Behaviour of materials containing actinides and long lived radionuclides

Part II

Natural analogues

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Background (1)

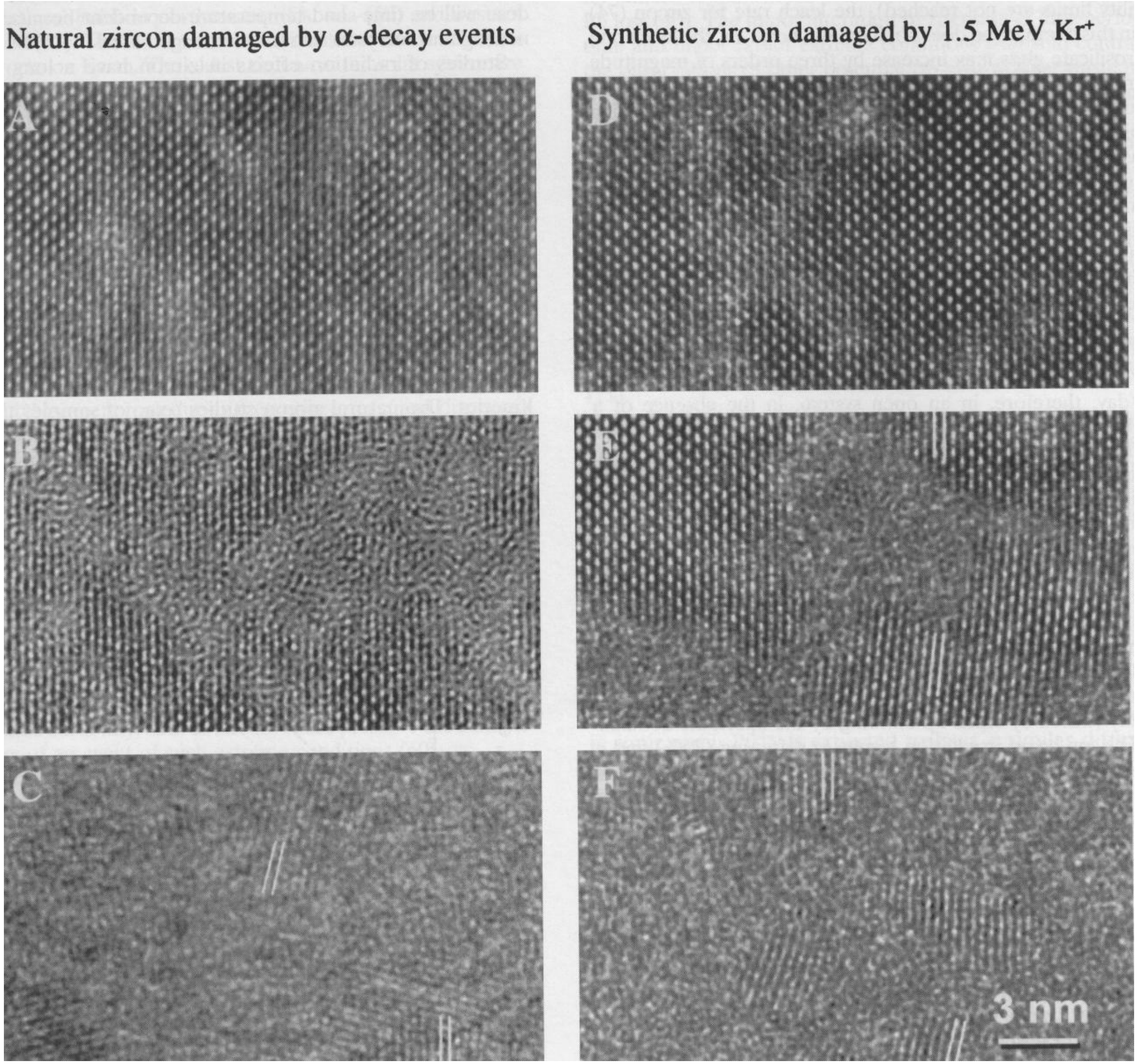
- Natural durable accessory minerals (zircon, monazite, zirconolite, pyrochlore, baddeleyite, xenotime, apatite, etc.) are considered as possible analogues of actinide host-phases for actinide immobilization
- Some of these minerals may contain admixture of natural radionuclides: U and Th from less than 0.0001 to several wt.% (even up to 15-20 wt.%)
- Some of these minerals became metamict (X-ray amorphous) as a result of self-irradiation during millions of years
- Metamict state is not glass-like. It is similar to solid gel: amorphous matrix + nano-crystallites

Background (2)

- Samples of accessory minerals accumulated very different doses of self-irradiation are available for research. Samples of natural radioactive glass do not exist.
- Some of these samples were affected in nature not only by self-irradiation but also chemical alteration and weathering
- Important information can be obtained from the study of radionuclide behavior inside crystalline structures of natural minerals under chemical alteration combined with self-irradiation

HRTEM images of non-radioactive natural and synthetic zircon after at different cumulated dose

(*Weber W.J. et al. 1994*)

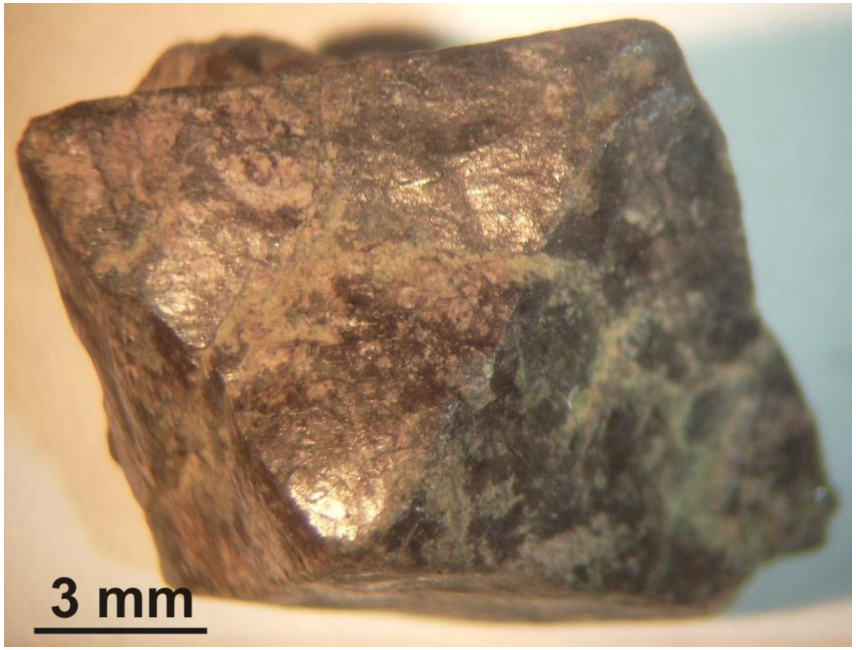


Two examples for consideration:
1) natural Th-U-containing metamict zircon and
2) natural U-bearing solid “gel-zircon”

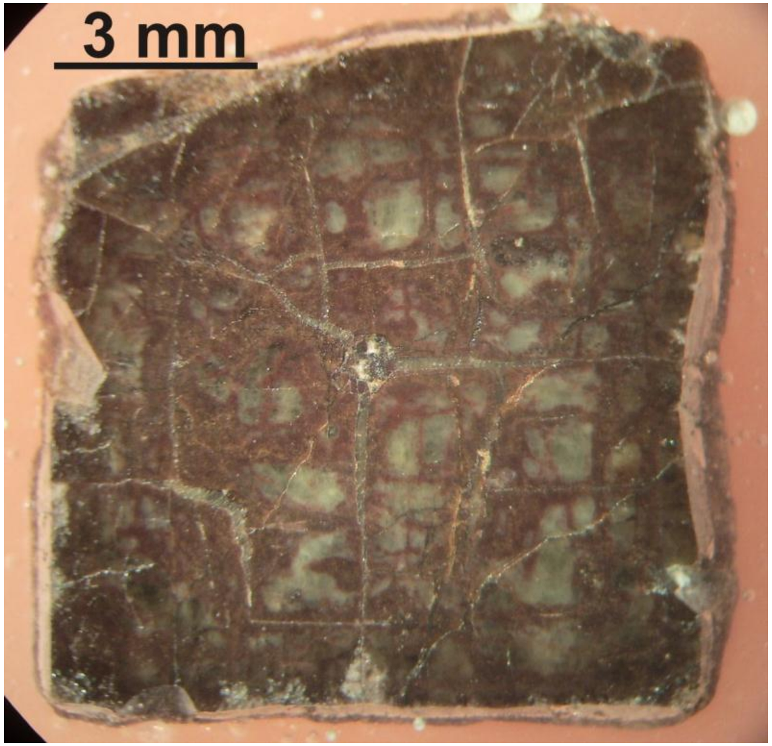
1) Single crystal of natural fully metamict (X-ray amorphous) zircon

Crystal of natural fully metamict zircon containing admixtures of Th and U

(granite pegmatite, Karelia, Russia)



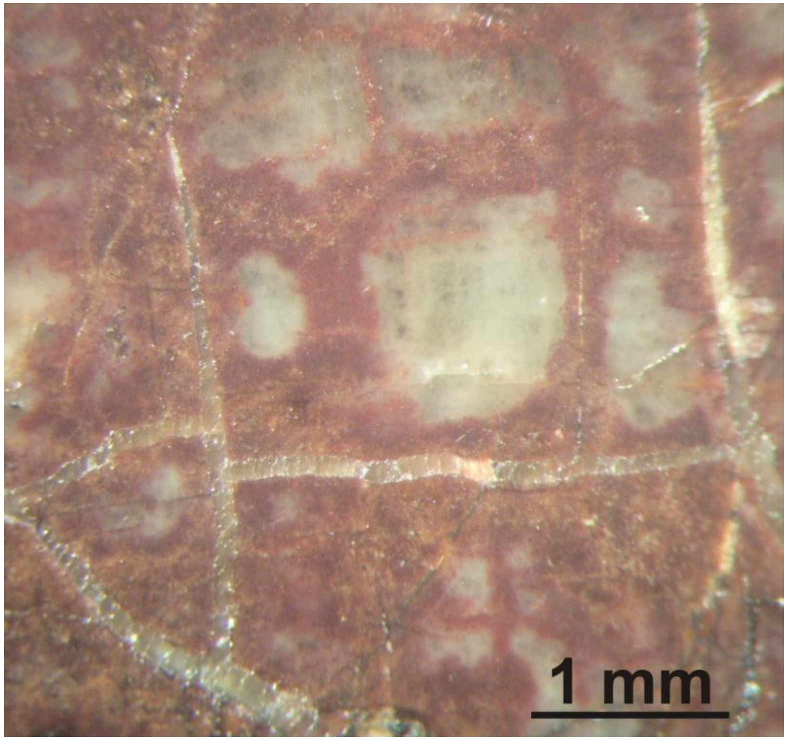
General image of initial crystal

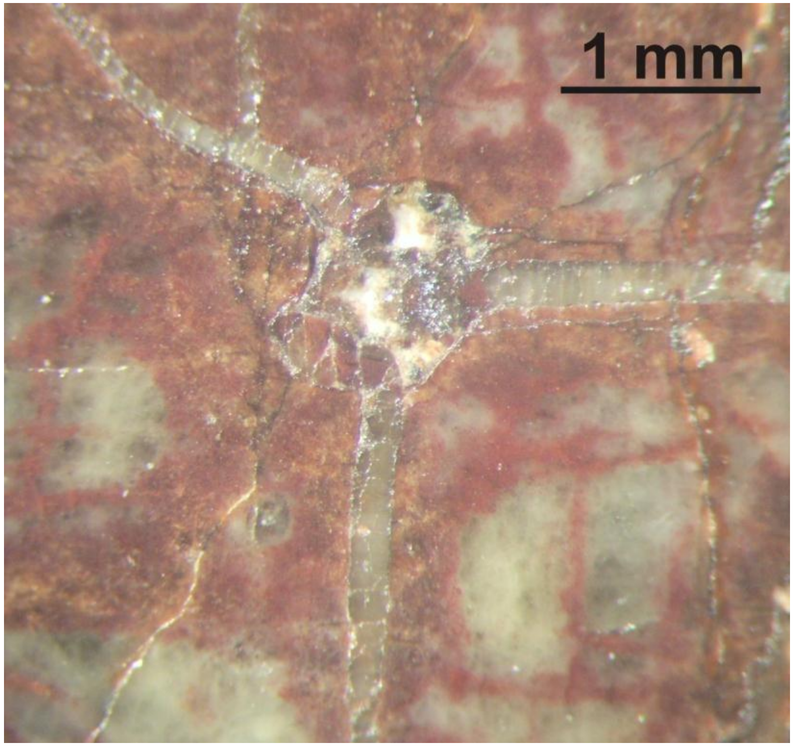


Polished cross-section

(colorless areas in brown matrix are clearly observed)

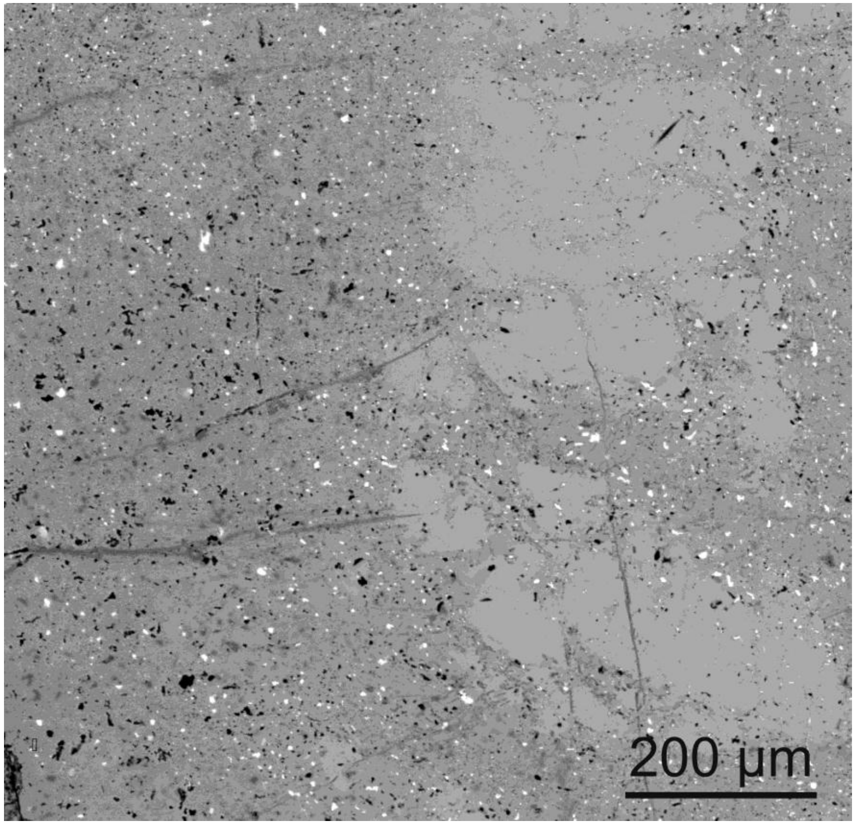
Optical microscope images of natural metamict zircon containing admixtures of Th and U

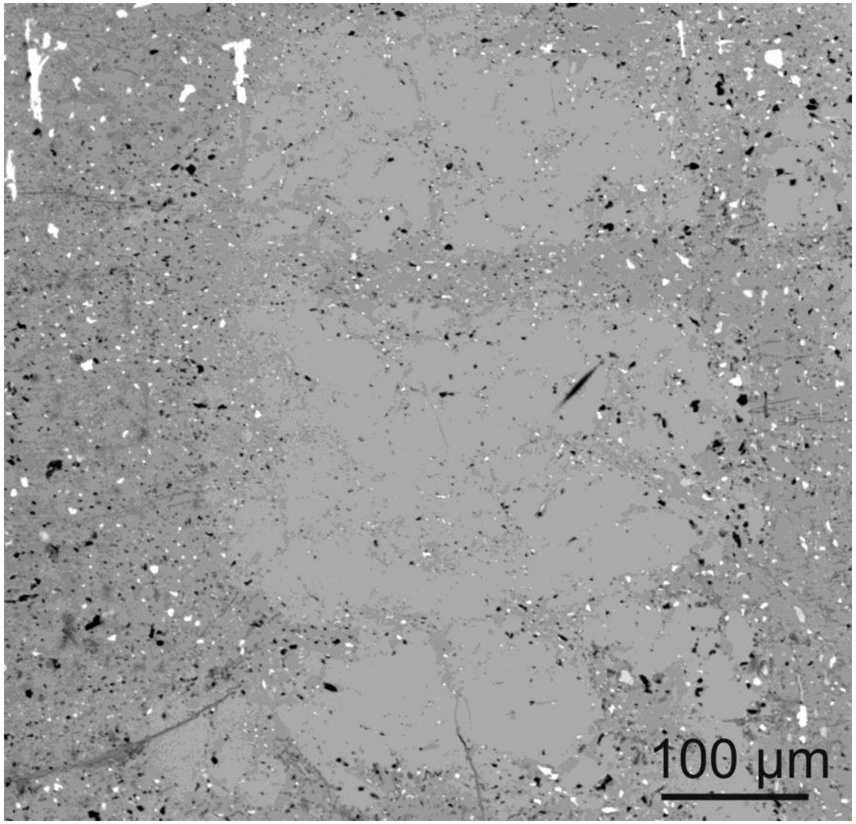




Cracks in crystal matrix are filled with calcite that indirectly confirms hydrothermal alteration. Colorless areas look like non-altered relicts. Both matrix and colorless areas are X-ray amorphous

SEM BSE images of natural metamict zircon containing admixture of Th and U





Homogeneous areas (non-altered?) contain 1.1-1.6 wt. Th and 1.3-2.0 wt.% U. White inclusions are Th-oxides with U admixture

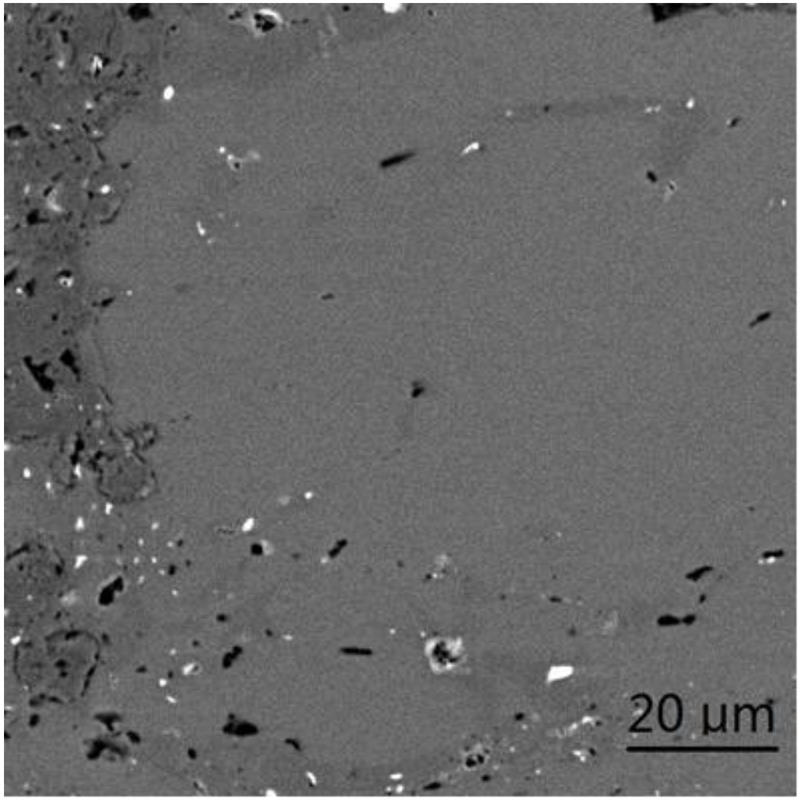
Possible explanation is that hydrothermal alteration caused destruction of solid solution and partial release of Th-U admixture in the form of separate inclusions

What about recovery of zircon structure under annealing?

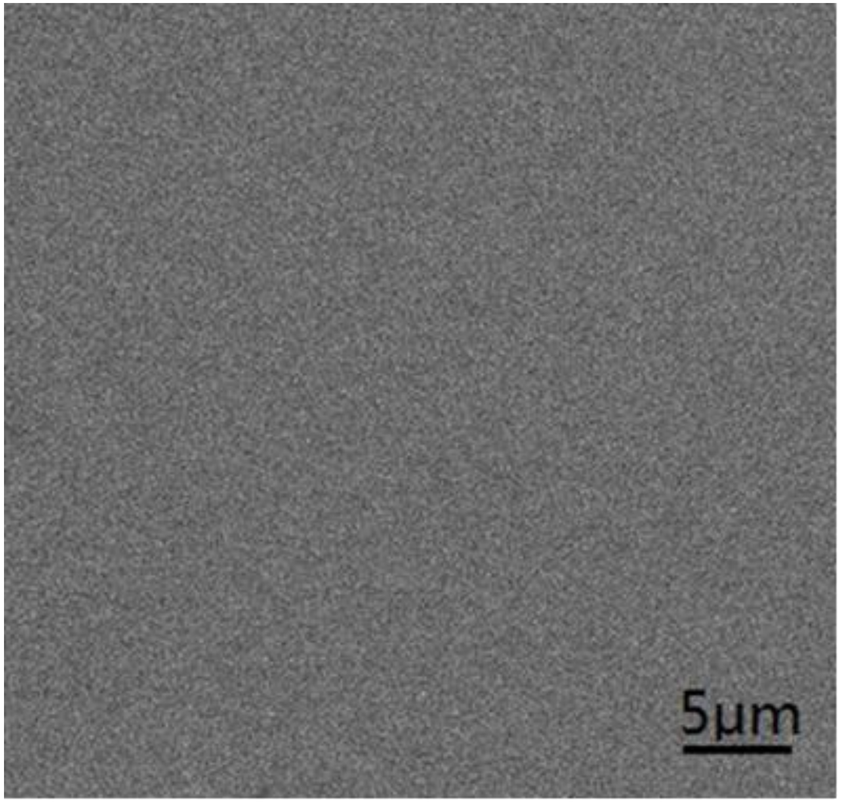
What about behavior of Th-U-admixture during recovery?

SEM BSE images of natural metamict zircon containing admixture of Th and U

after annealing and recrystallization at 1000°C for 1 hour



General view



Detailed image of initially homogeneous (non-altered?) area

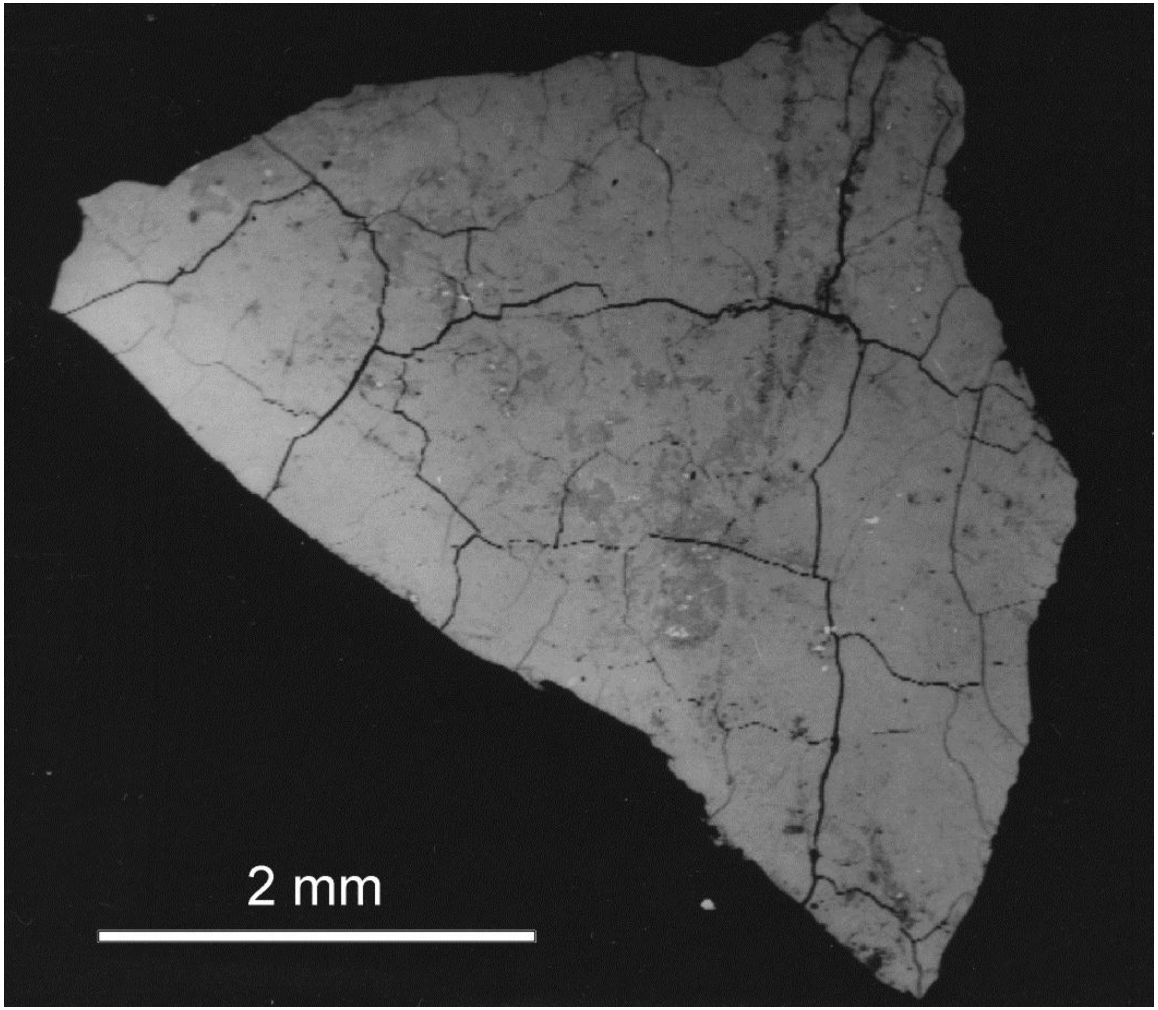
Recovery of zircon crystalline structure under annealing was accompanied with formation of chemical inhomogeneity – and even possible destruction of solid solution, formation of new phases and release of Th-U-admixture into separate inclusions!

2) Natural U-bearing solid Zr-silicate gel or “gel-zircon”

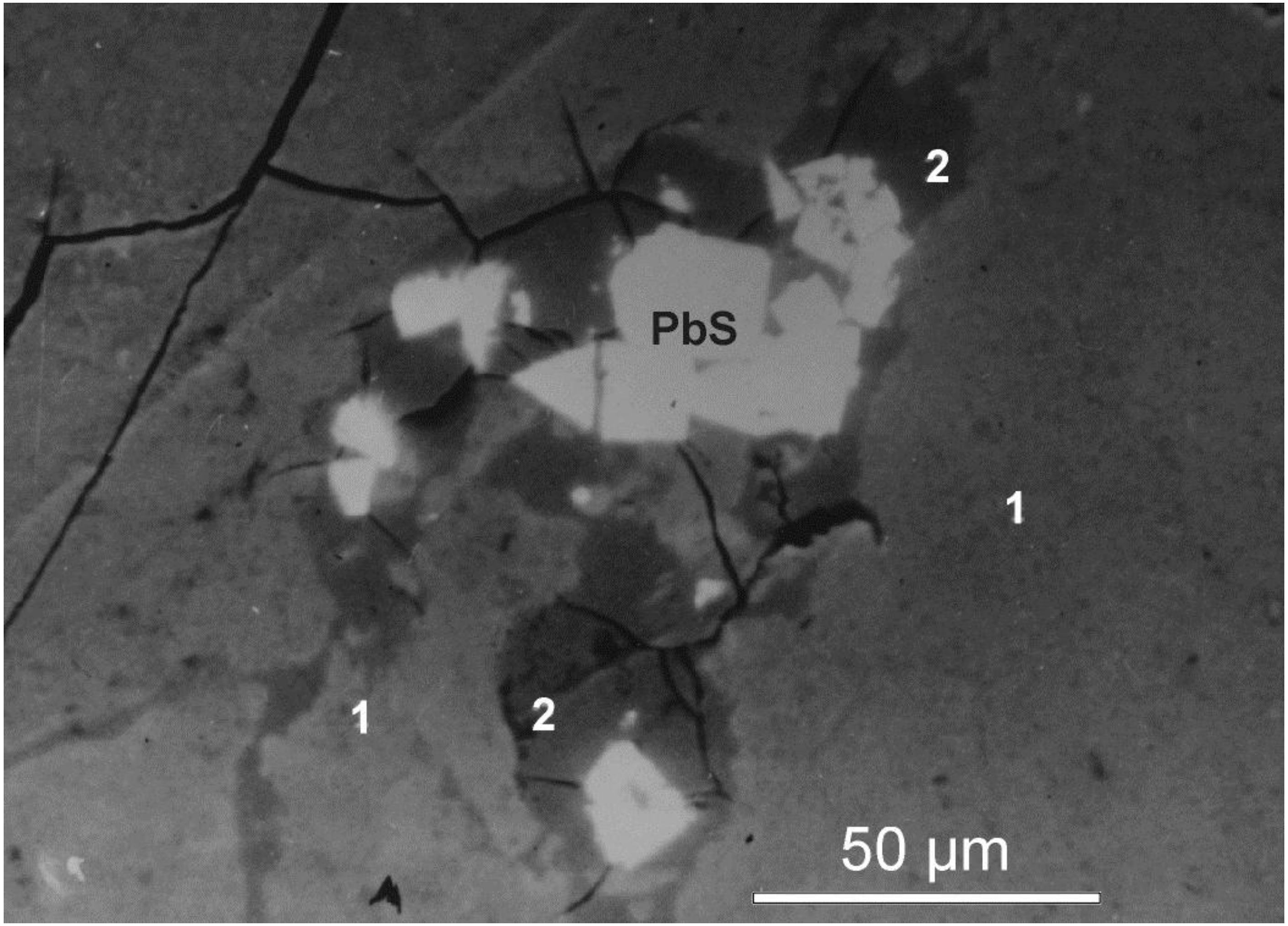
So called “gel-zircon” was discovered in uranium ores (with age about 400 million years) in Nothern Kazakhstan. These ores are not used for uranium extraction because “gel-zircon” is very chemically durable

Natural “gel-zircon” is not metamict zircon. This material was precipitated initially as a gel and it survived in open geochemical system during millions of years!

Back-scattered electron image of natural "gel-zircon"



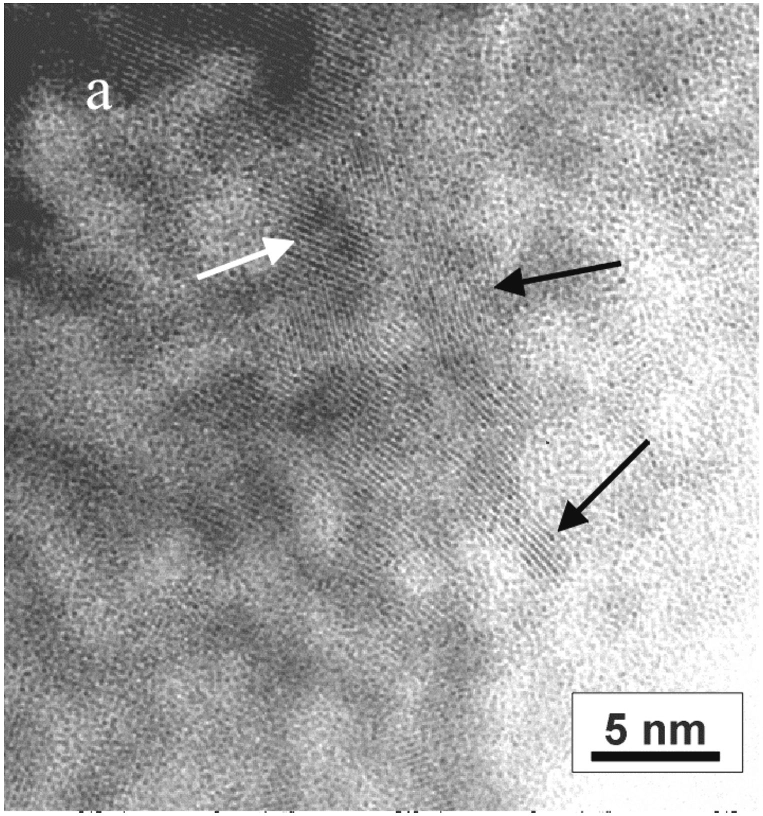
Back-scattered electron image of natural “gel-zircon”

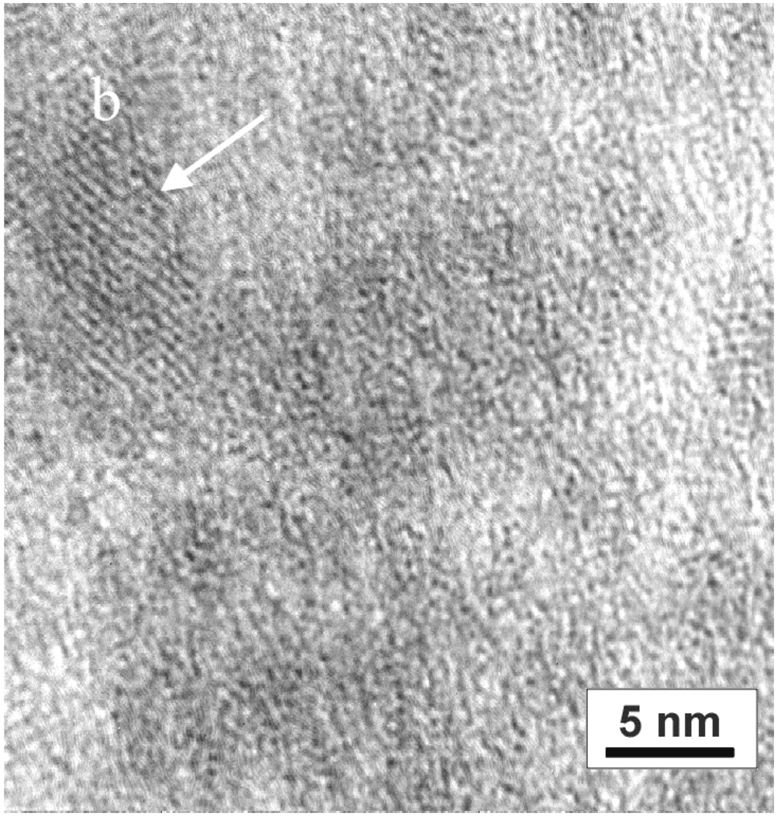


EMPA data of natural “gel-zircon”

Area	Content in wt.%						
	Ca	Mg	Al	Fe	Zr	Si	U
1	1.5	1.0	1.0	0.8	23.4	9.0	10.7
	1.0	-	0.5	0.7	23.5	9.4	10.3
	1.4	0.5	0.7	1.3	23.2	9.2	12.1
	1.2	-	0.8	1.3	24.8	10.0	12.8
	1.2	0.6	0.8	1.5	26.5	9.6	11.1
2	2.3	0.8	0.8	10.7	20.9	8.0	5.2
	1.1	1.2	2.0	13.8	11.7	9.8	8.4
	1.7	1.0	1.8	9.0	20.1	8.4	5.6
	2.3	0.9	2.5	5.0	23.7	10.4	3.6
	2.0	0.8	1.1	3.5	28.2	9.8	4.2

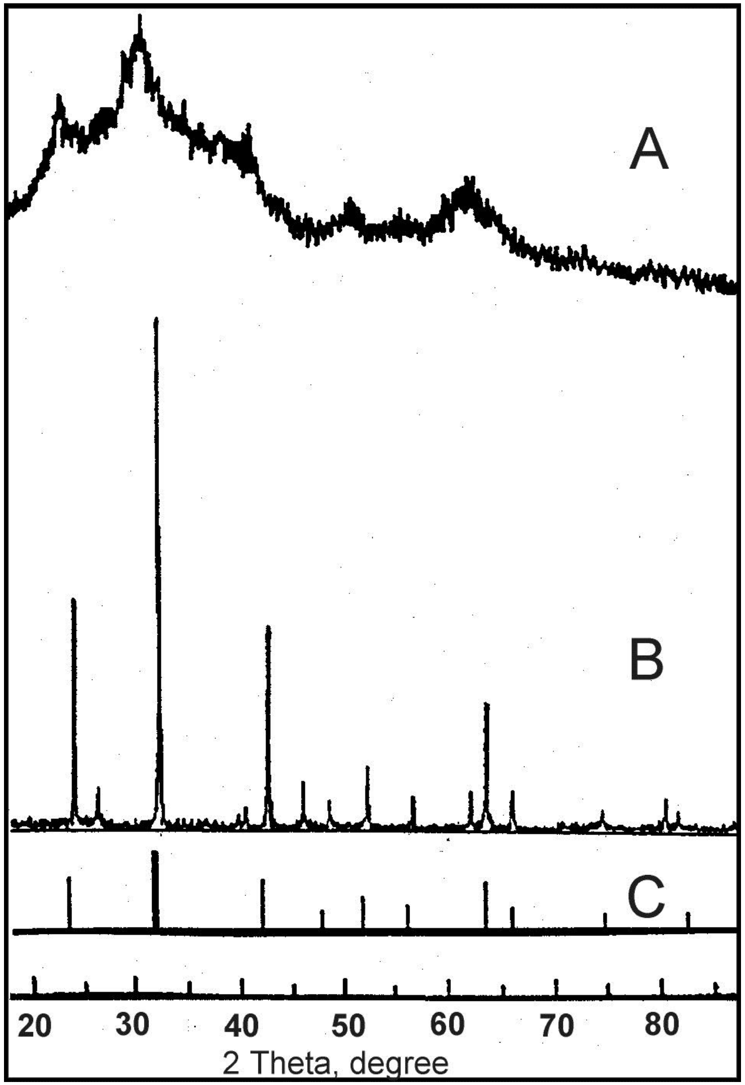
High resolution TEM images of gel





a – calcined synthetic Zr-Ce-silicate gel
b – natural “gel-zircon”

XRD analysis of natural “gel-zircon”

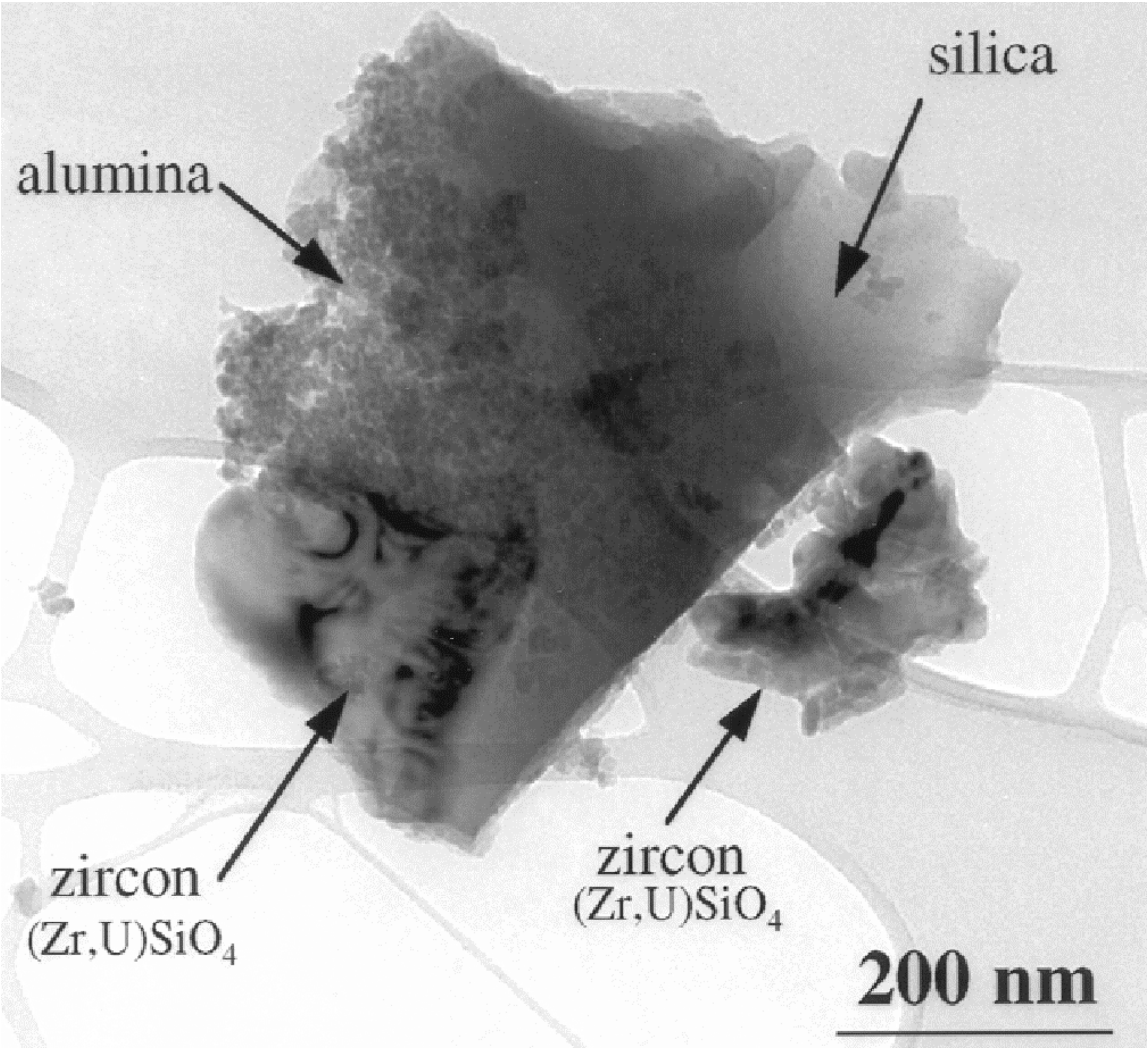


A – Initial “gel-zircon

B – After sintering in air (1400°C, 1 hour)

C – Patterns of standard zircon (JCPDS # 6-626)

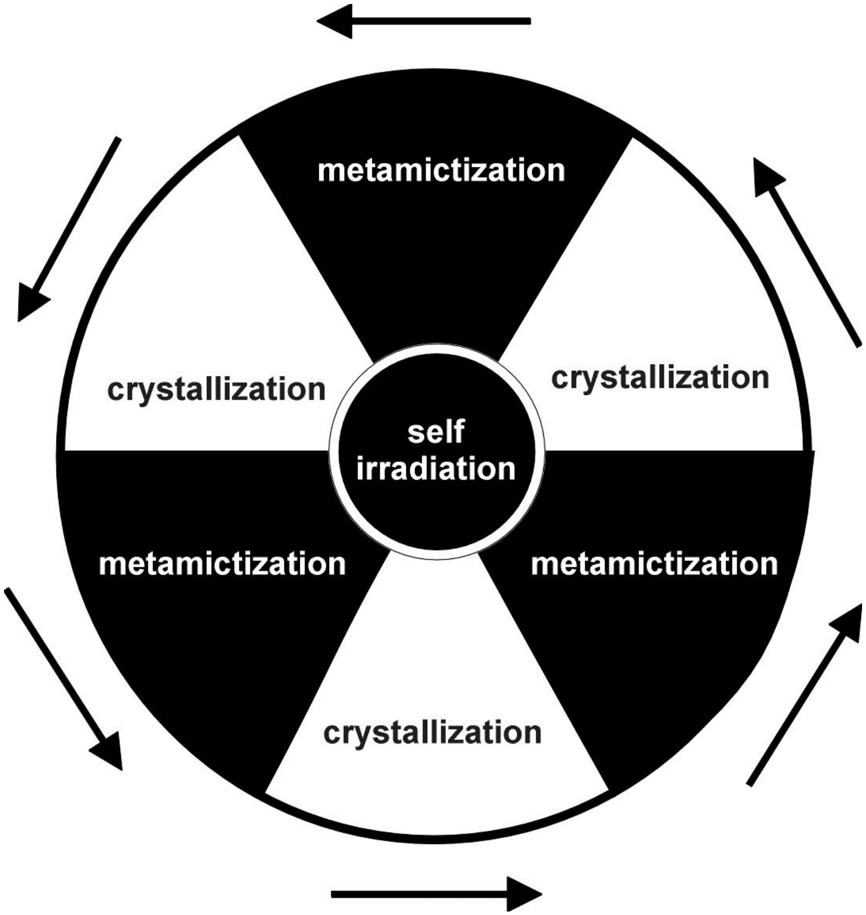
TEM image of natural "gel-zircon" after sintering in air (1400°C, 1 hour)



Stability of Zr-silicate gel during millions of years in open geochemical system in the presence of water

Self-irradiation causes equilibrium between two competitive processes:

1) gel crystallization favorably into zircon phase and 2) zircon metamictization (amorphization) – return back to the gel state



Conclusions

- Under self-irradiation crystalline mineral can become amorphous (metamict) and then after annealing can simply return back to crystalline state.

- Behavior of U-Th-admixtures incorporated into crystalline structures of natural minerals is not simple under self-irradiation, metamictization and recovery of crystalline structure. Destruction of solid solution accompanied with release of radionuclides into separate phases is possible.

- *Optimal equilibrium between metamictization and crystallization under self-irradiation is possible.*

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Thank you!