

Progressive oxidation in the U-O system: Structural relations around the U_3O_7 phase field

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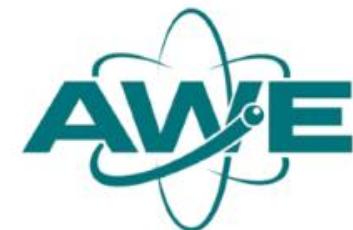
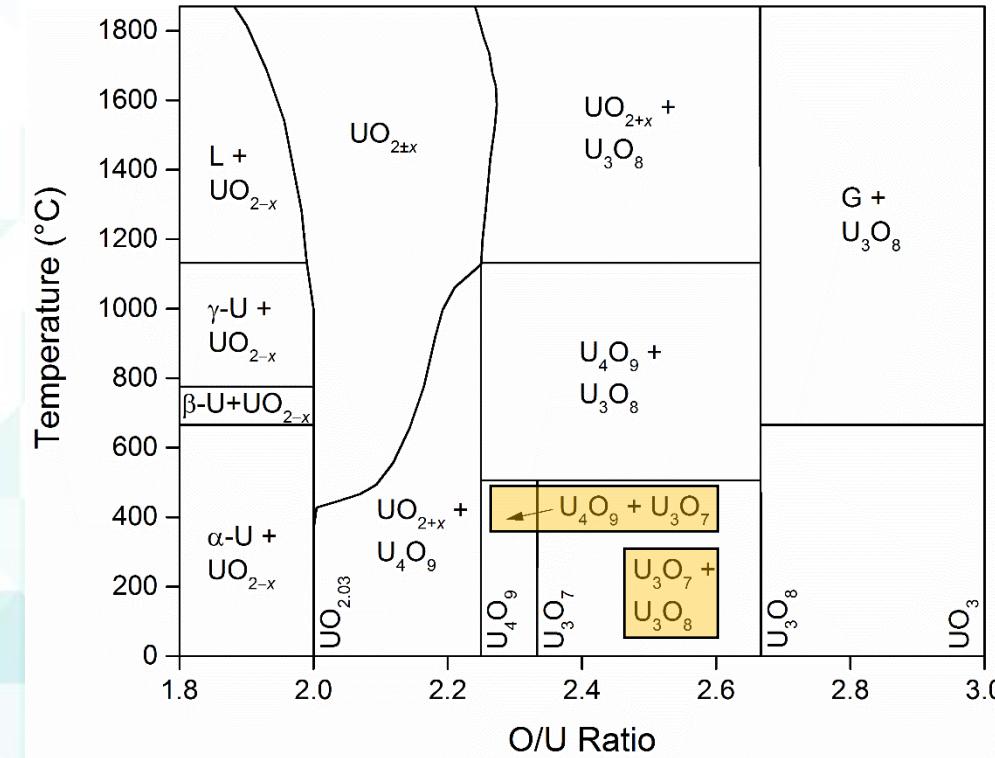
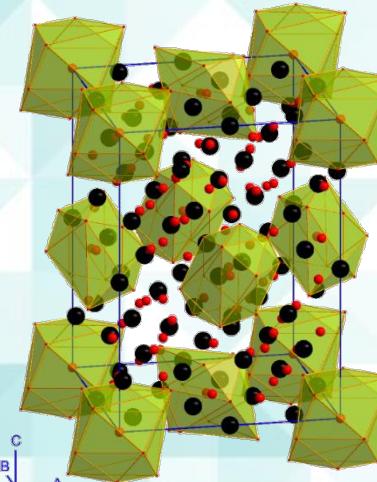
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^d UAntwerpen, Department of Physics

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Uranium is interesting!

Actinide series of elements:

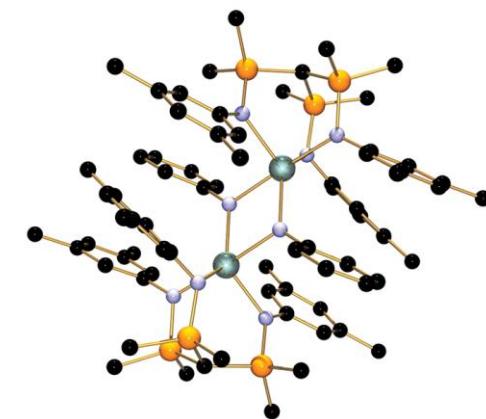
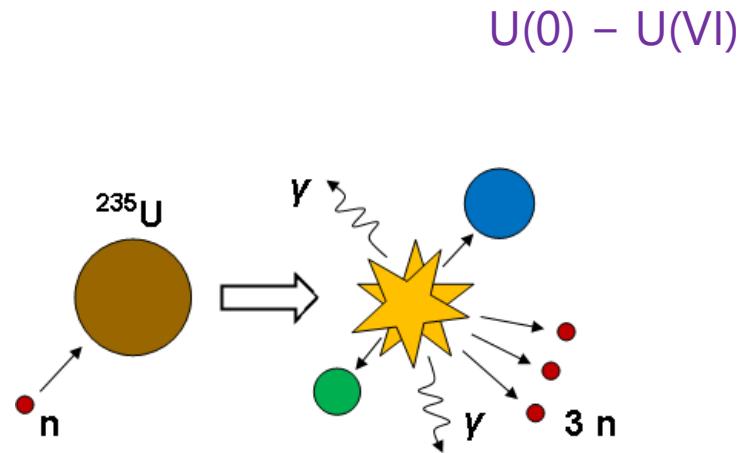
90 Th 232.04	91 Pa 231.04	92 U [Rn] 7s ² 6d ¹ 5f ⁶ 238.03	93 Np (237)	94 Pu (244)
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Applications:

- Nuclear fission fuel
- Catalysis
- Shielding materials

Fundamental:

- 5f electron physics and chemistry
- Orbital hybridization with ligands
- Experiment versus theory



Gardner, B. M., et al.
Nat. Commun. **2017**, *8*, 1898.

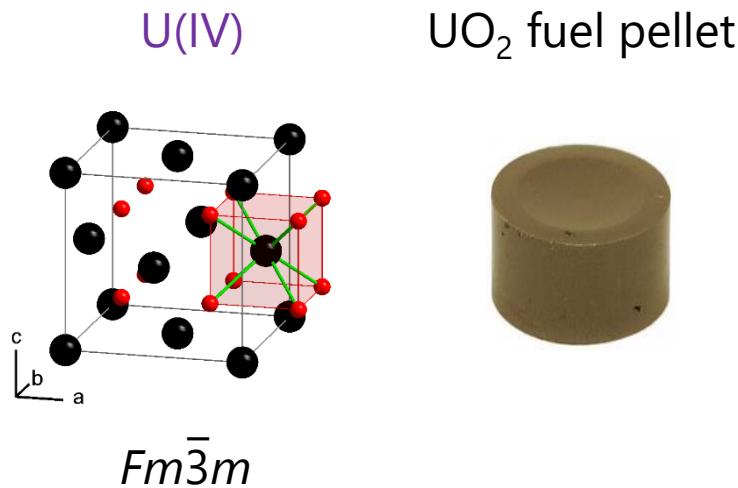
Nuclear fuel application

Uranium(IV)oxide (UO_2) is the preferred chemical form in nuclear applications

- Corrosion resistance to coolant
- Physical stability (e.g. limited swelling)
- Very high melting point
- "Flexible" crystallographic structure

- Low thermal conductivity
- Susceptible to oxidation

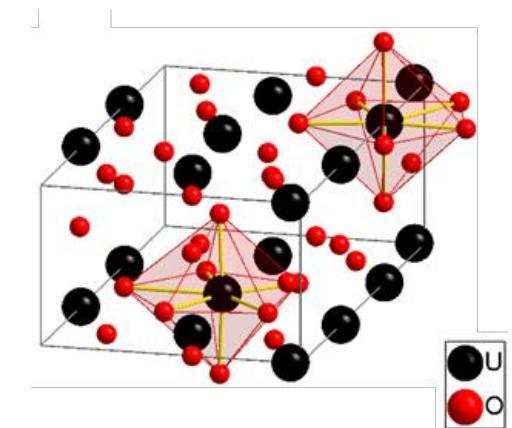
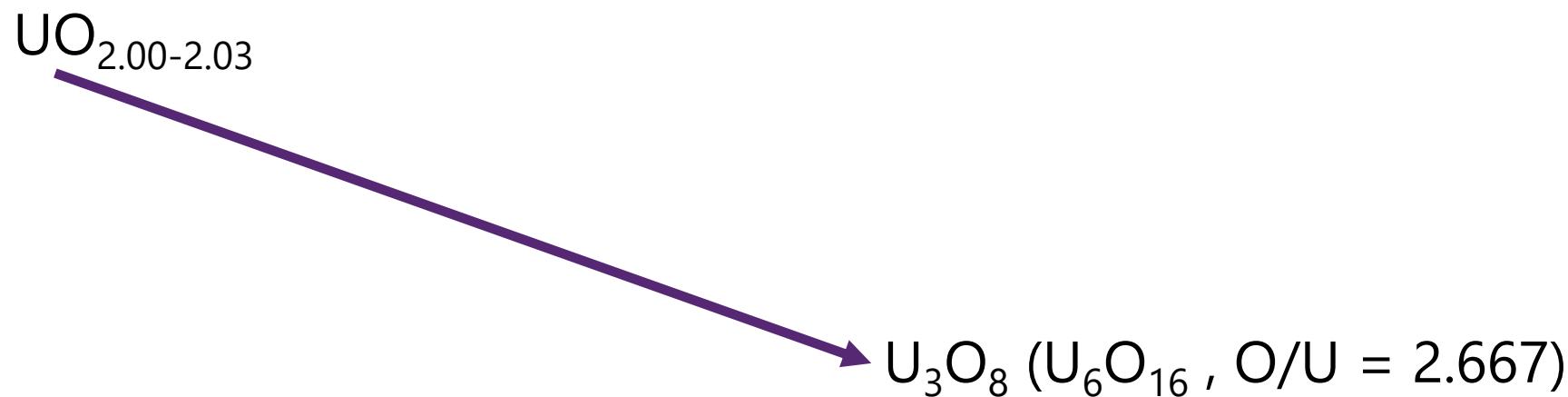
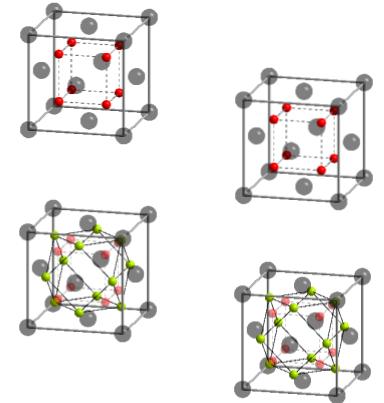
Affects the physico-chemical properties of UO_2



The U-O system

Oxidation pathway at temperatures < 500 °C [1-4]

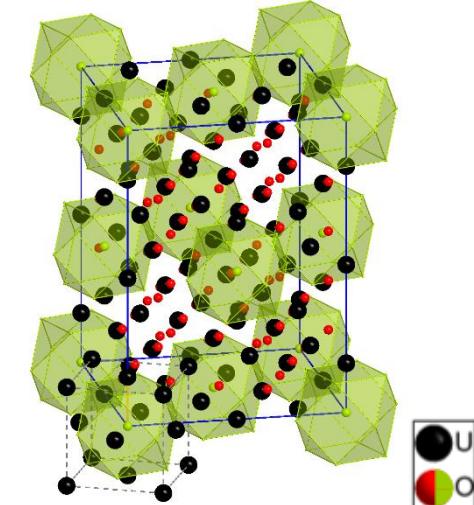
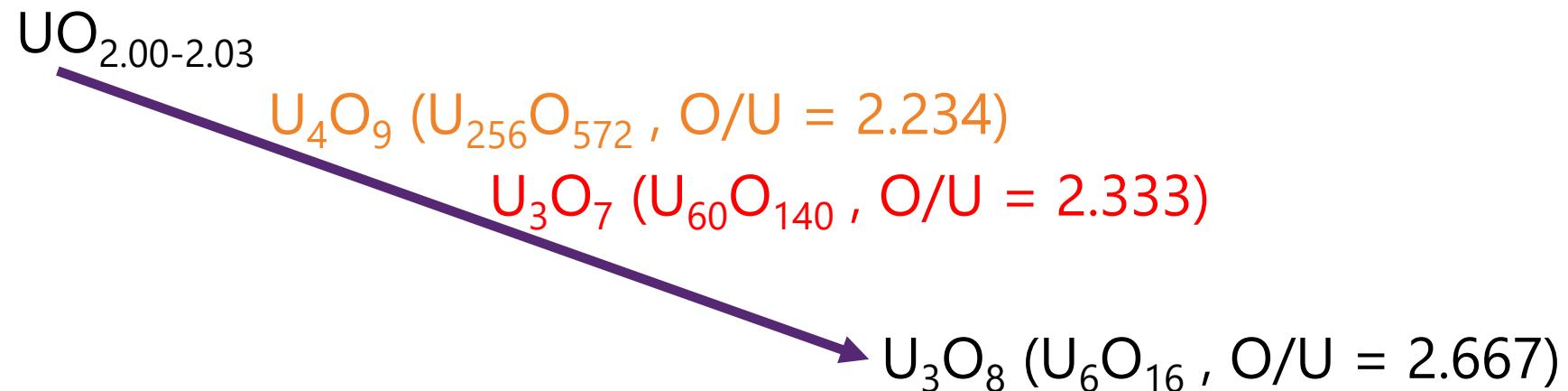
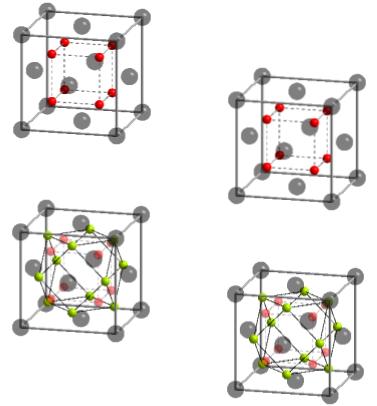
1. Incorporation of excess oxygen as point defects
2. Formation of defect clusters
3. Periodic (long-range) ordering of clusters



The U-O system

Oxidation pathway at temperatures < 500 °C

1. Incorporation of excess oxygen as point defects
2. Formation of defect clusters
3. Periodic (long-range) ordering of clusters
- 4. Formation of anion-excess intermediates [1-4]**

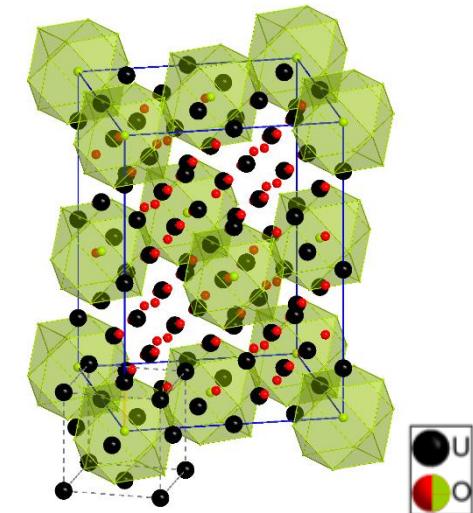
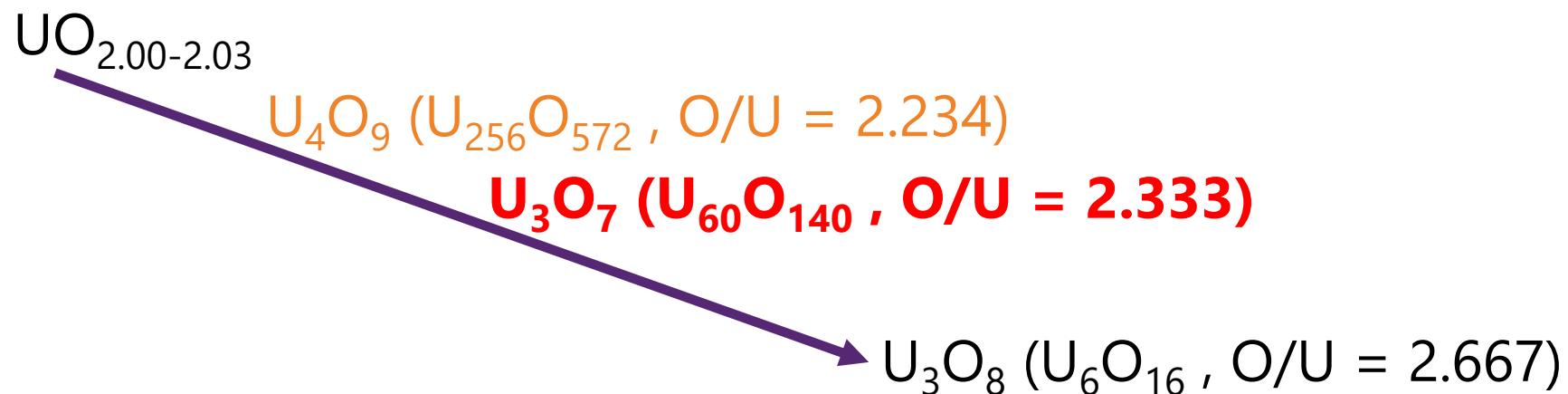


Objective

Understand and characterize the oxidation mechanism

→ Specifically: Focus on the anion-excess intermediate **U₃O₇**

Although first identified in 1947 [1], only recent progress in deriving its crystal structure [2-4], and the work continues [5]!



[1] Jolibois, P., *C.R. Acad. Sci.* **1947**, 224, 1395-1396.

[2] Desgranges, L., et al., *Inorg. Chem.* **2009**, 48, 7585-7592.

[3] Leinders, G., et al., *Inorg. Chem.* **2016**, 55, 9923-9936.

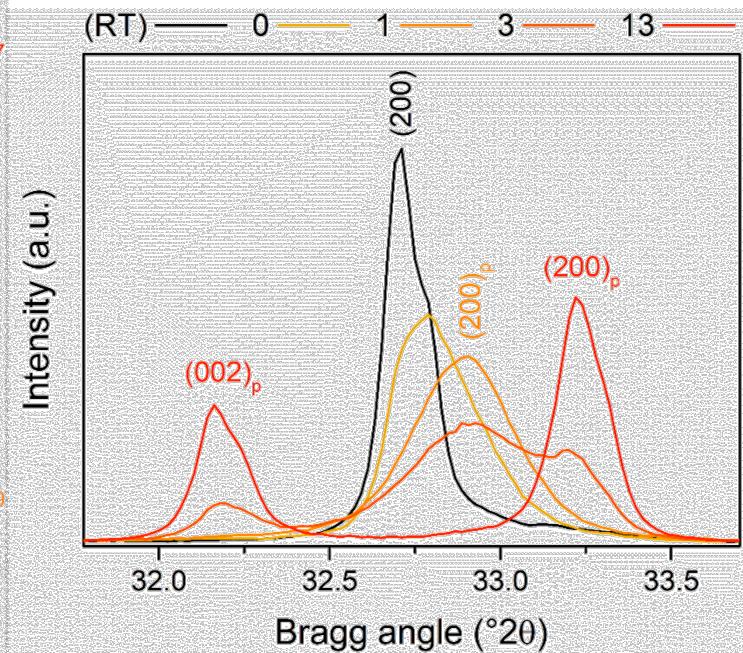
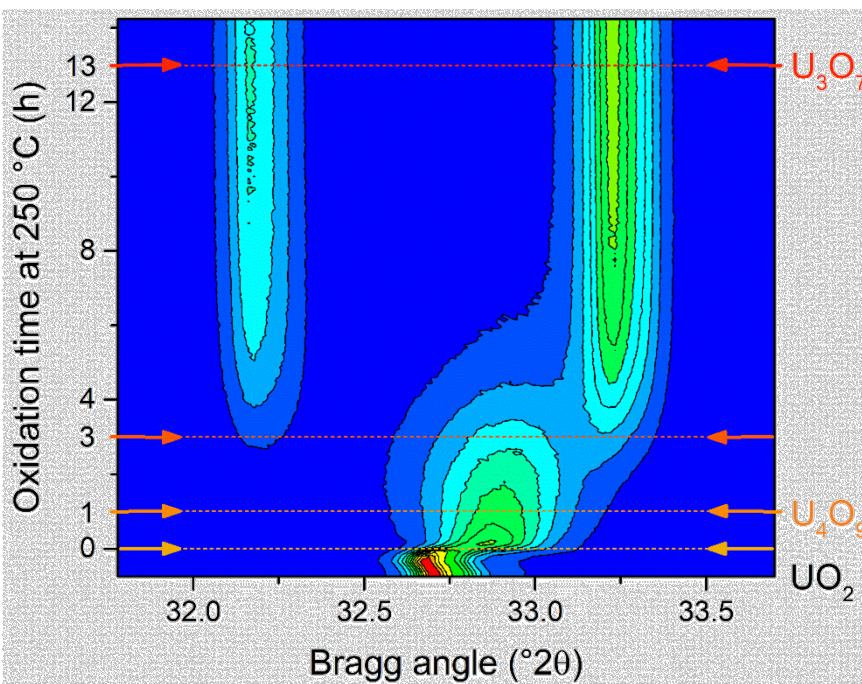
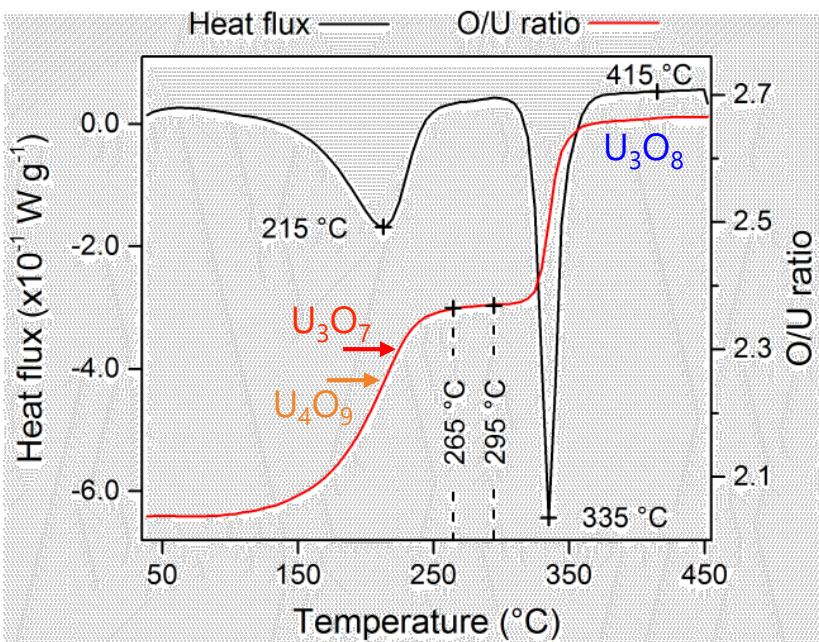
[4] Leinders, G., et al., *Inorg. Chem.* **2020**, 59, 4576-4587.

[5] Leinders, G., et al., *Inorg. Chem.* **2021**, in press.

doi: 10.1021/acs.inorgchem.1c01212

Finding and identifying U_3O_7

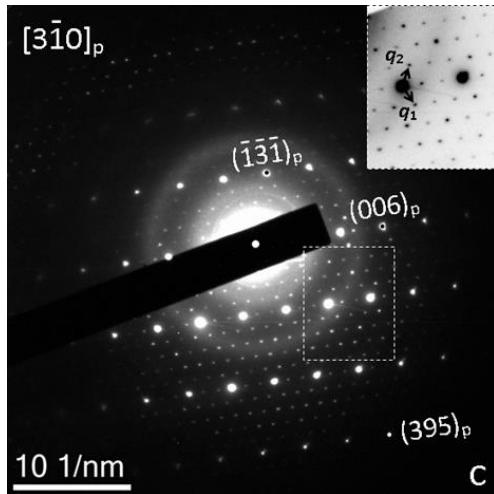
In-situ TG-DSC and XRD [1,2]



Assessing the crystal structure

Selected-area electron diffraction [1]

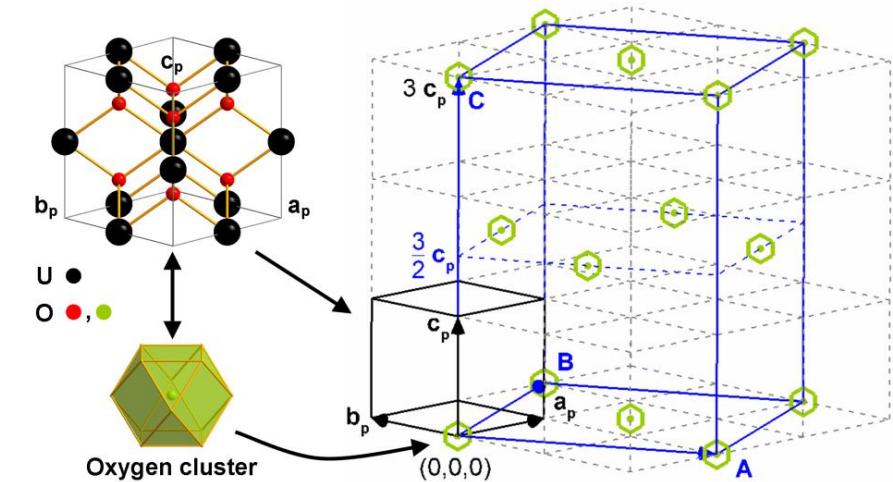
1. Main reflections: Fluorite parent structure
2. Satellite reflections: Periodic perturbation
3. Symmetry of the “superstructure”
 - Type of defect motif considered: Oxygen clusters



$$\mathbf{q}_1 = \frac{1}{15} \cdot [395]_p^* = \frac{1}{5} \cdot \mathbf{a}^* + \frac{3}{5} \cdot \mathbf{b}^* + \frac{1}{3} \cdot \mathbf{c}^*$$

$$\mathbf{q}_2 = \frac{1}{15} \cdot [\bar{3}\bar{9}5]_p^* = -\frac{1}{5} \cdot \mathbf{a}^* + -\frac{3}{5} \cdot \mathbf{b}^* + \frac{1}{3} \cdot \mathbf{c}^*$$

Space group $P4_2/n$

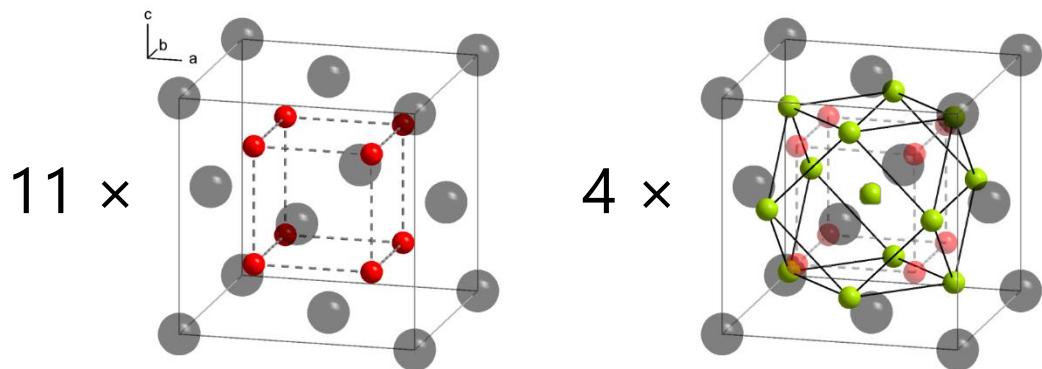


Building the trial model

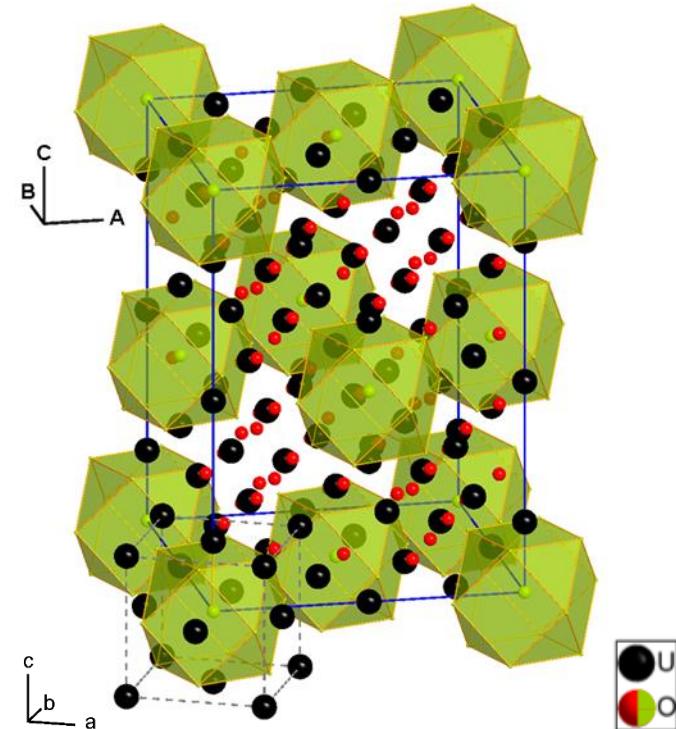
A “supercell” consisting of fluorite-type arranged U and O atoms and cubooctahedral oxygen clusters

$$V = (11 + 4) \times V_p = 15 \times V_p$$

- $(11 \times 4) + (4 \times 4) = 60$ U atoms
- $(11 \times 8) + (4 \times 13) = 140$ O atoms



$$140/60 = 7/3 = 2.333 (= \text{U}_3\text{O}_7)$$

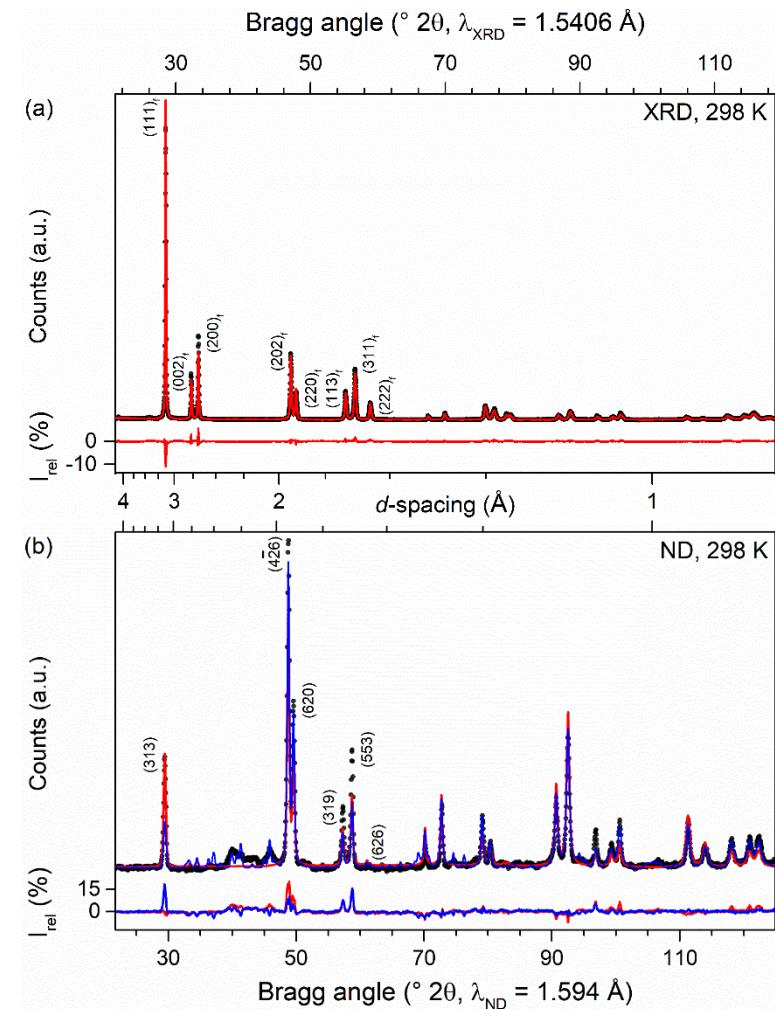


Validation of the trial model

1. XRD: Not sensitive to the oxygen clusters
 - Displays only the fluorite-type parent reflections

 2. ND: Sensitive to both U and O atoms
 - Displays fluorite-type parent reflections, and
 - Satellite reflections (visible between 30-50° 2θ)

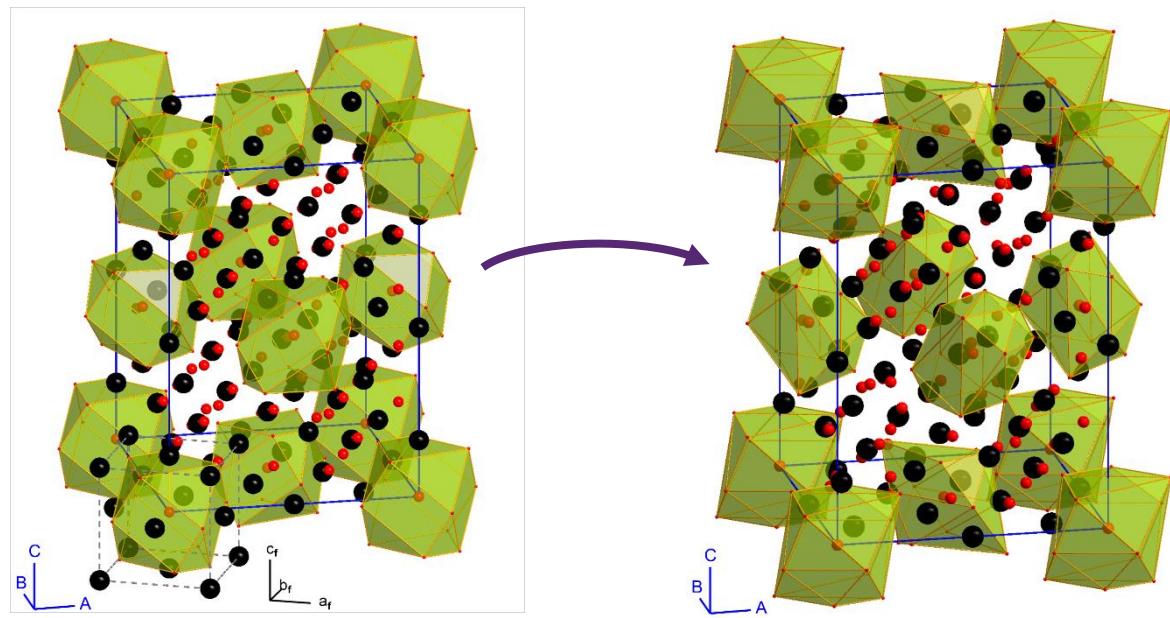
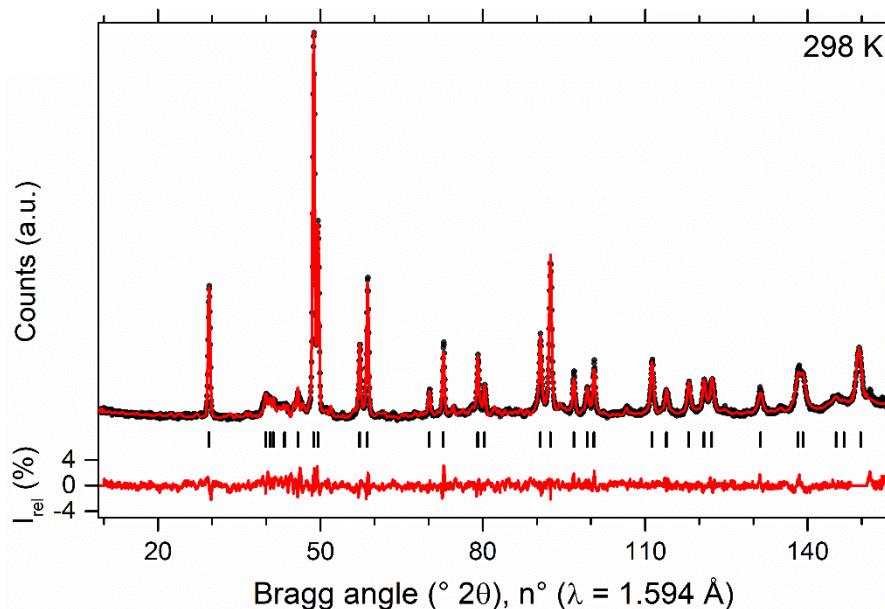
 - BUT: the trial model does not match well with the observations [1]
- **refinement of the model required!**



The refined U_3O_7 structure

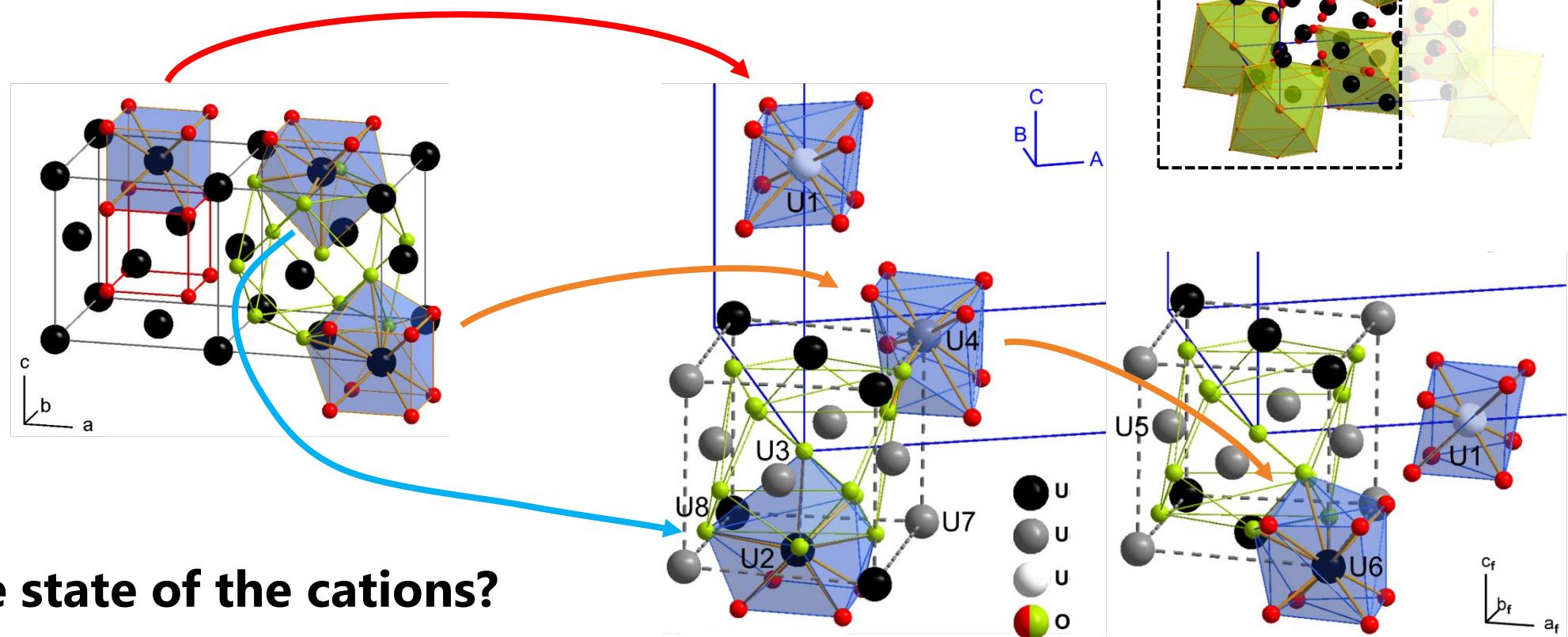
Refinement of atomic displacement factors and coordinates, respecting the derived space group symmetry

- U remain close to their original, fluorite-type positions
- O deviate more, leading to a distortion of the cuboctahedra



Atomic coordination

Distortion of the “regular” atomic environments in the trial model

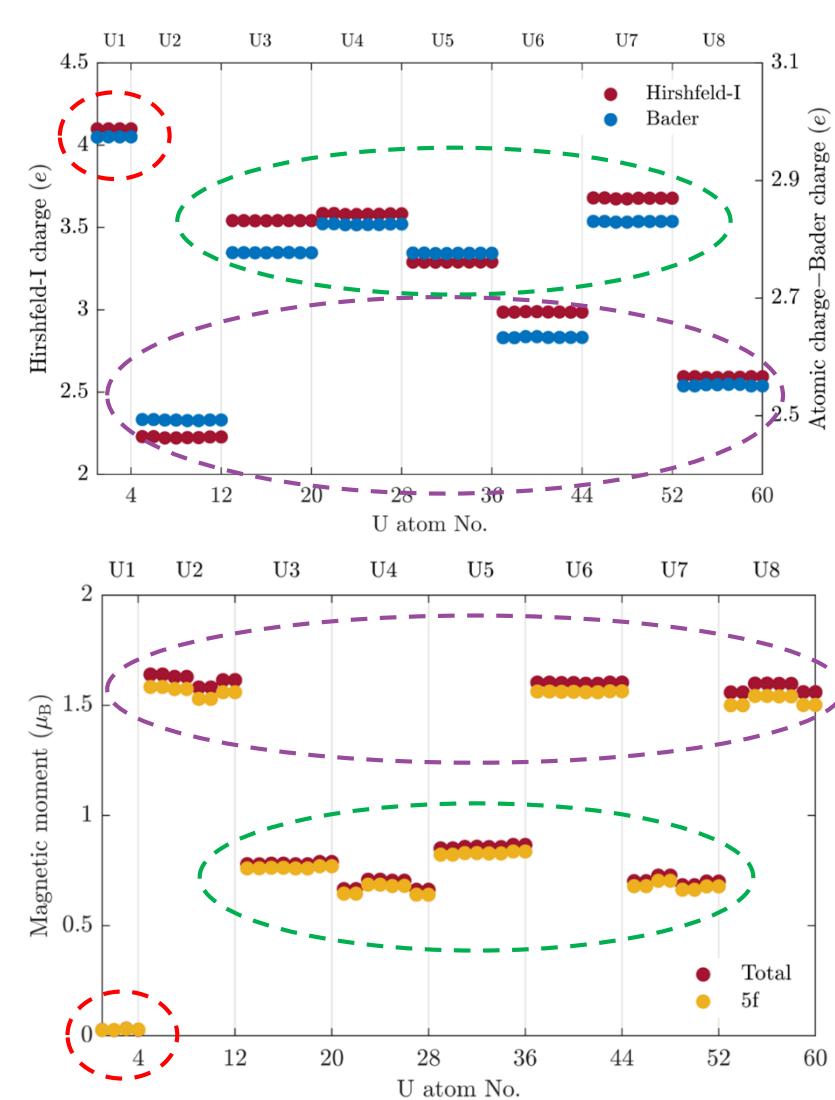


Uranium charge localization (PBE+ U)*

1. Bader and iterative Hirshfeld analysis
2. Magnitude of spin magnetic moments
3. Bond-valence-sum calculations

- U1: Highest charge, $\mu_B \approx 0$ → **U(VI)**
- U2,6,8: Lowest charge, $\mu_B \approx 1.6$ → **U(IV)**
- U3,4,5,7: Intermediate, $\mu_B \approx 0.8$ → **U(V)**

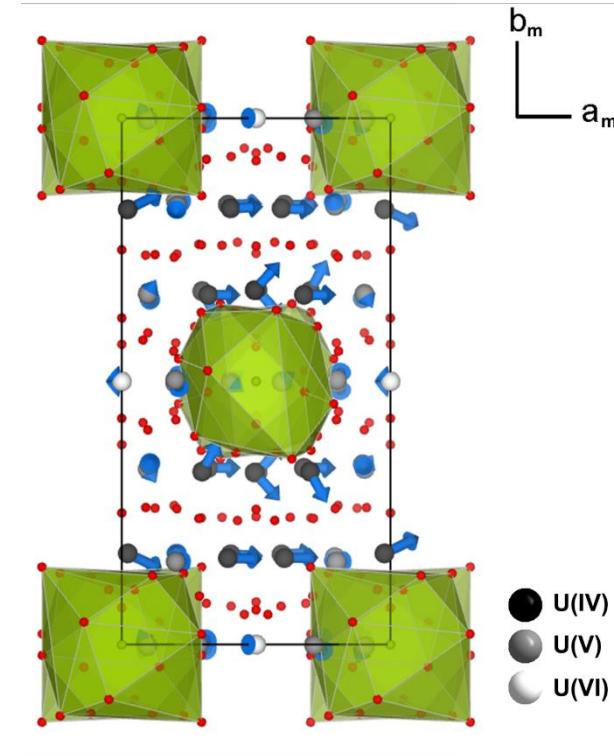
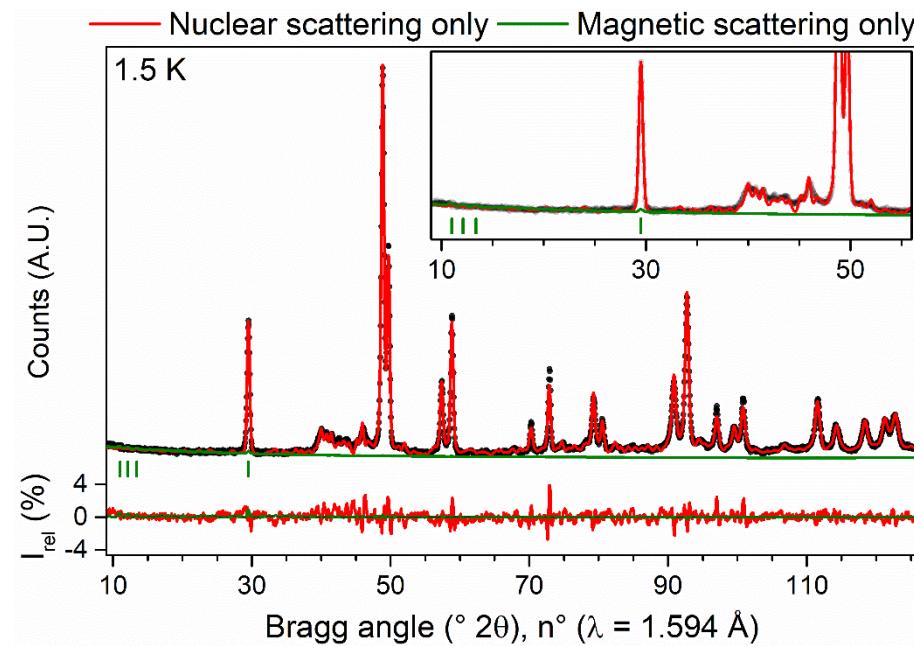
	U1	U2	U3	U4	U5	U6	U7	U8	All U	All O
Site mult.	4	8	8	8	8	8	8	8	60	140
Valence	(VI)	(IV)	(V)	(V)	(V)	(IV)	(V)	(IV)	...	(-II)
Charge distribution				$24 \times \text{U(VI)} = 96^+$					280^+	280^-
				$32 \times \text{U(V)} = 160^+$						
				$4 \times \text{U(VI)} = 24^+$						



Discussion: Magnetic ordering in U_3O_7

Canted ferromagnetic ground state predicted from the electronic structure calculations

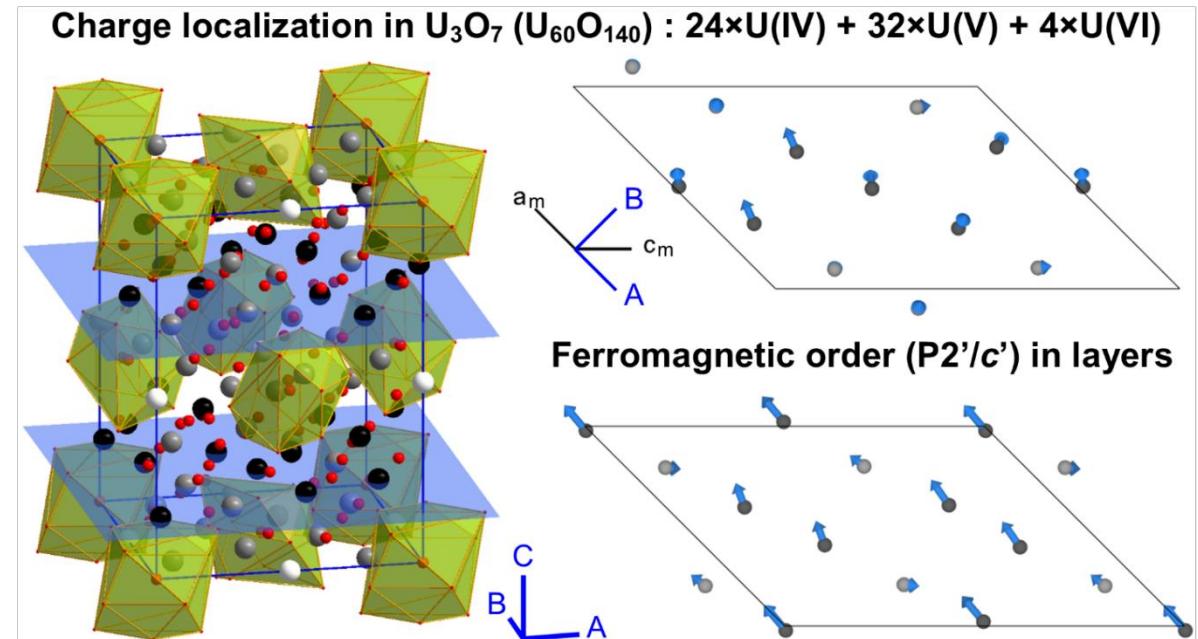
- Described in the monoclinic subgroup $\text{P}2'/c'$ of the tetragonal nuclear structure



Conclusion

Major steps forward in characterization of the anion-excess, fluorite-related intermediate U_3O_7

- Refined crystal structure
- Coordination environments
- Charge localization
- Electronic structure
- Magnetic correlations



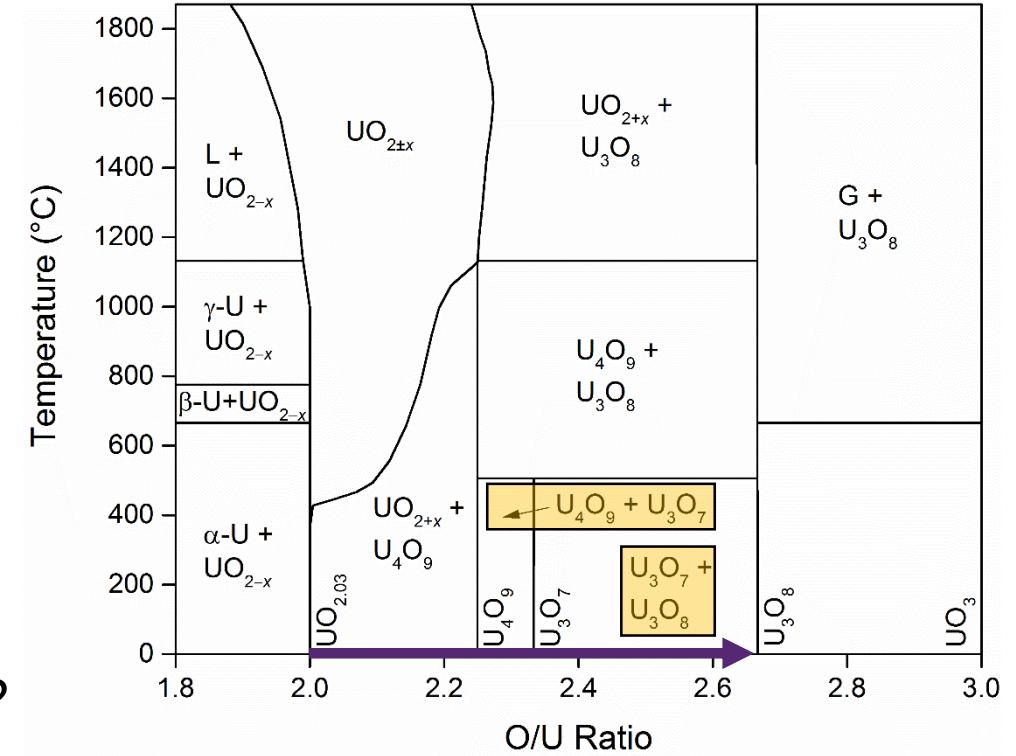
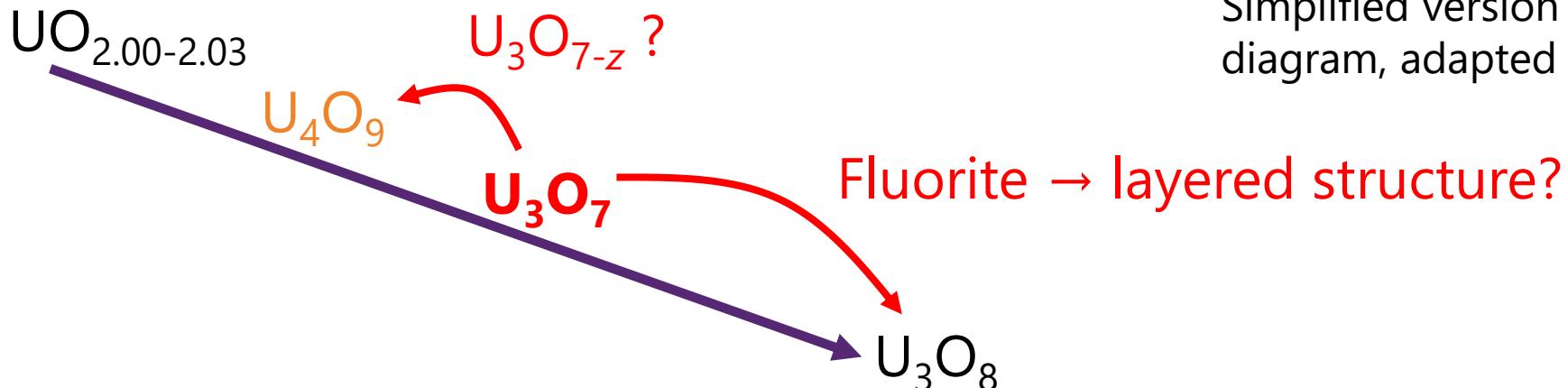
Outlook

U_4O_9 transition to U_3O_7

- Re-shuffling of the oxygen cuboctahedra
- sub-stoichiometric U_3O_{7-z} phase field?

U_3O_7 transition to U_3O_8

- Destruction of the oxygen cuboctahedra
- Role of the U(V) and U(VI) environments?



Simplified version of the U-O phase diagram, adapted from critical reviews [1-4].

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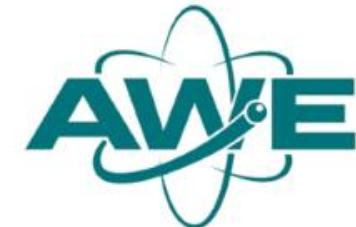
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^d UAntwerpen, Department of Physics

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Thank you for your attention

Questions?

→ **Save them for the virtual panel session!**

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