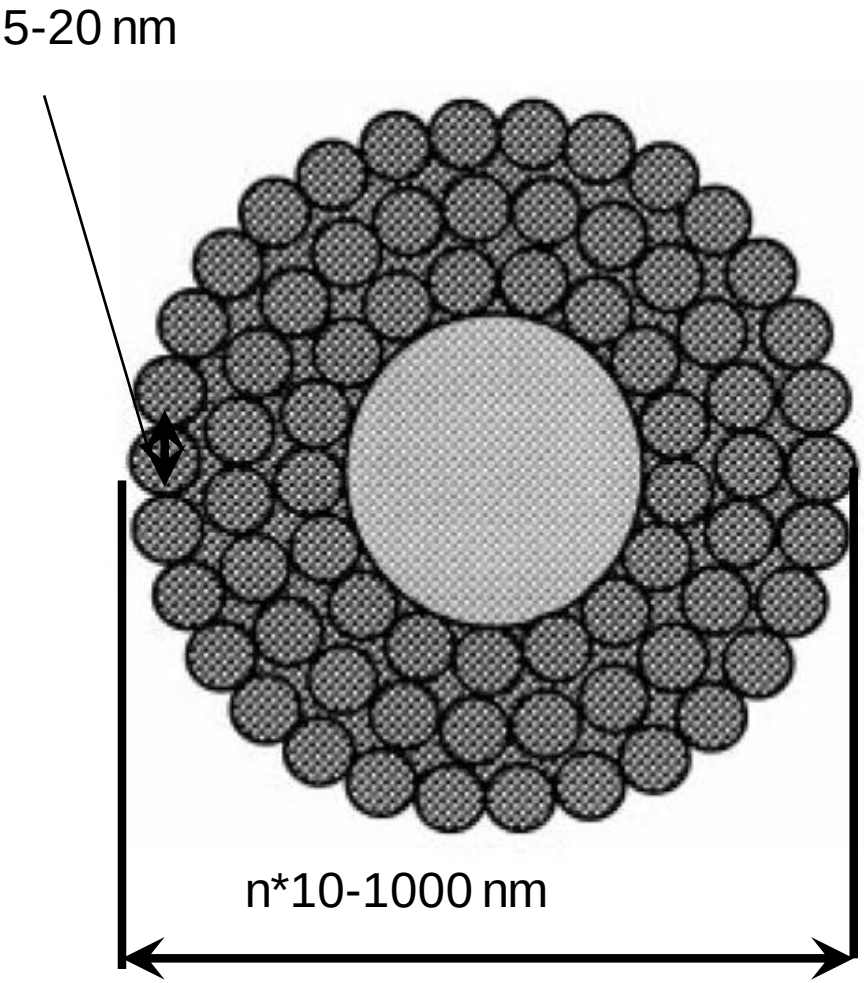


Rather small amount of degraded nanospheres is found.
Pu-rich particles are also present.

Structure of silica nanospheres

TEM (Darragh et al., 1966), positrons (Bardyshev et al., 2005, SAXS (our results) and calculations indicate that size of primary silica nanospheres may not exceed 5-20 nm. Larger particles consist of aggregates of “primaries”.

Results of our study confirm these early works: dissolution reveals internal structure.

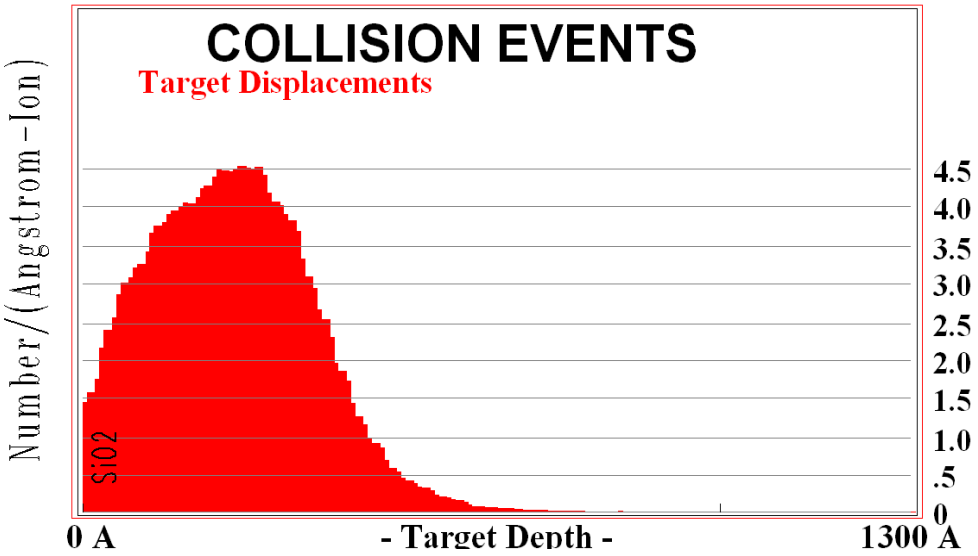


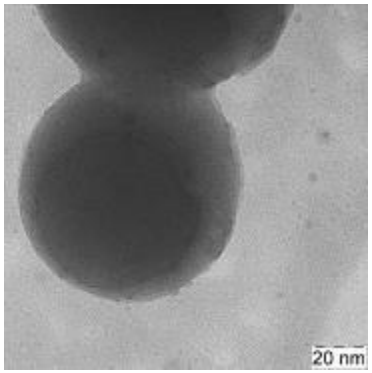
Influence of recoil atoms implantation

Recoil U from decay of a Pu ion at a nanosphere surface (normal incidence) produces ~1540 vacancies/ion (SRIM2008).

Maximum of damage is at depth of ~30 nm. This is similar to size of porous shell on partly destroyed spheres.

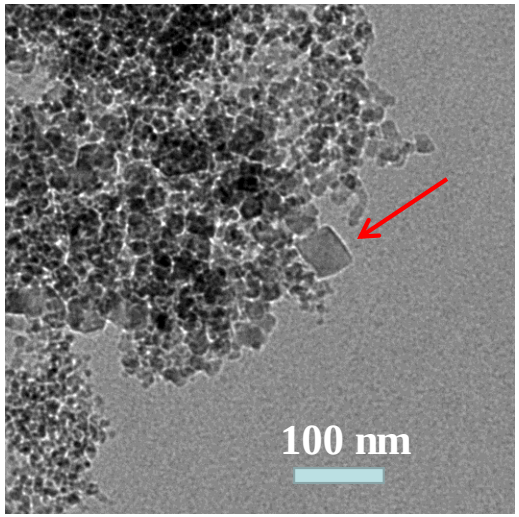
Sputtering.

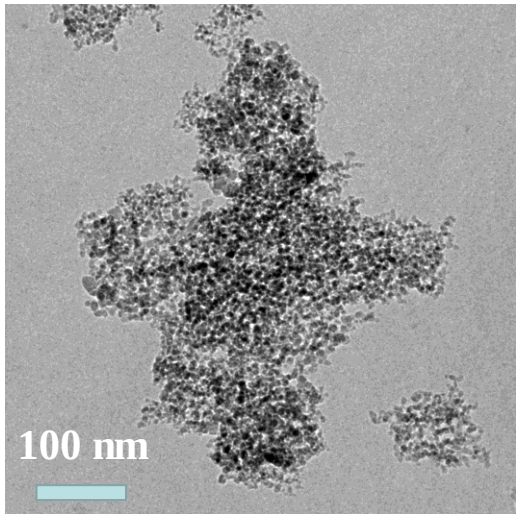




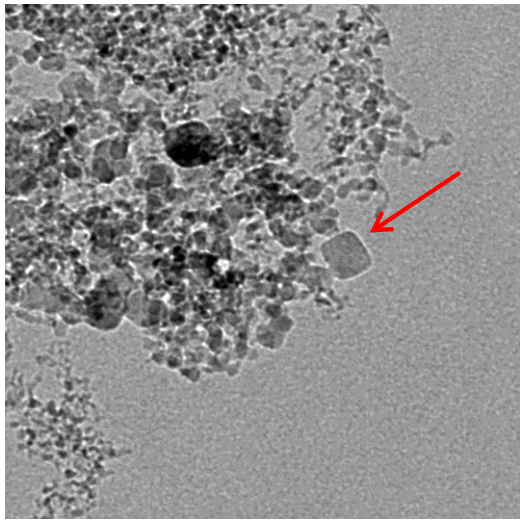
Xe implantation into nanodiamonds: *in situ* TEM

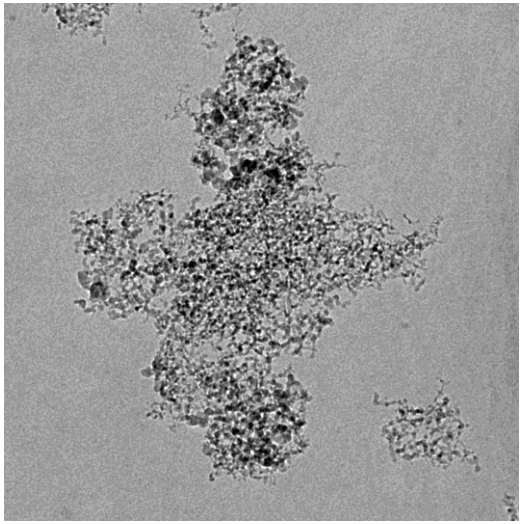
Initial state





After ~$6 \cdot 10^{14}$ Xe/cm^2 (6 keV)



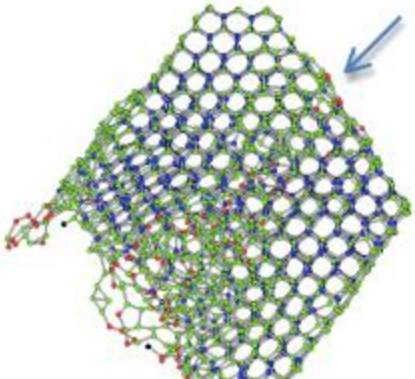


Shiryaev et al., Sci.Rep., 2018

Nanodiamonds under ion impact: molecular dynamics

1 keV Xe in 2 nm grain

6 keV Xe in 2 nm grain



At a “selected” ratio of ion energy and grain size the grains are *completely destroyed*!

Table 1. Composition of Non-radioactive and ^{238}Pu-doped glass samples

Element / Oxide	Content, wt.% (±0.02)	
	^{238}Pu-doped glass	Non-radioactive glass
SiO_2	47.86	47.71
Na_2O	14.60	14.52
B_2O_3	21.2	21.13
Al_2O_3	6.84	6.96
Eu_2O_3	3.02	3.84
CaO	5.87	5.84
PuO_2 (all isotopes)	**0.61**	-
$^{238}PuO_2$ (^{238}Pu)	0.53	-