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Title:	Structures and Stability of U-Containing Materials for Nuclear Waste Disposal
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Structures and Stability of U-Containing Materials for Nuclear Waste Disposal

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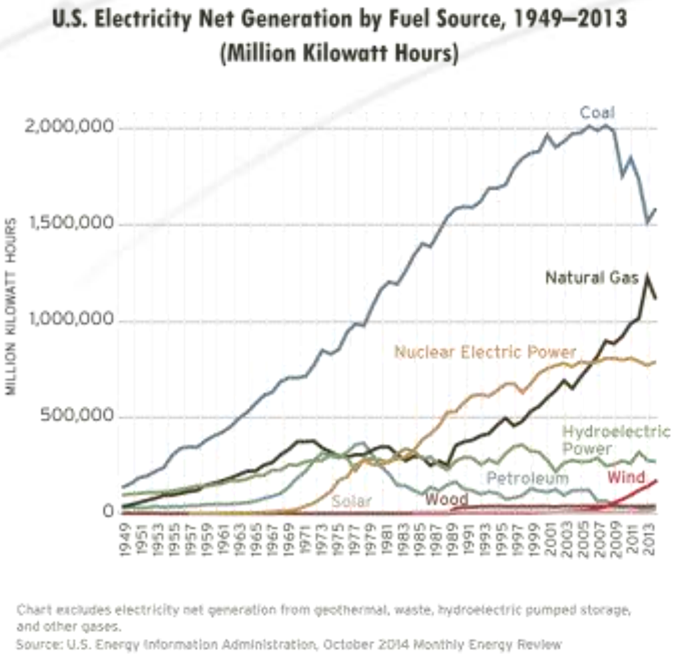
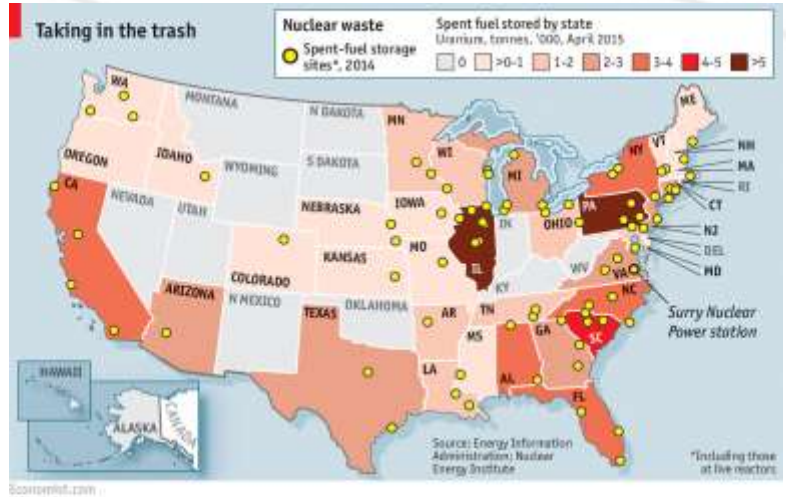
Earth and Environmental Sciences Division

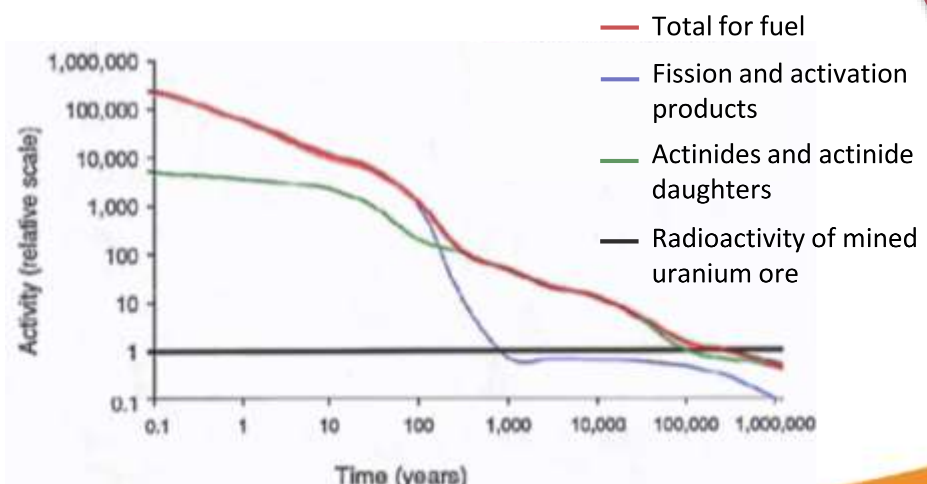
03/02/2016

Related to Nuclear Waste Disposal





~ 2000 tons SNF/yr   Legacy waste in Hanford, etc.



Source: IAEA 2016

In nuclear repository:

- High radiation
- Moderate high temperature
- Underground water
- Geological conditions

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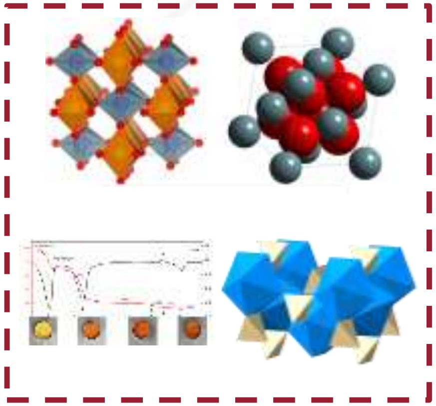
Research Experience

Issues important to safe waste disposal, environment protection, and basic (radiological) geochemistry.



Actinide materials/minerals in environment

- Metastudtite
- Amorphous UO_{3+x}
- U(V) uranate
- Coffinite
- Bulk and nano UO_{2+x}

Nuclear waste form and thermal stability

- Garnet
- Pyrochlore
- Polyhalite
- Monazite

Probe materials with X-ray, neutron, calorimetry

- HP/HT in-situ XRD
- Solid/Solution XAS
- HT Calorimetry
- Thermal analysis

Outline

- **Topic I**: Actinide Materials/Minerals in Environment

- **Topic II**: Nuclear Waste Form

- **Topic III**: Calorimetry on Transuranium (Pu)

Outline

- **Topic I: Actinide Materials/Minerals in Environment**
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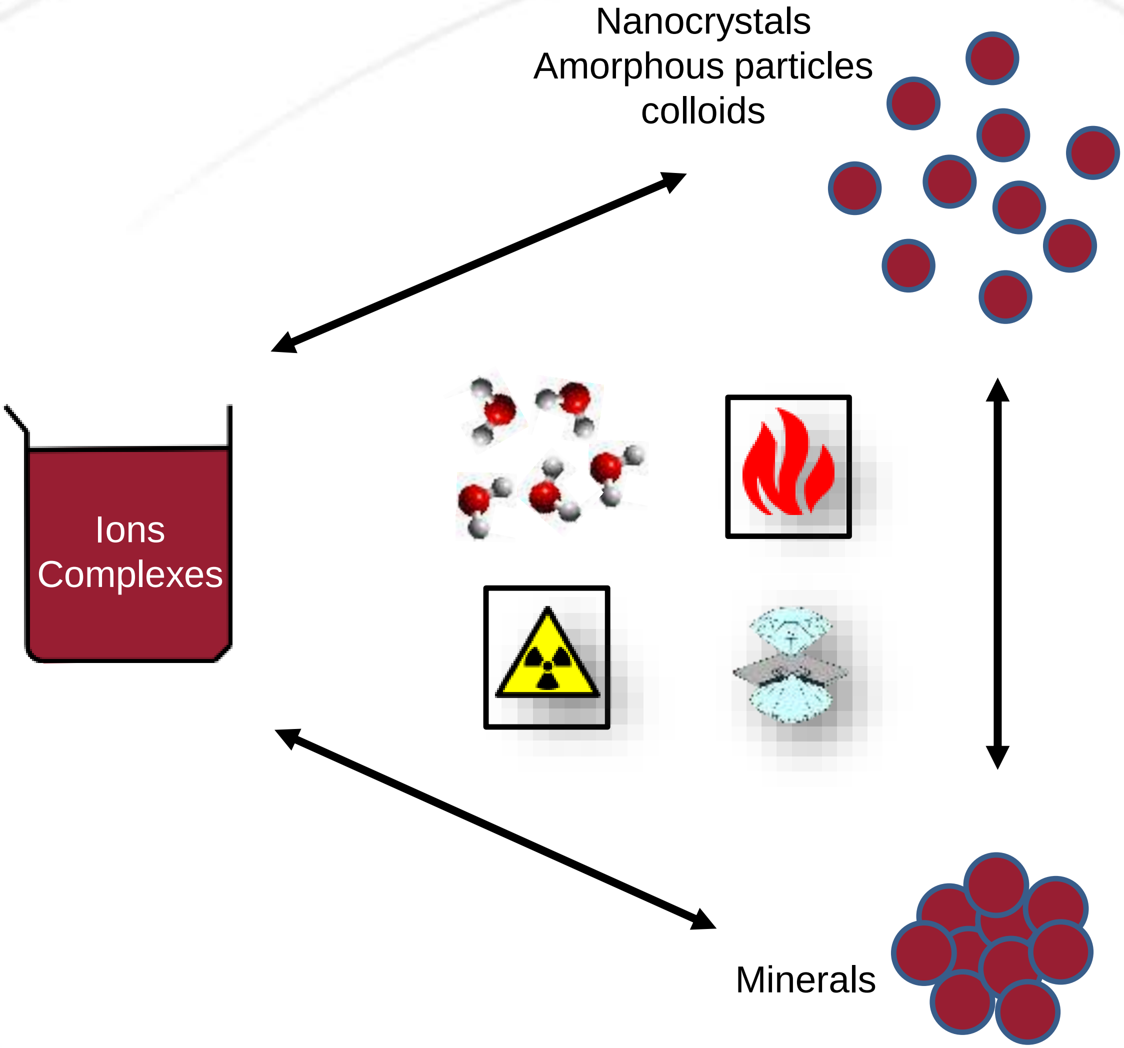
- **Topic III**: Calorimetry on Transuranium (Pu)

Actinides (Minerals) Originate, Alter, and Migrate in Environments



- Formation and dissolution
- Alteration and interaction
- Pathway of (im)mobilization

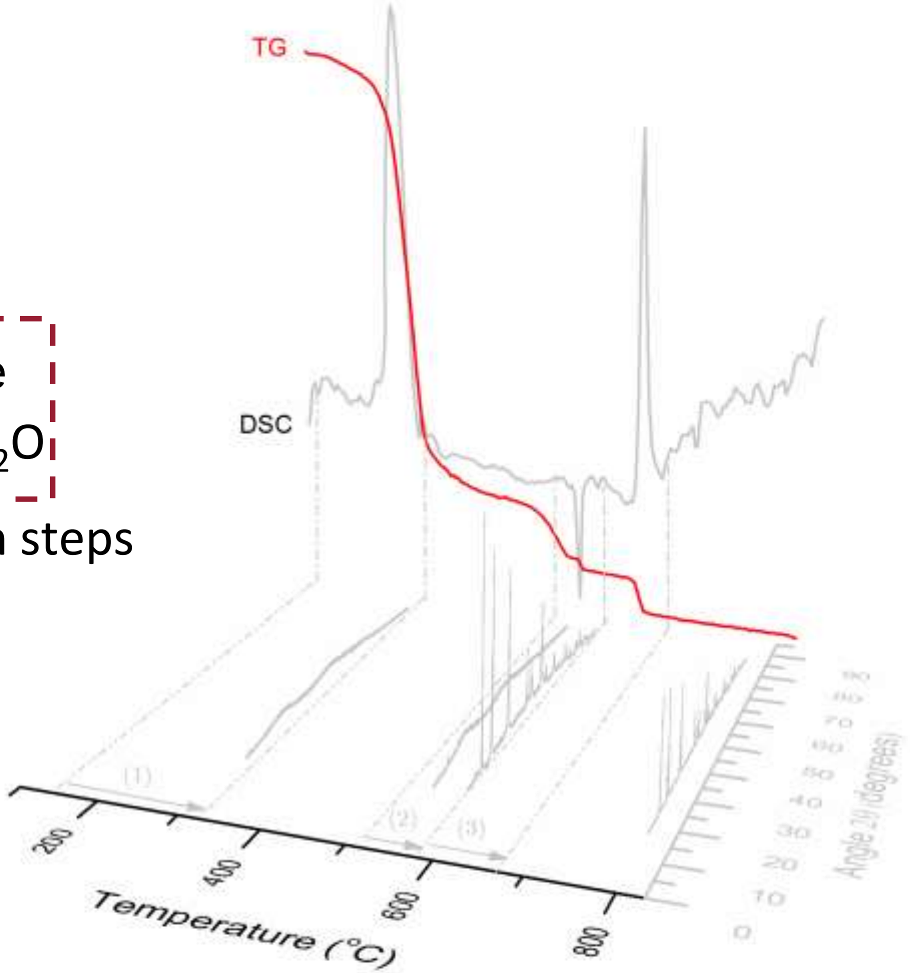
Thermochemistry of Metastudtite: SNF Alteration

Metastudtite

$UO_4 \cdot 2H_2O$:

Studtite

- Dehydration of $UO_4 \cdot 4H_2O$
- Thermal decomposition steps
- SNF implication

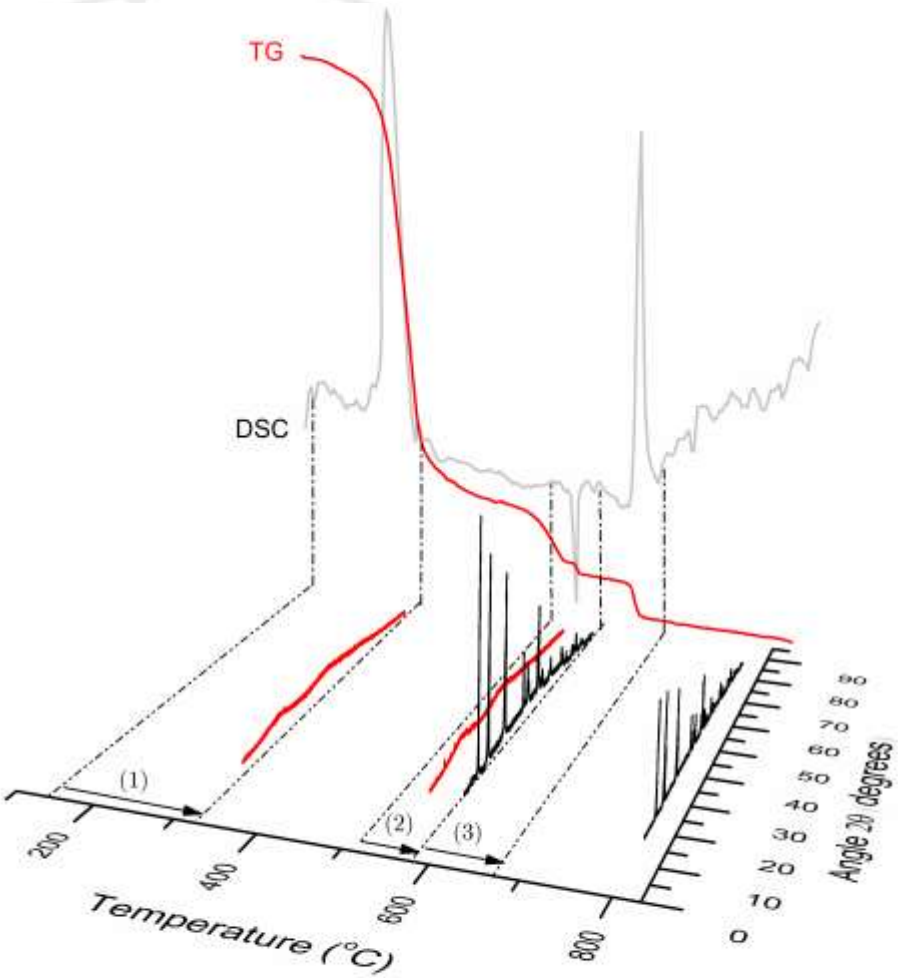


Guo et al., ***Proc. Natl. Acad. Sci. U.S.A***, *2014*

Thermochemistry of Metastudtite: SNF Alteration

Step features:

- Step-related phases
- Amorphous U phases
- Crystalline U phases



Thermochemistry of Metastudtite: SNF Alteration

Thermal stability:

- Metastable phase

  (UO_3, H_2O, O_2) 15.8 kJ/mol

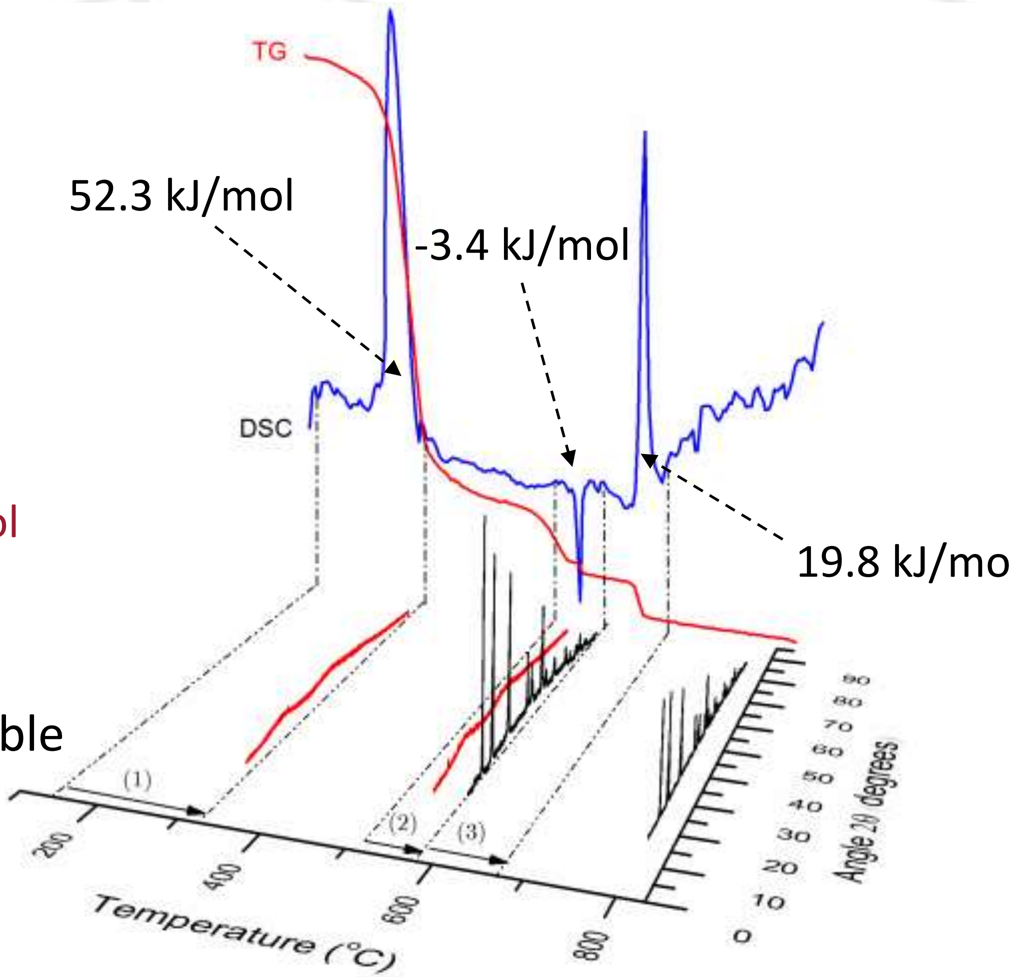
- Dehydration is irreversible

  $UO_4 \cdot 4H_2O \rightarrow UO_4 \cdot 2H_2O$

  -7.5 kJ/mol

- Favorable corrosion

  $UO_2 \rightarrow UO_4 \cdot 4H_2O \rightarrow UO_4 \cdot 2H_2O$ -217.1 kJ/mol



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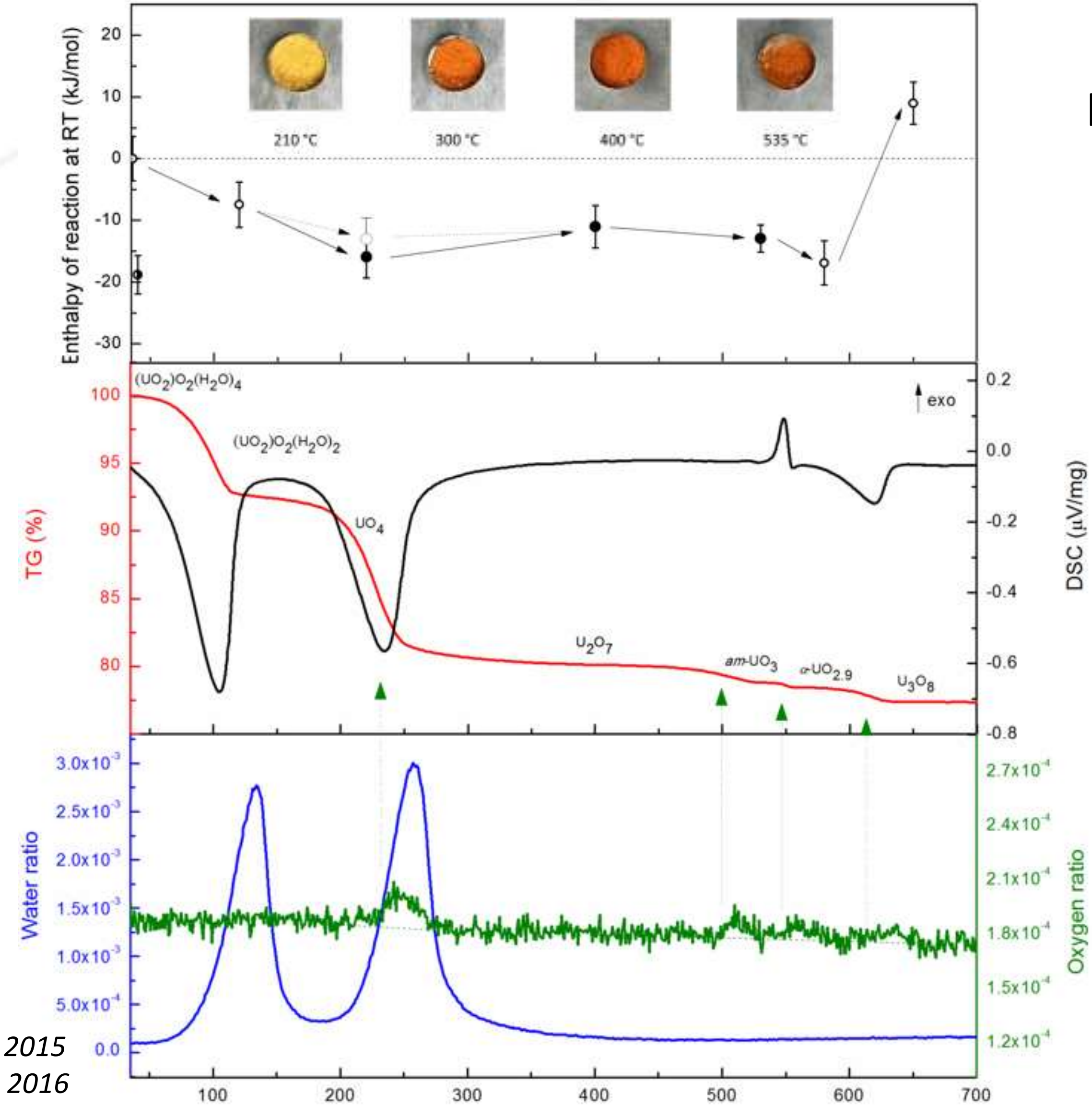
Thermodynamics of Amorphous UO_3, U_2O_7, and "UO_4"



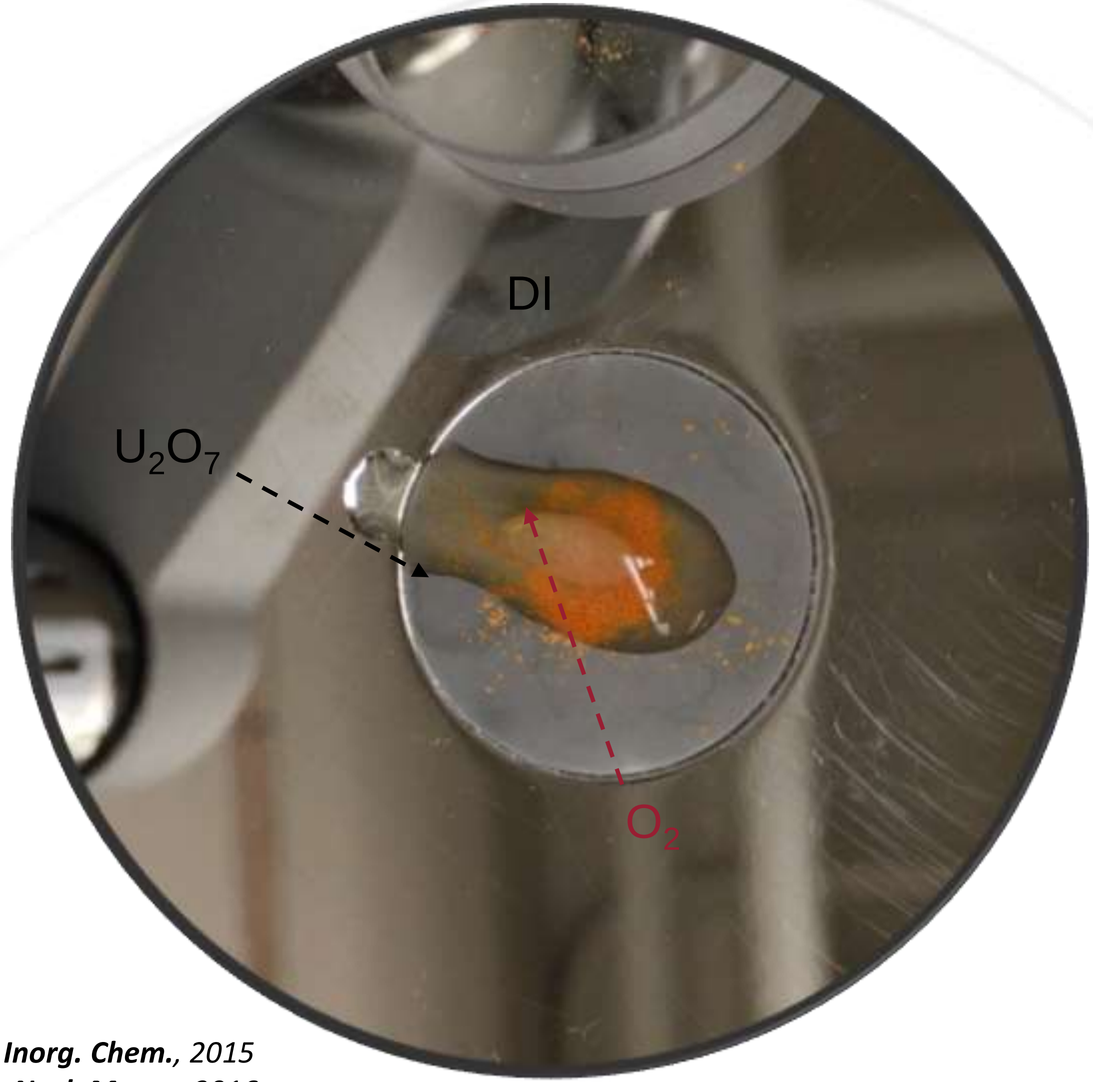
High Temperature Oxide Melt Calorimetry

STA

Mass Spectrometry

Odoh et al., ***Inorg. Chem.***, *2015*
Guo et al., ***J. Nucl. Mater.***, *2016*

Reaction of Amorphous U_2O_7 with Water



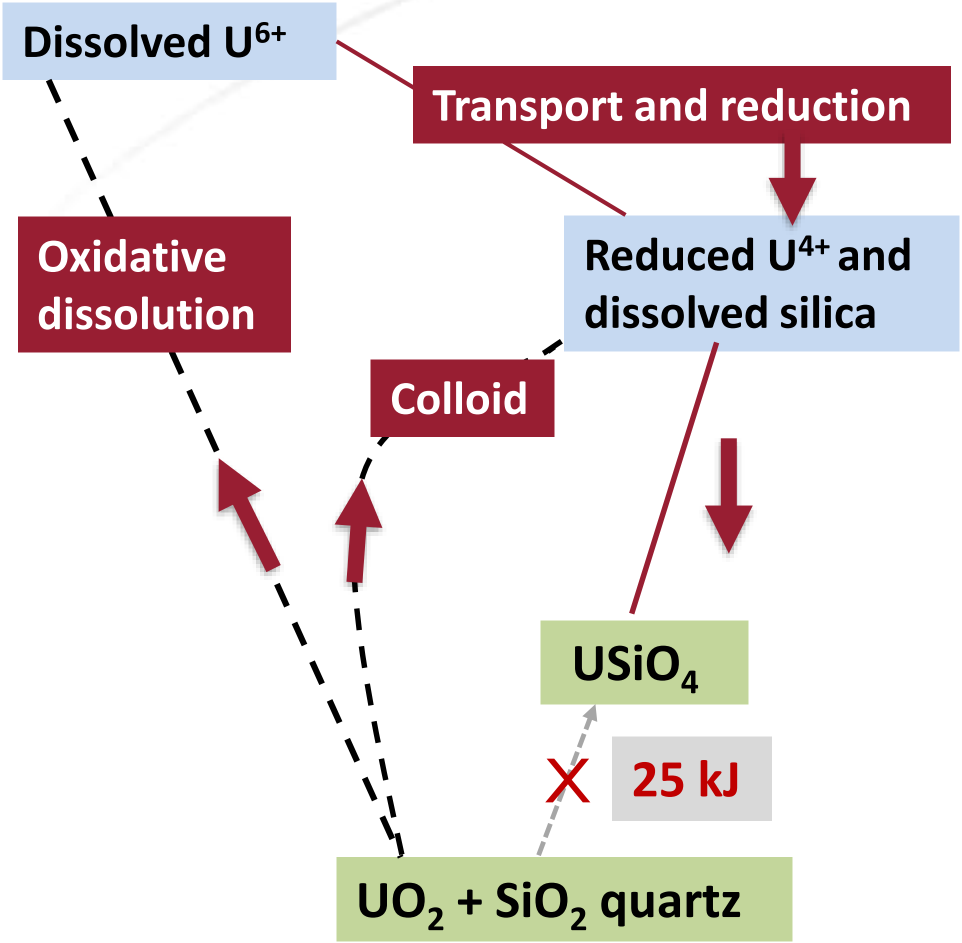
Have a rapid reaction with water, forming O_2

$U_2O_7 + ½\ H_2O$
→
$UO3·½H_2O + ¼O_2$

over-pressurization in container/drum

Odoh et al., ***Inorg. Chem.***, *2015*
Guo et al., ***J. Nucl. Mater.***, *2016*

Pathway to Form Metastable Coffinite, $USiO_4$



COFFINITE
with sooty uraninite

** Photo is Coffinite in uraninite from Minobras (Robert W. Jones collection)*

$UO_2 + SiO_2 = USiO_4$

$\Delta H = 25.6 \pm 3.9$ kJ/mol

$UO_2 + Si(OH)_2 \leftrightarrow USiO_4 + H_2O$

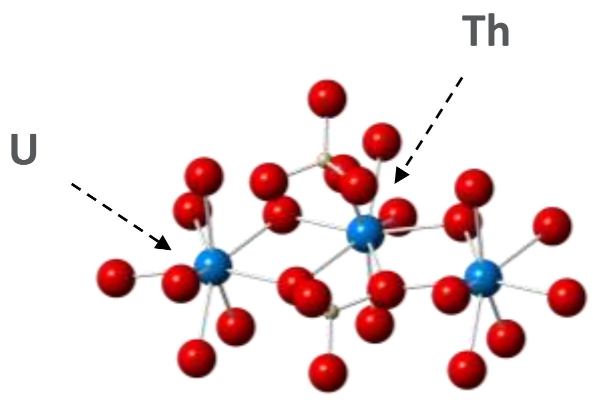
$\Delta G = -5.7 \pm 5.8$ kJ/mol

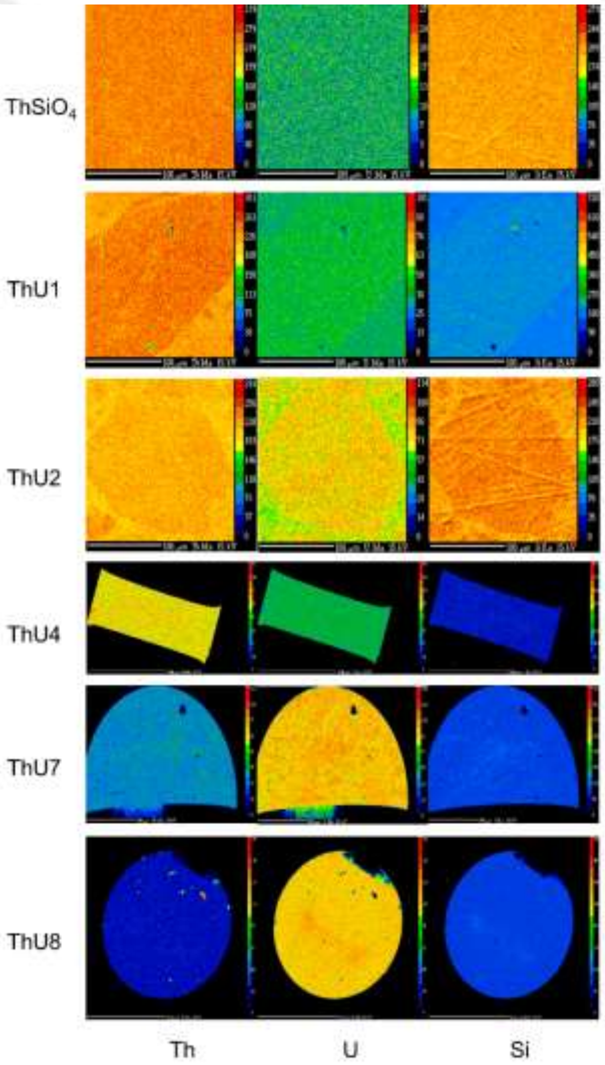
Guo et al., ***Proc. Natl. Acad. Sci. U.S.A***, *2015*

Thermodynamics of Uranothorite, $Th_{1-x}U_xSiO_4$

Significances:

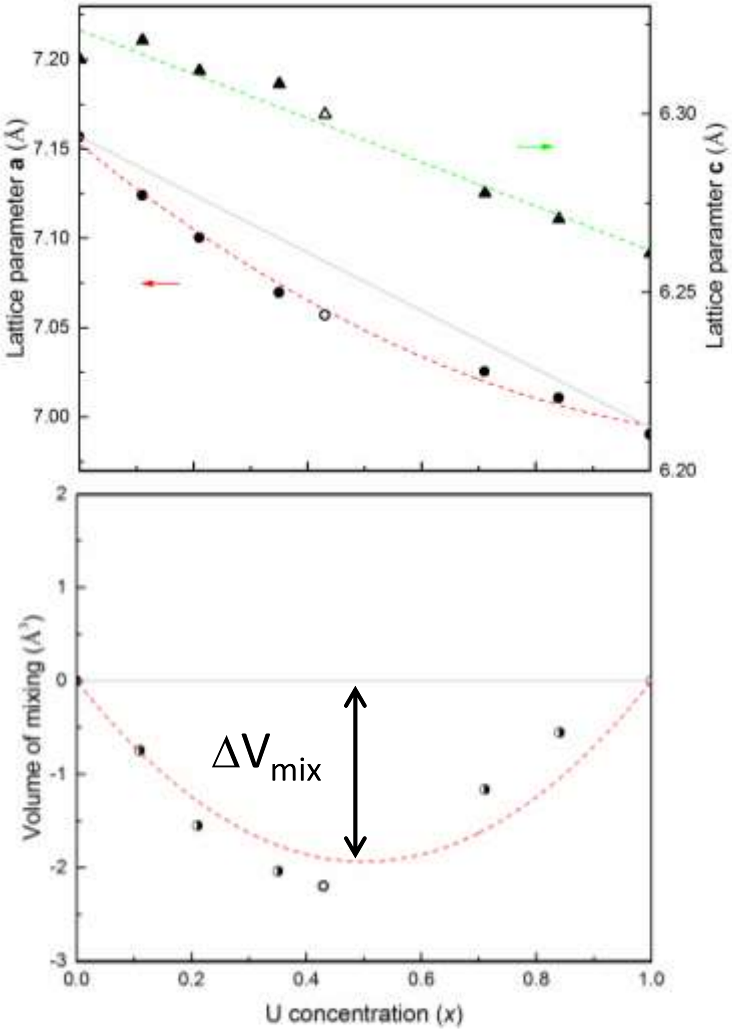
- Important U-, Th-silicate minerals
- Potential nuclear waste form
- Understand synthesis of coffinite



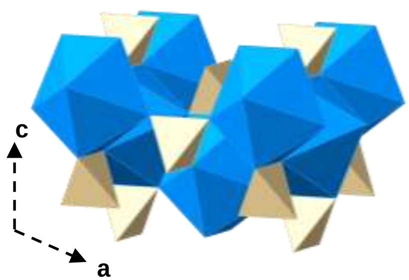


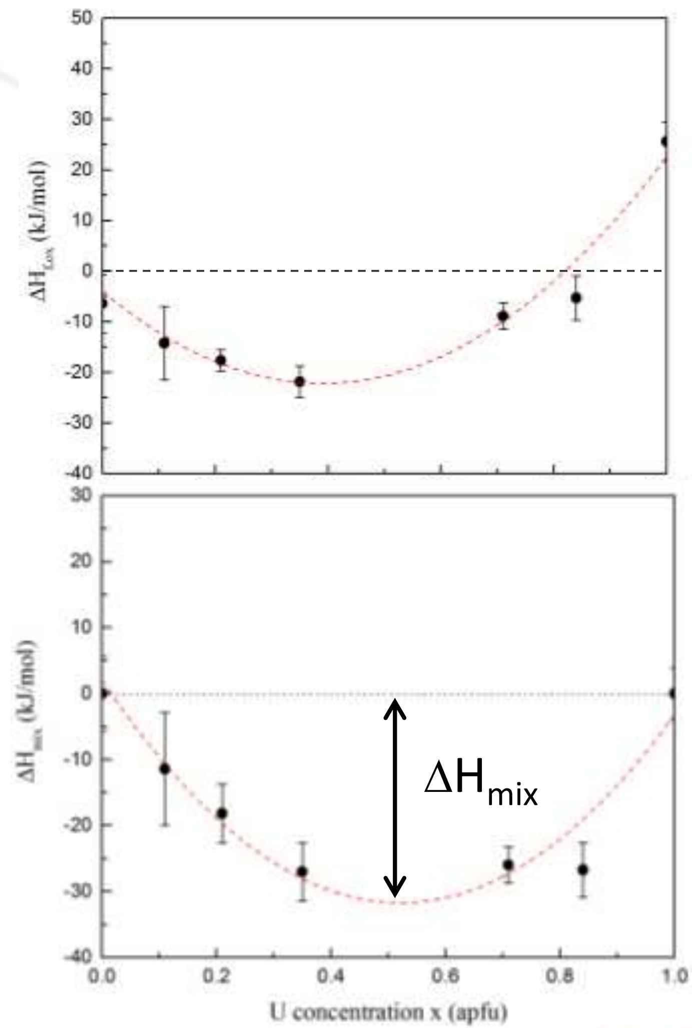
Guo et al., ***Chem. Mater.***, *2016*

Thermodynamics of Uranothorite, $Th_{1-x}U_xSiO_4$



$Th_{1-x}U_xSiO_4$

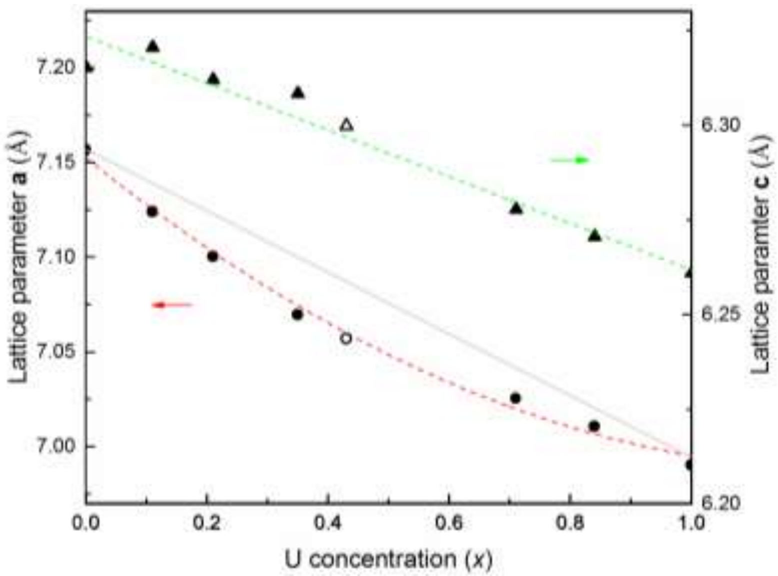




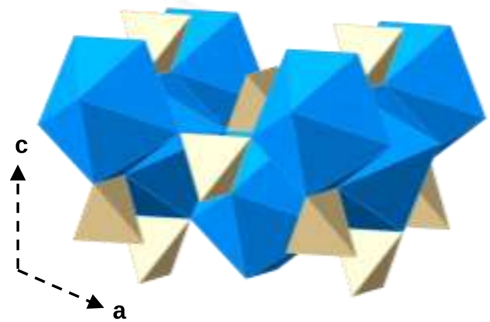
Guo et al., ***Chem. Mater.***, *2016*

Local Structure of Uranothorite, $Th_{1-x}U_xSiO_4$

- ***a*-** and ***c*-** axis have different structural features.
- Short range orderings in ***a*-**axis.



$Th_{1-x}U_xSiO_4$



Planned Structural Studies:

- Local structures revealed by neutron PDF (SNS)
- Short-range ordered patterns studied by HP diffractions and PDF (APS)

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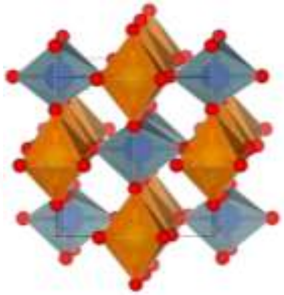
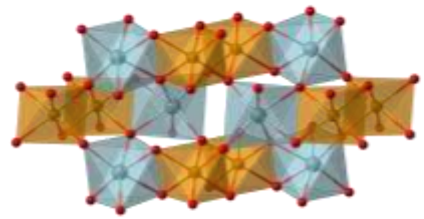
Structure and Thermodynamics of U(V) in Solids

Why U(V) is important:

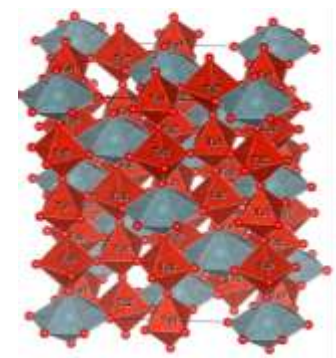
- Interstitial O.S.
- Unknown solid state structure/thermodynamics
- Roles in mineralization

MU(V)O_4





U(V)Ta3O_{10}



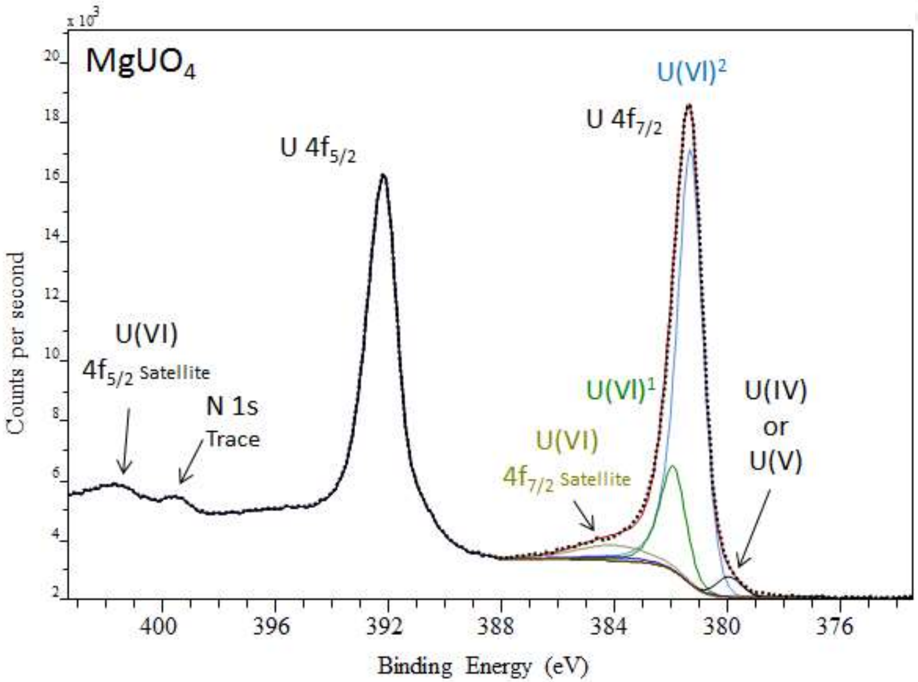
Investigations:

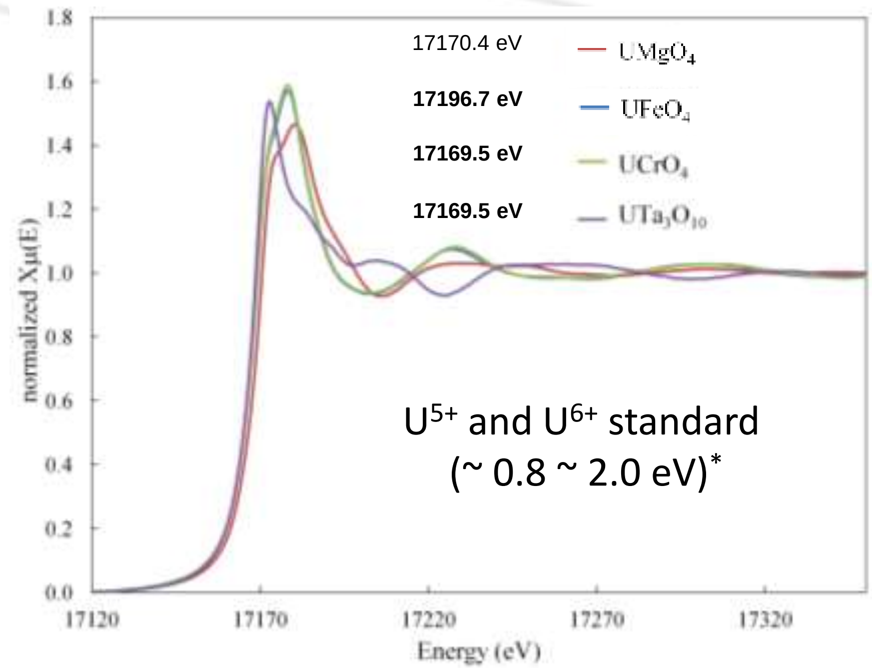
- Structural Features of U(V)
  - XANES/XPS/XRD, DFT
- Thermal stability of U(V)
  - High-T Calorimetry

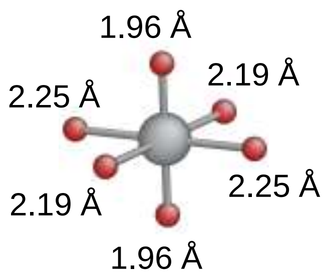
*Guo et al., **Dalton Trans.,** 2016*
*Guo et al., **Dalton Trans.,** 2016*

*Work was a science highlight at **EMSL at PNNL** in 2016 and **LANL** in 2017*

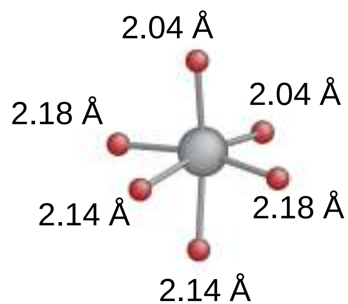
U^{5+}/U^{6+} in MUO_4



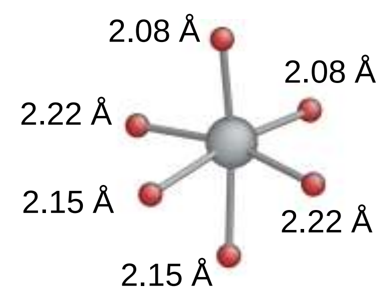




$MgUO_4$



$CrUO_4$



$FeUO_4$

Guo et al., ***Dalton Trans.**, 2016*
Guo et al.,, ***Dalton Trans.**, 2016*
Soldatov *et al.*. ***J. Solid State Chem***. 2007
Kelly *et al.*, ***Environ. Sci. Technol.*** 2008
Belai *et al.*, ***Inorg. Chem***. 2008.
Kosog *et al.*, ***Inorg. Chem***. 2012

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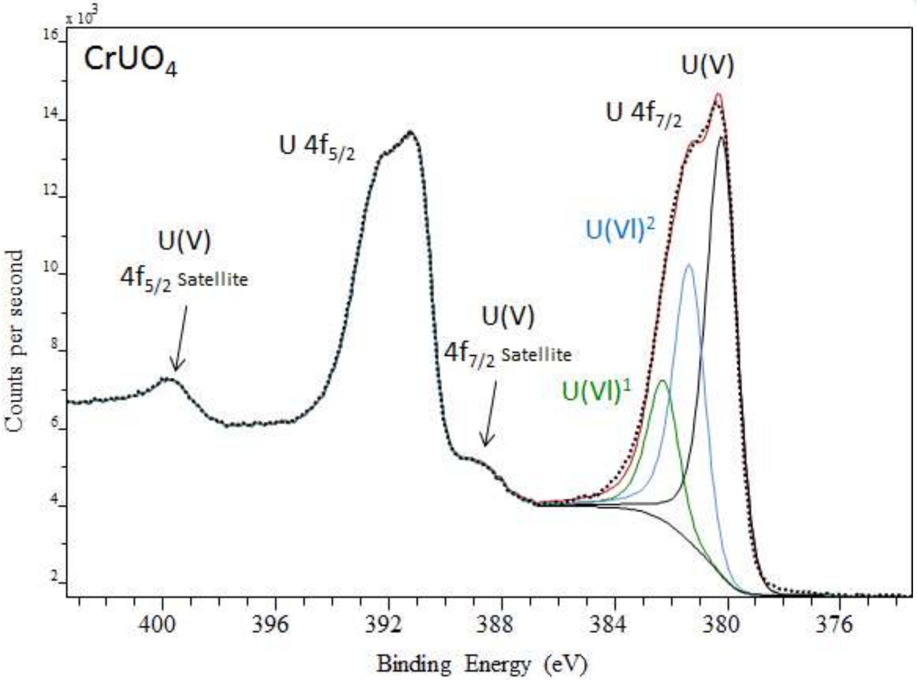
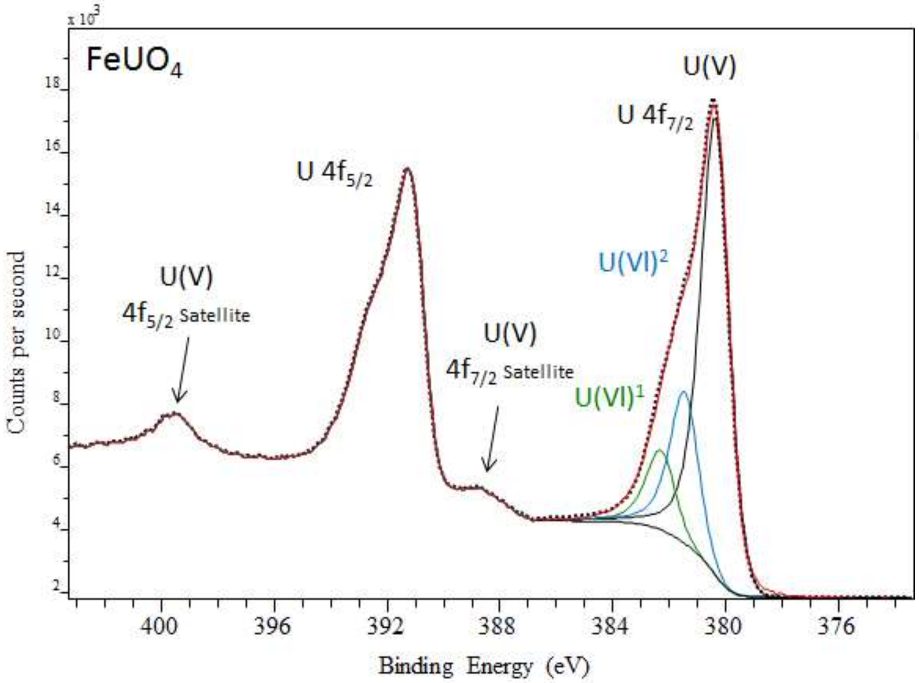
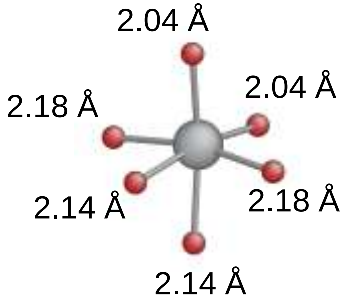
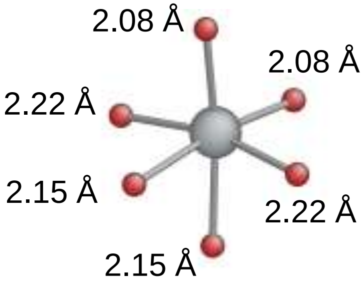
U^{5+} in MUO_4







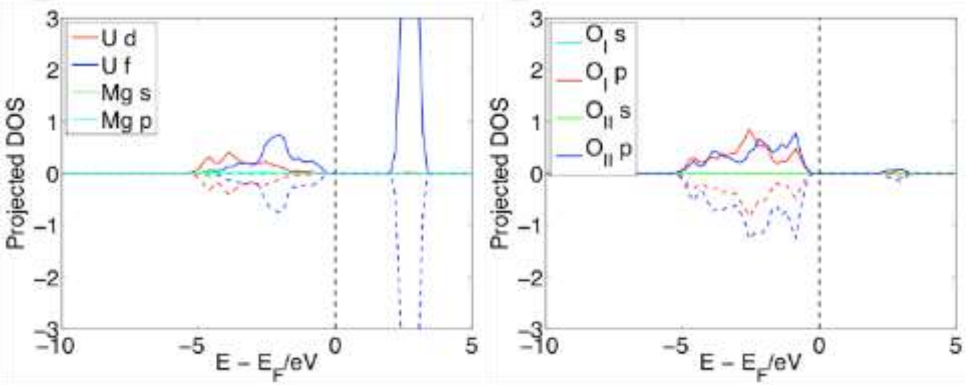
$CrUO_4$



$FeUO_4$

DFT + *U* Structural Investigation

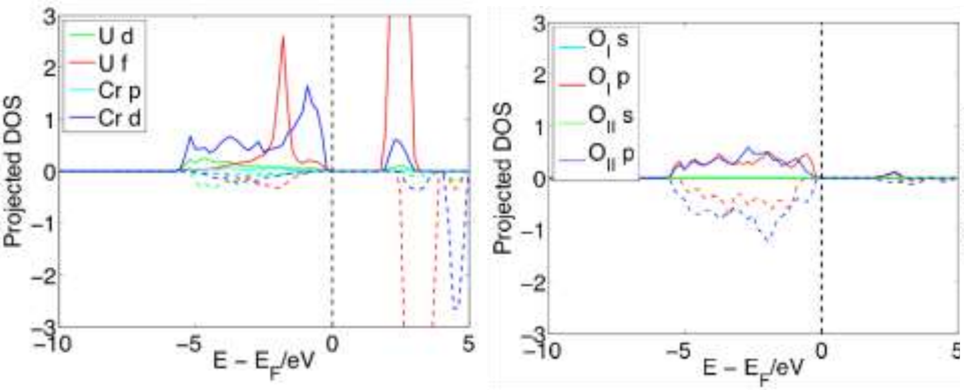
$MgUO_4$



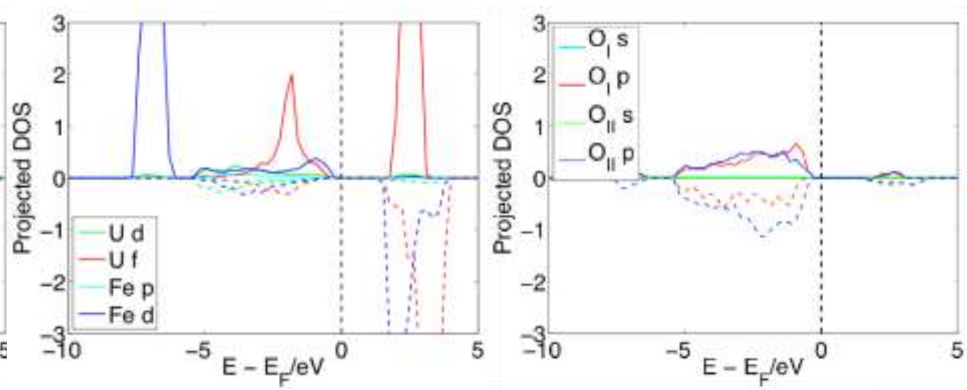
U^{6+}

U^{5+}

$CrUO_4$



$FeUO_4$



U^{5+} Stability in $FeUO_4$

Scenario 1: $Fe^{3+} + U^{5+} \rightarrow Fe^{2+} + U^{6+}$ ①

ΔE_t = 1.49 eV (143.8 kJ/mol)

→ Charge transfer is unfavorable

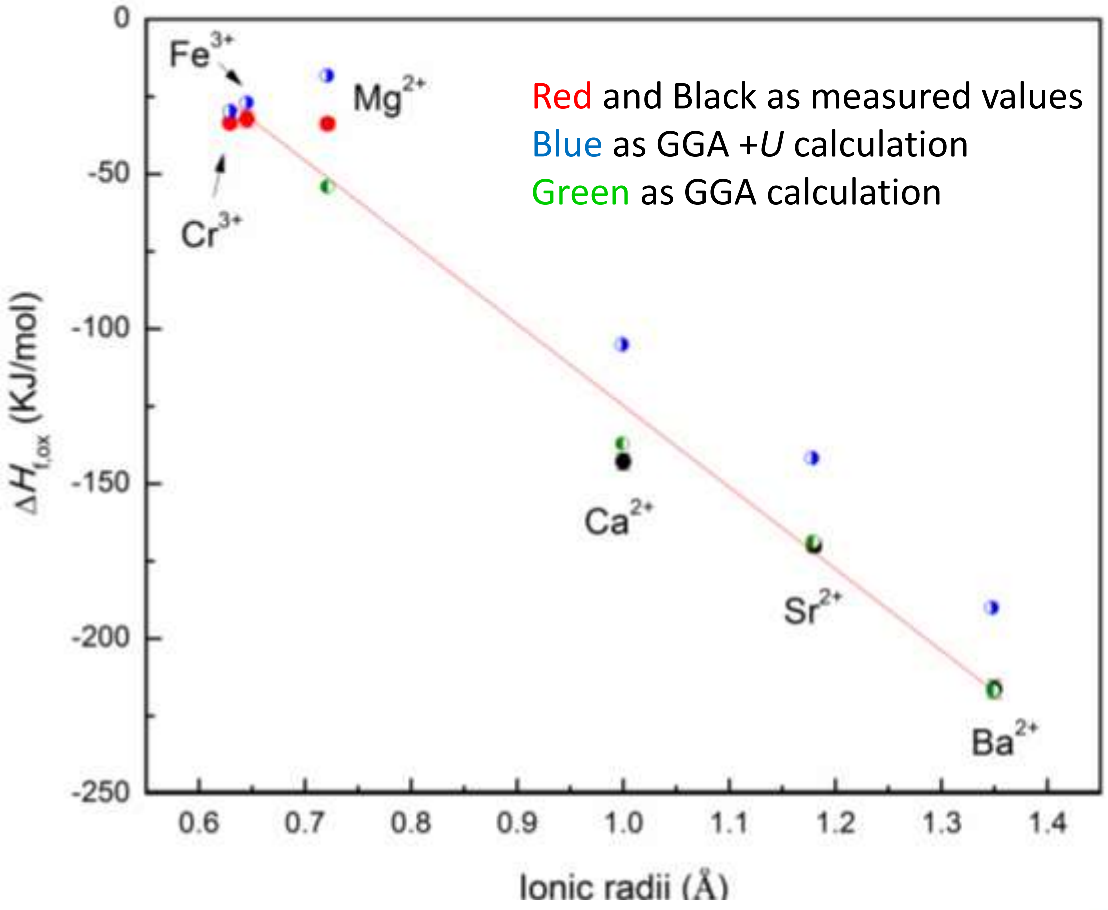
Scenario 2: $2U^{5+} \rightarrow U^{4+} + U^{6+}$ ②

ΔE_t = 1.39 eV (134.1 kJ/mol)

→ Only U^{5+} be allowed in $FeUO_4$

Enthalpies Formation of Metal Uranates

- Linear trend in $\Delta H_{f,ox}$ vs. Ionic radii
- Consistent trends from experiment and DFT
- Energetic competition



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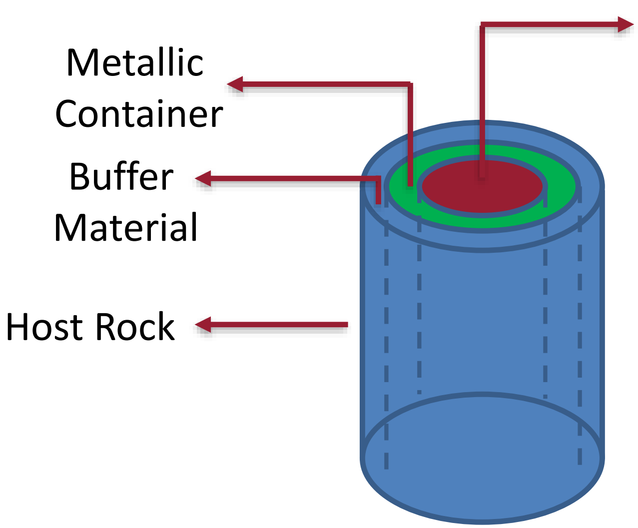
Outline

- **Topic I**: Actinide Materials/Minerals in Environment
- **Topic II**: Nuclear Waste Form
- **Topic III**: Calorimetry on Transuranium (Pu)

Nuclear Waste Forms

Focused Criteria:

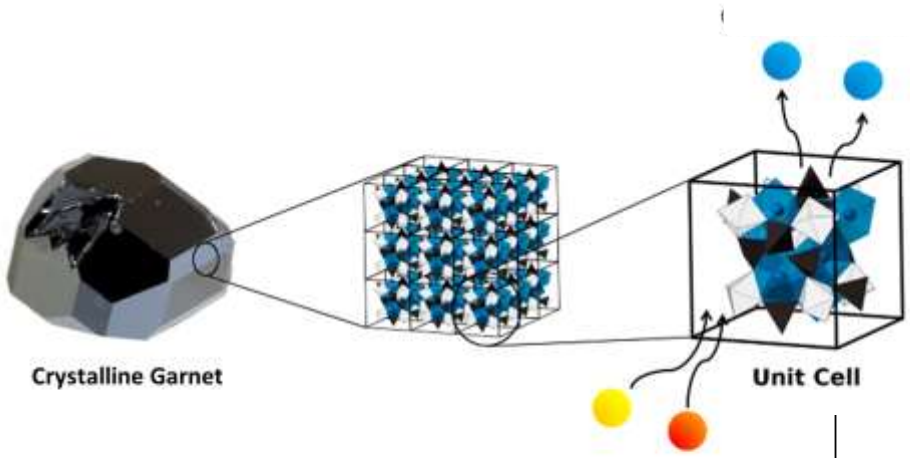
- Large loading of waste
- Long-term (thermodynamic) stability
- Homogeneous distribution of radionuclides

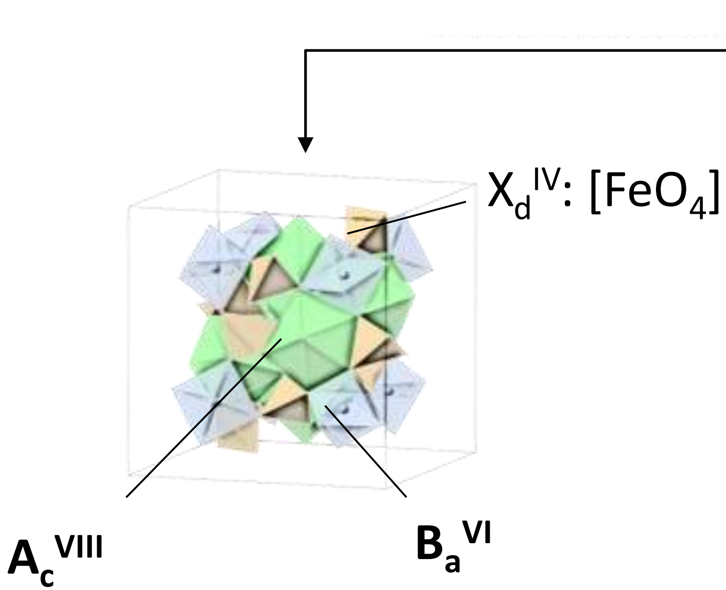


HLW/SNF/TRU Form Candidate:

- Glass
  - High chemical durability
  - Good radiation resistance
  - **Thermodynamic metastability**
- Ceramics
  - Good waste form
  - **Economic cost**
  - **Phase amorphization**

Garnet $A_3B_2Fe_3O_{12}$ as Nuclear Waste Form





Motivation:

- High affinity for Ln/Ac
- Radiation resistant
- Natural rad garnet: Elbrusite-(Zr)

Questions:

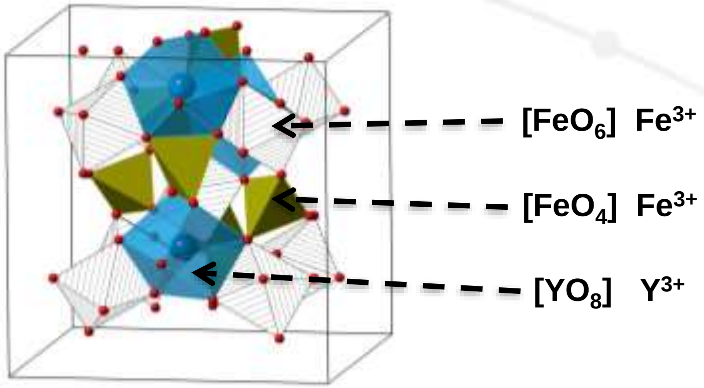
- O.S. of elements in matrix
- Energetics disturbed by Act

System studied:

- YIG: $Y_3Fe_5O_{12}$
- U-garnets: Ca-Zr-Fe based

Garnet Host: $Y_{3-x}M_xFe_5O_{12}$

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

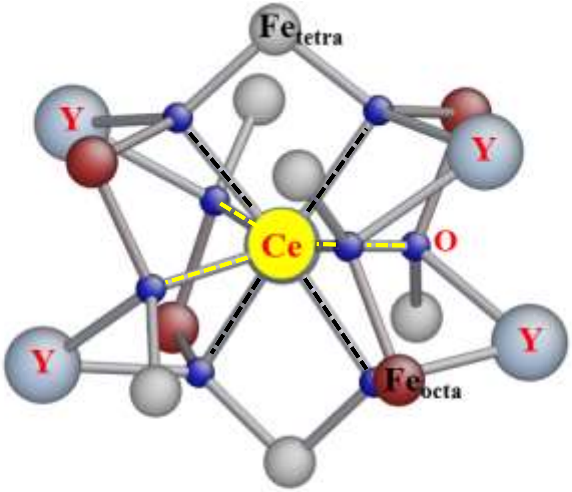


Ce, Th, U, Pu similarity

- Ce^{4+}: 0.97Å Th^{4+}: 1.05Å U^{4+}: 1.00Å Pu^{4+}: 0.96Å
- Variations of charge states.
- Chemical properties.

Substitution reactions

- Y^{3+} → Ce^{4+}
- Fe^{3+} → Fe^{2+}

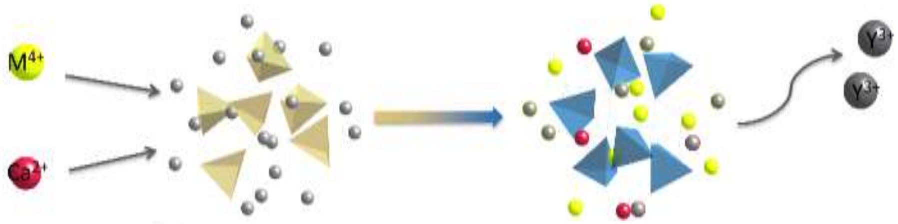


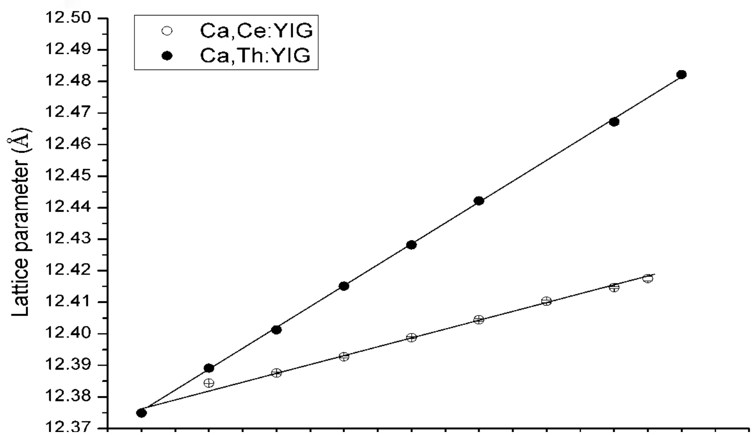
Charge transfer between one Ce and its first nearest neighbor Fe at tetrahedral site (1NN Fe_{tetra}):

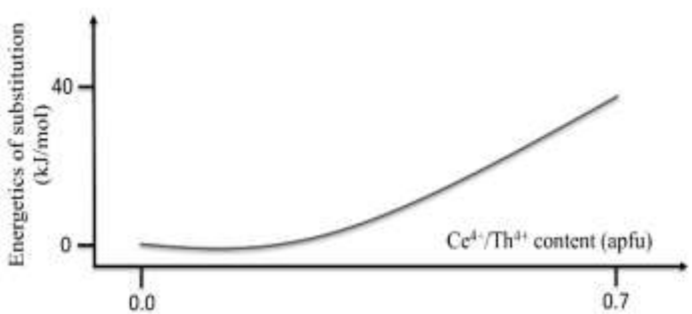
$Ce^{3+}/Fe^{3+} \rightarrow Ce^{4+}/Fe^{2+}$

*Guo et al., **Chem. Mater.,** 2014*
*Guo et al., **J. Mater. Chem. A,** 2015*

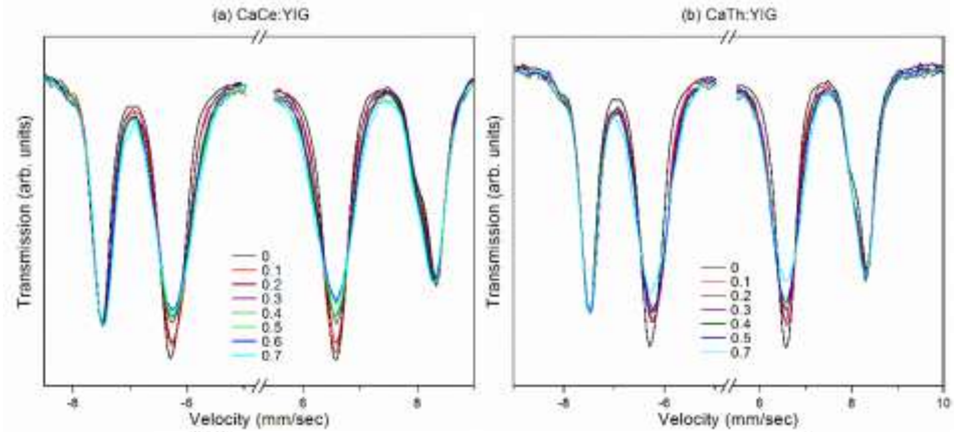
Charge-coupled incorporation: $(Y_{3-x}Ca_{0.5x}M_{0.5x})Fe_5O_{12}$

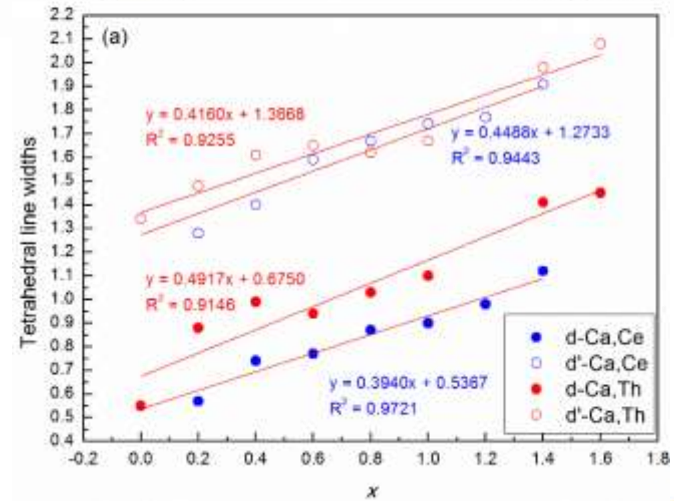






Tetrahedral systematic distortion



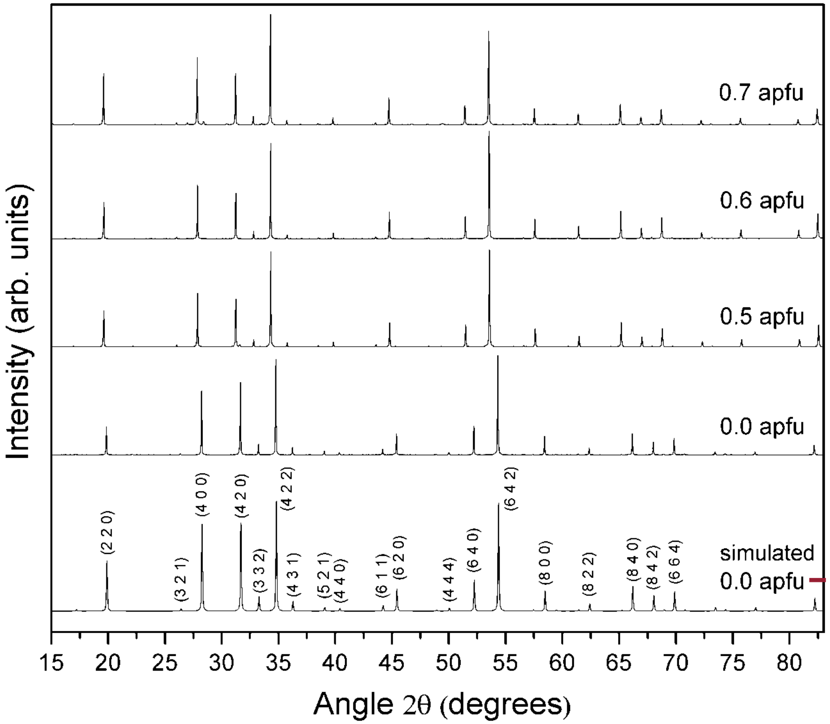


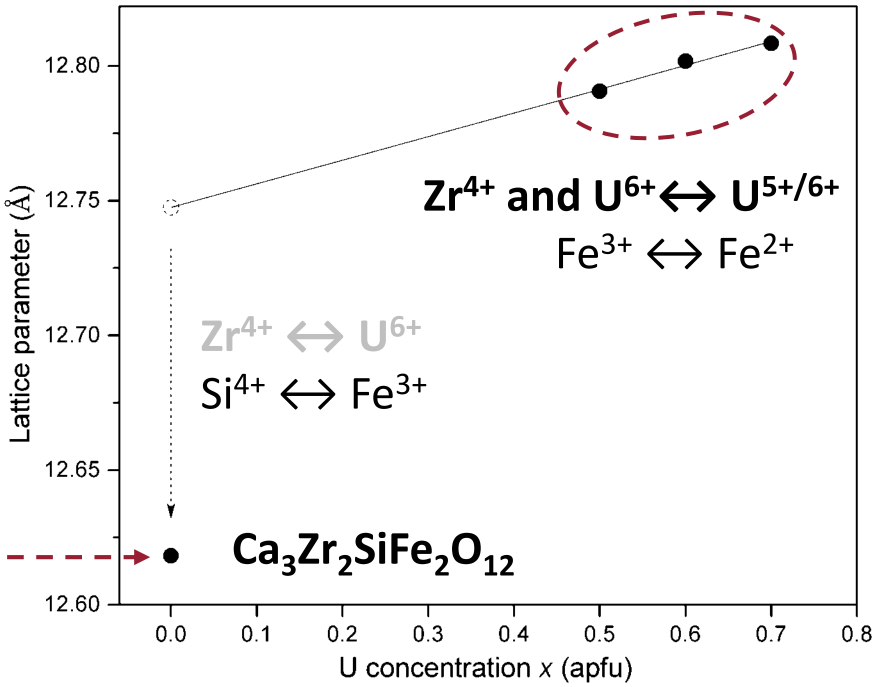
*Work was a science highlight at **EFRC-Actinide** in 2016*

*Guo et al., **Inorg. Chem.**, 2015*

High-loading U Garnet: $(Ca_3)(Zr_{2-x}U_x)Fe_3O_{12}$

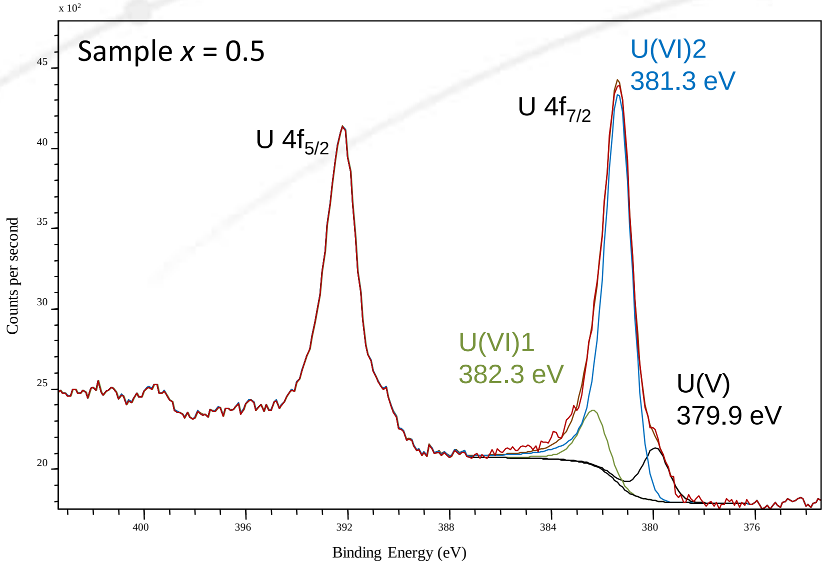
- 50 mol % ~ 70 mol % (22 wt. %) U
- Mix states of **U^{5+}** and **U^{6+}**
- Increased stability of U garnet phase





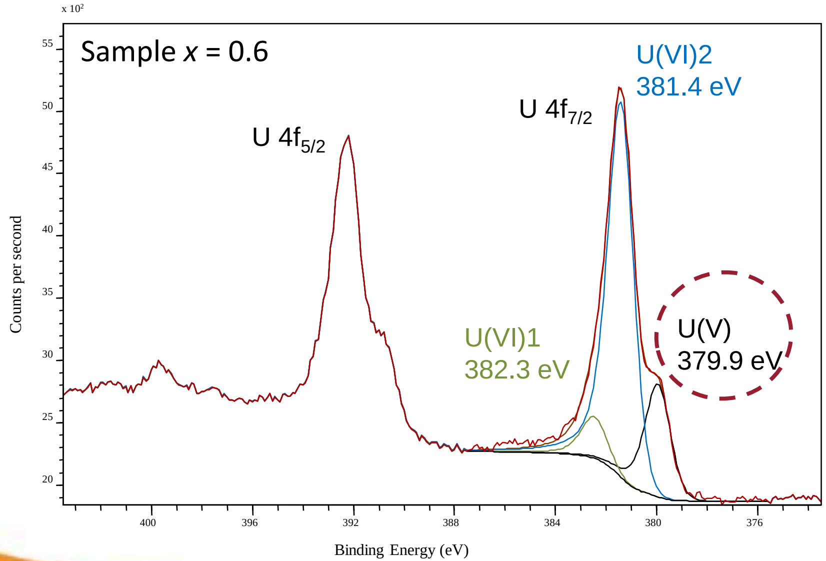
*Guo et al., **Geochim. Cosmochim. Ac.**, 2016*

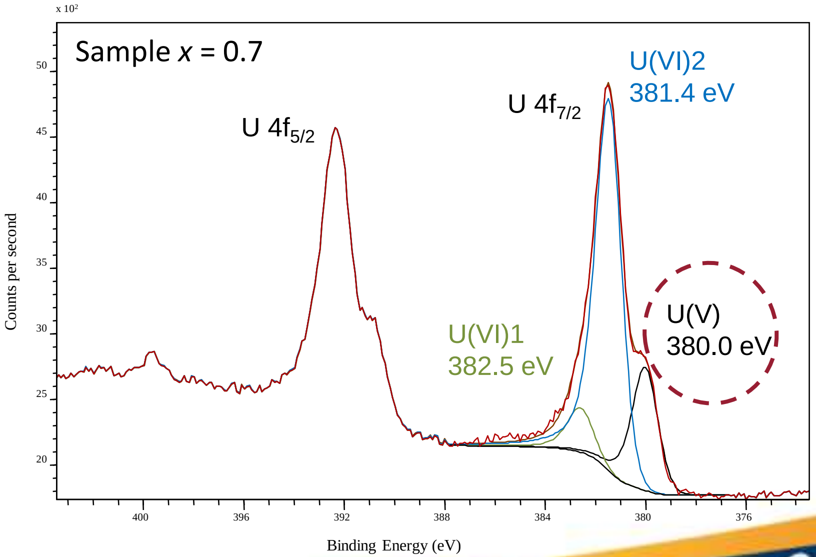
O.S. of U in $(Ca_3)(Zr_{2-x}U_x)Fe_3O_{12}$



X-ray photoelectron spectroscopy

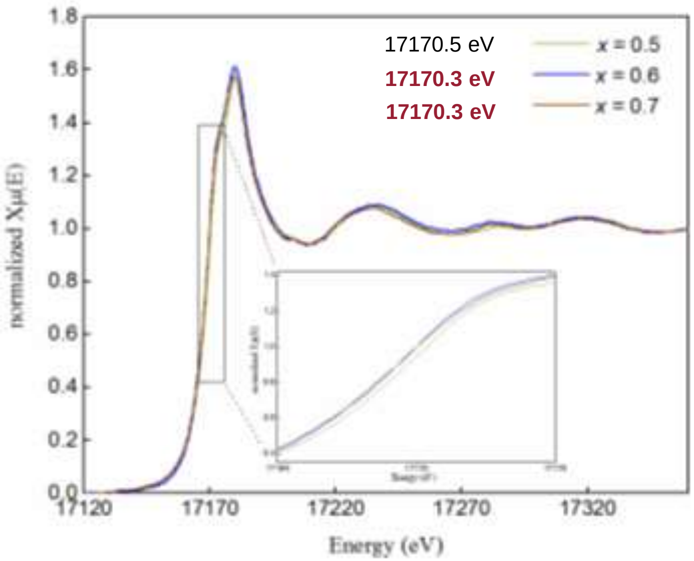
- Mix U states
- Reduce U increases

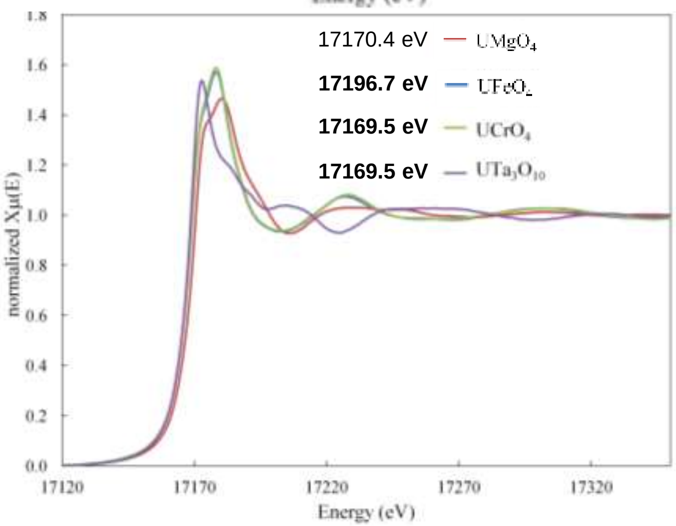




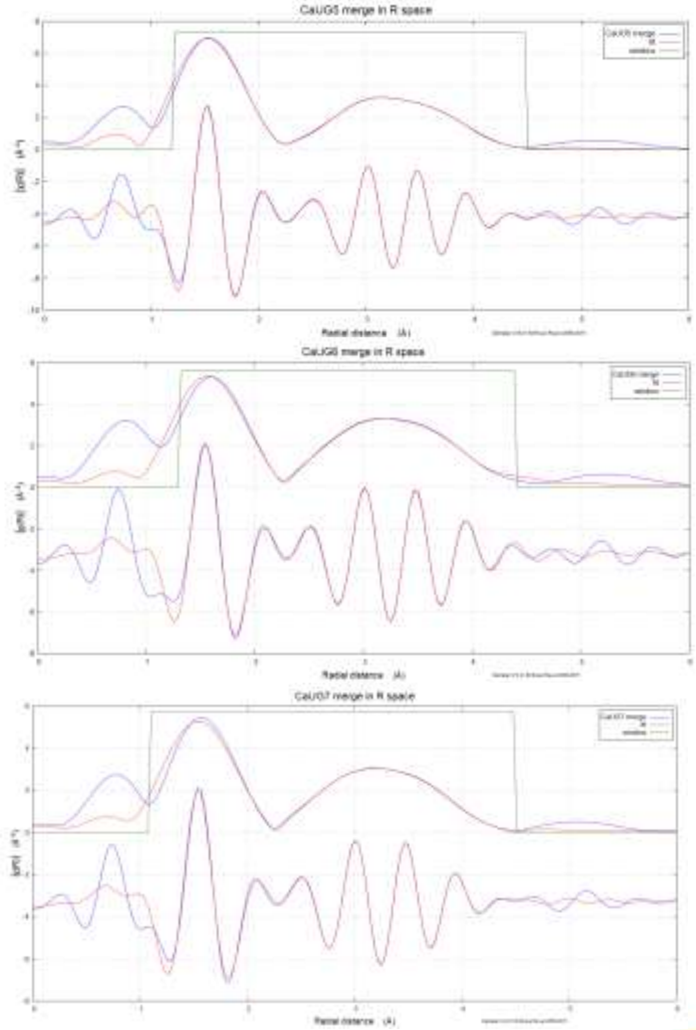
O.S. of U in $(Ca_3)(Zr_{2-x}U_x)Fe_3O_{12}$

U L_{III} XANES Spectra





EXAFS Fitting



U-O: 2.07 ± 0.01 Å

U-O: 2.10 ± 0.02 Å

U-O: 2.10 ± 0.02 Å

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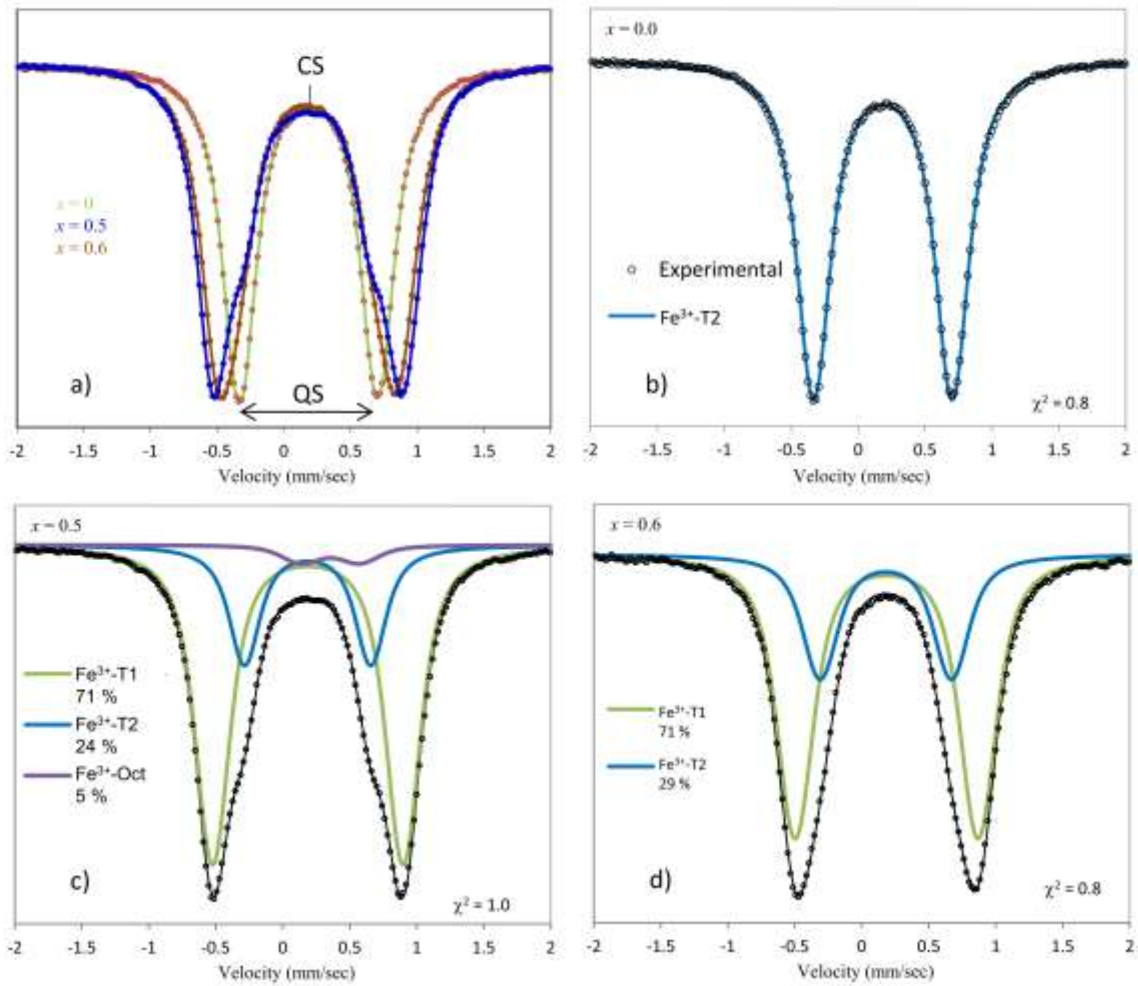
O.S. of Fe in $(Ca_3)(Zr_{2-x}U_x)Fe_3O_{12}$

Mössbauer Spectroscopy

- No Fe^{2+} presence
- Distorted tetrahedral Fe sub-lattice



x = 0.5, $Ca_3(U^{6+}_{0.5}Zr_{1.5})^{VI}(Fe^{3+}_3)^{IV}O_{12}$

x = 0.6, $Ca_3(U^{6+}_{0.4}U^{5+}_{0.2}Zr_{1.4})^{VI}(Fe^{3+}_3)^{IV}O_{12}$

x = 0.7, $Ca_3(U^{6+}_{0.3}U^{5+}_{0.4}Zr_{1.3})^{VI}(Fe^{3+}_3)^{IV}O_{12}$

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Implication for U Immobilization at Repository Conditions

Oxidative reaction (RT): $Ca_3Zr_2SiFe_2O_{12}$, γ-UO_3, Fe_2O_3

45.6 ~ 82.0 kJ/mol → NOT stable

Reducing associated-mineral environment (RT): $Ca_3Zr_2SiFe_2O_{12}$, γ-UO_3, FeO

-99.2 ~ -65.3 kJ/mol → Very stable

Phase formation condition (T ~ 800 – 1000 ℃): $Ca_3Zr_2SiFe_2O_{12}$, U_3O_8, Fe_2O_3

x = 0.5, 32.0 ± 5.3 kJ/mol
x = 0.6, 11.5 ± 5.2 kJ/mol
x = 0.7, -19.7 ± 5.3 kJ/mol → $\Delta G^{800\,^\circ C}_{sub} \approx -28.4$ kJ/mol

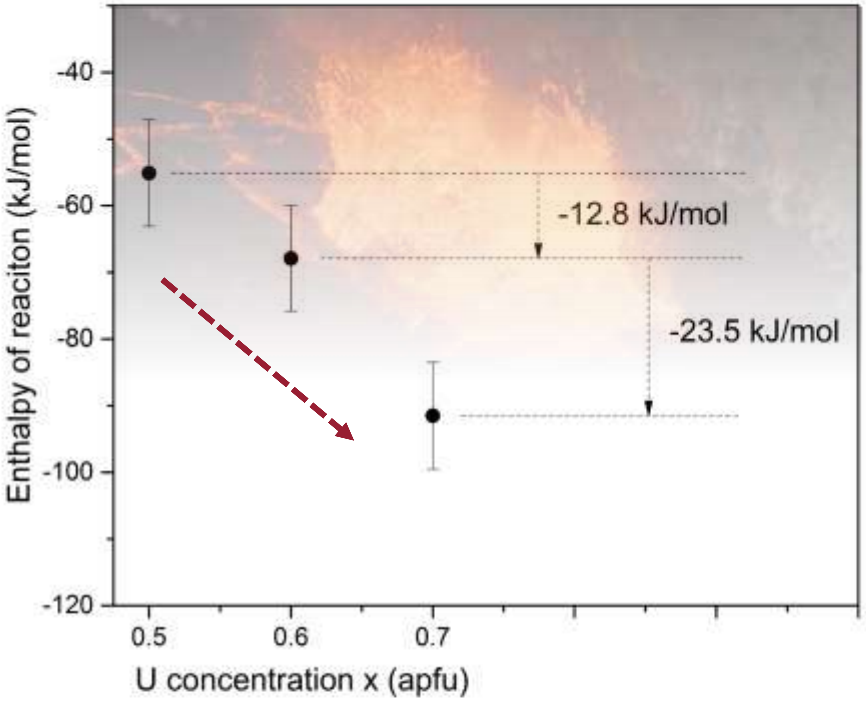
Geological/repository Implication from Thermodynamics

How increased U influences Ca-Zr-Fe garnet phase:

$$Ca_3(U_xZr_{2-x})Fe_3O_{12} + \Delta x\ \gamma\text{-}UO_3 \rightarrow Ca_3(U_{x+\Delta x}Zr_{2-x-\Delta x})Fe_3O_{12} + \Delta x\ ZrO_2 + \Delta x/2\ O_2$$

Implications:

- Higher U content stabilize the phase
- Unlikely to decompose to oxides



Outline

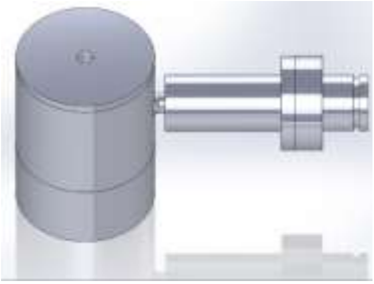
- **Topic I**: Actinide Materials/Minerals in Environment
- **Topic II**: Nuclear Waste Form
- **Topic III**: Calorimetry on Transuranium (Pu)

Thermodynamics for Actinides (U, Th, Np and Pu)

- **Relocated and reinstalled during year 2015 ~ 2017**:

Fully operational

Challenges for setting up actinide calorimetry capability



Control team

- Safety documents
- Waste stream approval
- Experiment coordination

Our team

- Lab arrangement
- Critical designs
- IWD
- Handling ACT
- Minimize waste

Pu team

- Sample preparation
- Transuranium Transfer

Uniqueness of Rad Calorimetry

Targets:

- PuO_2, $PuO_{2\pm x}$, $PuO_2 \cdot xH_2O$
- PuO_2-UO_2, NpO_2-UO_2
- U-, Th-, materials
- UN, USi
- Nano materials

Also applied to:

- Transuranium
- Air-, humidity- sensitive materials

Summary

Research Topics

Topic I:
Actinides in Environment

Topic II:
Nuclear Waste Form

Topic III:
Pu Calorimetry

Techniques

Synthesis:
Solid state, schlenk line, sol-gel, hydrothermal, vacuum seal, etc.

Characterization:
XRD, EPMA, SEM synchrotron X-ray, Neutron Scattering, BET, MS, IR

Thermal analysis:
DSC, TG, water adsorption calorimetry, high-T reaction calorimetry

Collaborators

- LANL
- UC Davis
- WSU
- UC Berkeley
- U Tennessee
- Stanford
- Notre Dame
- Lanzhou U

- EMSL, PNNL
- APS
- SSRL
- CHESS
- SNS, ORNL
- NIST

- Institue de Chimie Séparative de Marcoule
- French Alternative Energies and Atomic energy Commission
- Nuclear Research Center – Negev Be'er-Sheva
- Forschungszentrum Jülich
- GSI Helmholtz Centre for Heavy Ion Research

Acknowledgement

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- Dr. Jeremy N. Mitchell
- Dr. Albert Migliori
- Dr. Alexandra Navrotsky

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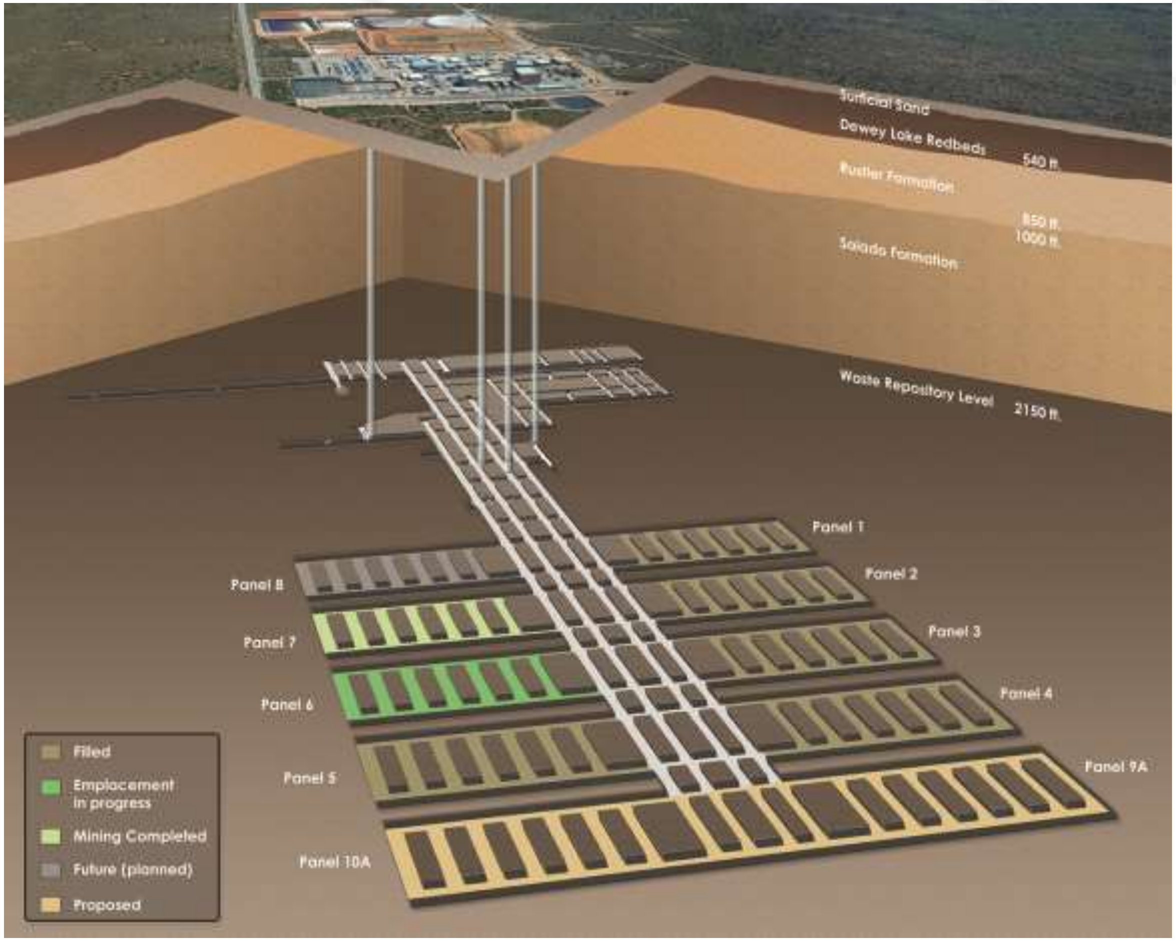
- EFRC-Actinides

- Seaborg Institute

Research related to a salt repository

Features of WIPP:

- Salt repository
- Low permeability
- Self-healed
- High thermal conductivity
- High solubility



https://nukewatch.org/activemap/NWC-WIPP.html

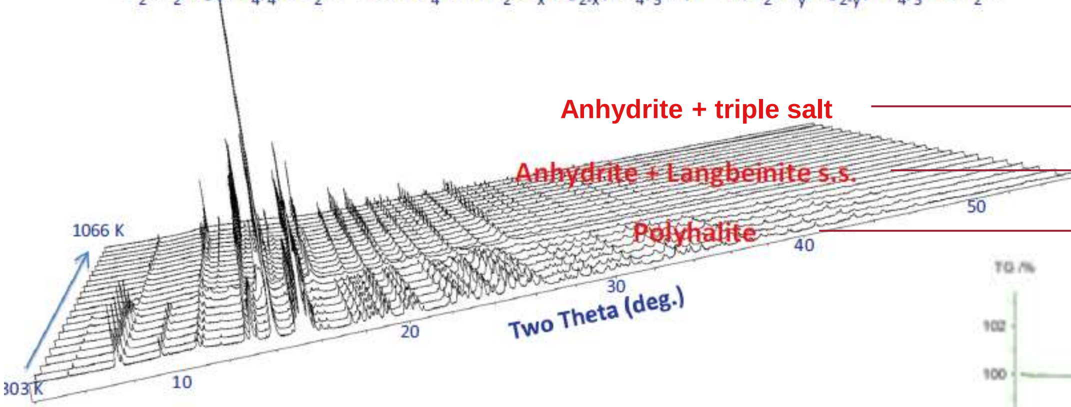
Polyhalite: Thermal Behavior and Thermodynamics

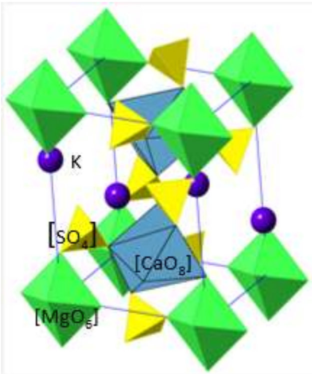
Motivation:

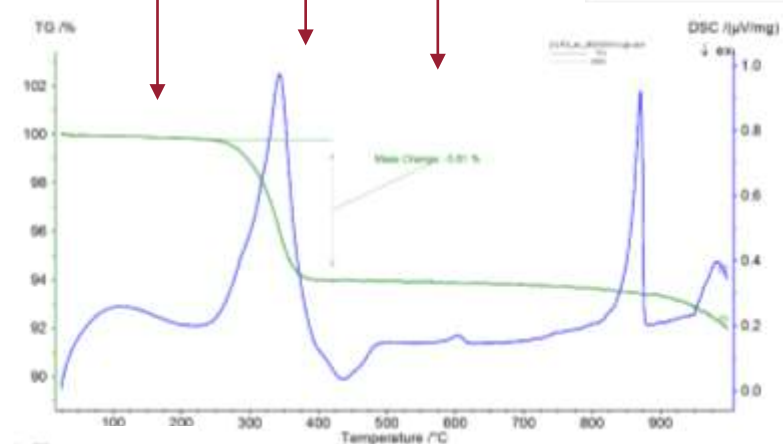
- A coexisting mineral with halite in salt repositories (such as WIPP)
- Dehydrating at high T, dissolving halite and affecting repository integrity

Heating in-situ Synchrotron XRD

$$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O \rightarrow CaSO_4 + (A)K_2Ca_xMg_{2-x}(SO_4)_3 + (1-A)K_2Ca_yMg_{2-y}(SO_4)_3 + 2H_2O$$







Enthalpies and thermal stability

-152.5 kJ/mol

*Xu et al., **J. Chem. Thermo.**, 2016*
*Guo et al., **J. Chem. Thermo.**, 2017 (submitted)*