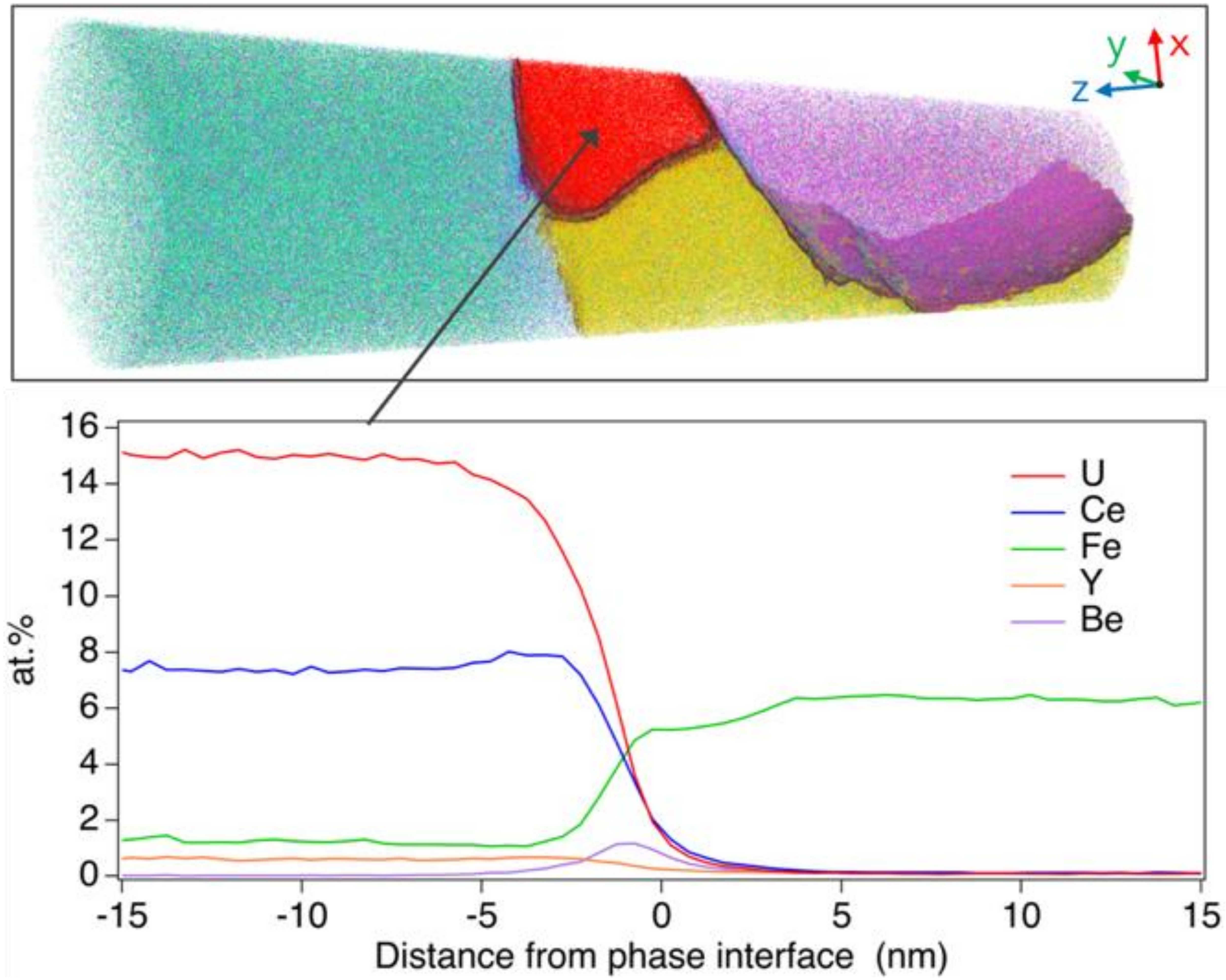

Formation of mineralogical interfaces as radionuclide repositories

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CSIRO Environment

Remplex 2023 Summit

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The Challenge

- Nuclear wastes encompass a diversity of chemical reactivity/half-lives that constitute a pervasive challenge for safe disposal into the millennia
- Fukushima contaminated waters highlight need for a multi-radionuclide capture/containment technology
- Need rapid, broad spectrum uptake capacity for aqueous/colloidal phases for recovery or long-term disposal

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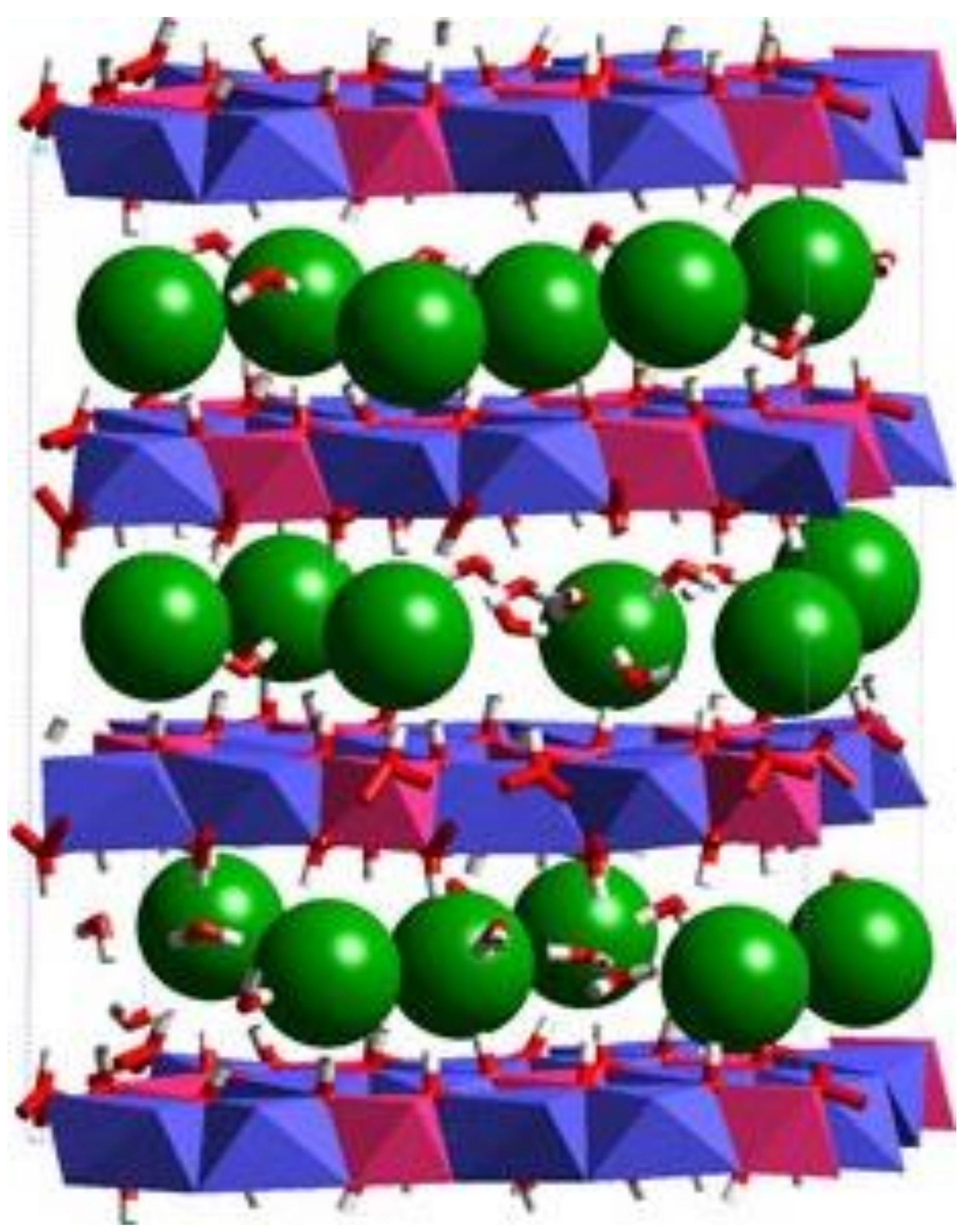
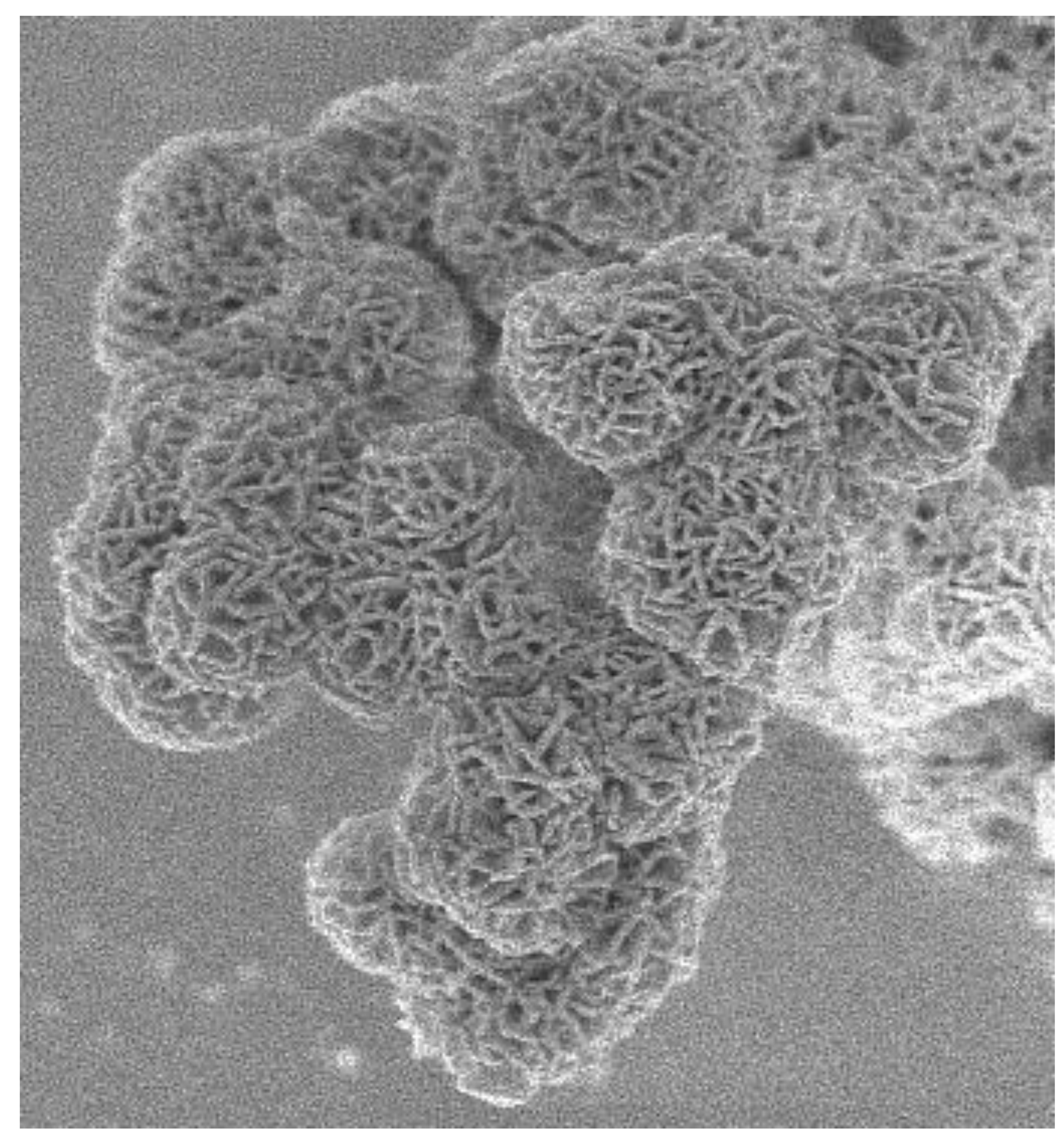
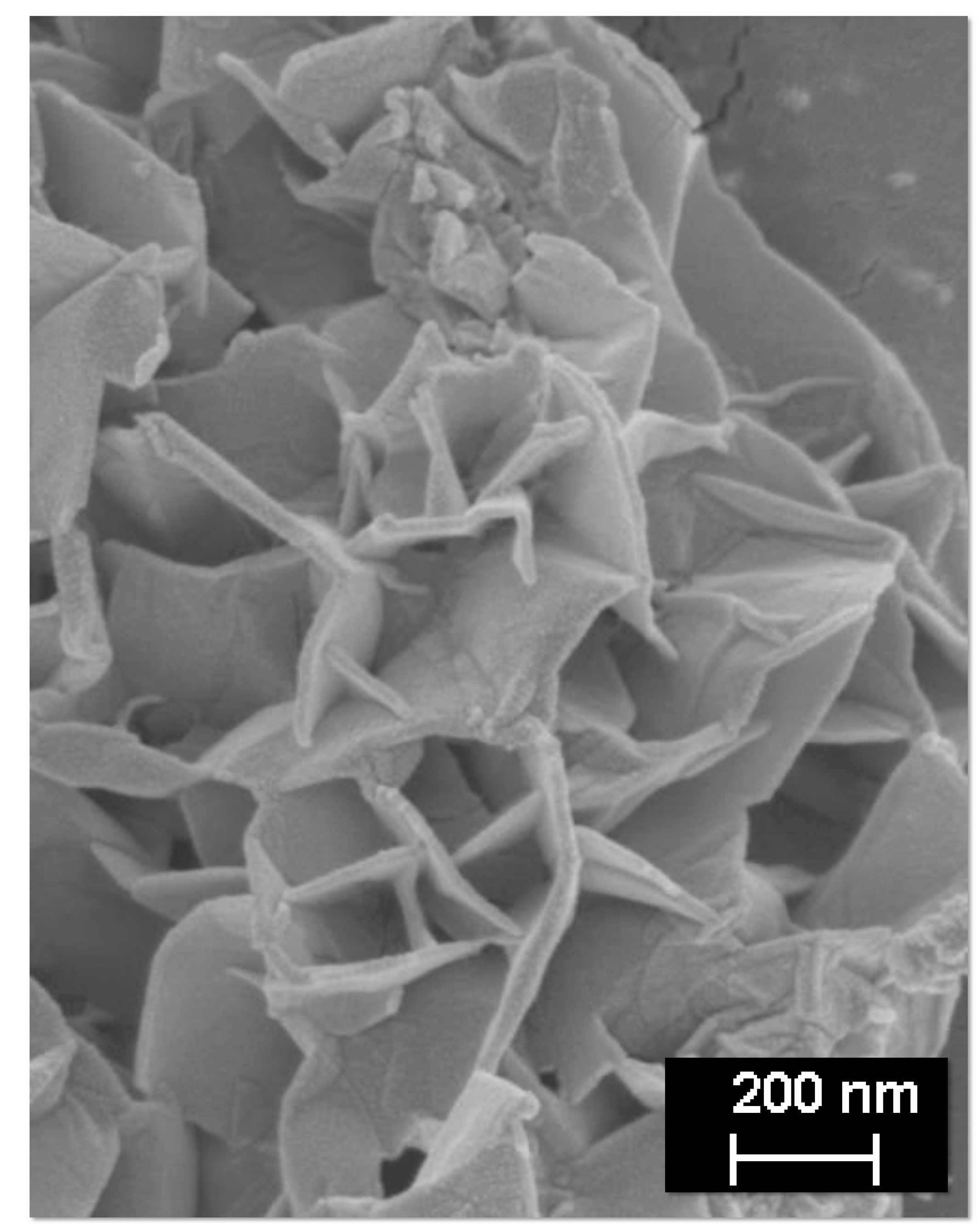
The Solution – based on in-situ hydrotalcite (HTC) formation

- Radionuclides, other contaminants form building blocks of a polymetallic HTC*
- HTC structure: + charged metal-OH layers with interstitial anions + H_2O
- Broad composition: 2:1 to 4:1 M^{2+}:M^{3+} ratios: $Mg_4Al_2(OH)_{12}CO_3.4H_2O$ to $Mg_8Al_2(OH)_{20}CO_3.4H_2O$
- M^{2+}: Mg^{2+}, Cu^{2+}, Zn^{2+} UO_2^{2+}, with M^{3+}: Al^{3+}, Fe^{3+}, $REE^{3+/4+}$ as transuranic analogues
- HTCs constitute a multi-element/contaminant repository







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HTC removal efficiency from a U mine In-Situ Recovery (ISR) barren lixiviant

Four major element groupings:

*U (1%), REE (2.5%), Th, Fe, Al;

*Transition Metals, Metalloids

*Alkalis, Alkaline Earths

*NaCl, Bicarbonate

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Major, REE and trace elements in HTC - U mine In-Situ Recovery (ISR) barren lixiviant

Major elements/oxides (wt%)	
MgO	26.78
Al_2O_3	12.83
Fe_2O_3	8.92
SO_3	7.26
SiO_2	6.54
Na_2O	1.50
CaO	1.16
Cl	0.39
P_2O_5	0.05
TiO_2	0.02
MnO	0.02
K_2O	0.01
Rare Earth Elements (REE) + Y (µg/g)	
Ce	618
Y	277
Nd	275
La	169
Sm	62
Yb	12

Trace elements (µg/g)	
Zn	9896
V	4455
U	2220
As	433
Cu	328
Ni	254
Th	238
Cr	166
Co	144
Mn	134
Sr	120
Ga	40
Sc	39
Ta	38
Cd	32
Cs	22
Pb	22
Tl	22
Ba	21

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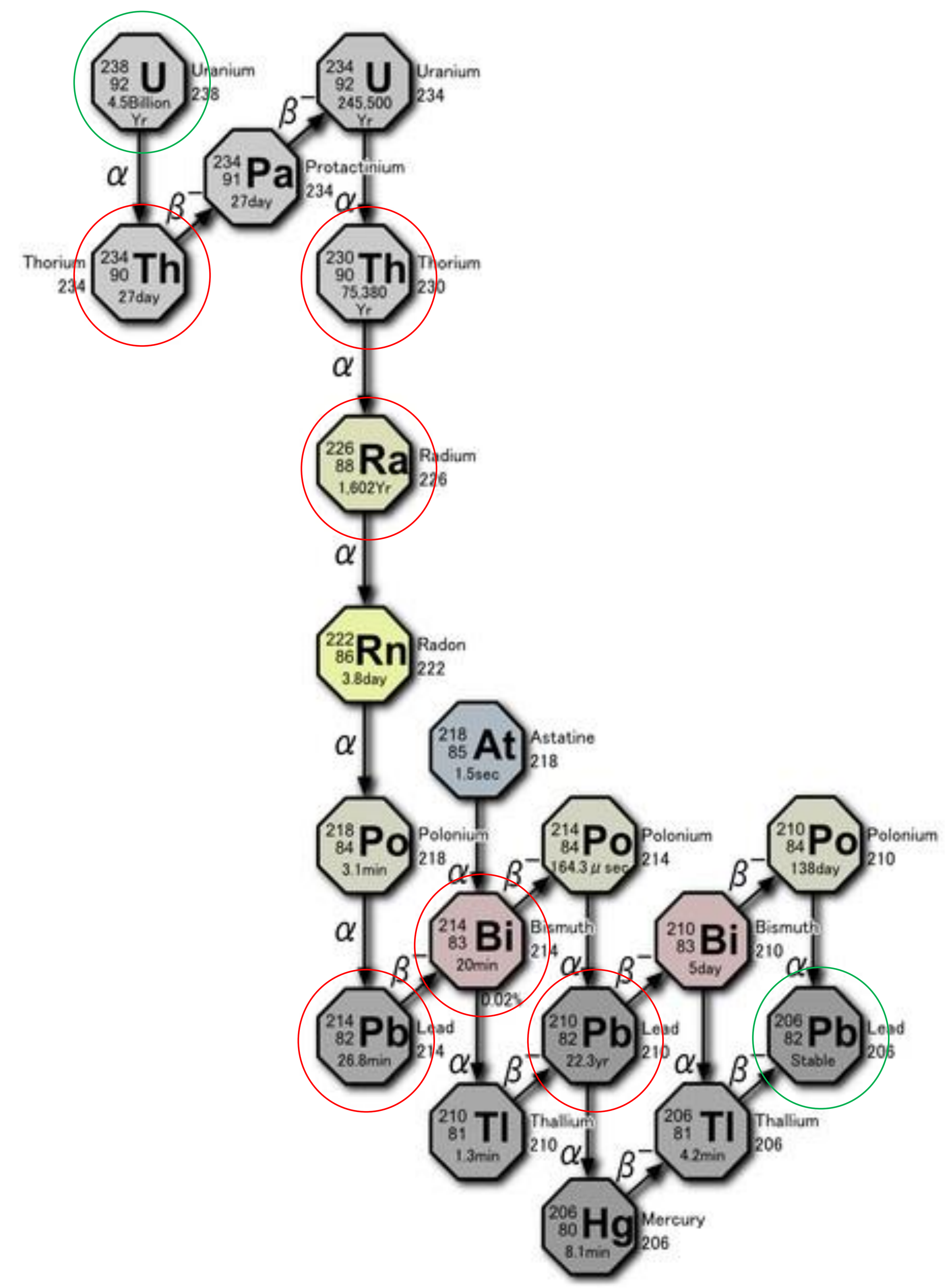
Radionuclide removal efficiency from U mine ISR barren lixiviant

- HTC effectively removes U + daughter radionuclides
- High concentration factors for U-Th decay chain radionuclides
- Removal efficiencies of 92.0 to 99.9%

Radionuclide	Barren lix (Bq/L)	Treated lix (Bq/L)	Percent removal	HTC (Bq/g)
^{238}U	225	2	99.1	67194
^{234}Th	557	<1	99.9	120986
^{230}Th	8683	66	99.2	1955469
^{226}Ra	324	26	92.0	55282
^{214}Pb	326	26	92.1	53822
^{214}Bi	322	26	92.0	57013
^{210}Pb	2193	4	99.8	488302



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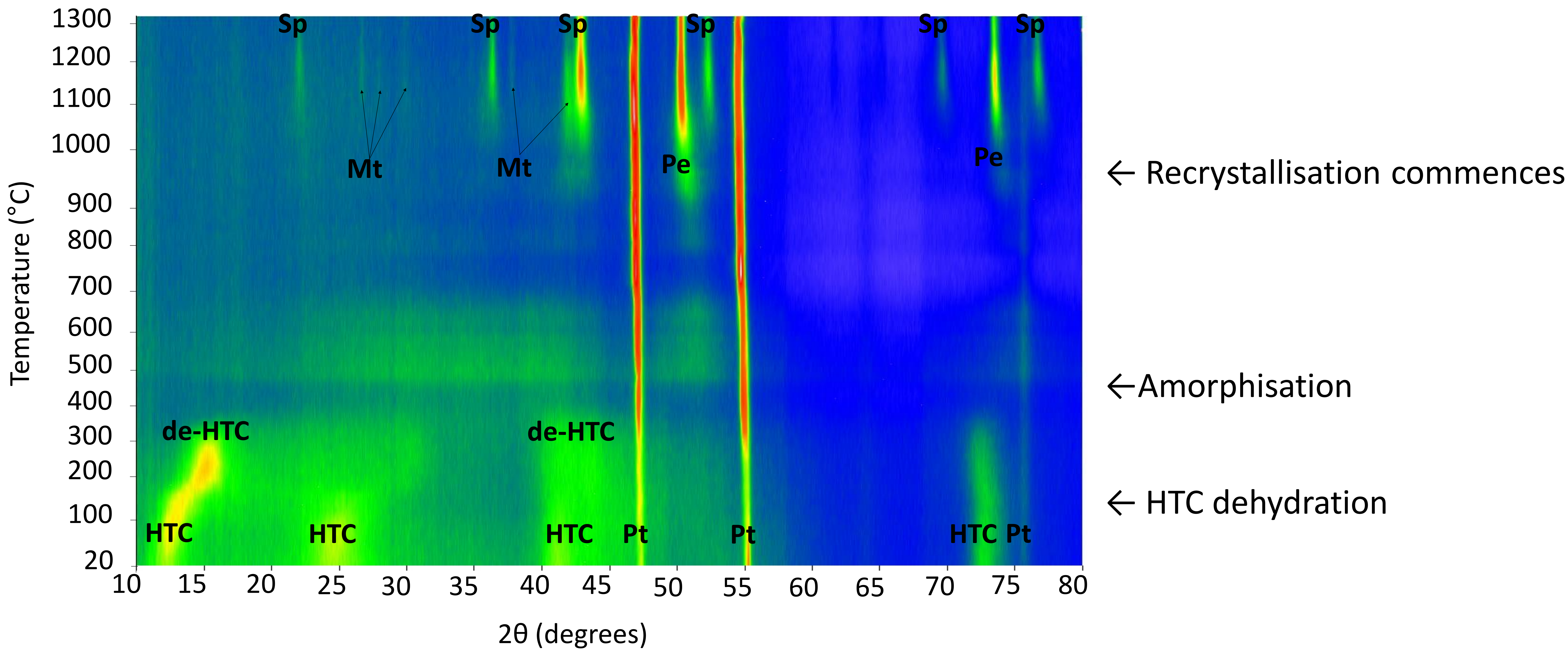
Thermal X-Ray Diffraction (XRD) analysis – HTC calcination (20 to 1320°C)

- HTC → Periclase (Pe), Spinel (Sp), Monticellite (Mt), Platinum (Pt – crucible/internal standard)



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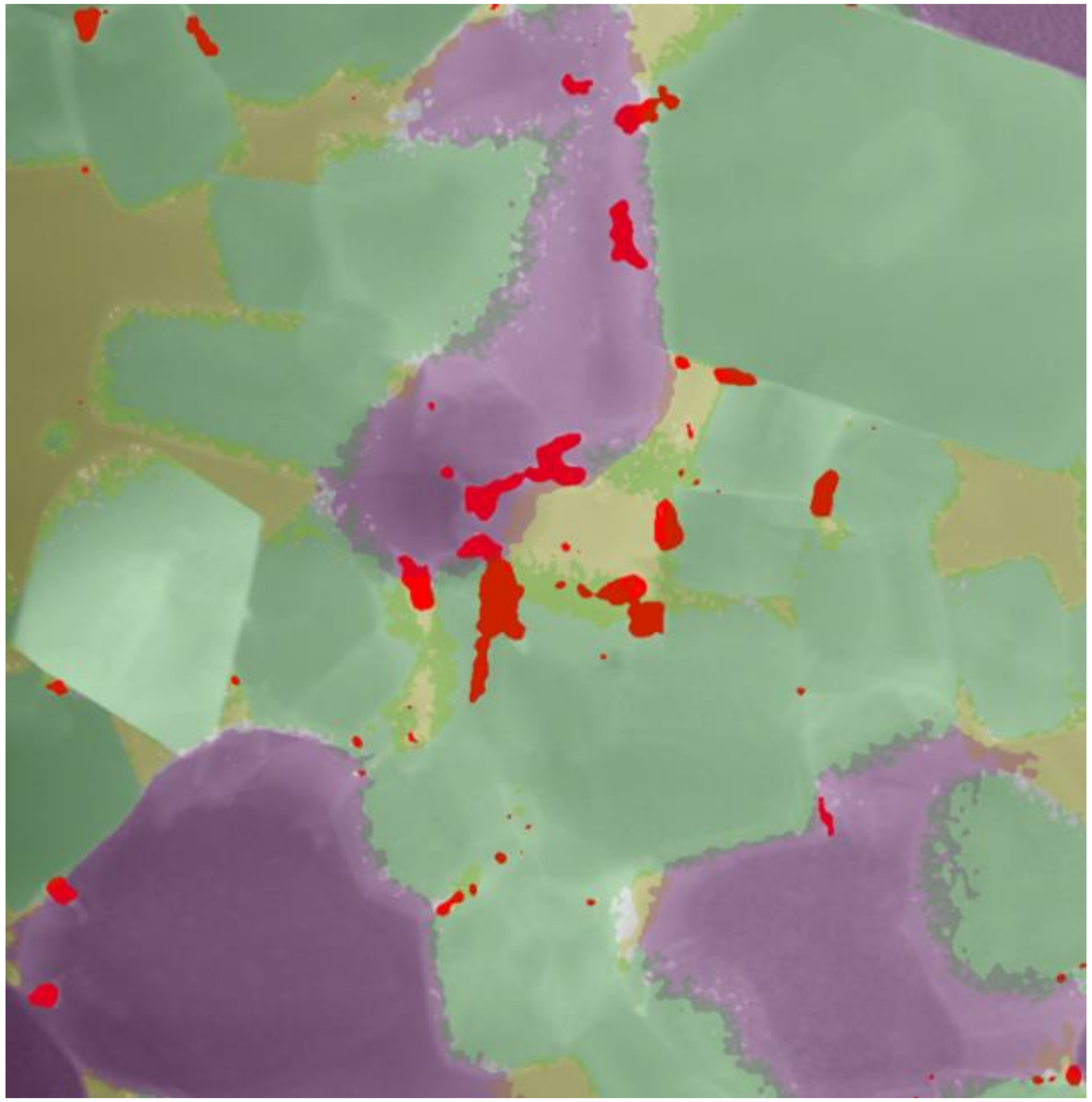
SEM analysis U mine ISR calcined HTC precipitate

Post-calcination mineral phases

- Spinel (green), periclase (purple), monticellite (yellow)
- Lower mantle mineral analogues, high T-P stability
- Cooling, incompatible element exsolution
- U-REE phase (red) along grain boundaries
- Pliniusite (V-apatite) within monticellite (not shown)



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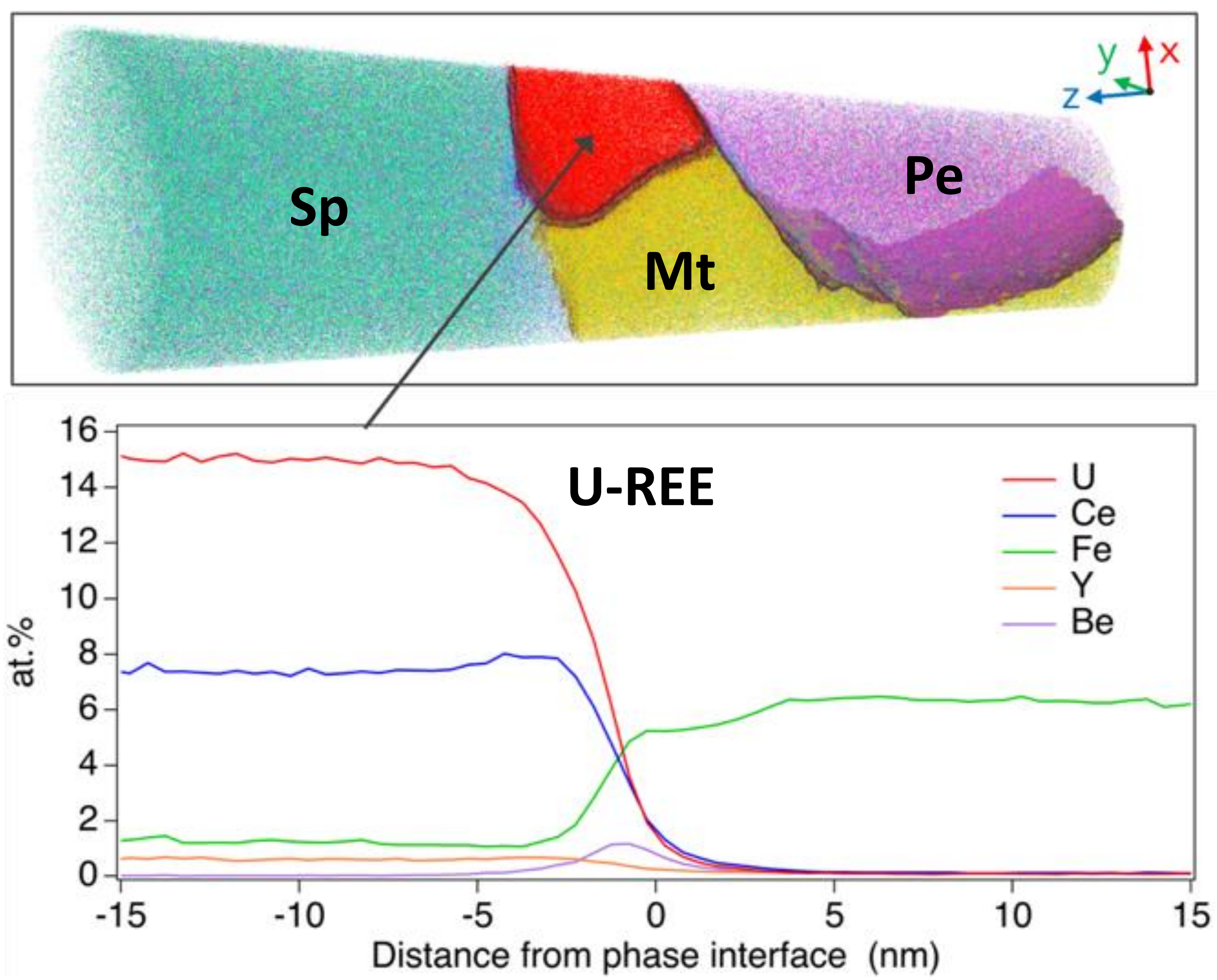
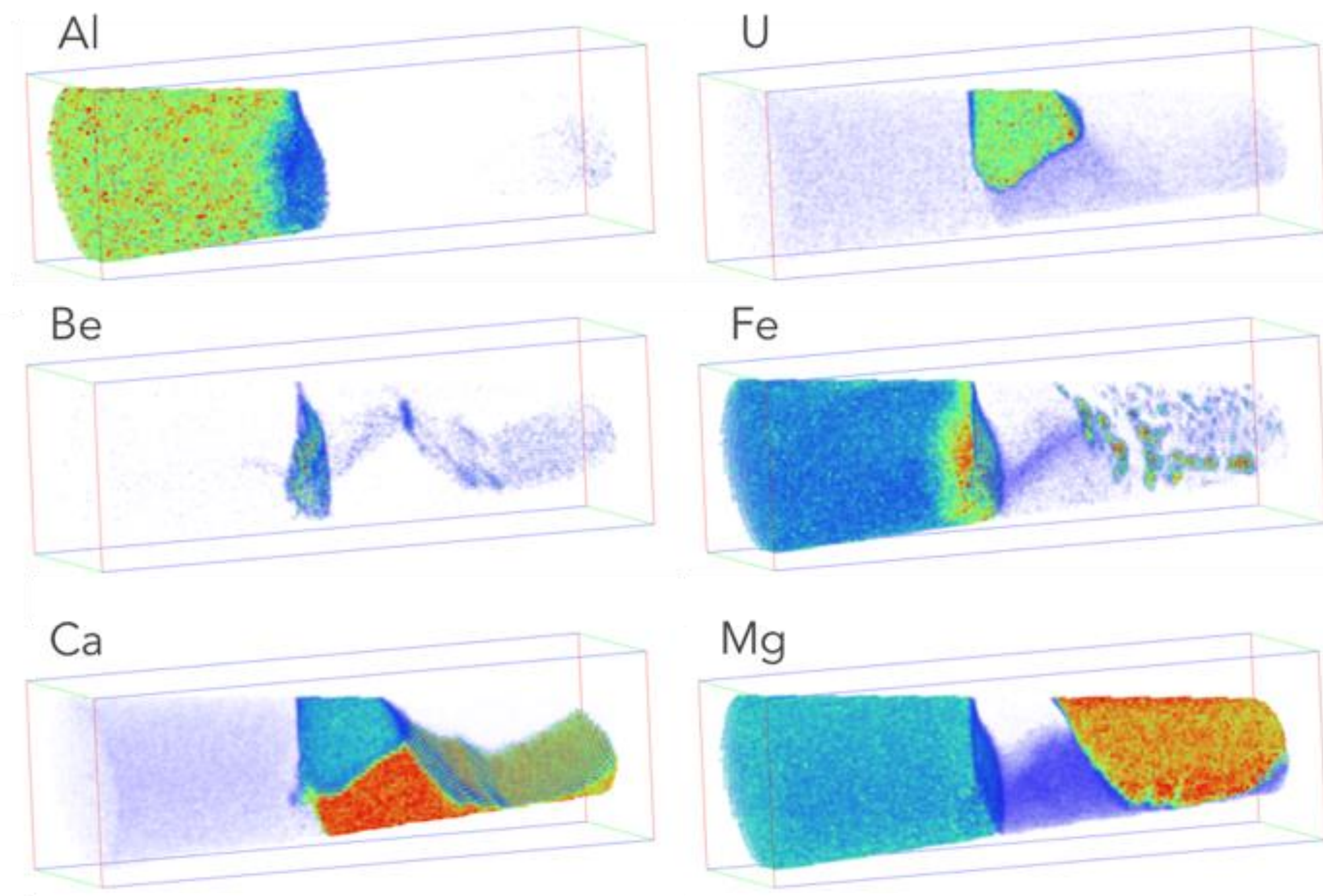
Atom Probe Analysis of U ISR mine calcined HTC precipitate

- Atom Probe analysis (34M atoms, 3D reconstruction, 300 nm)
- New U-bearing phase: Becquerelite family (red)
- 71% U_3O_8, 19% $TREE_2O_3$ (transuranic analogues), Th, ^{210}Pb





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Strong element partitioning

- U as U_3O_8 ~50K enrichment in becquerelite-like phase (71% U_3O_8, 19% $TREE_2O_3$) + Th + ^{210}Pb
- REE as transuranic analogues (Np, Pu, Am) in +II to +IV oxidation states
- Sr as a fission product analogue to ^{90}Sr in V-apatite (pliniusite)

Elements	U-REE oxide	Apatite-V	Monticellite	Spinel	Periclase
Radionuclides (wt%)					
U_3O_8	**70.90**	0.22	-	-	-
ThO_2	**2.05**	0.36	-	-	-
^{210}Pb	**0.02**	-	-	-	-
REE (wt%)					
REE_2O_3	**19.31**	**3.23**	0.12	-	-
Major element oxides (wt%)					
SiO_2	-	3.87	33.62	0.01	0.07
Al_2O_3	-	-	0.36	50.31	1.93
Fe_2O_3	1.39	-	-	34.20	21.34
MgO	0.12	2.08	30.60	14.99	75.97
CaO	5.89	65.67	35.23	0.01	0.01
P_2O_5	-	3.47	0.04	-	-
Trace elements (wt%)					
Sr	0.16	**2.79**	-	-	-
V	0.11	**16.41**	0.03	-	-
Zn	-	-	-	0.17	0.56

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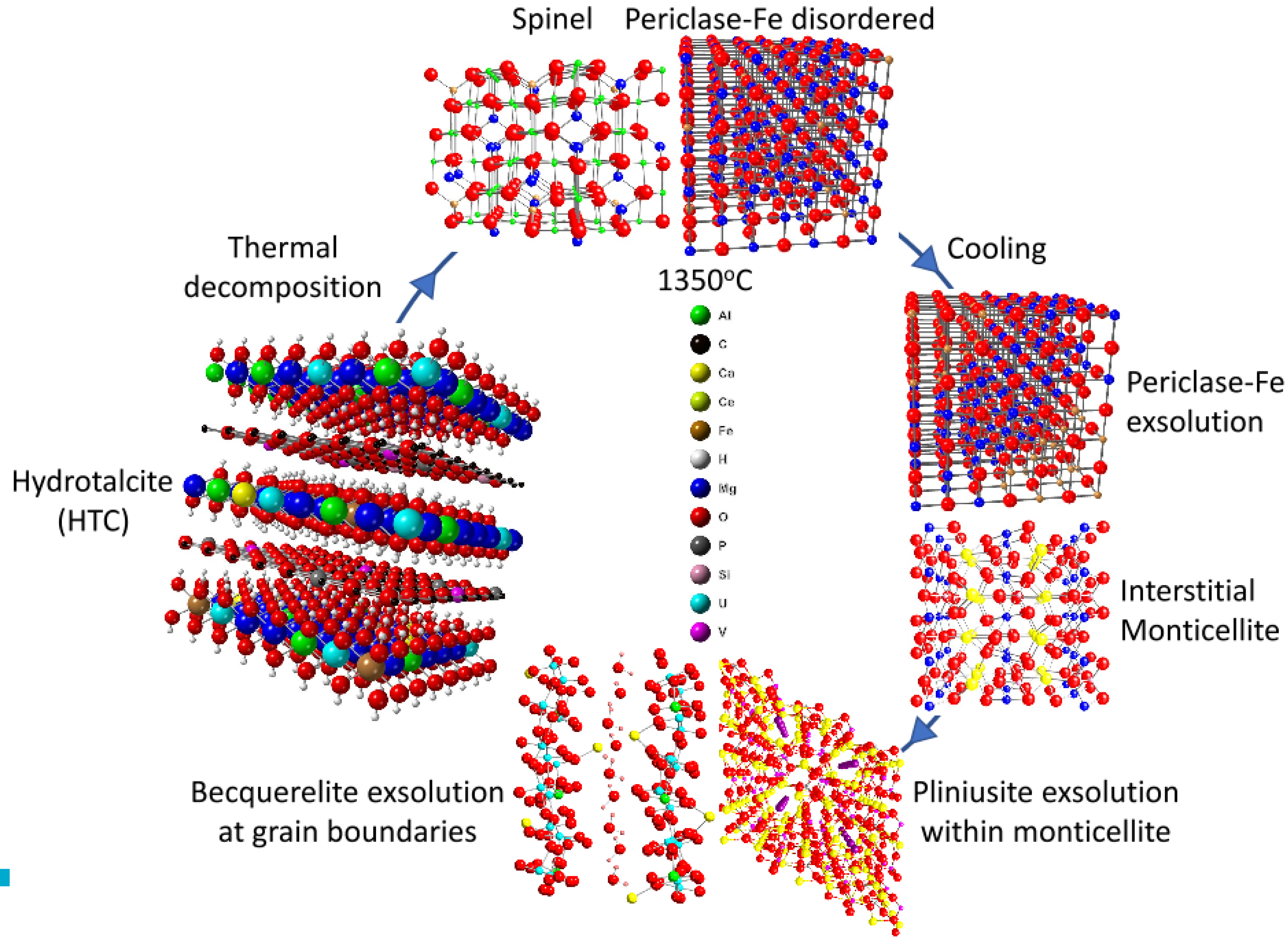
Reaction sequence

- HTC formation from ISR solution
- Recrystallisation during heating
- Novel mineral formation during cooling/exsolution
- Concentrates:

  (a) U, Th, REE/transuranics, and
  (b) fission products (Sr) into two mineral phases within:
- Lower mantle high (P-T) spinel, periclase and olivine mineralogy
- Create bespoke mineralogy via Si, Al addition (nuclear repository)



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Thank you

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