Vibrational and raman spectroscopy of nuclear waste forms and technogenic radioactive minerals from severe nuclear accidents

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Outlook

- Nuclear cycle & Nuclear waste
- Selected examples of spectroscopic applications
- “Mineralogy” of nuclear accidents

Spectroscopy of radioactive materials:
Just a scientific curiosity?

Immobilisation of actinides – background

- 17% of electricity in the world is generated by Nuclear Power Plants (NPP).
- Average civilian NPP produces 10-12 kg of plutonium per year per MWt + several kilogramms of “minor” actinides (Am, Np, Cm) => tens of tons per year globally.
- Half-life of ^{239}Pu is 24100 years. $T_{1/2}$ ^{237}Np = 2.14 million years. “Full” decay requires 10 half-lifes…
- Plutonium and neptunium are highly dangereous due to high specific activity and are chemically toxic.
- Danger of proliferation (~6 kg of ^{239}Pu metal or ~60 kg of ^{237}Np is sufficient for a bomb…).

Immobilisation of actinides – background

<u>Activity units:</u>

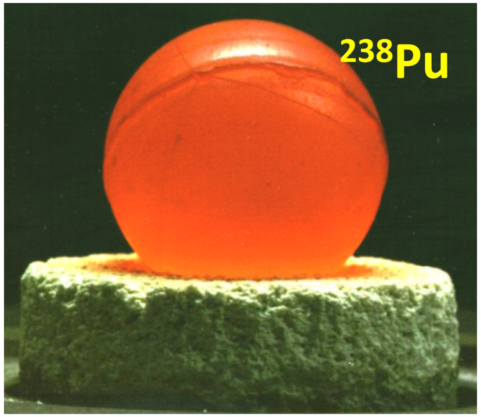
Becquerel – one decay per second - **very low activity**.

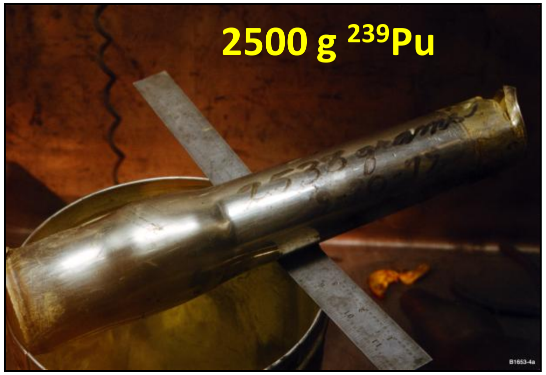
Activity of 1 gram of potassium due to ^{40}K is approx. 31 Bq.

Curie – 3.7×10^{10} decays per second – **very high activity!!!**

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)



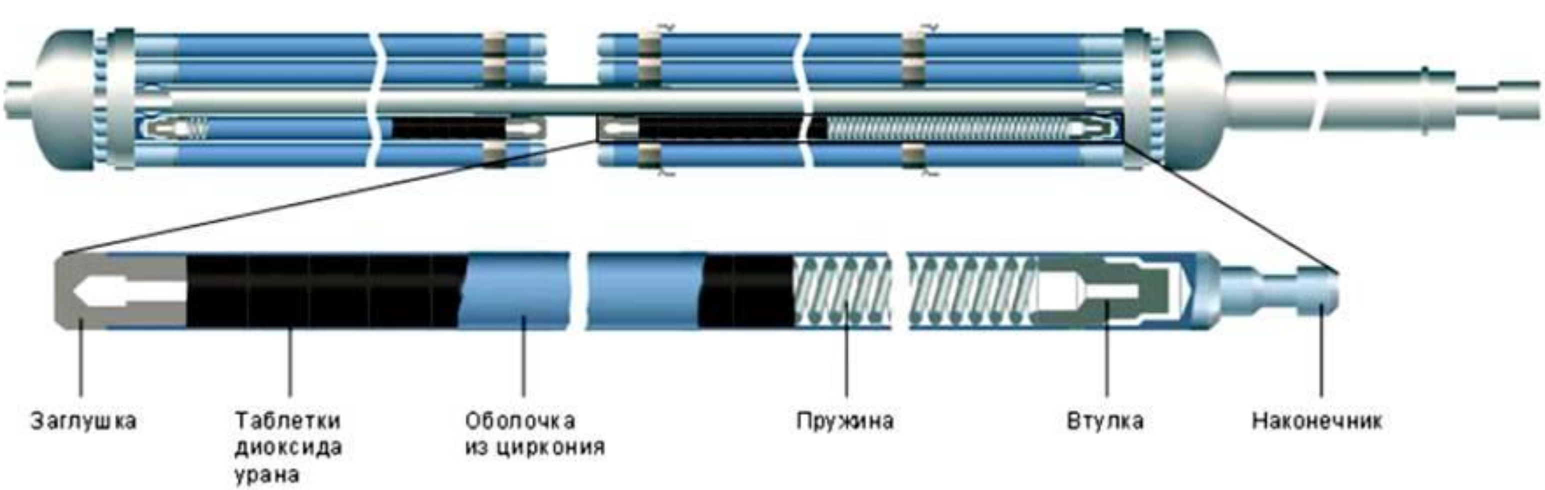


Nuclear power generation: Fuel

- UO_2 pellets. ^{235}U content varies from natural (0.7%) to 2-8%. Advantages: mature technology, high thermal conductivity, relatively low swelling, not very reactive (e.g. with water)
- Rarely: UC, UN, U metal (old reactors), U-Be…. for special purposes or experimental reactors. Unclear behaviour in operation conditions and complicated reprocessing.
- Thorium cycle (India). Waste with nasty ^{233}U. Reprocessing differs from conventional.
- MOX (Mixed Oxide) (and ReMiX)– UO_2 + 5-10% PuO_2. Potentially very promising; employed in some European and Russian reactors.

Nuclear power generation: Fuel

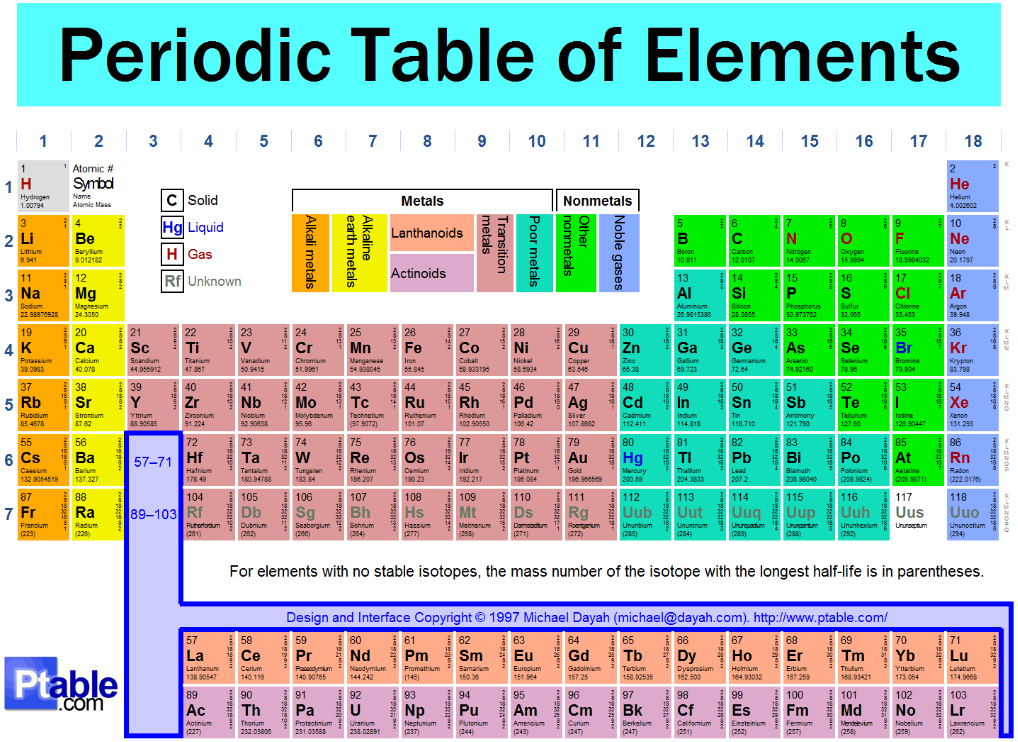
UO_2 pellets are packed into sealed fuel rods 3-6 meters long made from corrosion-resistant alloys (often Zr-Nb - zircalloy, sometimes Al-alloys; stainless steel).



Core: 86 600 kg U, 2.6% ^{235}U; critical mass 38.5 kg ^{235}U; burn-up 27 500 MWd t^{-1}; refueling 1/5 of core annually; storage pool for 125 t fuel; core volume 38 m^3.

Fuel element: UO_2 pellets, 1.43 cm diameter; 49 rods per assembly; 444 assemblies in core; enrichment 2.6% ^{235}U; Gd_2O_3 burnable poison; zircaloy cladding 0.8 mm.

' fuel (SNF)



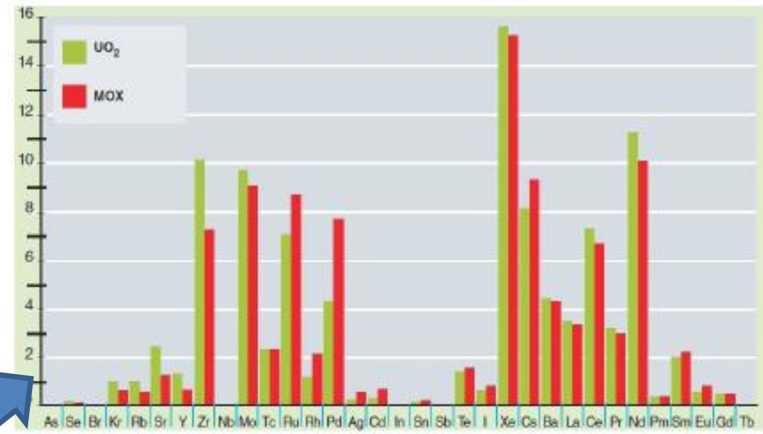


Рис. 2. Различия в составе продуктов деления (масс.%, сумма всех ПД принята за 100 масс.%) в ОЯТ UO_2 и ОЯТ $UO_2 - PuO_2$ (МОХ), выгорание 60 ГВт сутки / тонна (Nuclear Waste…, 2009).

Элемент (изотоп)	Содержание элементов при выгорании (ГВт*сут/т ТМ) Грамм на т		
	0,5	40	70
^{232}U	-	0,0015	0,004
^{235}U	6550	12500	6200
^{236}U	270	5000	7700
Np	0,5	700	1320
Pu	500	9 900	12900
Am	0,5	480	1080
Zr	66	5 240	7200
Mo	53	4 260	6400
Tc	16	1 090	1350
Sr	18	1 440	1920
Cs	68	5 120	6950
Ba	31	2 460	3490
РЗЭ + Y	220	~16 000	~23000
Σ ПД	550	~44000	~78000

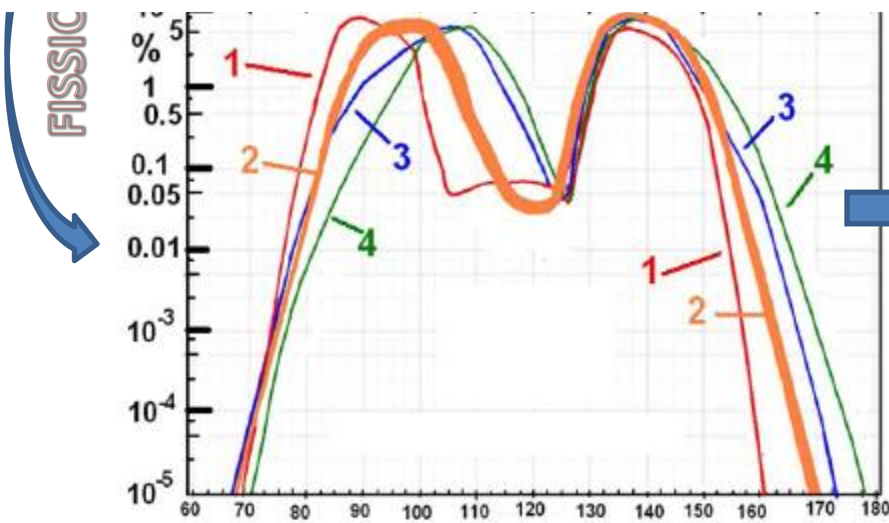


Рис. 1. Кривые распределения продуктов деления актинидов в зависимости от их масс и энергии нейтронов: 1 – ^{232}Th (быстрые нейтроны), 2 – $^{235}U + ^{238}U$ (быстрые нейтроны), 3 – ^{245}Cm (тепловые нейтроны), 4 – ^{252}Cf (спонтанное деление). Данные (The JEFF-3.1/-3.1.1…, 2009).

At average burn-up SNF contain approx. 35 kg of fission products (partly gaseous) per ton of U

Handling of Spent Nuclear Fuel

- Irradiated fuel rods are physically chopped into pieces and dissolved in concentrated nitric acid.
- U and Pu could be extracted chemically with ~99% yield (e.g. PUREX-process).
- Some extraction processes may remove minor actinides (Np, Am, Cm…). Room for further work…

Chemical composition of vitrified waste (wt.%)

Waste composition:
Major Fe, Al, Na, U (~12 wt.%) and minor Sr;
corrosion products (Cr, Mn, Co, Ni, Zr);
process contaminants (Si, P, S, F, Cl, etc.).

Oxides	Waste	Frit 320	S1-45		S2-50		S3-55		S4-60		S5-65	
			T	V	T	V	T	V	T	V	T	V
Li_2O	-	8.00	4.40	nd	4.00	nd	3.60	nd	3.20	nd	2.80	nd
B_2O_3	-	8.00	4.40	nd	4.00	nd	3.60	nd	3.20	nd	2.80	nd
Na_2O	12.08	12.00	12.04	11.86	12.04	12.00	12.04	11.53	12.05	13.61	12.05	14.11
MgO	0.24	-	0.11	0.47	0.12	0.84	0.13	0.87	0.14	0.88	0.15	0.94
Al_2O_3	16.83	-	7.57	7.42	8.41	7.62	9.26	8.68	10.10	9.75	10.94	12.07
SiO_2	1.98	72.00	40.47	41.56	37.01	38.25	33.47	35.80	30.00	33.34	26.48	32.65
CaO	3.76	-	1.69	1.66	1.88	1.88	2.07	2.16	2.25	2.78	2.44	3.01
Cr_2O_3	0.37	-	0.17	0.13	0.19	0.06	0.21	0.13	0.22	0.14	0.24	0.06
MnO	3.89	-	1.75	1.47	1.94	1.47	2.14	1.67	2.33	1.34	2.53	1.24
Fe_2O_3	42.26	-	19.02	16.91	21.14	18.26	23.24	20.04	25.36	15.28	27.46	12.61
NiO	2.17	-	0.98	0.43	1.08	0.23	1.19	0.21	1.30	0.18	1.41	0.10
CuO	0.20	-	0.09	0.15	0.10	0.18	0.11	0.18	0.12	0.30	0.13	0.17
ZnO	0.39	-	0.18	0.22	0.19	0.12	0.21	0.28	0.23	0.25	0.25	0.12
ZrO_2	0.79	-	0.35	0.38	0.39	0.42	0.43	0.23	0.47	0.56	0.51	0.13
U_3O_8	11.75	-	5.29	5.22	5.87	5.89	6.46	6.55	7.05	7.35	7.64	8.61
Others*	3.29		1.49	2.94	1.64	4.71	1.84	4.61	1.98	4.78	2.17	4.20
Total	100.0	100.0	100.0	90.82	100.0	91.93	100.0	92.99	100.0	90.54	100.0	90.02
WL, wt.%			45		50		55		60		65	

T – target composition, V – vitreous phase composition, WL – waste loading, nd – not determined, * F,Cl, P_2O_5, SO_3, SrO, Cs_2O, PbO, REEs, actinides.

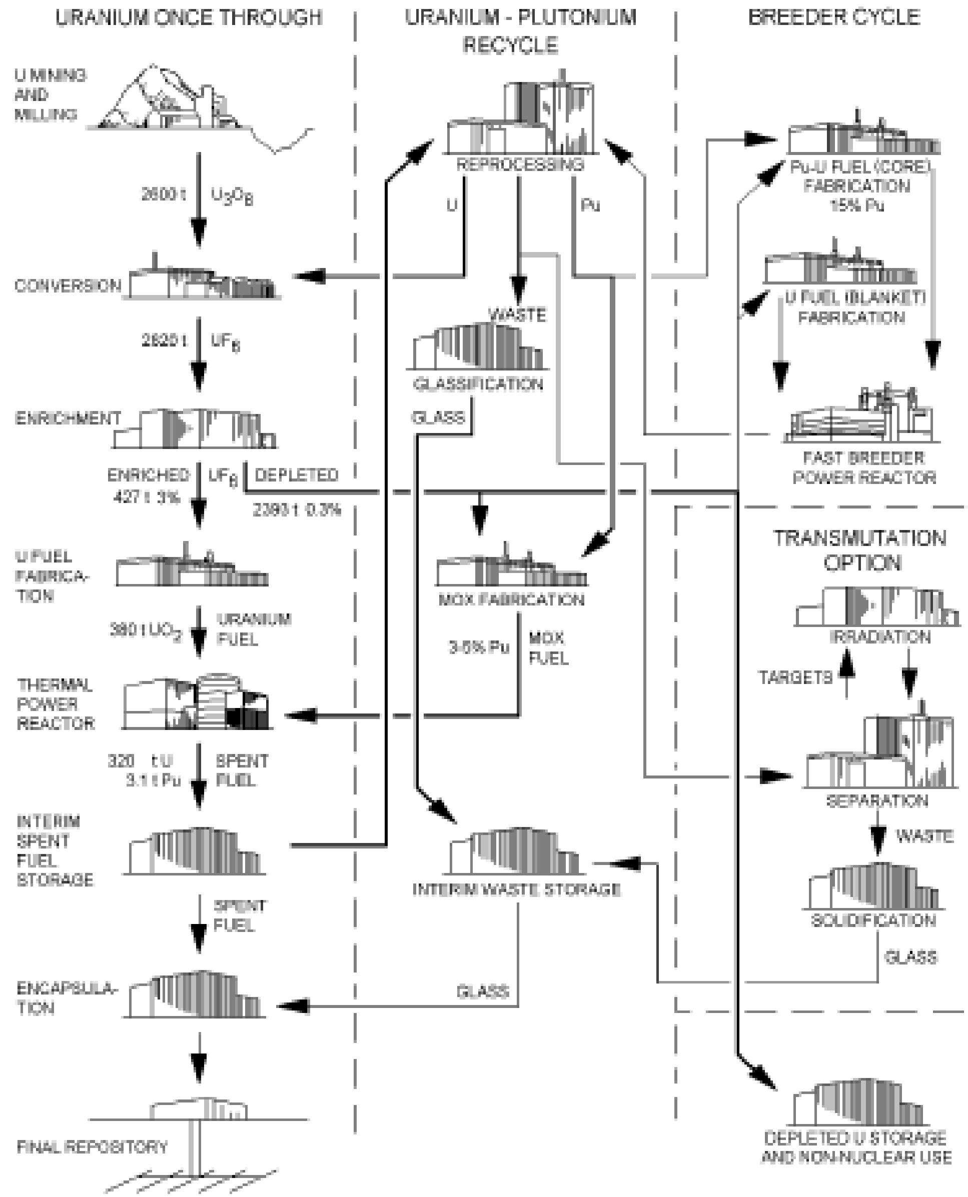
Open and closed cycles

Due to accumulation of neutron absorbers (neutron poisons), swelling, cracking etc. only 3-5% of U contained in fuel can be used in one campaign. This fraction can be increased by use of higher ^{235}U enrichment or MOX.

Fuel rods are removed from reactor and cooled in pools for several years.

Two principal further ways of handling SNF:

- Recycling of Pu and U with production of radioactive waste (Russia, France…)
- Disposal of SNF (USA…)



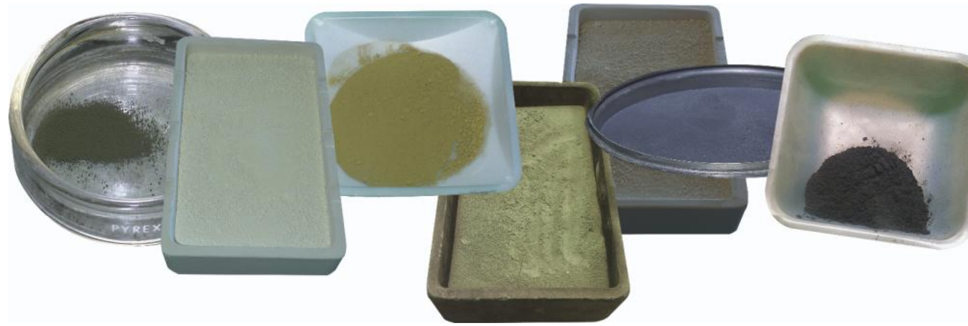
Role of spectroscopy

- Fundamental physics/materials science
- Understanding of structural peculiarities of the forms
- Non-destructive measurements (attention to sample heating)
- Possibility of investigation of very small samples and/or high spatial resolution
- Environmental studies of highly diluted actinides

Actinide Oxygen Systems (from talk by Prof. D.L. Clark)

- Deceptively simple formula (AnO_2) and cubic structure masks an incredibly complex behavior

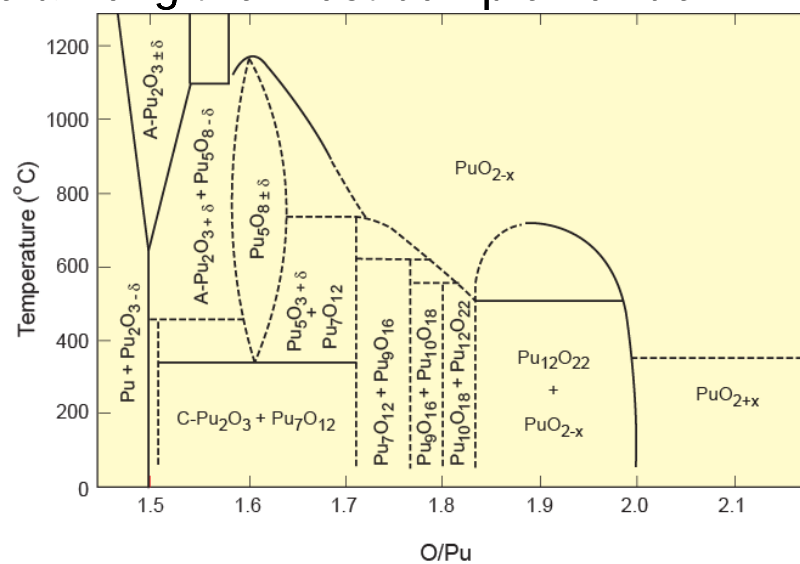
- Due to multiplicity of oxidation states (III-VI), actinides are prone to formation of nonstoichiometric systems – PuO_{2+x}



Clark, et al *Chem Act Transact Elements*, **2006**, *813*

- Uranium and plutonium oxygen systems are among the most complex oxide systems known

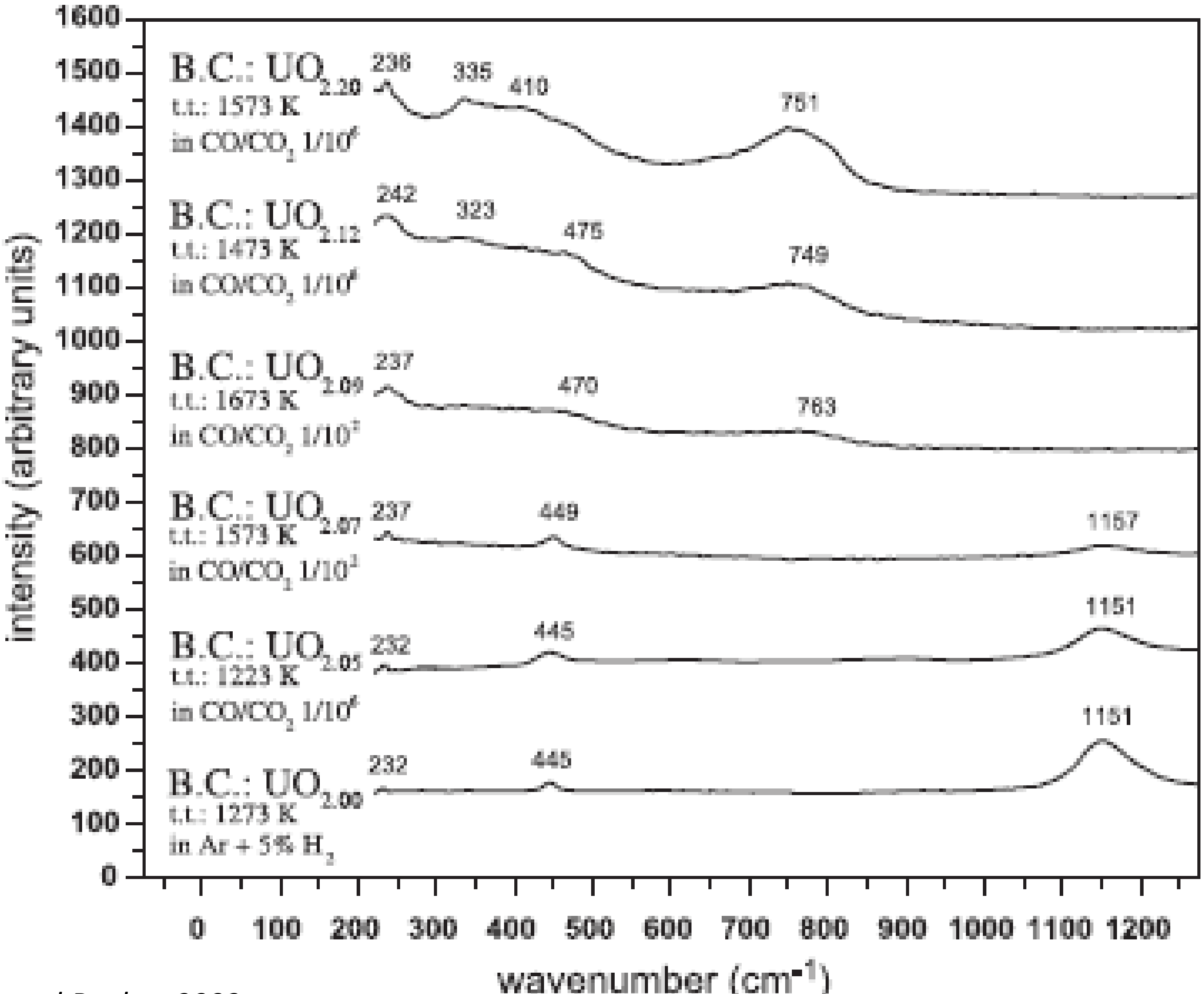
Edelstein, et al *Chem Act Transact Elements*, **2006**, *1753*



- Despite years of effort, the picture, including the phase diagram, is far from complete
  - discrepancies and contradictory results

- Understanding ordered $AnO_{2.0}$ is the prerequisite to understanding impure, or disordered materials found in most use scenarios

Raman of AnO_{2+x}



Manara and Renker, 2003

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.

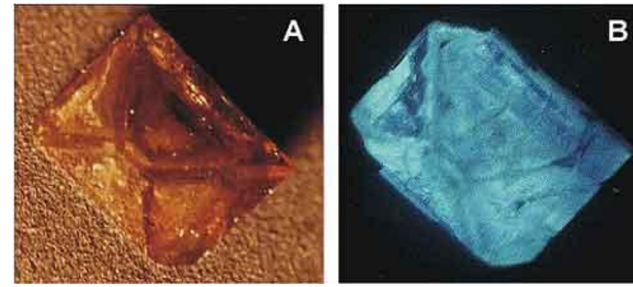
↓

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

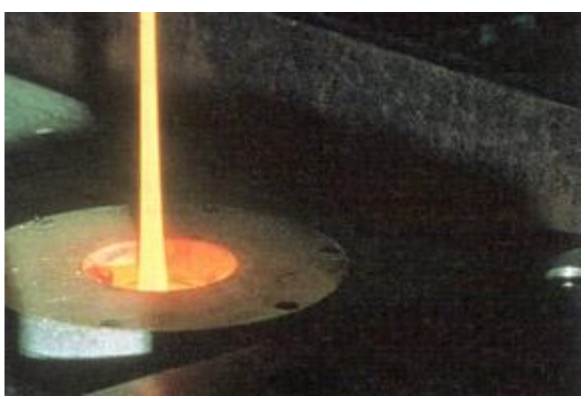
Waste separation for subsequent separate immobilisation is extremely important.

Forms for immobilisation

- Cements (for low-activity waste)
- Glasses (e.g., borosilicate, phosphate)
- Glass-ceramics
- Ceramics



Courtesy by B.Burakov



VITRIFICATION Pouring glass to immobilize radioactive waste.

Forms for immobilisation: Principal requirements

- **High capacity** for waste incorporation *without* formation of individual phases.
- Radwaste may release considerable amount of heat: a canister may be heated to 200-300 °C => **thermomechanical stability.**
- **Low leach rate** of radionuclides on contact with hot water/steam (MCC tests – 90 °C).
- **Technological feasibility**.

Glasses

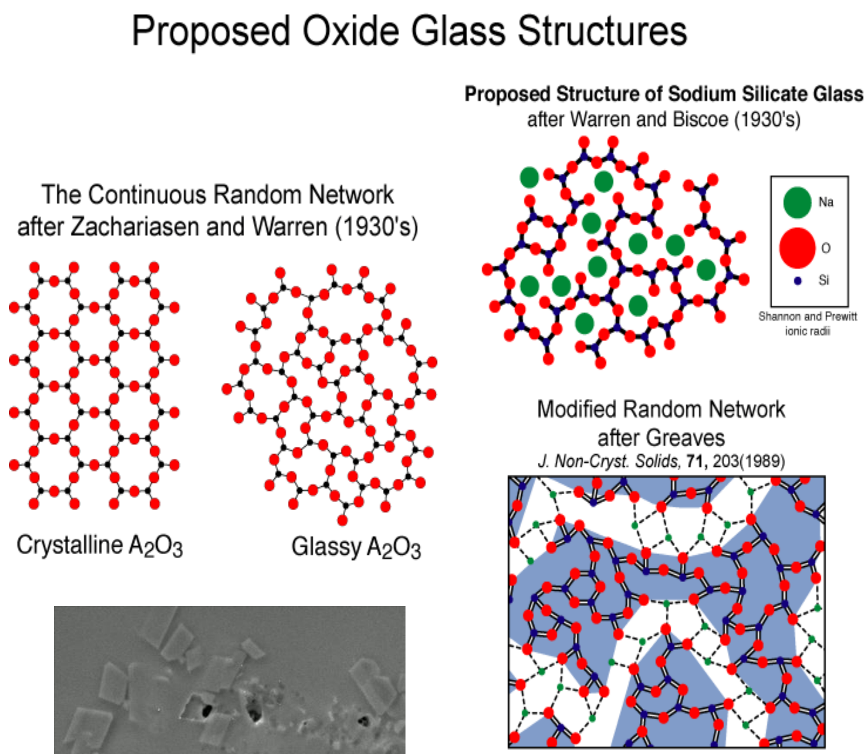
Disordered structure allows incorporation of many elements

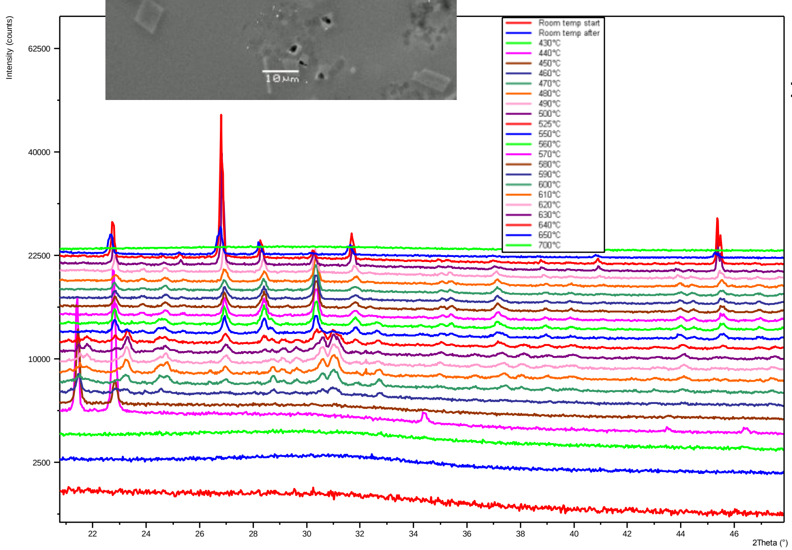
<u>Borosilicate glasses:</u>

- **<u>Advantages:</u>** rather resistant to corrosion; matured technology.
- **<u>Drawbacks:</u>** require high temperatures; limited capacity for some important waste streams (e.g., negligible solubility of Mo-Tc-Ru-Pd or alkalis).

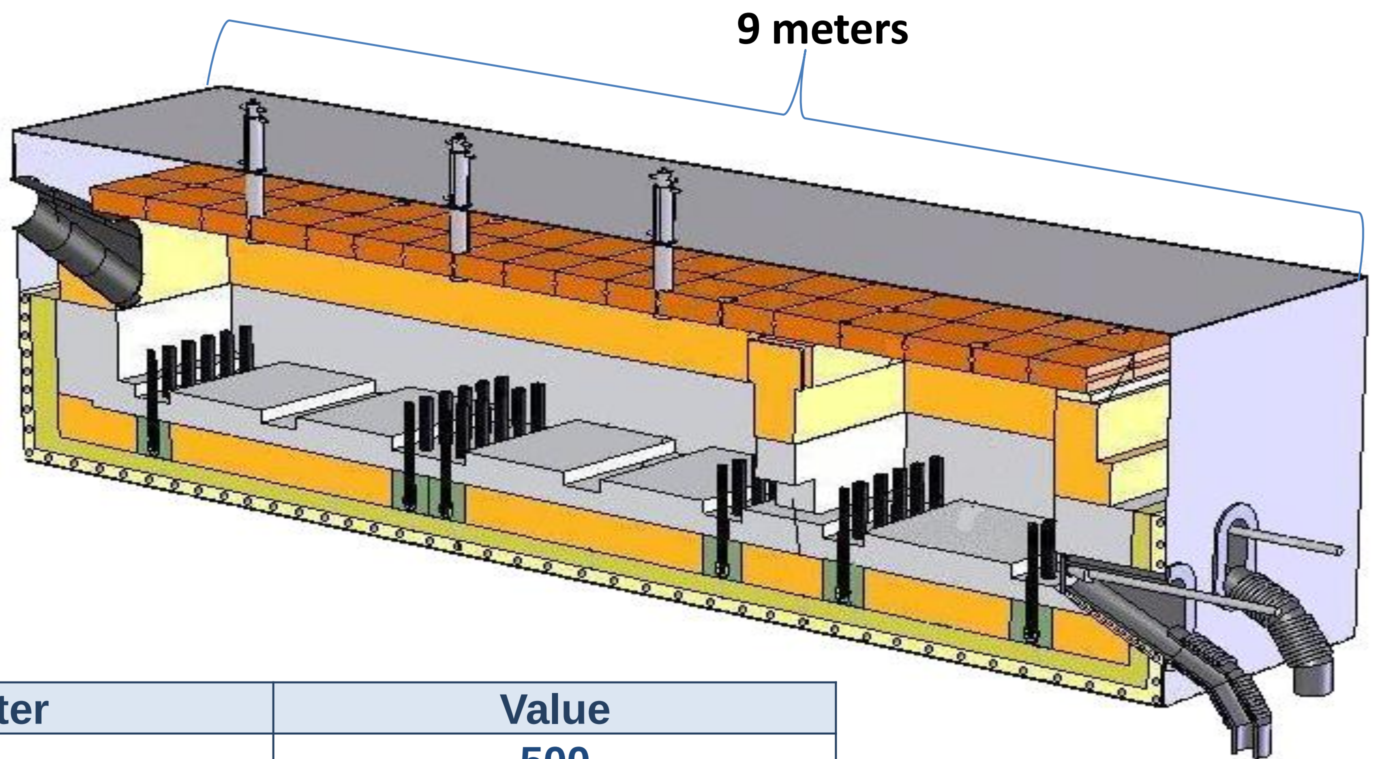
<u>Phosphate glasses:</u>

- **<u>Advantages:</u>** matured technology less sophisticated than for borosilicate glasses; easily adapted for waste composition (e.g. accepts alkaline stream).
- **<u>Drawbacks:</u>** less resistant to corrosion; devitrified at relatively low temperatures.





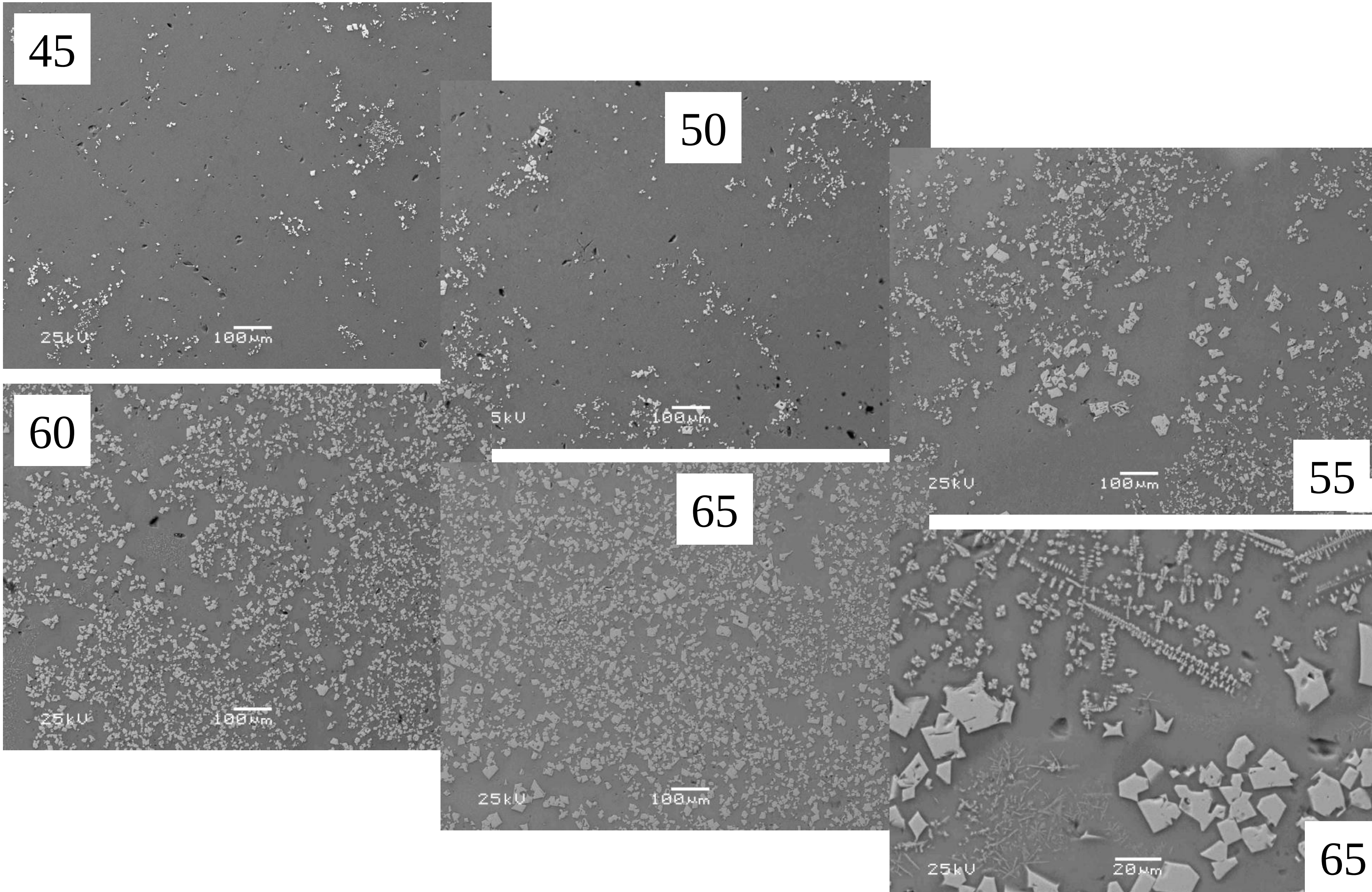
Furnace EP-500/5 (Mayak, Russia)



Parameter	Value
Initial solution l/h	**500**
Annual glass production, tons	**800**
Weight, t	**130**
Exploitation duration, years	**6**
Glass type	**alumophosphate**

Kozlov V.P.

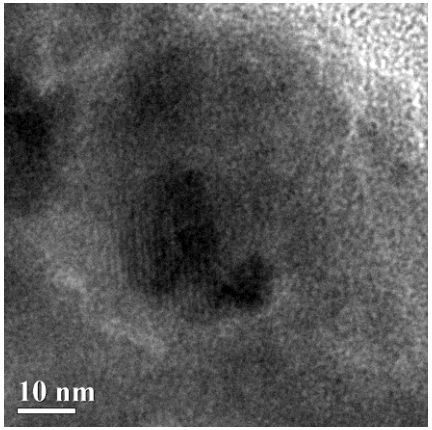
Scanning Electron Microscopy of Uranium-loaded glass

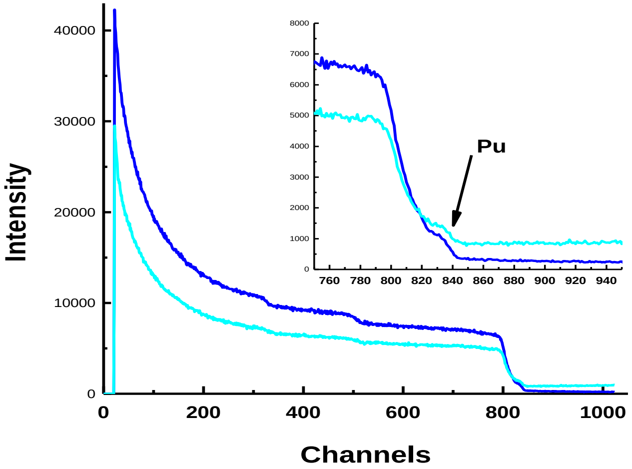


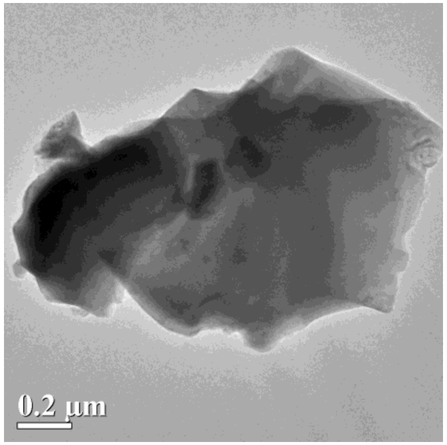
A case study:
Pu-loaded Lanthanide-Borosilicate glass

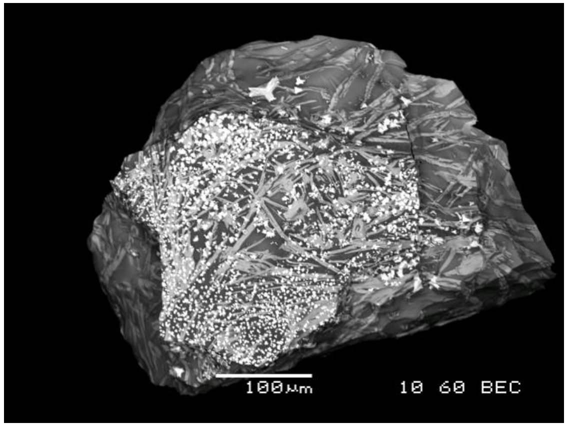
- Maximum PuO_2 concentration in conventional borosilicate glasses is ~2-3 wt.%. Lanthanide-Borosilicate (LaBS) glasses were designed to incorporate up to ~10 wt.% PuO_2 (*Strachan et al.*, 1998).
- ***Behaviour of Pu and of some other constituents in LaBS glasses and its long-term stability is still poorly constrained.***

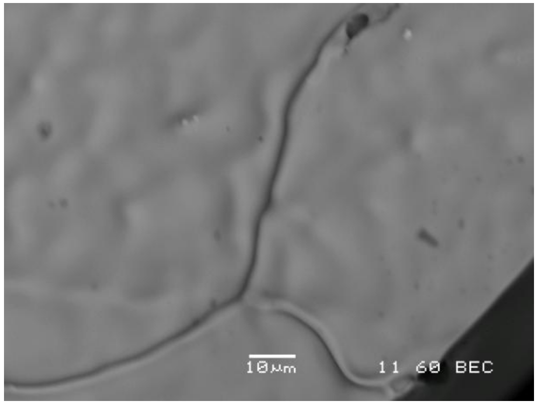
The glass seems to be homogeneous on mm-scale (RBS data), but is **markedly** heterogeneous on sub-mm scale if high PuO_2 loads are used!

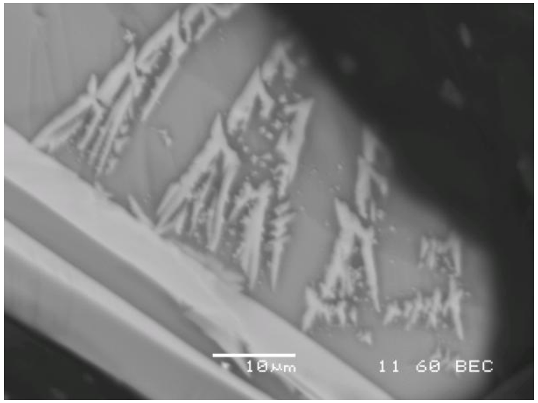




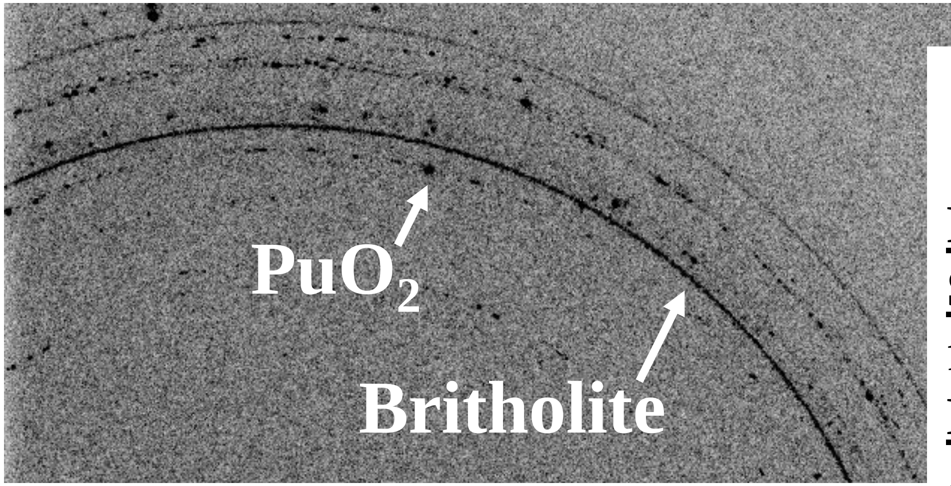






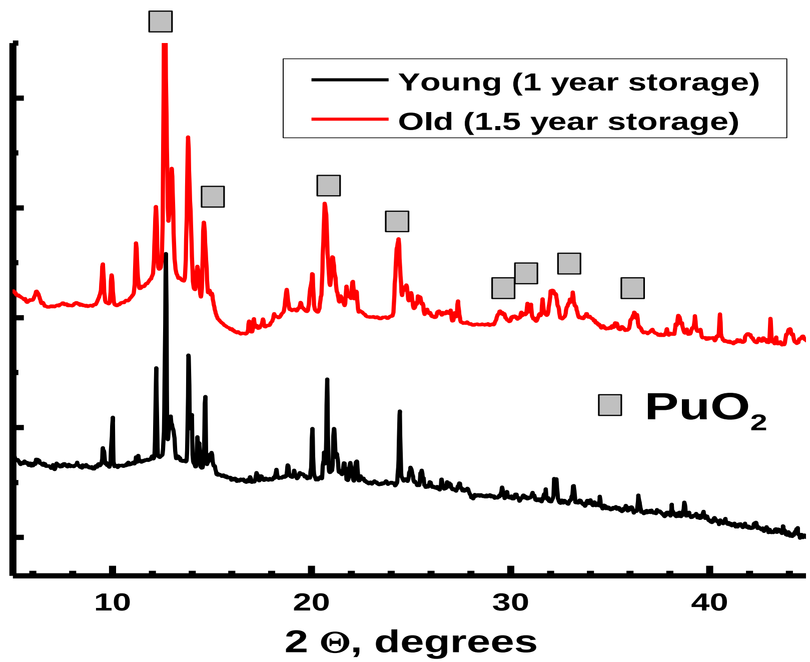


Phase composition of the LaBS glass
(9.5 wt% PuO_2)

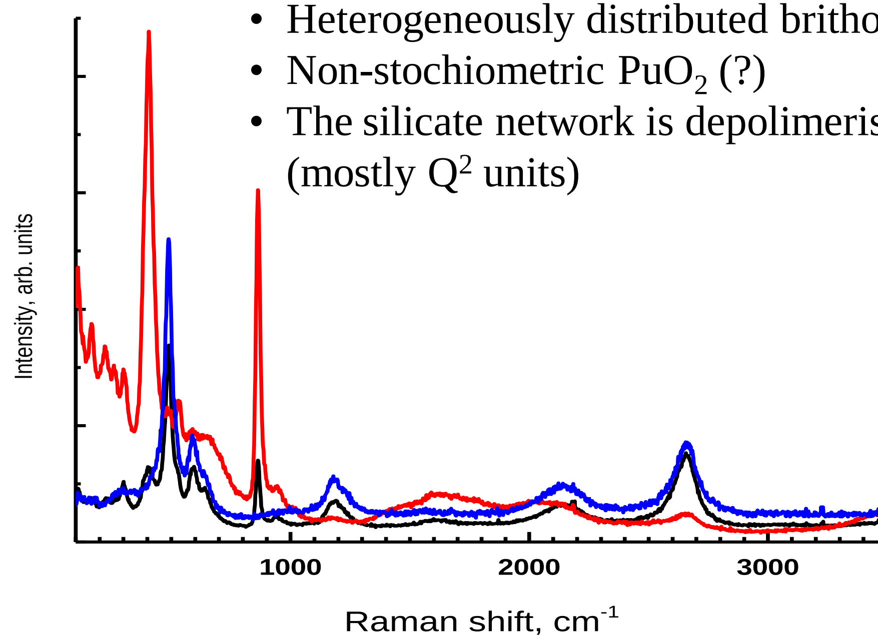


Identified phases (XRD+SEM/EDX)

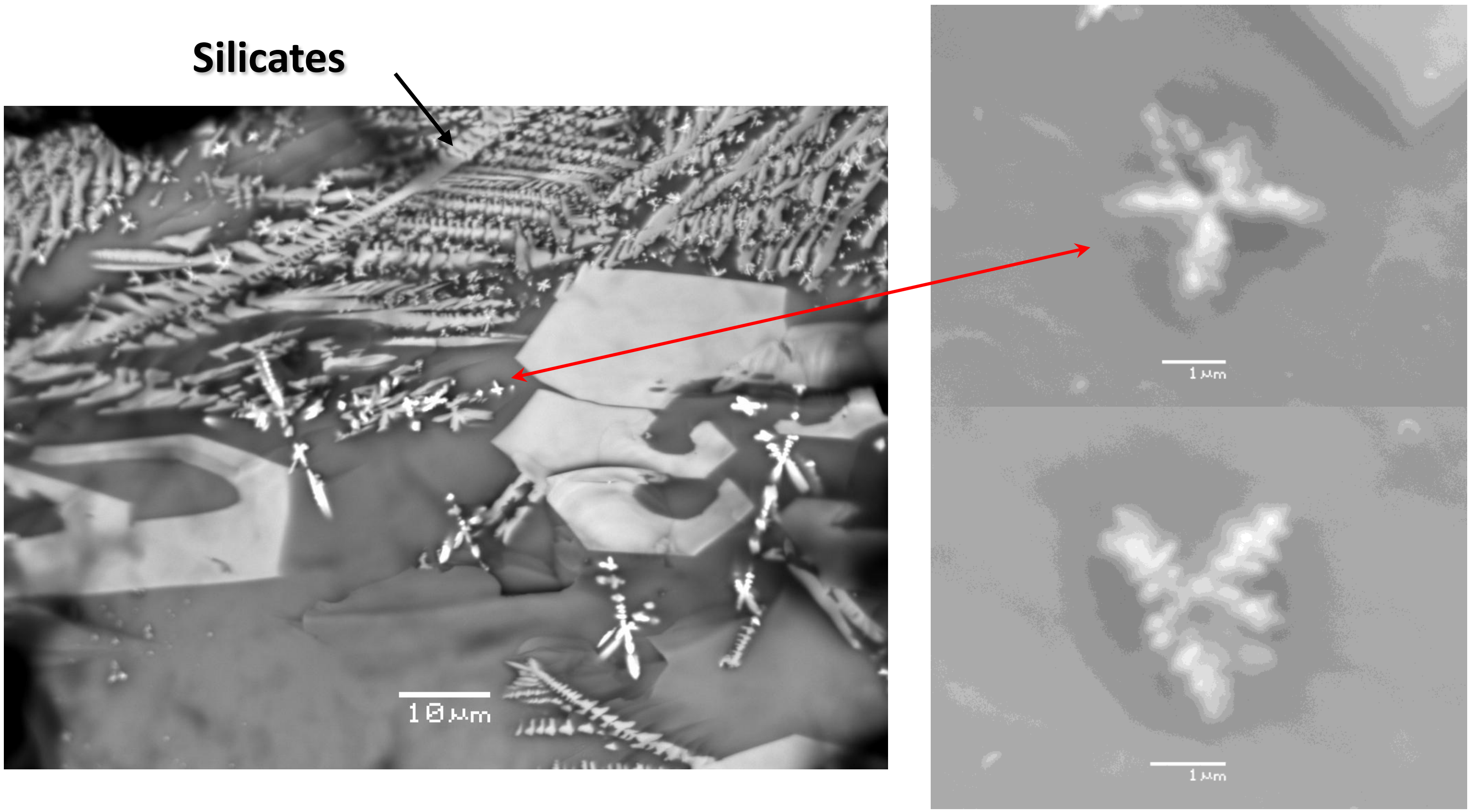
PuO_2: crystallites with sizes of >50 nm.
Solid solution of (Pu, Hf)O_2 with a fluorite structure (SEM/EDX/XRD)
Britholite: (approx. $REE_{10}Si_6O_{24}(OH)_2$) is a "real" powder.



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

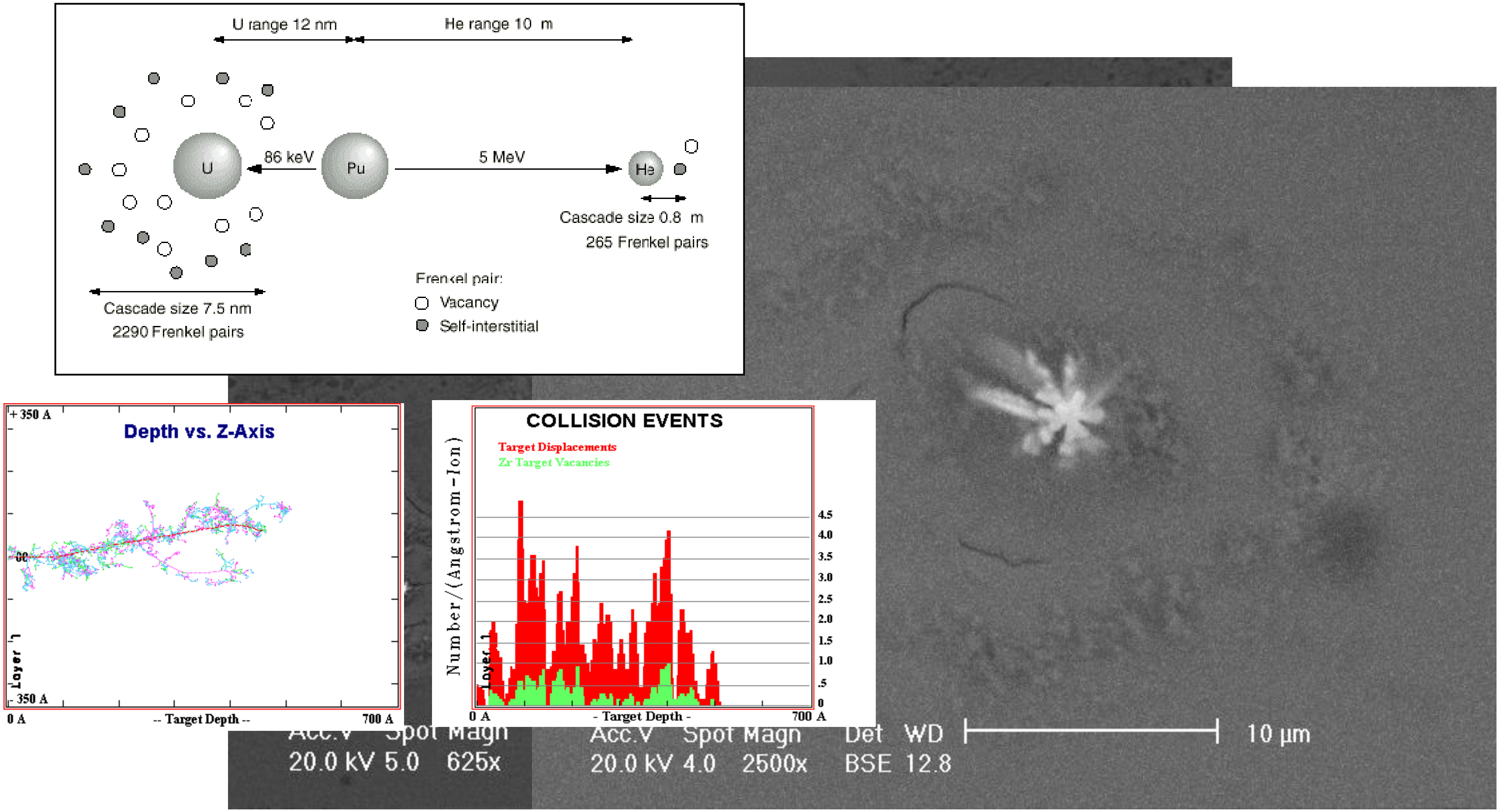


The “heavy spots”: a closer look

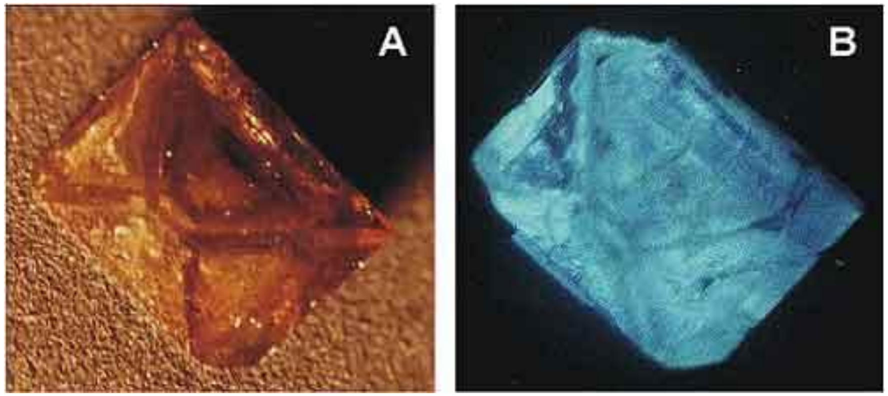


Precipitates of (Pu, Hf)O_2 solid solution and of REE-Al phase!!
Dendritic morphology consistent with CaF_2-structural type dendrites
Exsolution (rapid?) of excess PuO_2?

Alteration of Pu-rich glass



Mineral-like ceramics
Zircon as a form for actinides immobilisation



Flux-grown zircon with 6 wt% of Pu

- XANES confirms that Pu is tetravalent, i.e. most likely it substitutes Zr^{4+} in zircon lattice.

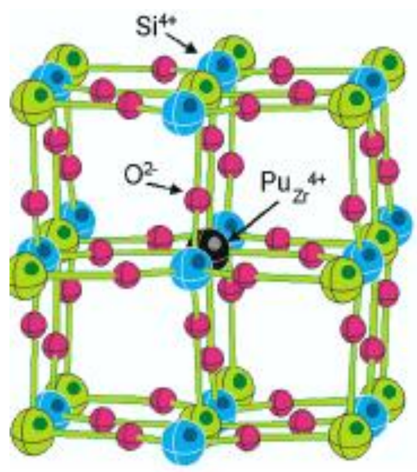
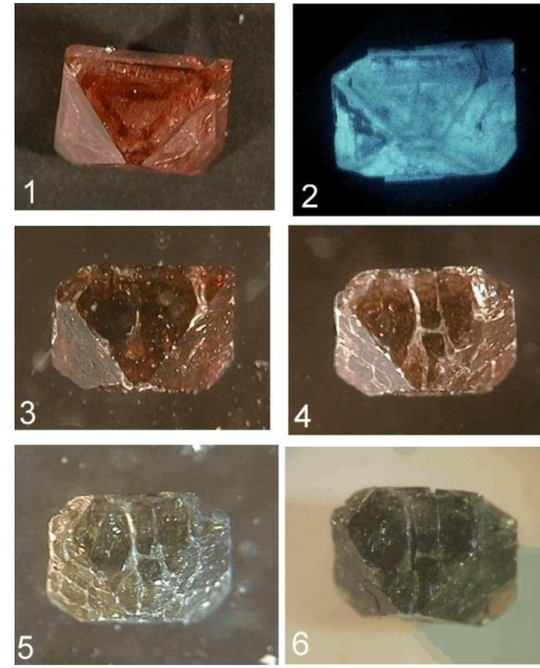


Image by R.E.Williford, PNNL

Principal problem: degradation due to self-irradiation

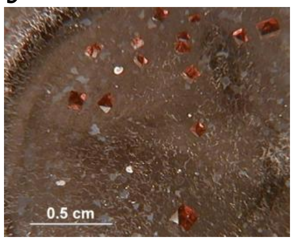
Zircon amorphises under irradiation (metamictisation). Still conflicting results on amorphisation dose and chemical resistance of metamict zircon.

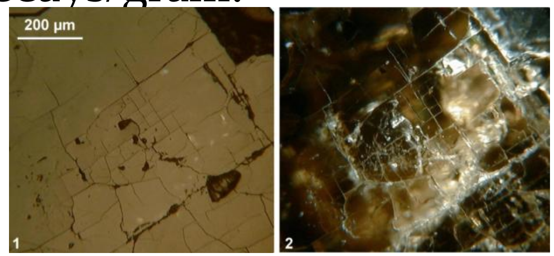
Samples



Single crystals:

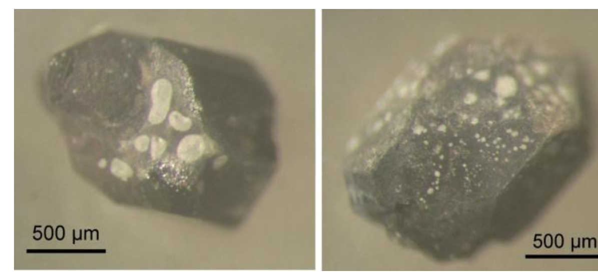
a) Zircon doped with 2.4 wt% ^{238}Pu ($T_{1/2}$ = 87.7 y), grown in July 2001. ~5x10^{17} decays/gram.





b) Eu-monazite doped with 4.9 wt% ^{238}Pu, grown in Dec. 2003. Now approx. ~1x10^{19} decays/gram.

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

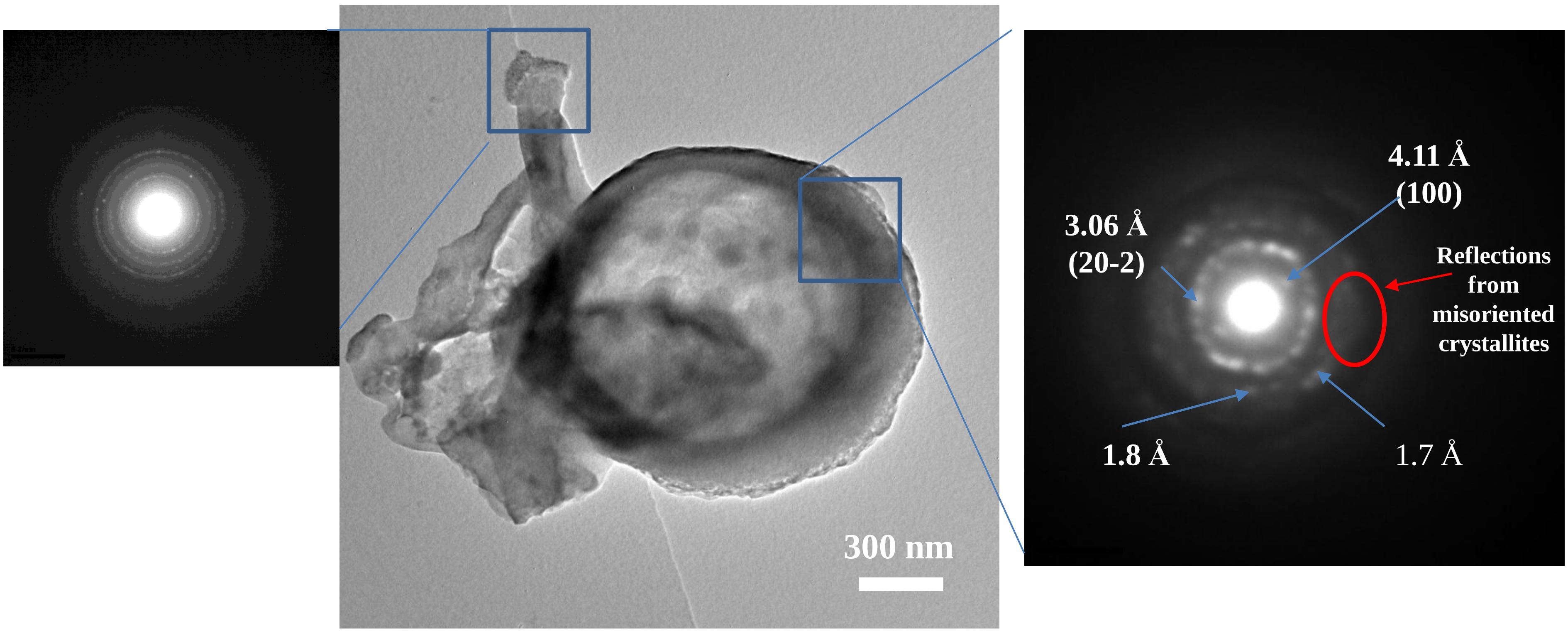


Polycrystalline ceramic:

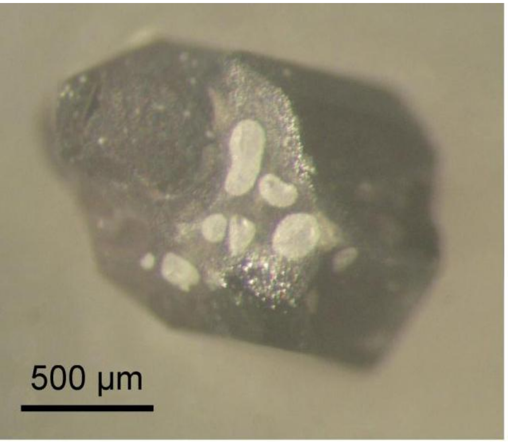
La-monazite doped with **8.1 wt.% of ^{238}Pu**. Synthesized in 2002.

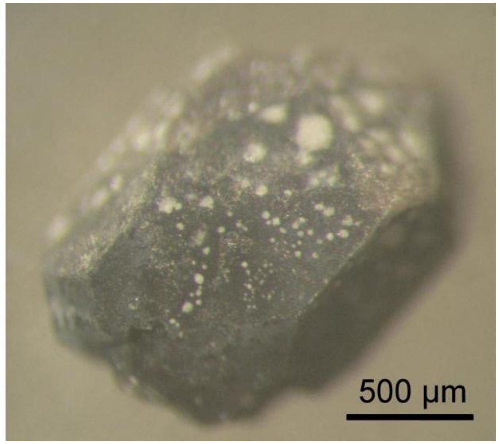
Methods: Raman, SC-XRD, XAFS, TEM

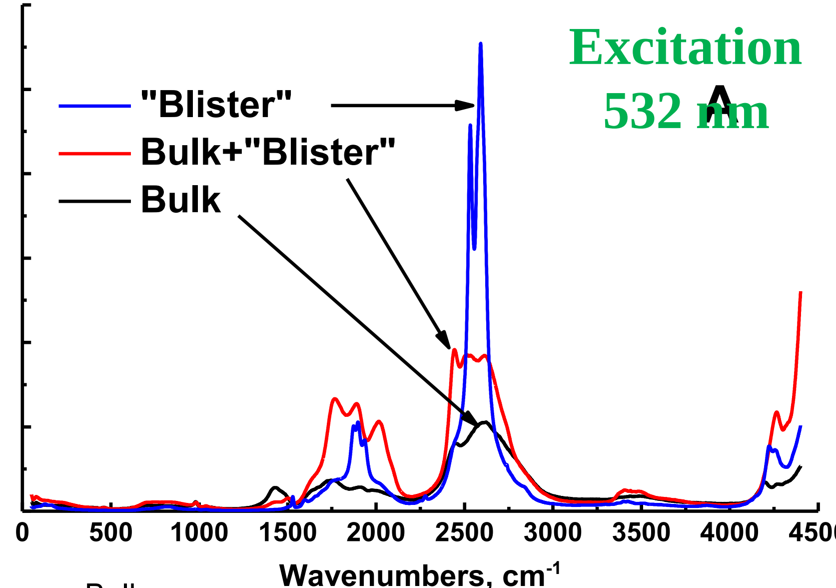
Single crystals of $Eu_{0.95}Pu_{0.05}PO_4$

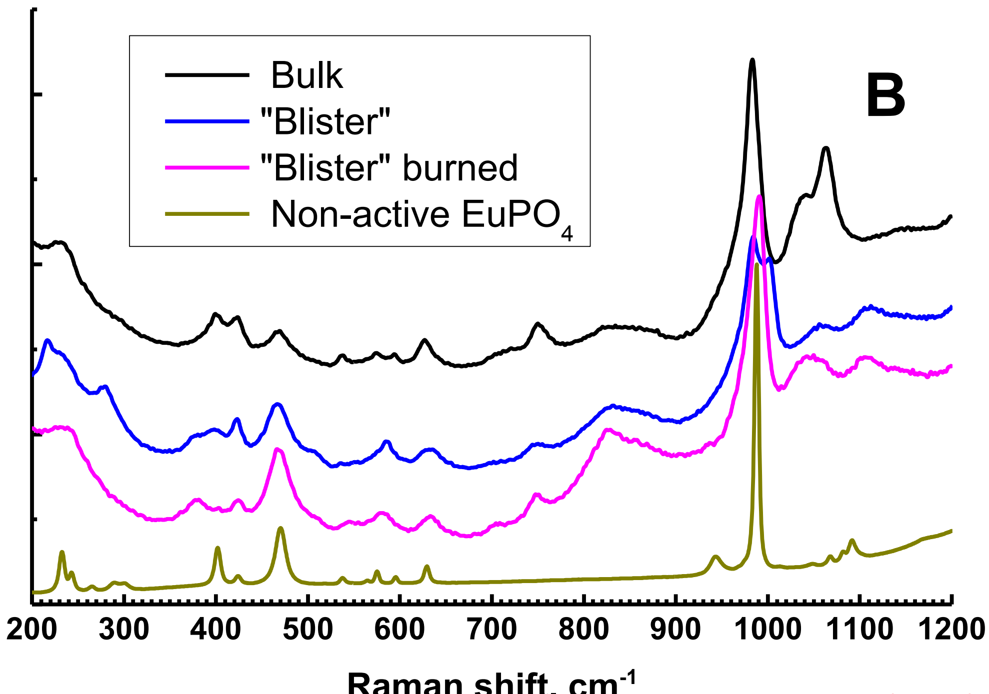


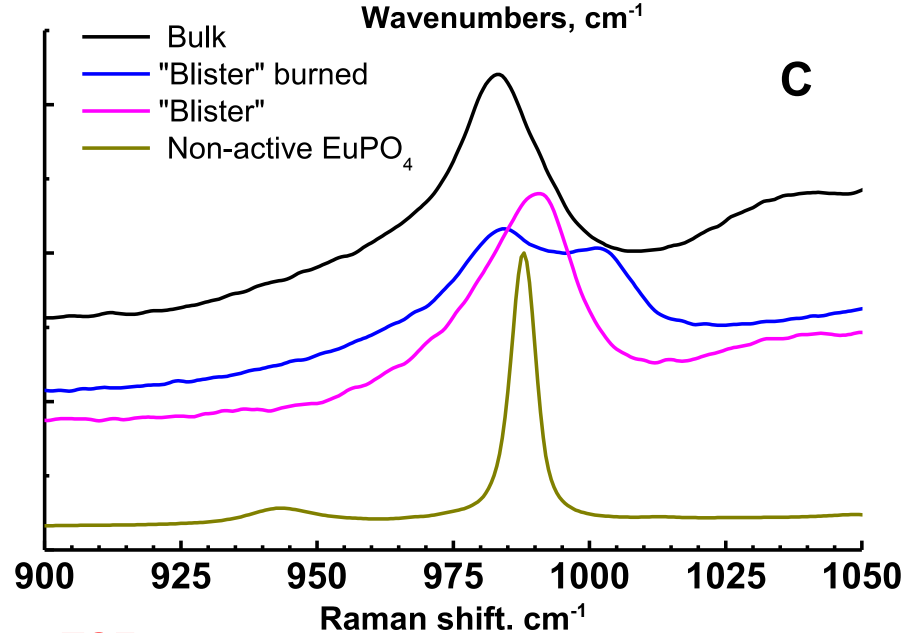
Single crystals of $Eu_{0.95}Pu_{0.05}PO_4$











Excitation 785 nm

Environmental studies

Pu/Am Soil Contamination – 903 Pad (from talk by Prof. D.L. Clark)

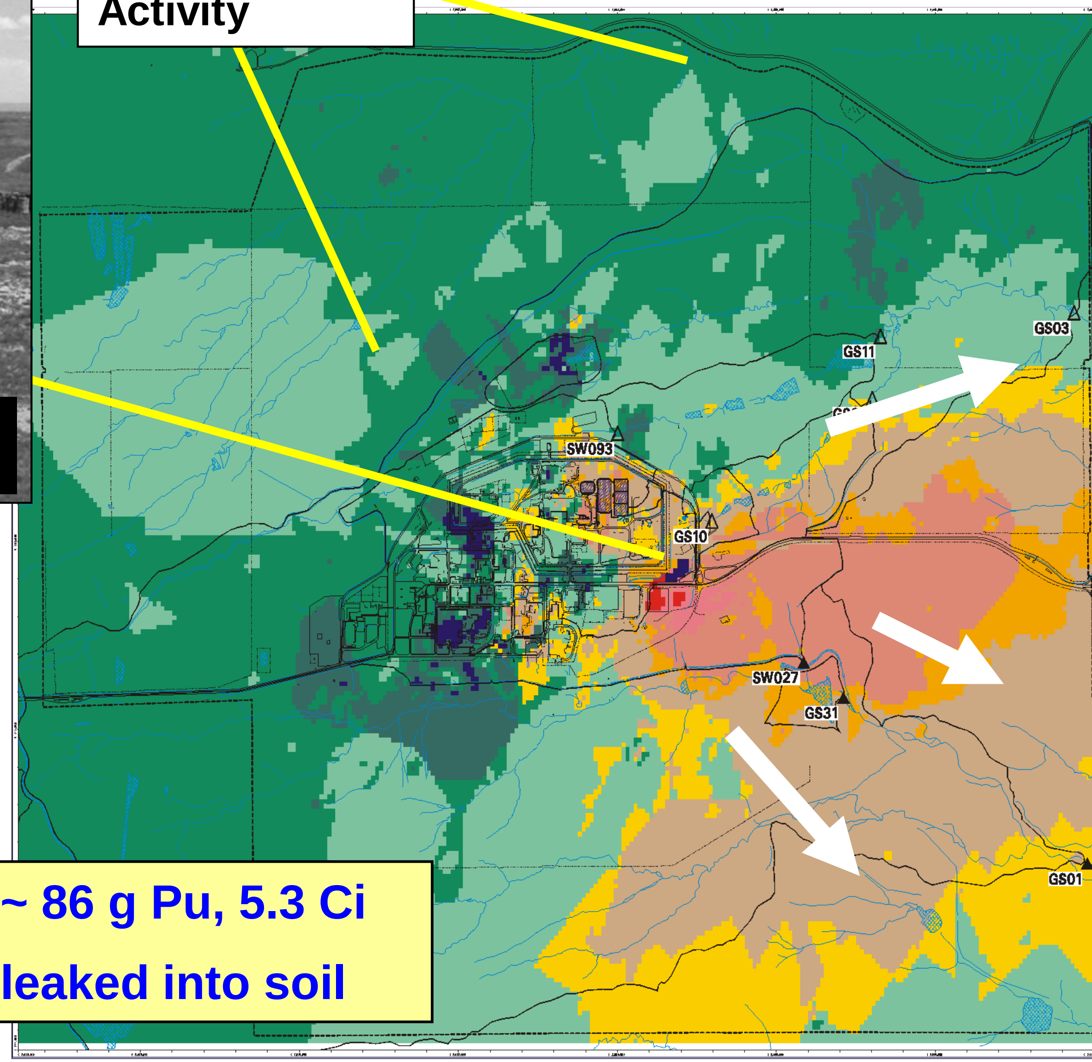
wind & rain spread Pu/Am-contaminated soils to east & southeast

Legend

Red	> 1000 pCi/g
Pink	1000 – 100 pCi/g
Pink’	100 – 10 pCi/g
Orange	10 – 5 pCi/g
Brown	5 – 1 pCi/g

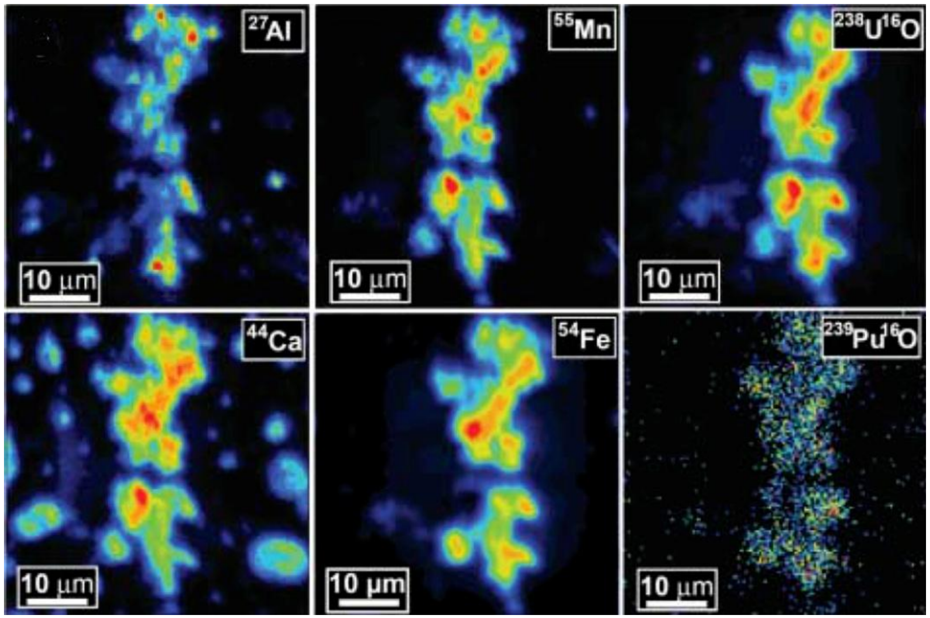
RFCA : 0.15 pCi/L

“Background” Activity

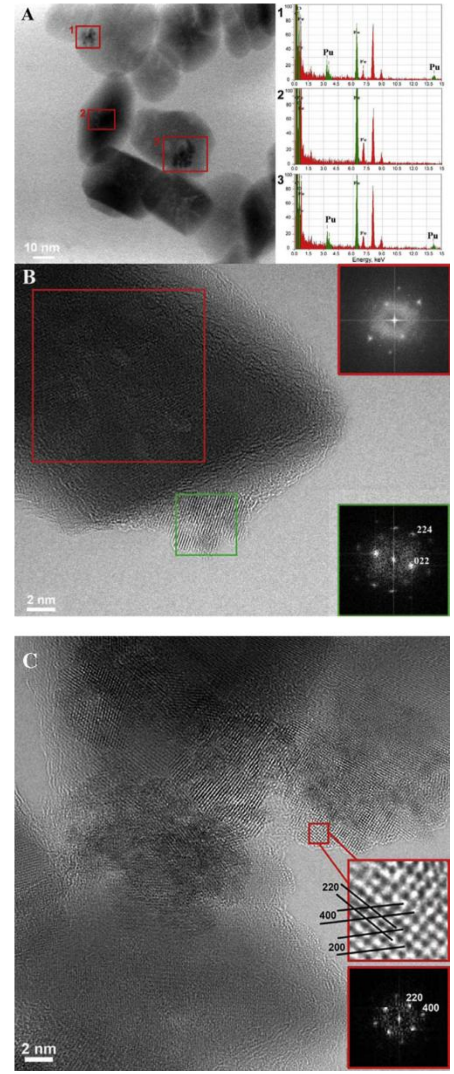


~ 86 g Pu, 5.3 Ci leaked into soil

Environmental studies
Colloids-assisted transport of actinides

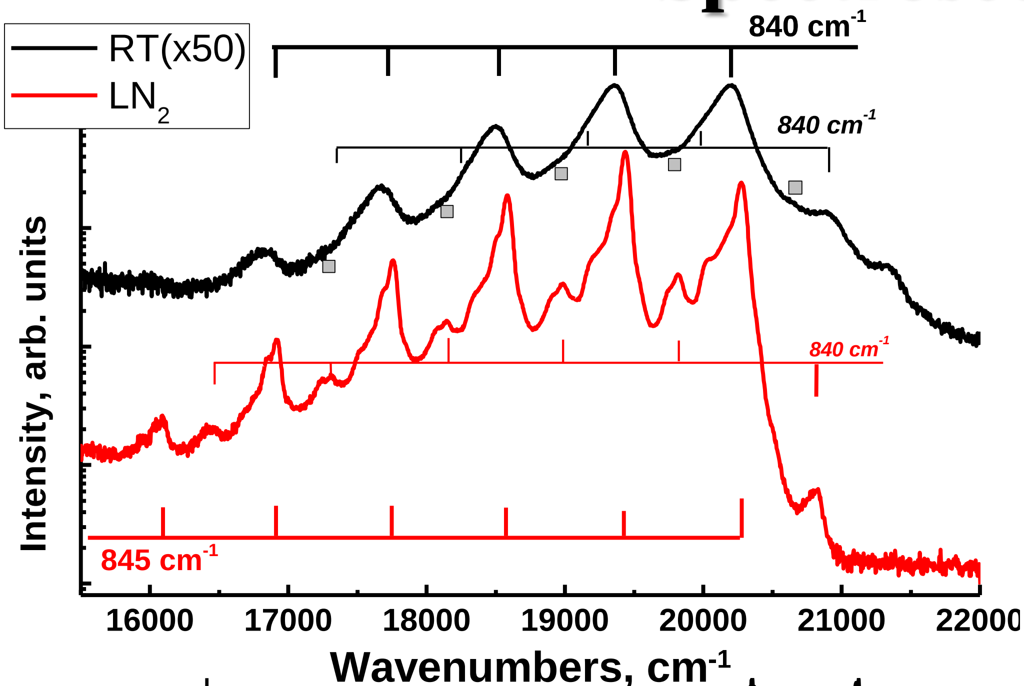


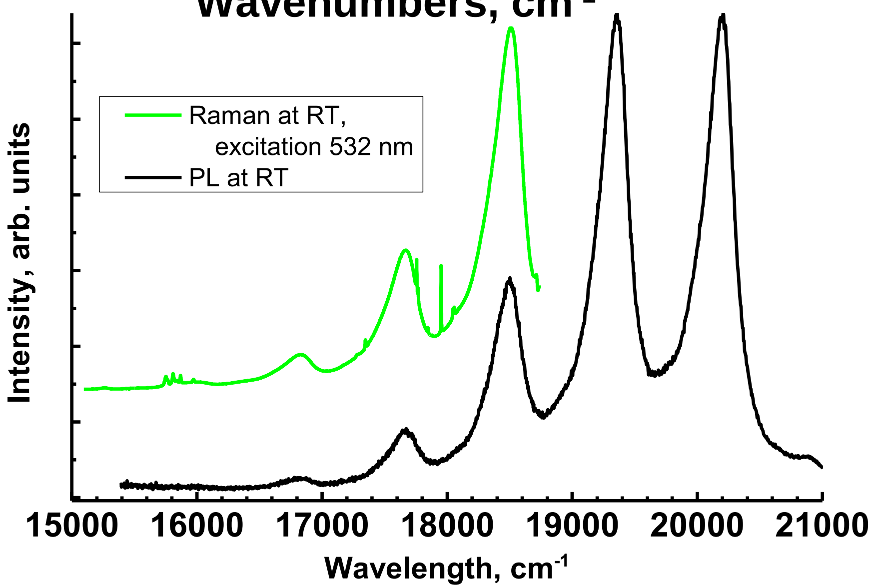
- Novikov A.P., Kalmykov S.N., et al., Colloid Transport of Plutonium in the Far-Field of the Mayak Production Association, Russia. Science, 2006, 314, 638-641
- Kersting et al., 1999



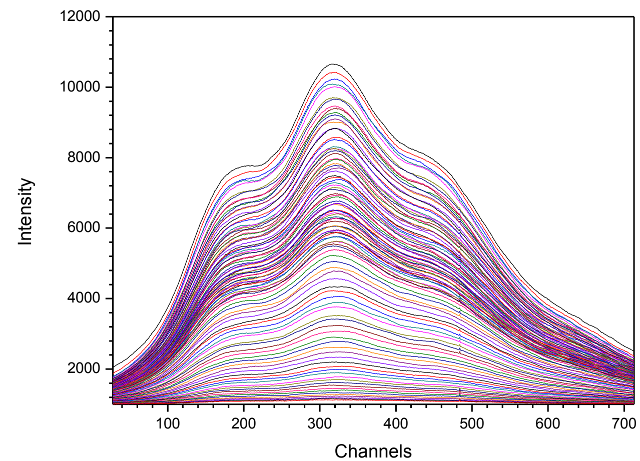
Romanchuk et al., GCA, 2014

Colloids-assisted transport of actinides: Spectroscopy

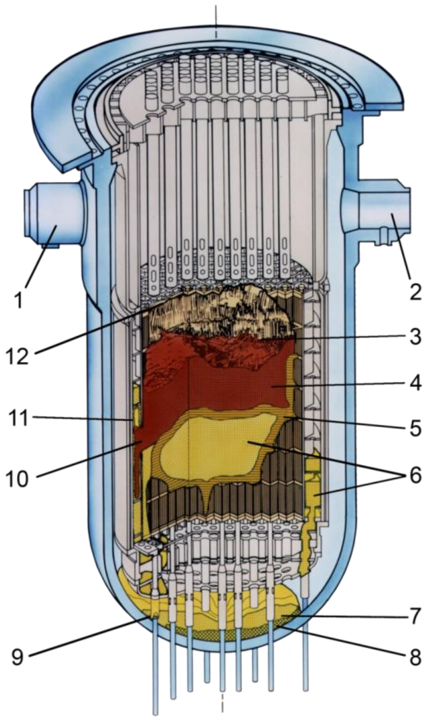




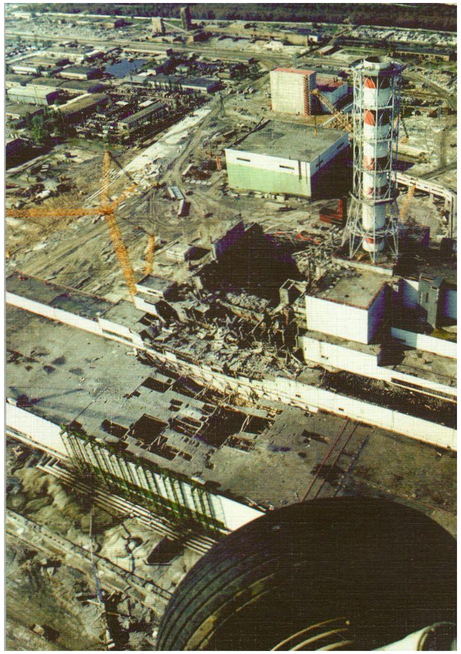
U(VI), Pu and Cm possess bright and characteristic fluoresence.
Time-resolved life-time fluorescence (TRLIFS) is widely used for examination of actinides species.



Nuclear accidents



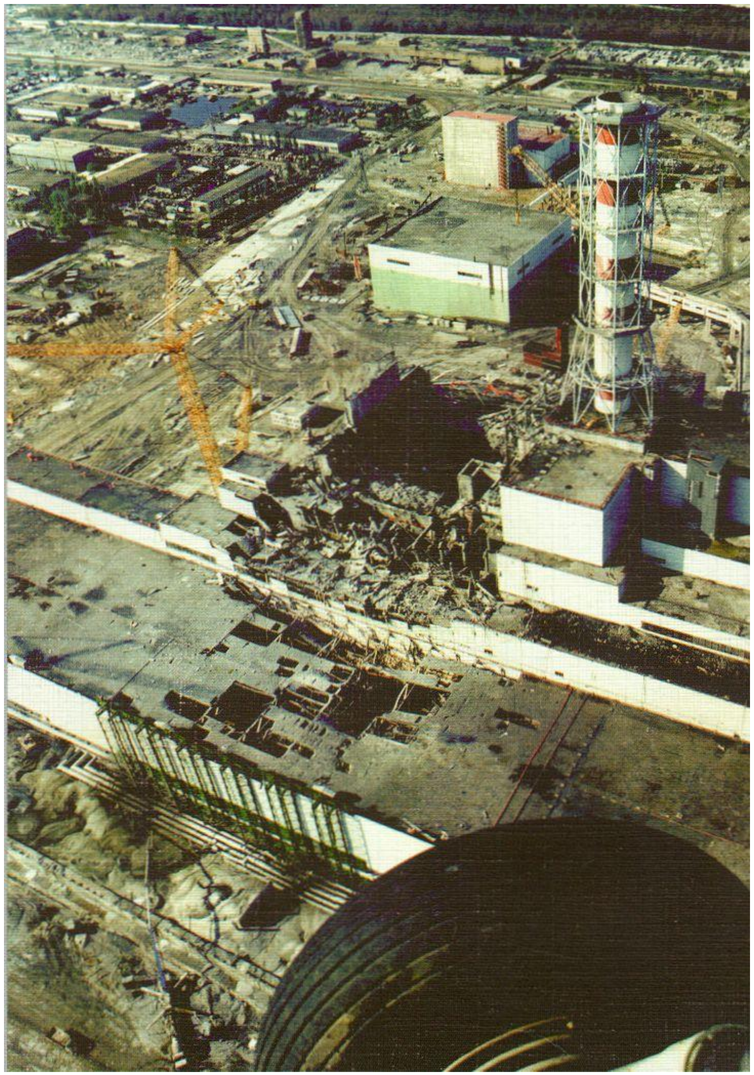
Three-mile island NPP, USA March 28, 1979



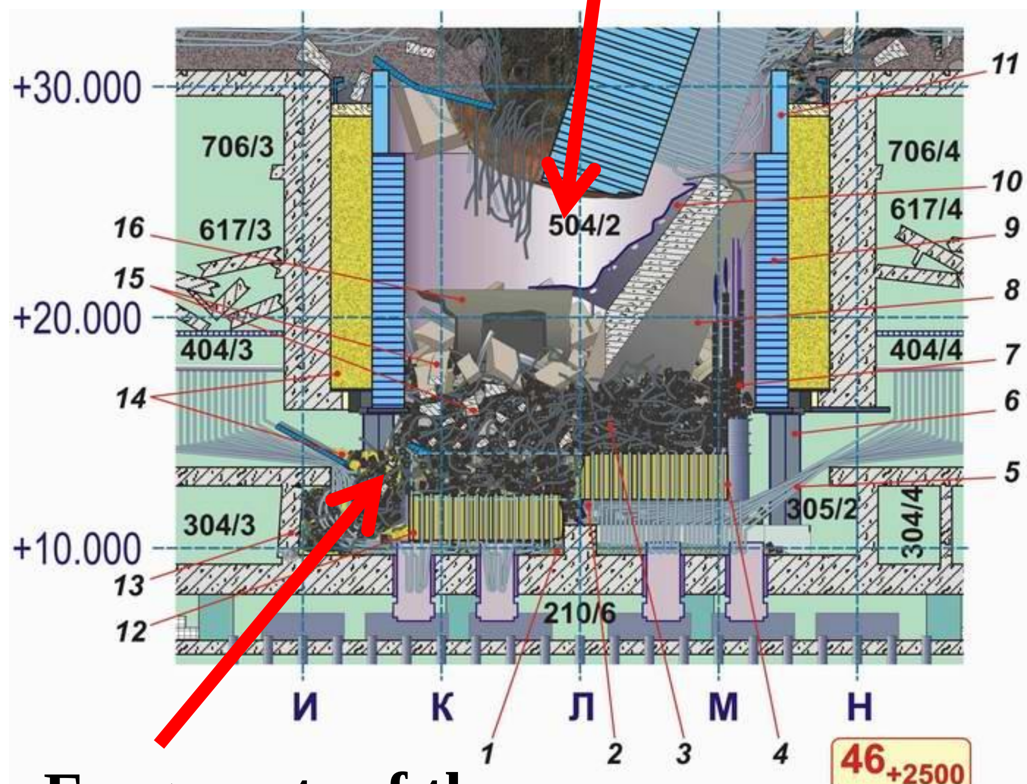
Chernobyl NPP USSR, April 26 1986

Fukushima Japan, March 11, 2011

Chernobyl lavas



Reactor shaft

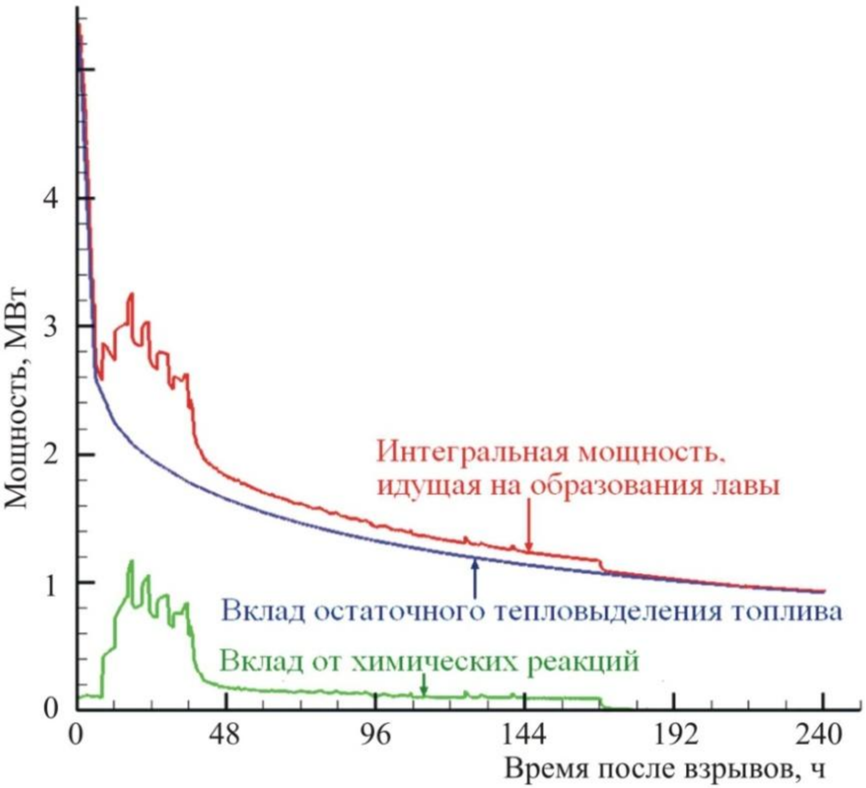


Fragments of the core
Fractured construction materials

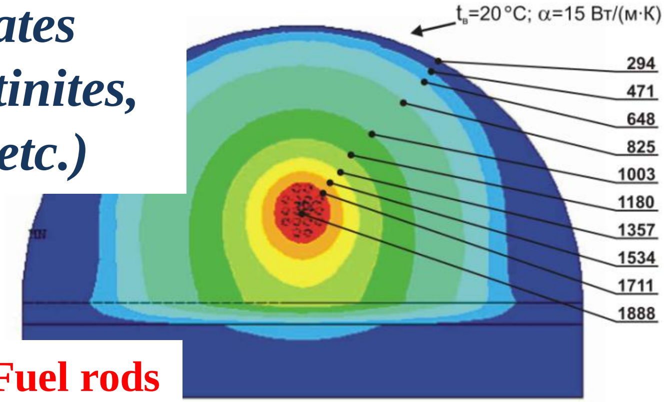
Kurchatov Institute Report

Heat generation

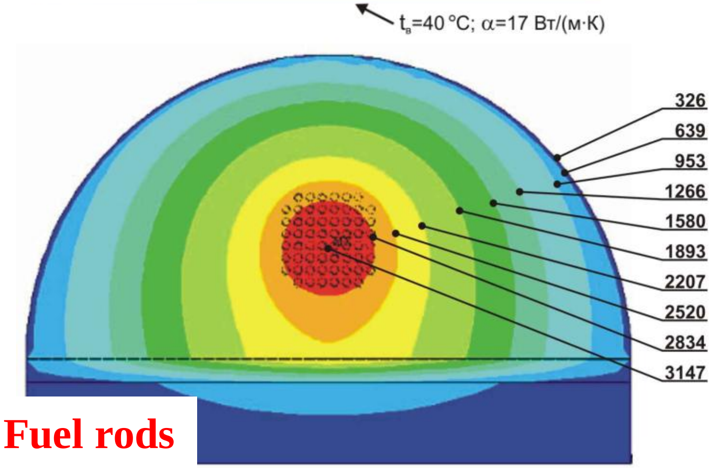
Power, MWt



Silicates (serpentinites, sand etc.)



16 Fuel rods



60 Fuel rods

Lagunenko, 2008

System **UO_2+ZrO_2+Al,Mg-silicates**

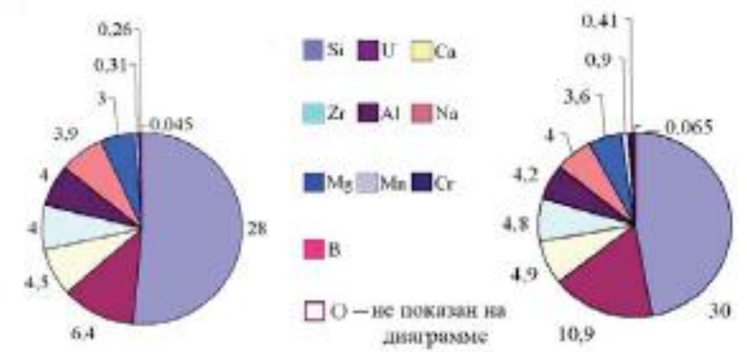
(+steel)

Interaction of UO_2+ZrO_2+ concrete/sand

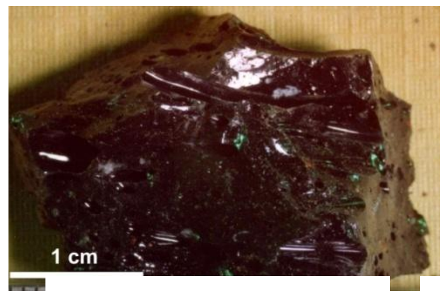
Krasnorutskii et al.

Chernobyl lavas

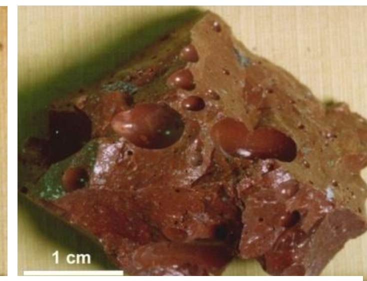
Hot (1600-2300 °C) UO_2 fuel alloyed with zircalloy cladding contacted with concrete and metal constructions forming lava-like fuel-rich flows. They contain major fraction of the fuel from the reactor (>90 tons).



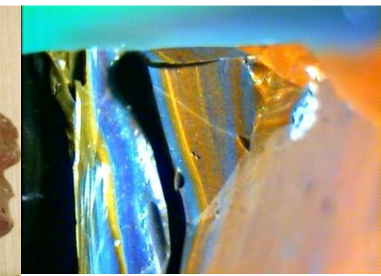
black ceramics **brown ceramics**



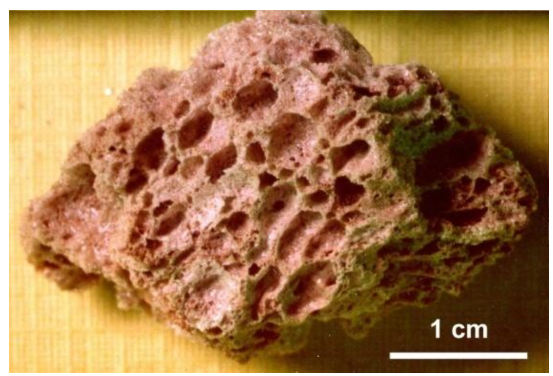
black ceramics



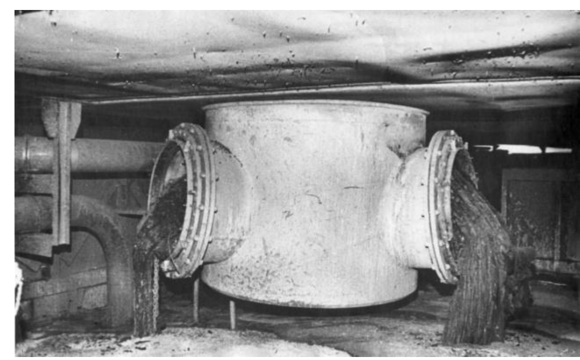
brown ceramics



Polychromatic ceramics

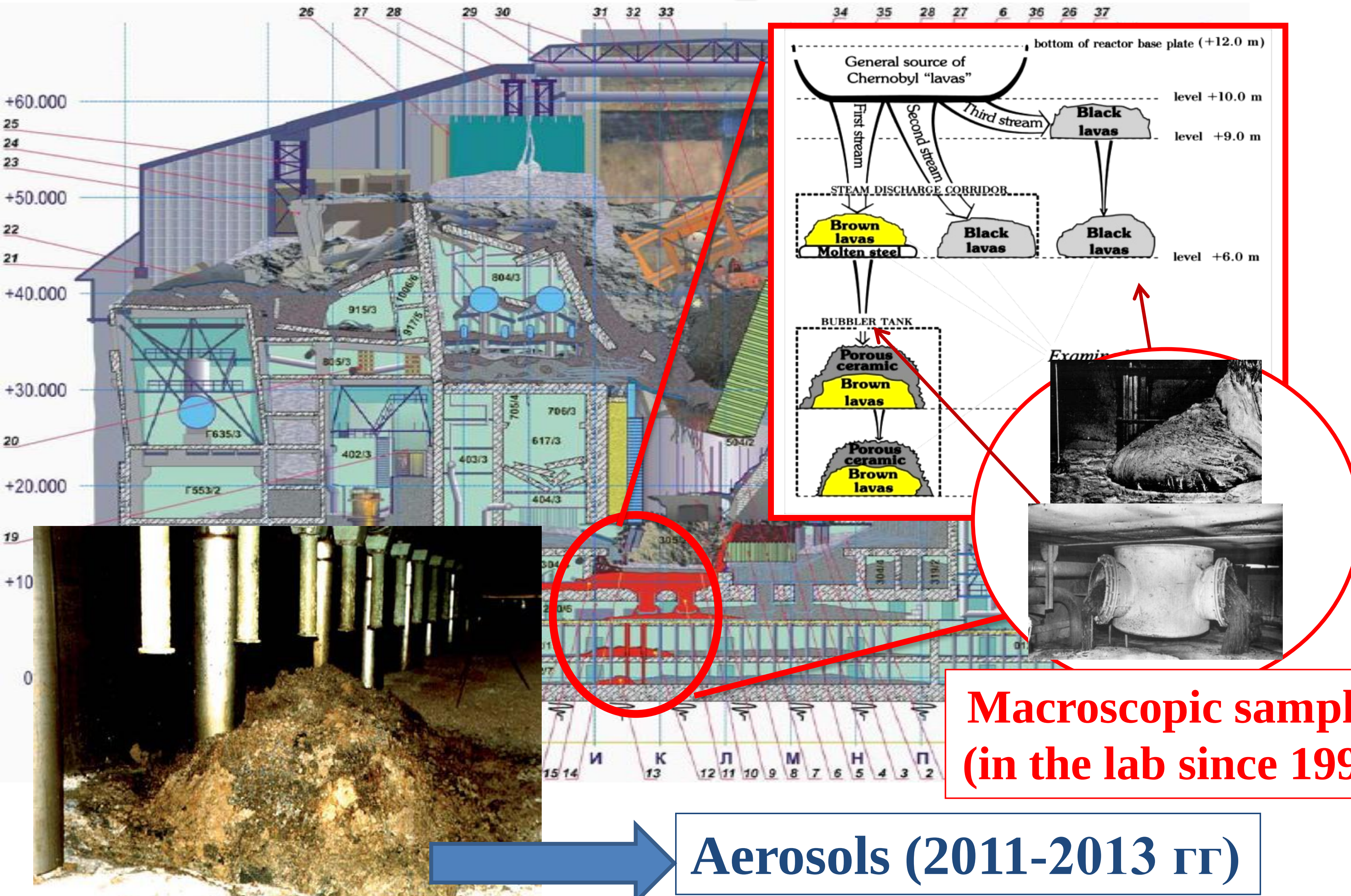


pumice



Kurchatov Institute Report; B.E.Burakov, KRI

Samples

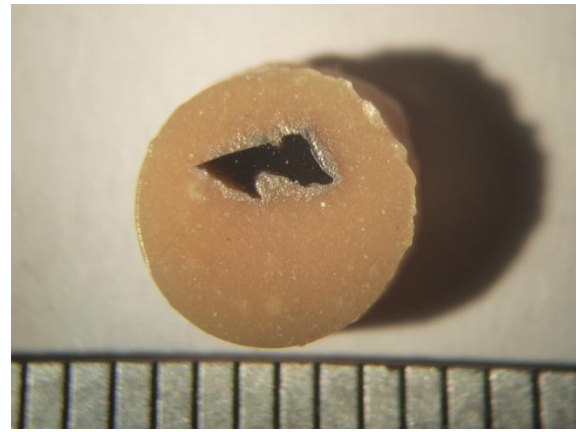


Macroscopic samples (in the lab since 1991)

Aerosols (2011-2013 гг)

Samples

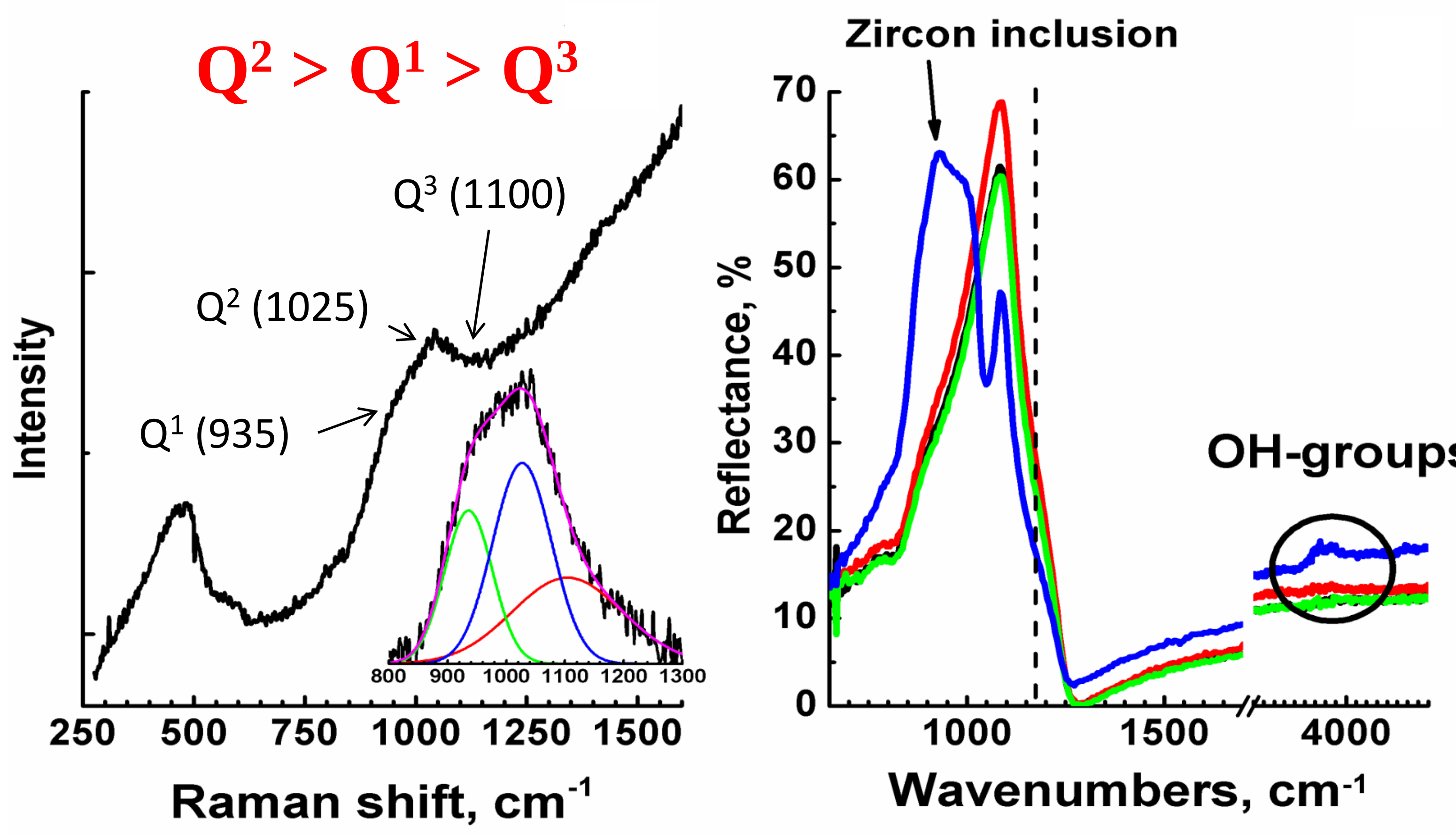
- Bulk pieces of black and brown bulk lava.



•Aerosols collected in the vicinity of a lava heap in 2011-2013 using dedicated air pump (10-12 hours).

•Particles collected during several months exposure (2012-2013) on a tray <1 meter from the lava heap (“jumping particles”).

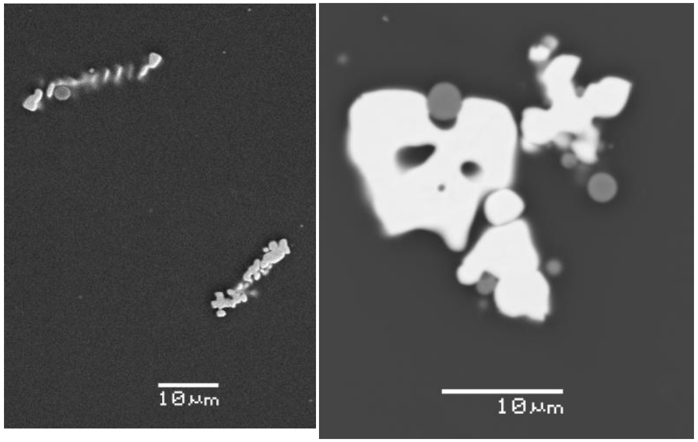
Vibrational spectroscopy: glassy matrix



Spectra typical for depolymerised metaluminous silicate glasses *(e.g., Mysen and Toplis, 2007)*. The matrix is **anhydrous**, OH-groups are associated with inclusions.

Inclusions

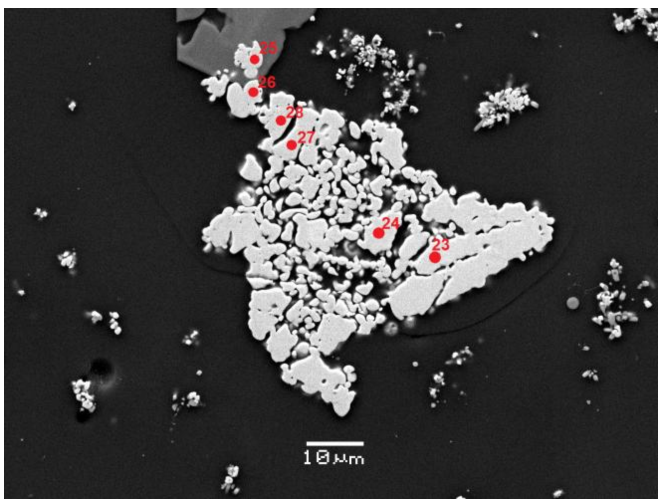
UO_{2+x} inclusions



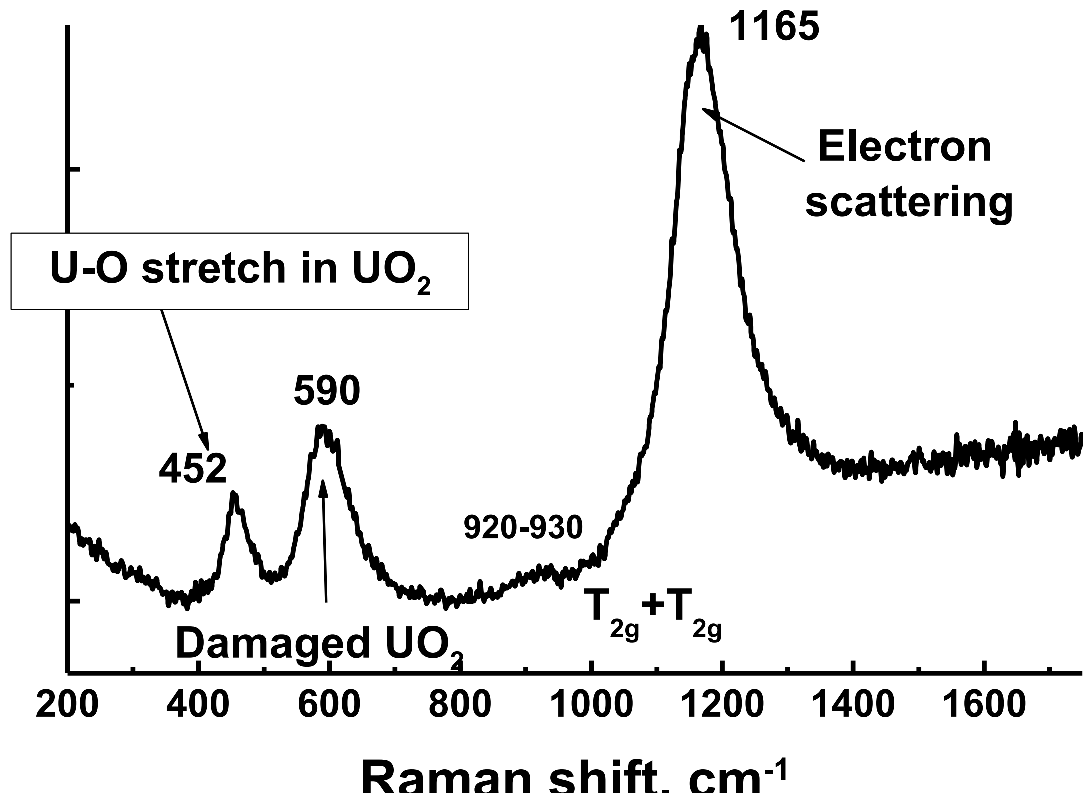
Variable morphology :

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

Presence and strength of the electron scattering band indicates minor deviations from UO_2 stochiometry (x<2.07) *(Manara et al.)*



Undissolved fuel pellet?

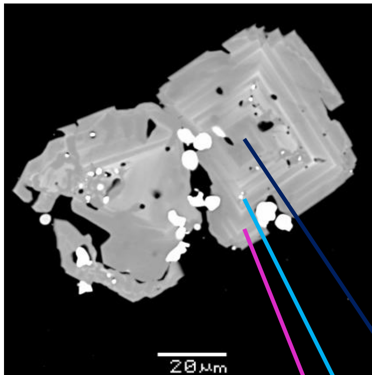


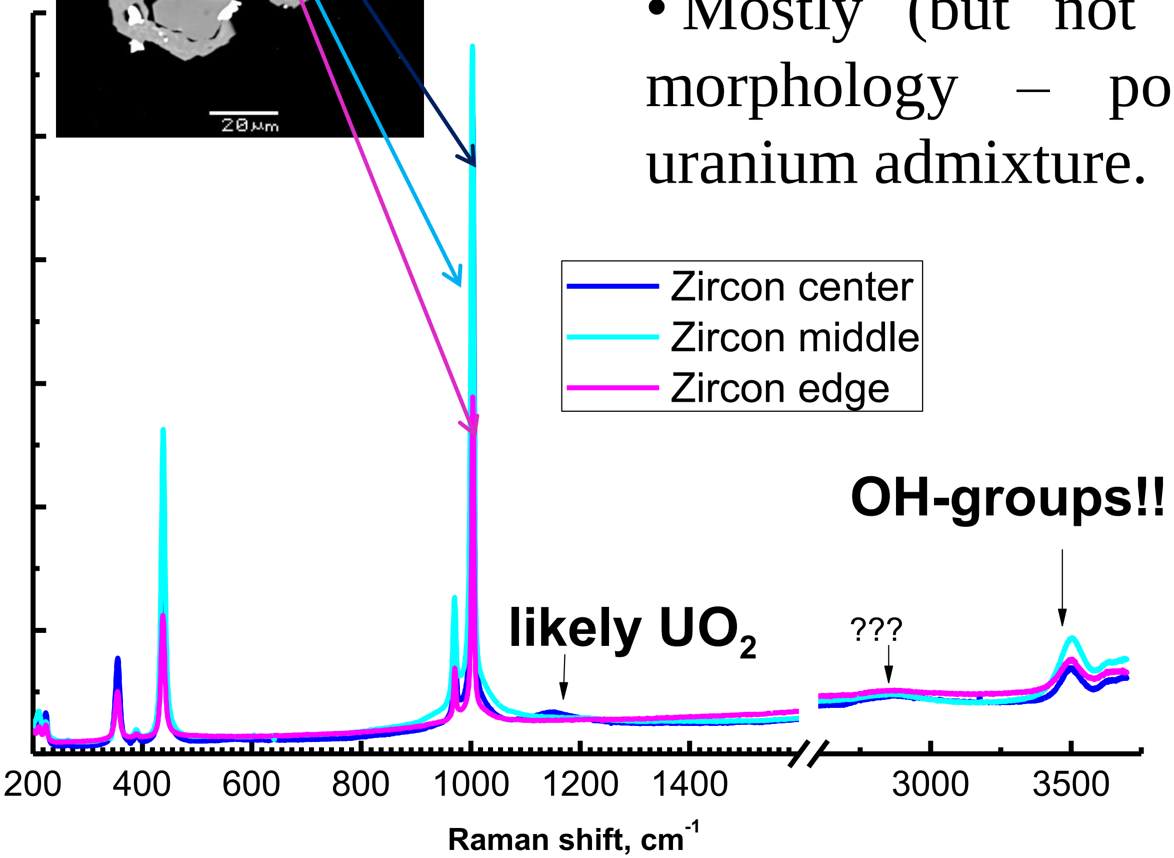
UO_2 precipitated from the melt *always* contains Zr admixture

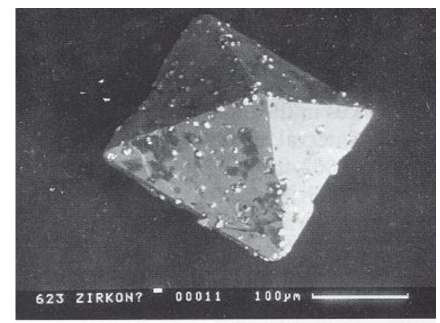
Excitation 532 nm

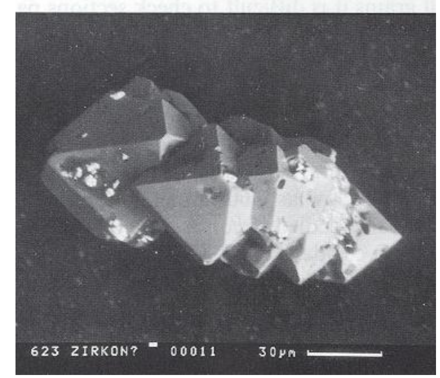
Inclusions of high-U zircon (chernobylite)

- Despite U content of up to 15 wt% they are perfectly *crystalline* with pronounced zonation
- Presence of OH-groups (raman and IR)!
- Mostly (but not always) dipyramidal morphology – possibly influence of uranium admixture.



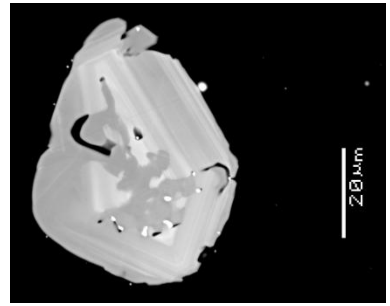


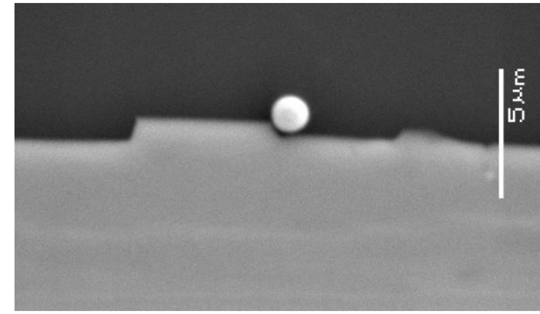




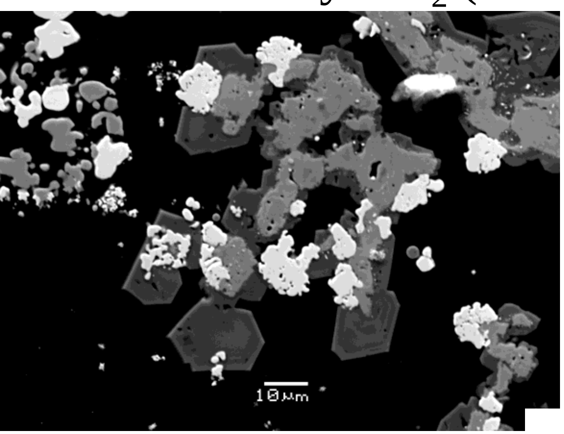
Inclusions of high-U zircon (chernobylite), Zr-U-O and ZrO_2

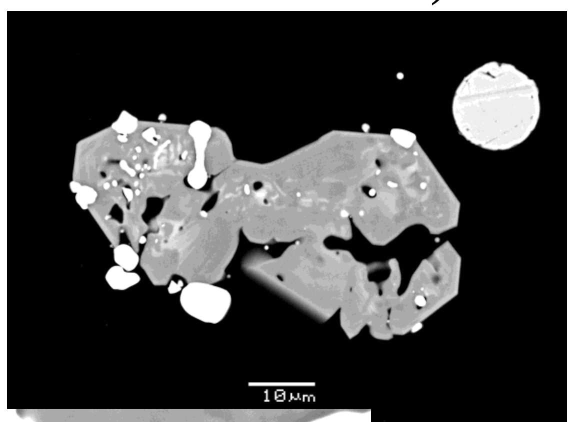
- Often complicated internal structure.

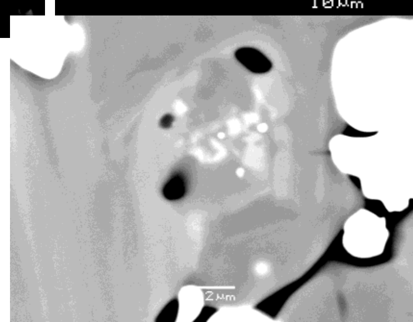


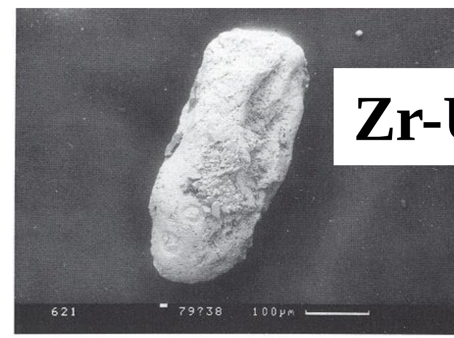


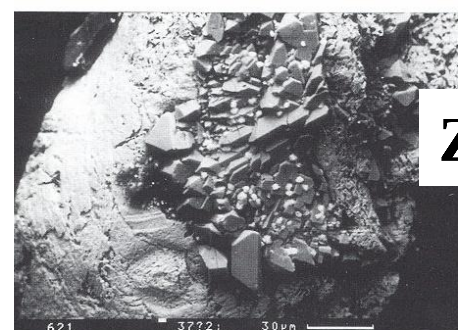
- Principal inclusions are ZrO_2, UO_2. Can be present in all growth zones. Steel balls are never trapped.
- Formation temperature: 1200<T<1650 °C.
- Zircons grew at the expense of Zr-U-O phase and high-temperature tetragonal ZrO_2, stabilised by UO_2 (EBSD and Raman results).





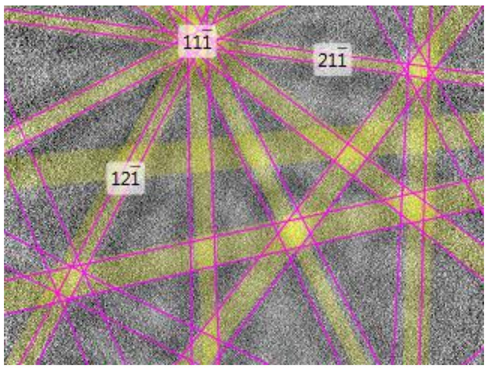


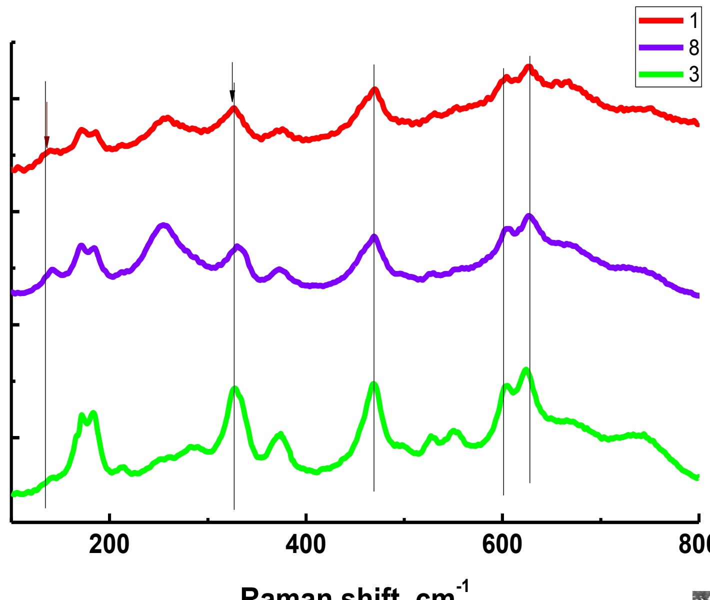




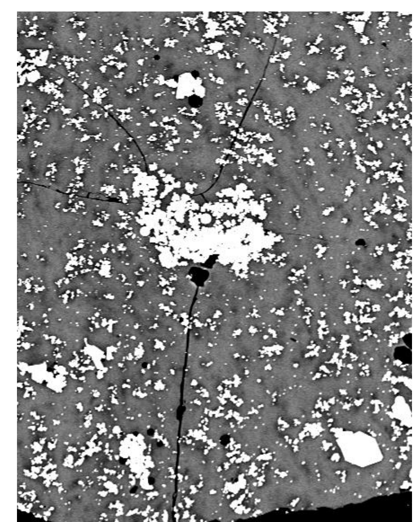
Inclusions of high-U zircon (chernobylite), Zr-U-O and ZrO_2

Contrary to expectations zirconia is ***not*** exclusively monoclinic! Raman and EBSD suggest presence of tetragonal modification (U-stabilised?).





Moisture-induced spontaneous transition of tetragonal zirconia to monoclinic phase is accompanied by considerable volume increase: possible mechanism of the lava cracking.



Spectroscopy of radioactive materials:
Just a scientific curiosity?

NO!
It is an important and versatile tool