

Assessment of the U_3O_7 crystal structure

A missing piece in the UO_2 oxidation mechanism puzzle

Gregory Leinders, Rémi Delville, Janne Pakarinen, Thomas Cardinaels,
Koen Binnemans and Marc Verwerft



Outline

Scope

- o Background
- o Objective

Results

Conclusions and outlook

Outline

Scope

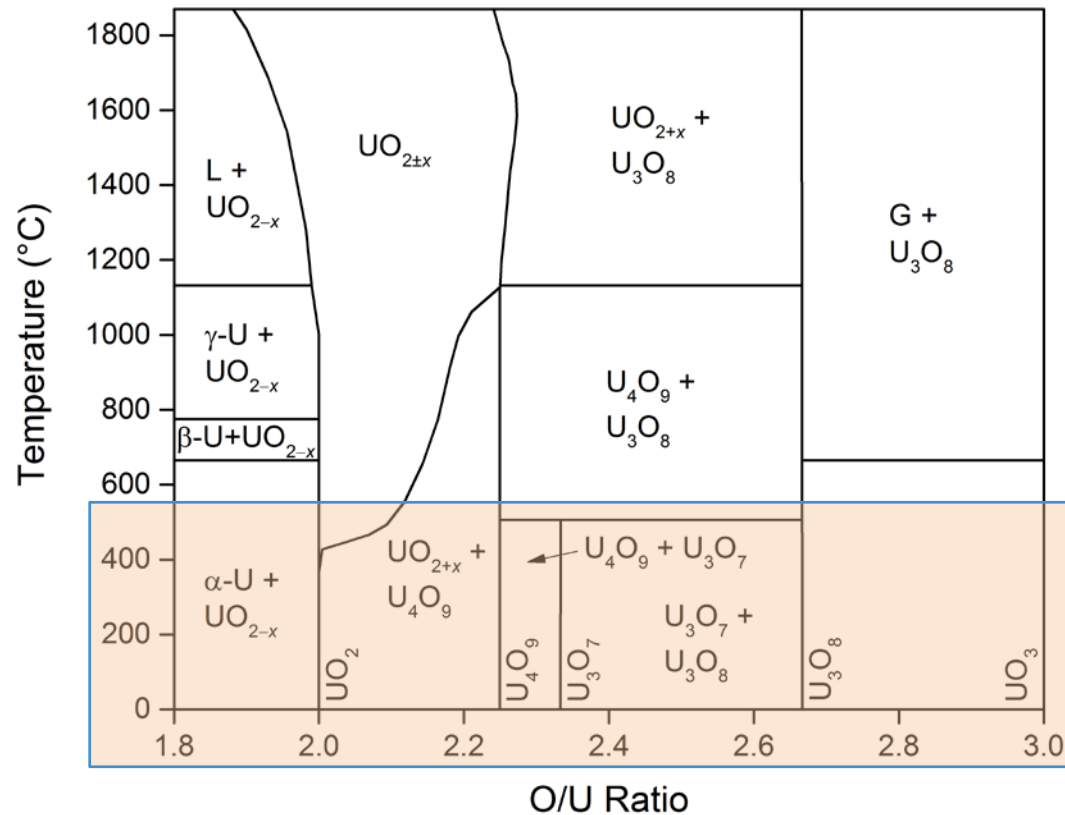
- o **Background**
- o **Objective**

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Conclusions and outlook

Uranium and Oxygen...

...live together in (perfect) harmony?



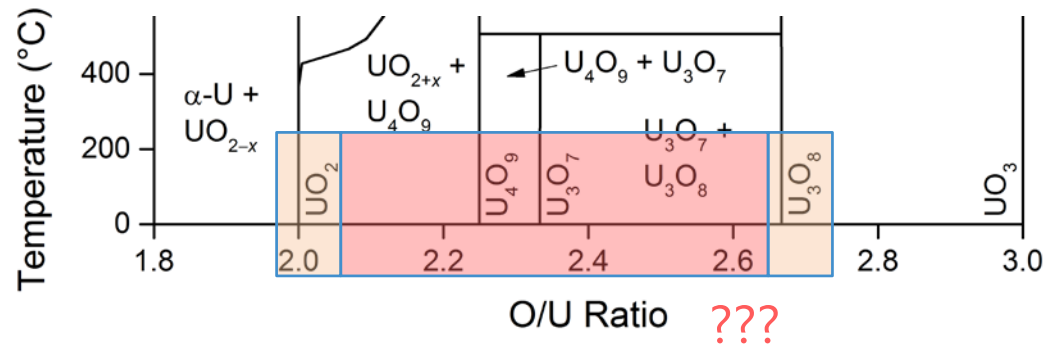
Simplified version of the U-O phase diagram, adapted from critical reviews [1-4].

- [1] P. Y. Chevalier, *et al.*, *J. Nucl. Mater.* **2002**, 303, 1.
[3] J. D. Higgs, *et al.*, *J. Nucl. Mater.* **2007**, 366, 99.

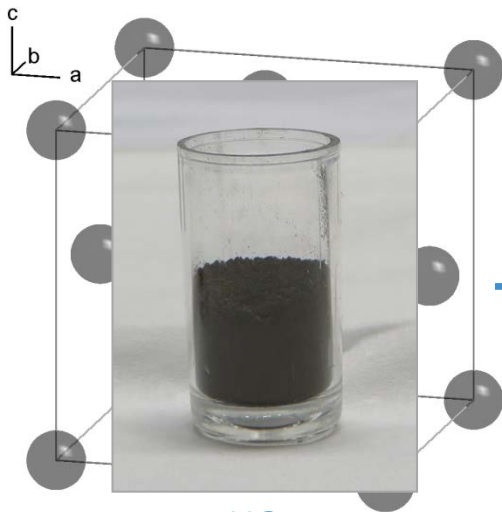
- [2] D. Labroche, *et al.*, *J. Nucl. Mater.* **2003**, 312, 50.
[4] C. Guéneau, *et al.*, *J. Nucl. Mater.* **2011**, 419, 145.

Uranium and Oxygen...

...a low-temperature oxidized family



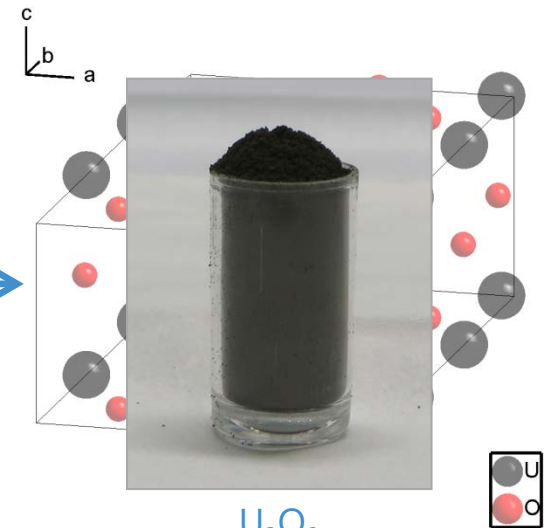
O/U = 2.00



UO_2
 UO_2 crystal structure ($Fm\bar{3}m$):
 $a = b = c$ [5]

Crystallographic
 transformation: 36%
 increase in volume

O/U = 2.67

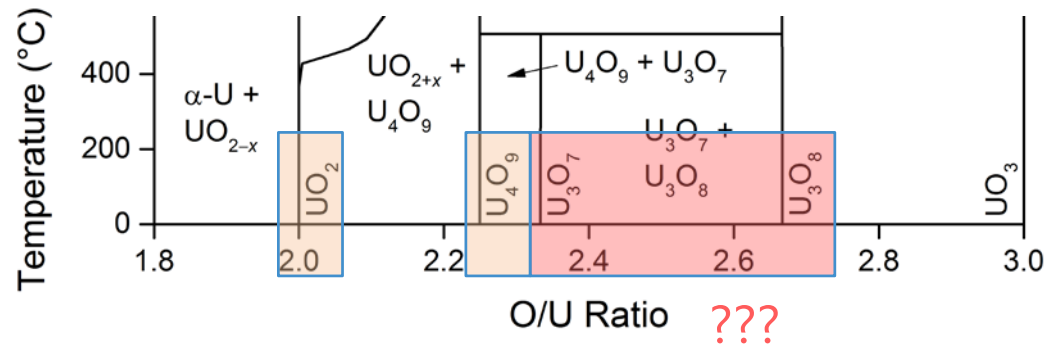


U_3O_8
 U_3O_8 crystal structure ($C2mm$):
 $a \neq b \neq c$ [6]

- [5] V. M. Goldschmidt & L. Thomassen, *Videnskapsselskapets Skrifter*. **1923**, 48.
 [6] B. O. Loopstra, *Acta Cryst. A* **1964**, 17, 651.

Uranium and Oxygen...

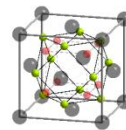
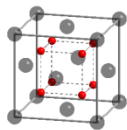
...a low-temperature oxidized family



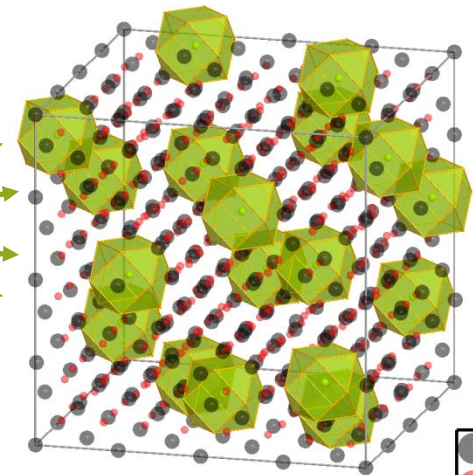
O/U = 2.00

2.00 < O/U < 2.25

O/U = 2.25



Building block of long-range ordered structure!



UO₂ crystal structure ($Fm\bar{3}m$):

[7] D. J. M. Bevan, *et al.*, *J. Solid State Chem.* **1986**, 61, 1.

[8] R. I. Cooper & B. T. M. Willis, *Acta Cryst. A* **2004**, 60, 322.

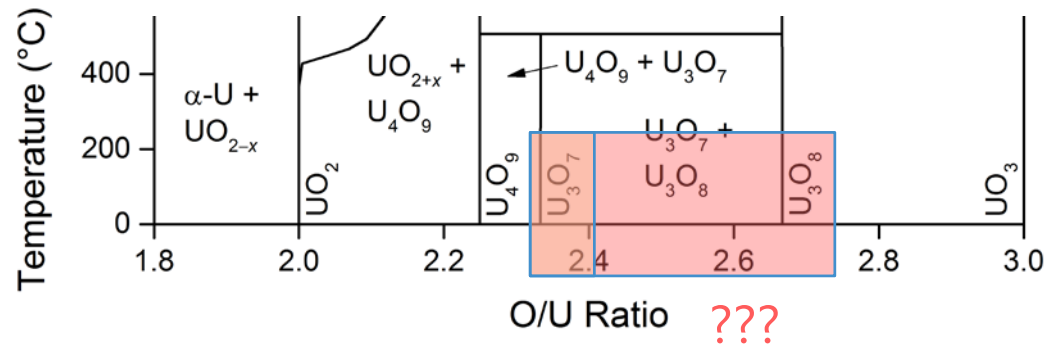
Cuboctahedral oxygen cluster

U₄O₉ crystal structure ($I\bar{4}3d$):

4×a, 4×a, 4×a [7,8]

Uranium and Oxygen...

...a low-temperature oxidized family



O/U = 2.33

O/U = 2.67

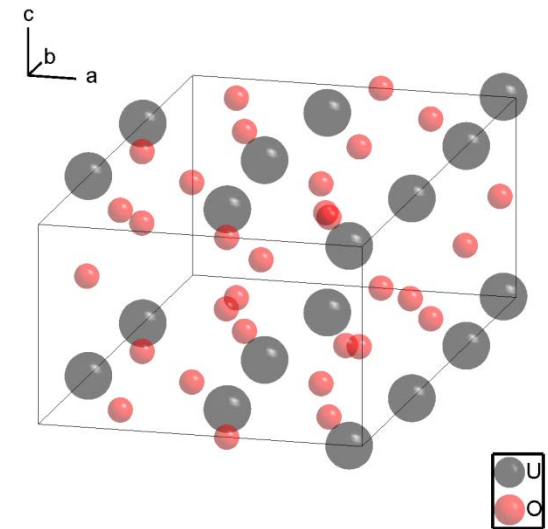
Long-range
ordered structure?

$\sqrt{5} \times a, \sqrt{5} \times a, 3 \times c$ [9]

$5 \times a, 5 \times a, 3 \times c$ [10]

$4 \times a, 4 \times a, 4 \times c$ [11]

Other ... [12,13]



U_3O_8 crystal structure ($C2mm$):
 $a \neq b \neq c$ [6]

[9] R. J. McEachern & P. Tayler, *J. Nucl. Mater.* **1998**, 254, 87.

[10] L. Nowicki, *et al.*, *Phys. Chem. Solids* **2000**, 61, 1789.

[11] L. Desgranges, *et al.*, *Inorg. Chem.* **2009**, 48, 7585.

[12] D. A. Andersson, *et al.*, *Inorg. Chem.* **2013**, 52, 2769.

[13] N. A. Brincat, *et al.*, *J. Nucl. Mater.* **2015**, 467, 724.

Objective

Assess the crystal structure of U_3O_7 using appropriate methods

Find the missing piece in the UO_2 oxidation mechanism puzzle!

Outline

Scope

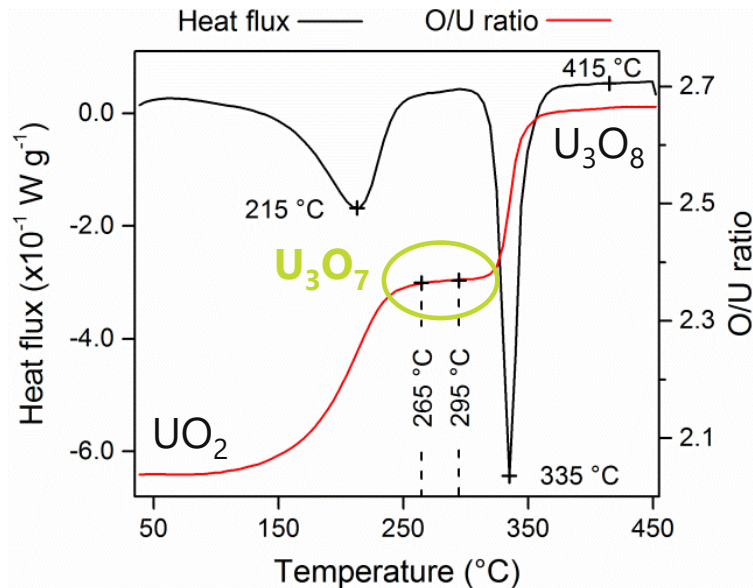
- o Background
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Sample preparation

Simultaneous thermal analysis to determine optimal temperature



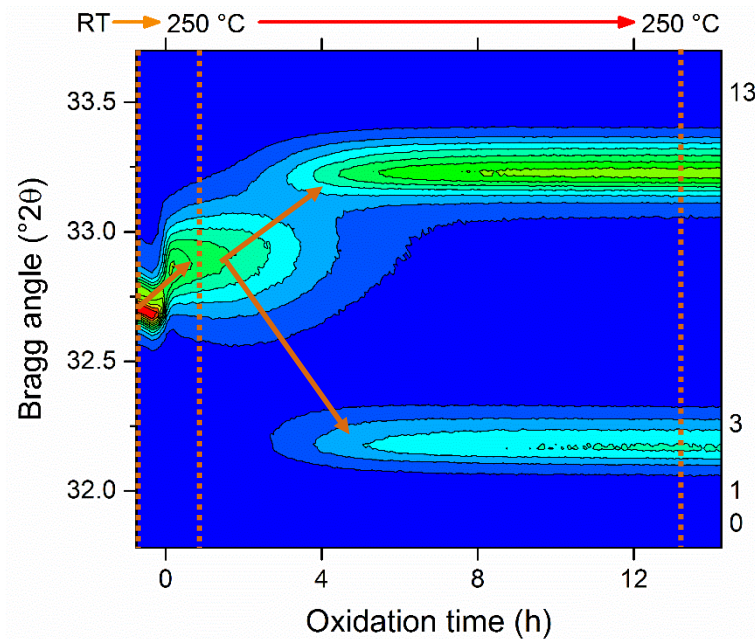
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STA data of UO_2 oxidation, showing the increase in mass (red line) and the associated heat flux (black line), a measure of the reaction enthalpy.

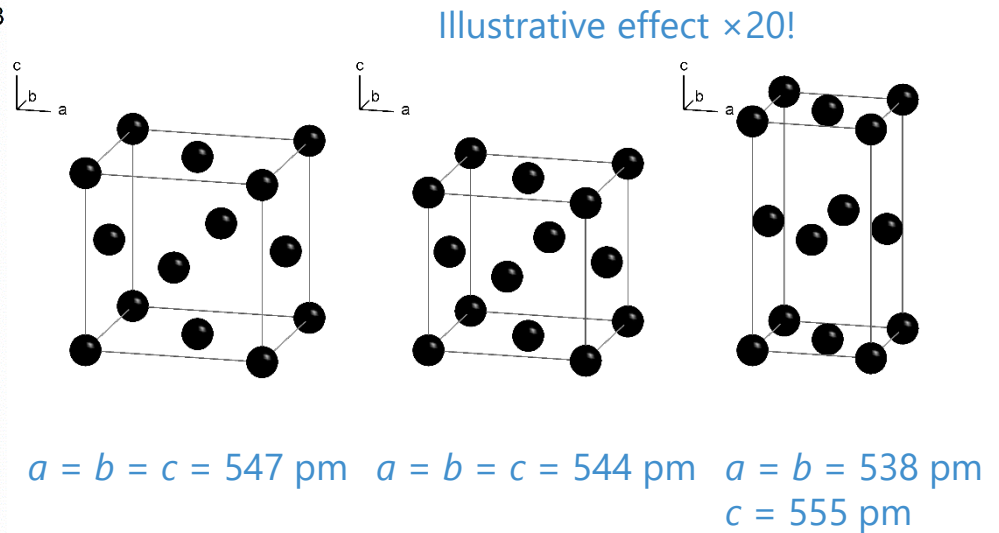
Sample preparation

In-situ X-ray diffraction to investigate crystallographic changes

→ Uranium atomic positions



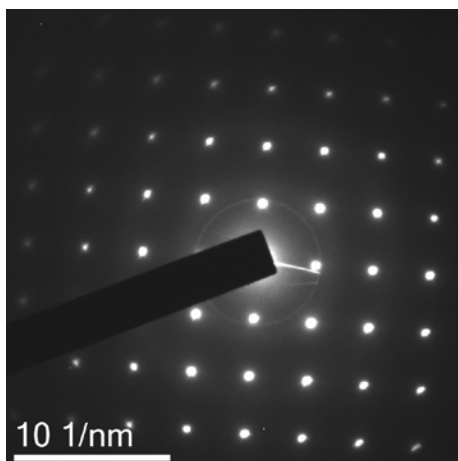
In-situ XRD of UO_2 oxidation, showing evolution of the tetragonal U_3O_7 phase.



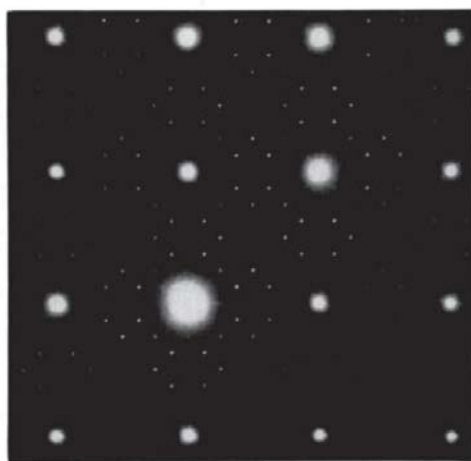
Superstructure analysis

Electron diffraction patterns gathered and analyzed during 1.5 years

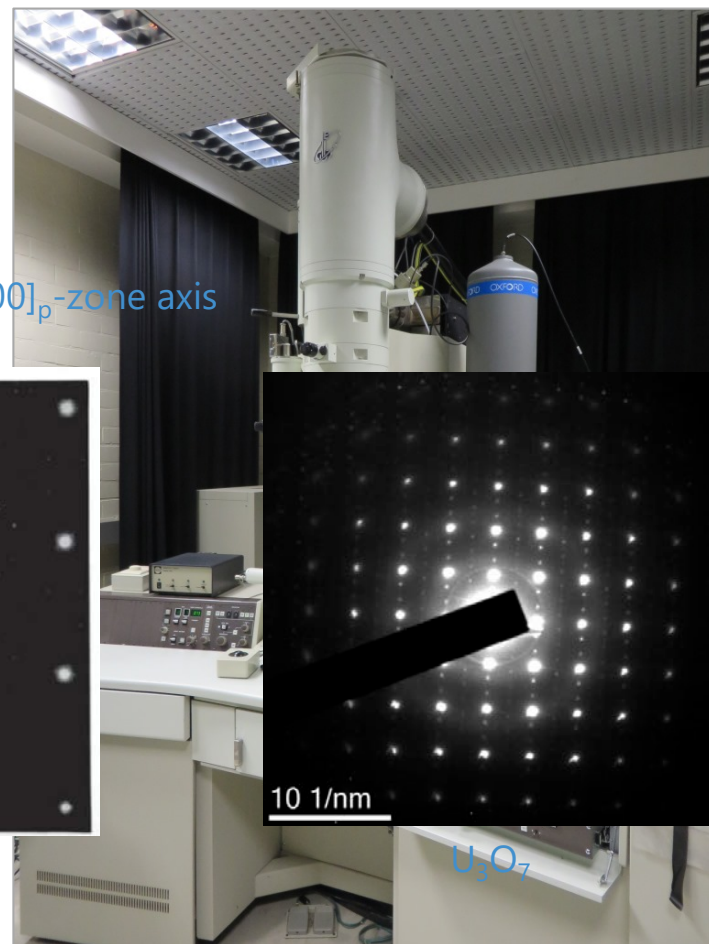
ED patterns oriented along the $[100]_p$ -zone axis



UO_2



U_4O_9 [14]



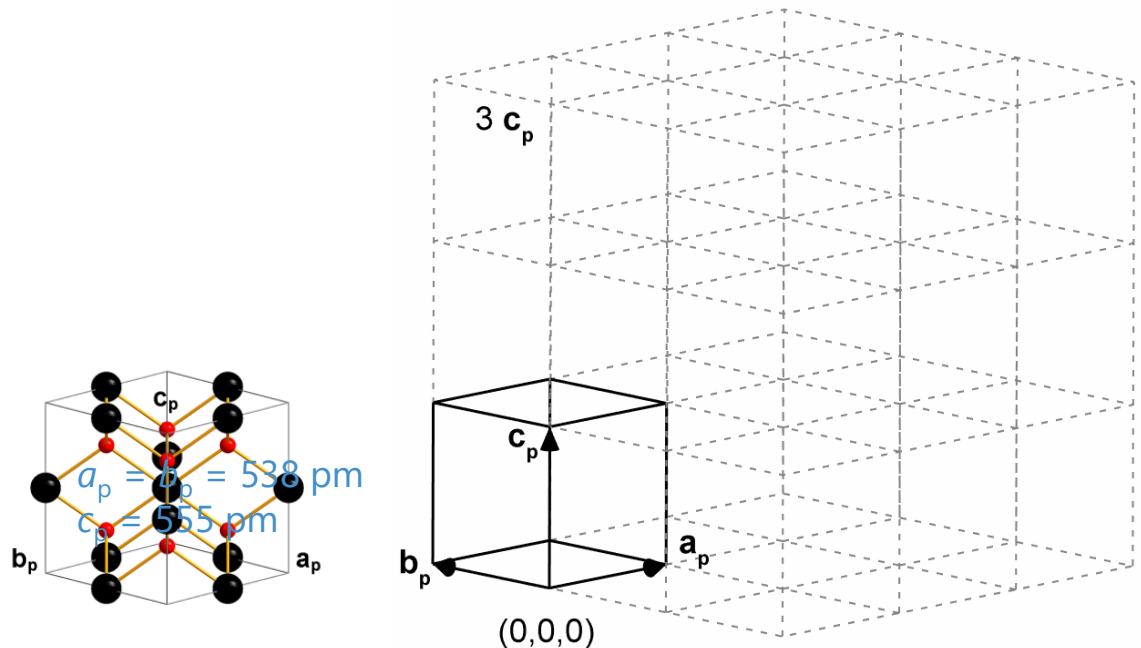
U_3O_7

Superstructure analysis

Interpretation of results: Deriving the structural model

1. U positions determined from XRD, assume O positions cf. UO_2

$$\rightarrow \text{O/U} = \frac{8}{4} = 2.00 \quad (< 2.33, \text{U}_3\text{O}_7)$$

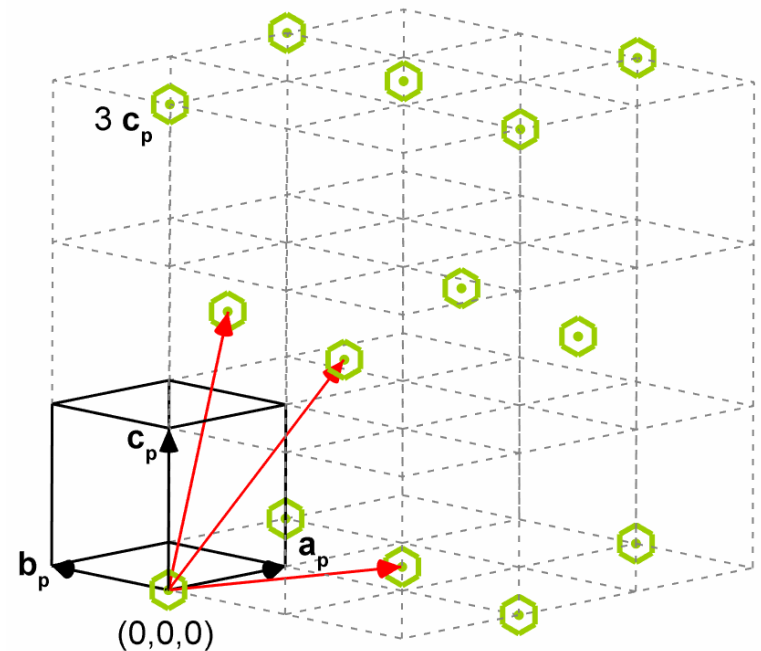
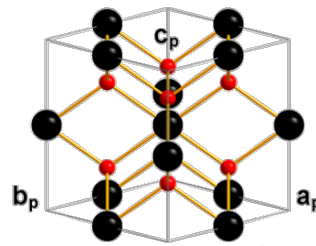


Superstructure analysis

Interpretation of results: Deriving the structural model

2. Additional oxygen in cuboctahedral clusters

→ Coordination determined from ED results

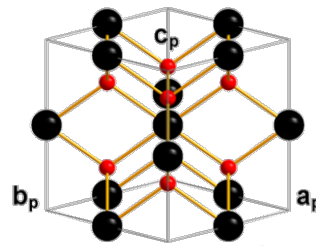


Superstructure analysis

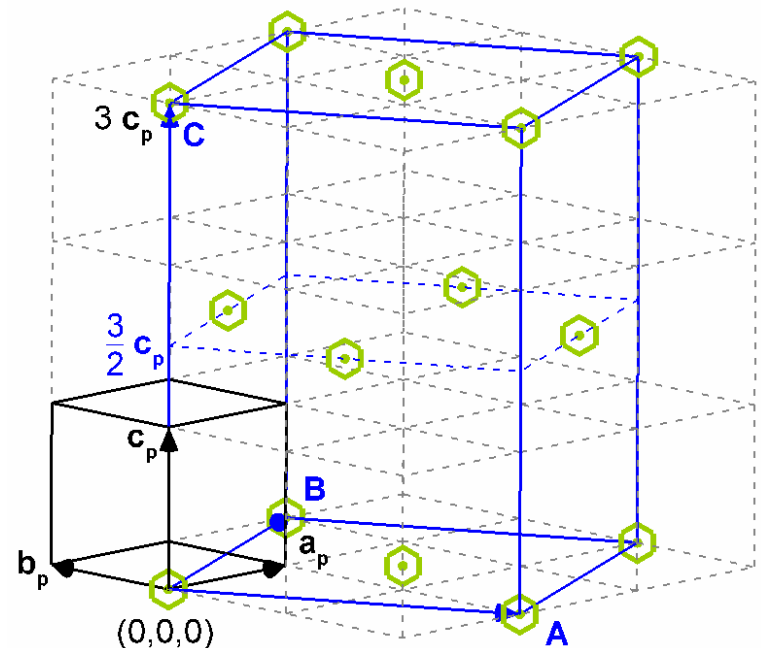
Interpretation of results: Deriving the structural model

3. Unit cell identified: A, B, C

→ Based on relative positions of oxygen clusters



Oxygen cluster

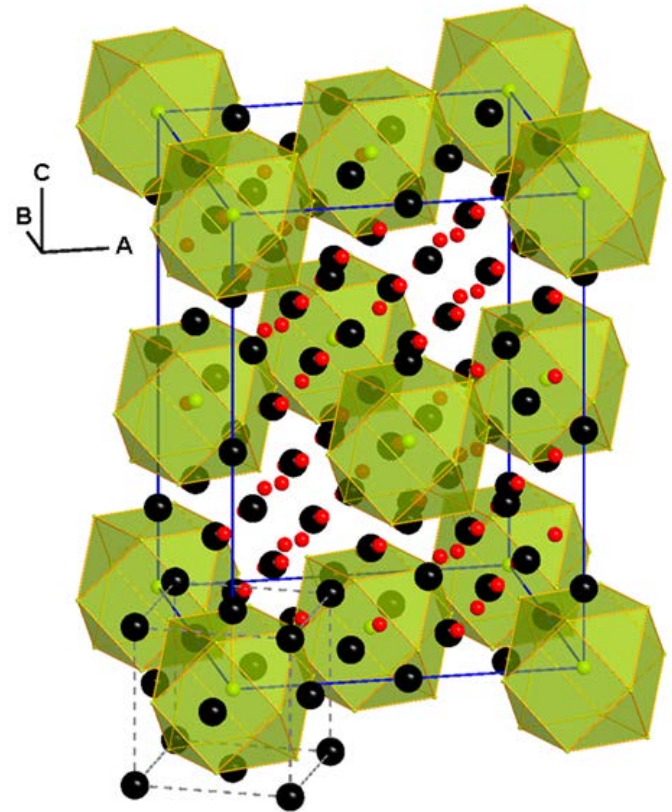


Superstructure analysis

Interpretation of results: Deriving the structural model

3. Unit cell identified: A, B, C

→ Fill out remaining U and O atoms



Superstructure analysis

Interpretation of results: Deriving the structural model

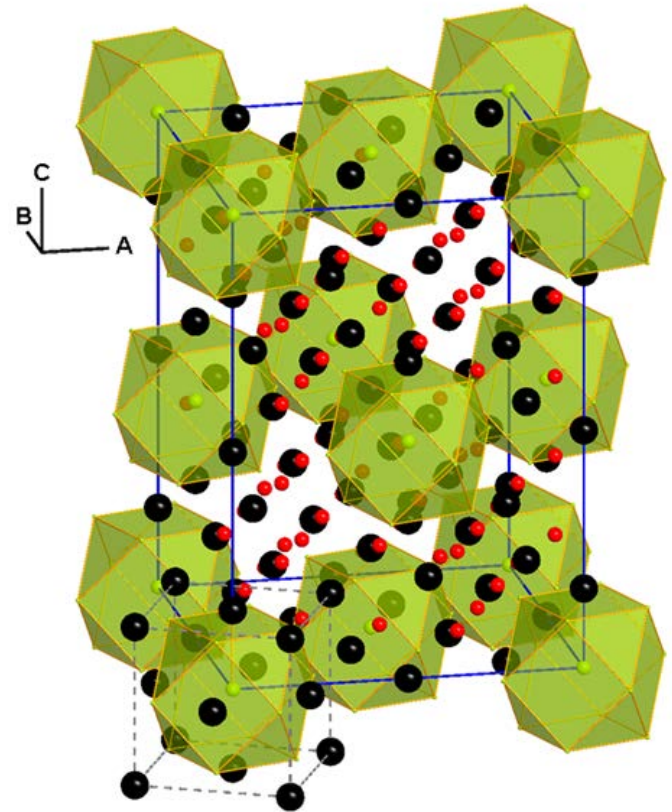
3. Unit cell identified: A, B, C

→ Fill out remaining U and O atoms

4. Composition = U_3O_7 ?

$$\text{O/U} = 2.33 ?$$

$$\rightarrow \text{O/U} = \frac{140}{60} = 2.33 !!!$$



Objective

Assess the crystal structure of U_3O_7 using appropriate methods

Find the missing piece in the UO_2 oxidation mechanism puzzle!

First reference to U_3O_7 :

→ P. Jolibois, A new oxide of uranium, U_3O_7 . *C.R. Acad. Sci.* **1947**, 224, 1395.

70 years until present: no complete and consistent structure derived

Outline

Scope

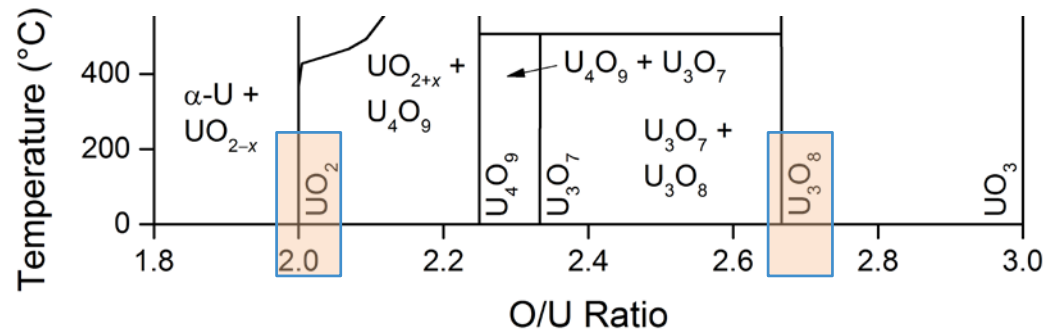
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...a low-temperature oxidized family



O/U = 2.00

O/U = 2.67



UO_2

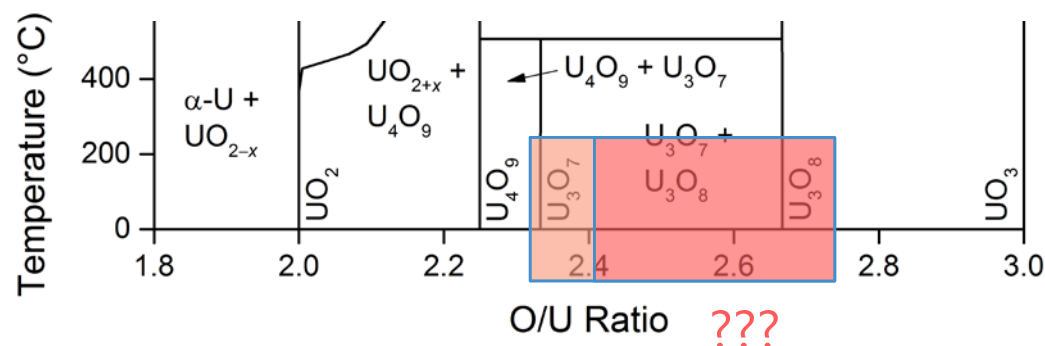
Crystallographic
→ transformation: 36% →
increase in volume



U_3O_8

Uranium and Oxygen...

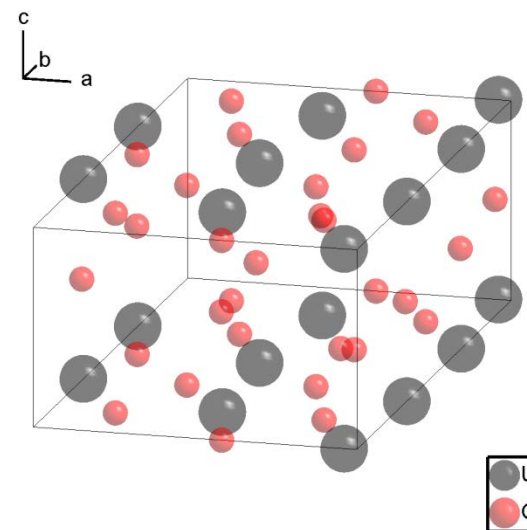
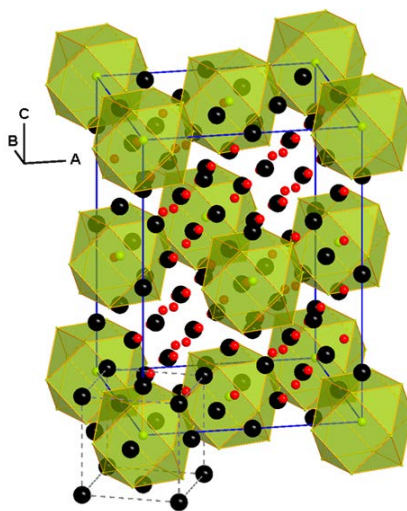
...a low-temperature oxidized family



O/U = 2.33

O/U = 2.67

Long-range
ordered structure?



U_3O_8 crystal structure ($C2mm$)

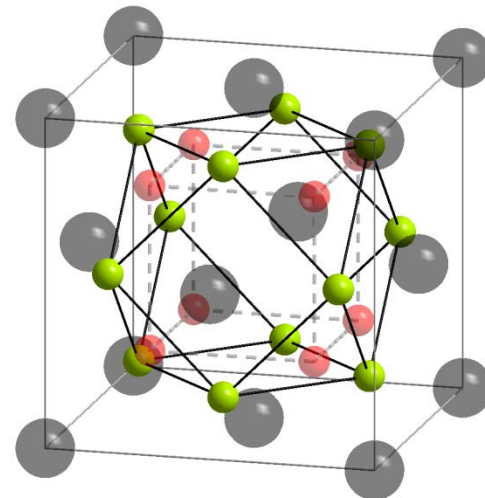
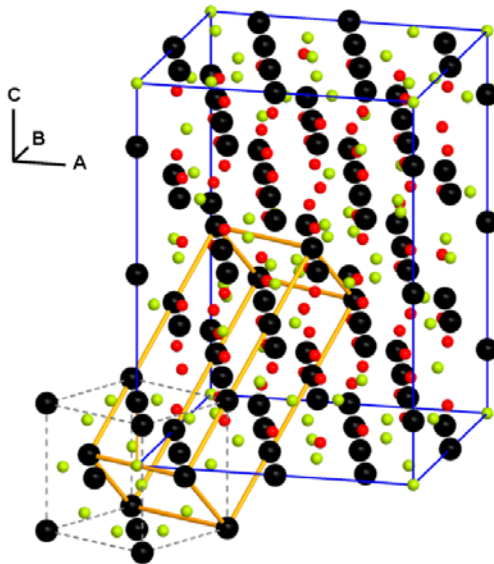
Outlook

Further explore crystallographic relations between the different uranium oxides

Refinement of the crystal structure:

- Transformation of U_3O_7 into U_3O_8
- Configuration and geometry of the cuboctahedral oxygen cluster

Master thesis
topic available!



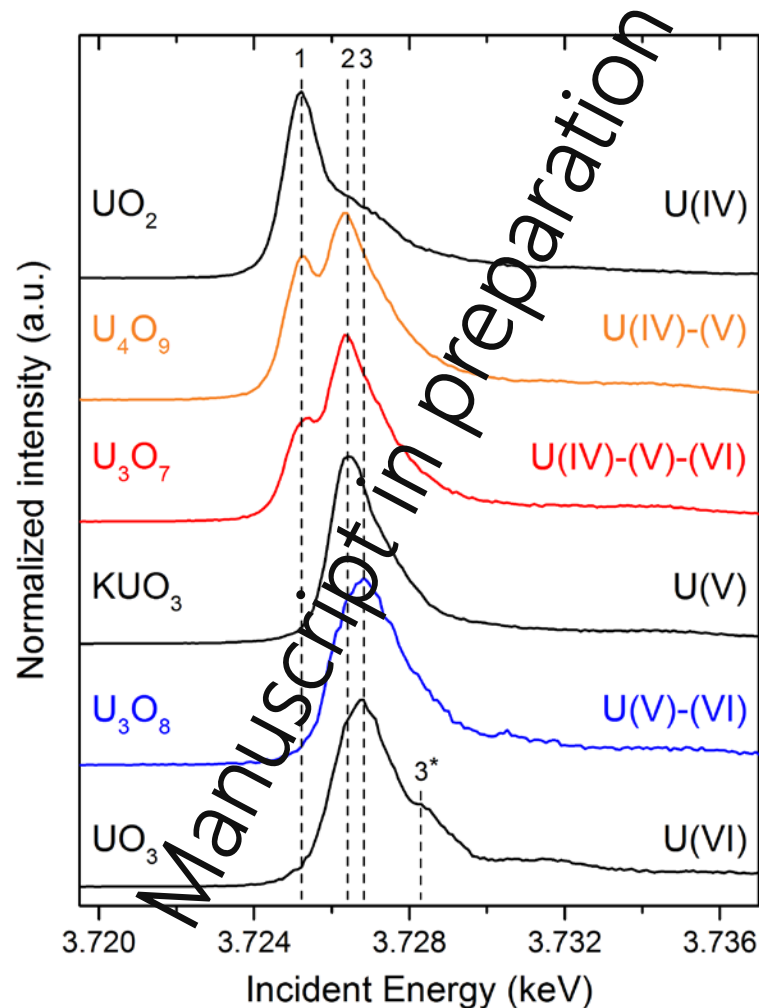
Outlook

Further explore crystallographic relations between the different uranium oxides

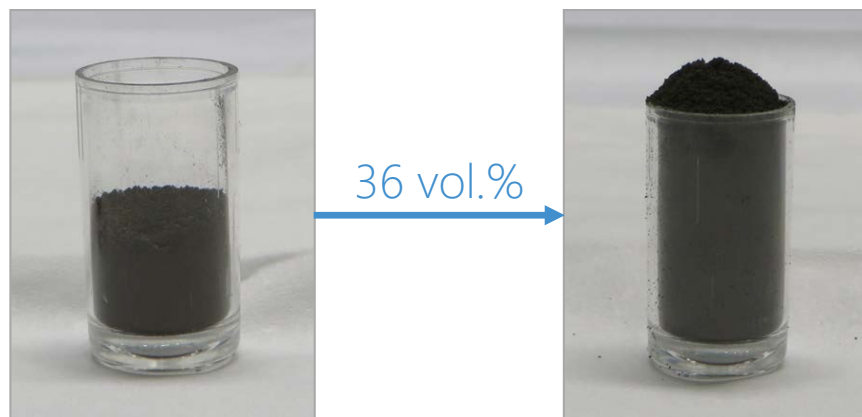
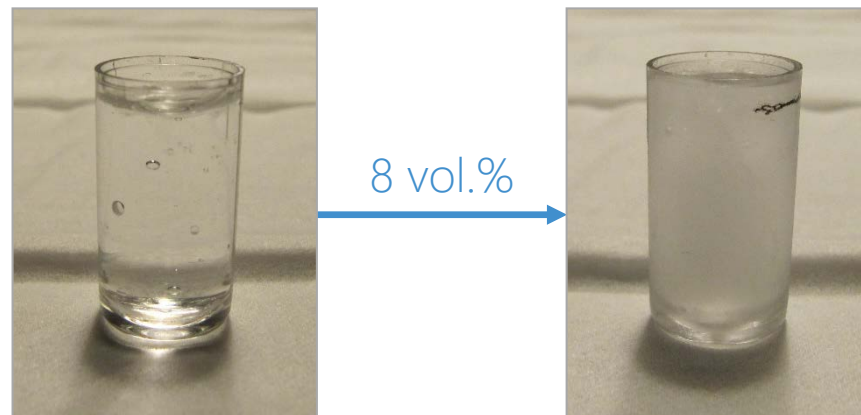
Evolution of U valence state



- X-ray absorption spectroscopy
HERFD XANES U_{M_4} -edge



Thank you!



Questions?

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