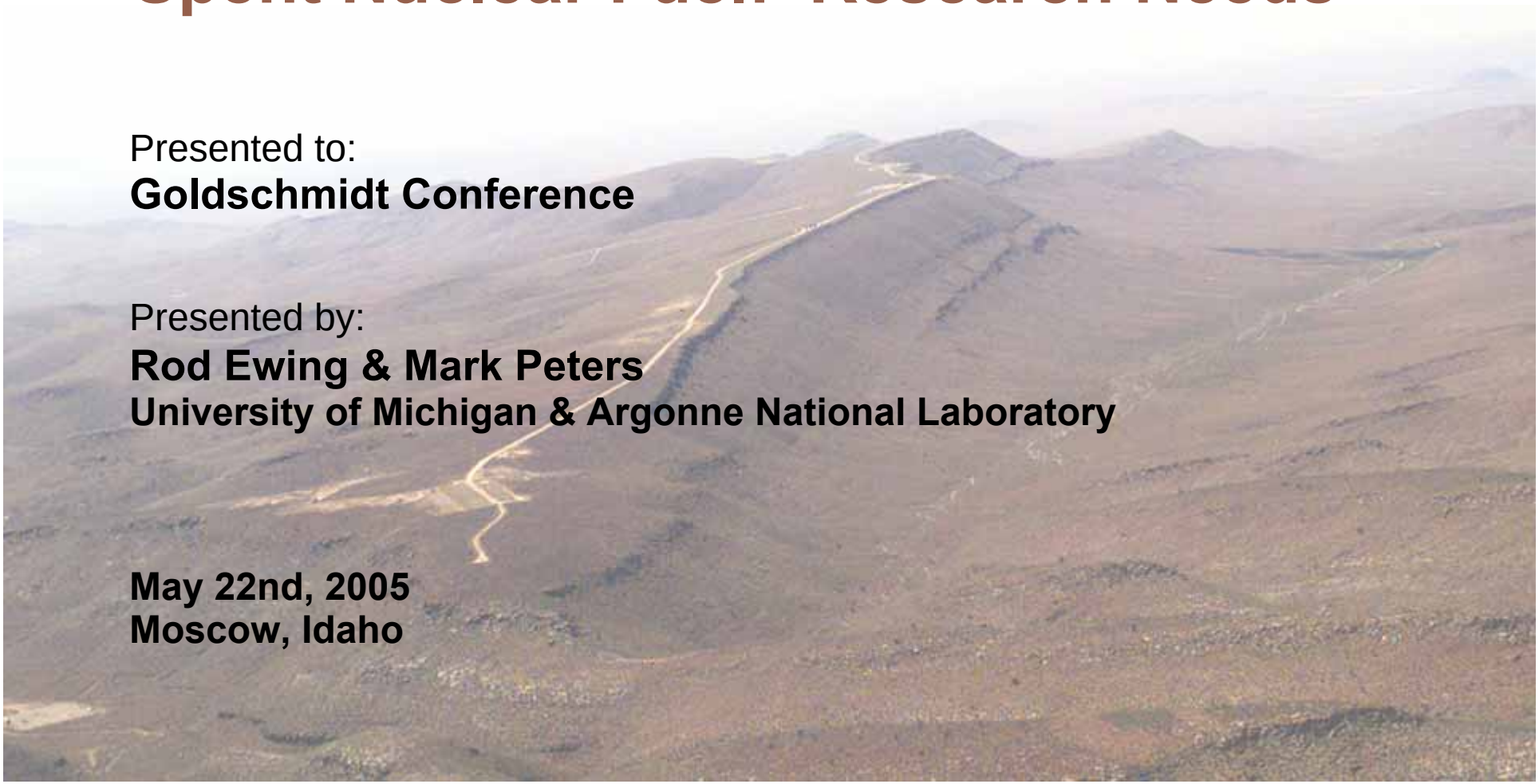
U.S. Department of Energy
Office of Civilian Radioactive Waste Management

www.ocrwm.doe.gov

Spent Nuclear Fuel: Research Needs



Presented to:
Goldschmidt Conference

Presented by:
Rod Ewing & Mark Peters
University of Michigan & Argonne National Laboratory

May 22nd, 2005
Moscow, Idaho

Office of Science and Technology and International (OST&I)

Mission

“ Provide advanced science and technology to continually enhance our understanding of the repository system and to reduce the cost and schedule for the OCRWM mission.”

Office of Science and Technology and International (OST&I)

Major Elements

- **Targeted Thrusts**
- **Advanced Technology**
- **International Collaborations**

Office of Science and Technology and International (OST&I)

Targeted Thrusts

- **Natural Barriers**
- **Materials Performance**
- **Radionuclide “Getters”**
- **Source Term**

Importance of Spent Nuclear Fuel

Rationale

- **Spent nuclear fuel is the major source (>95%) of the radioactivity**

- **At the longest times, the behavior of spent nuclear fuel will continue to control the release of the activity**

Source Term Targeted Thrust of OST&I

Integration

Research program is focused on the changing conditions over *time*, identifying the *critical processes* within each time interval, and with attention to the *radionuclides* that are the *major contributors to dose*

Source Term Targeted Thrust

Integration

- **Time**
- **Critical Processes**
- **Radionuclide Inventories**
- **Pathways to Radionuclide Release**

Source Term Targeted Thrust

Critical Processes

- **Kinetics of waste form corrosion**
- **Formation of secondary, alteration phases**
- **Sorption/reduction on the surfaces of near-field materials**
- **Formation and mobility of colloids**

Source Term Targeted Thrust

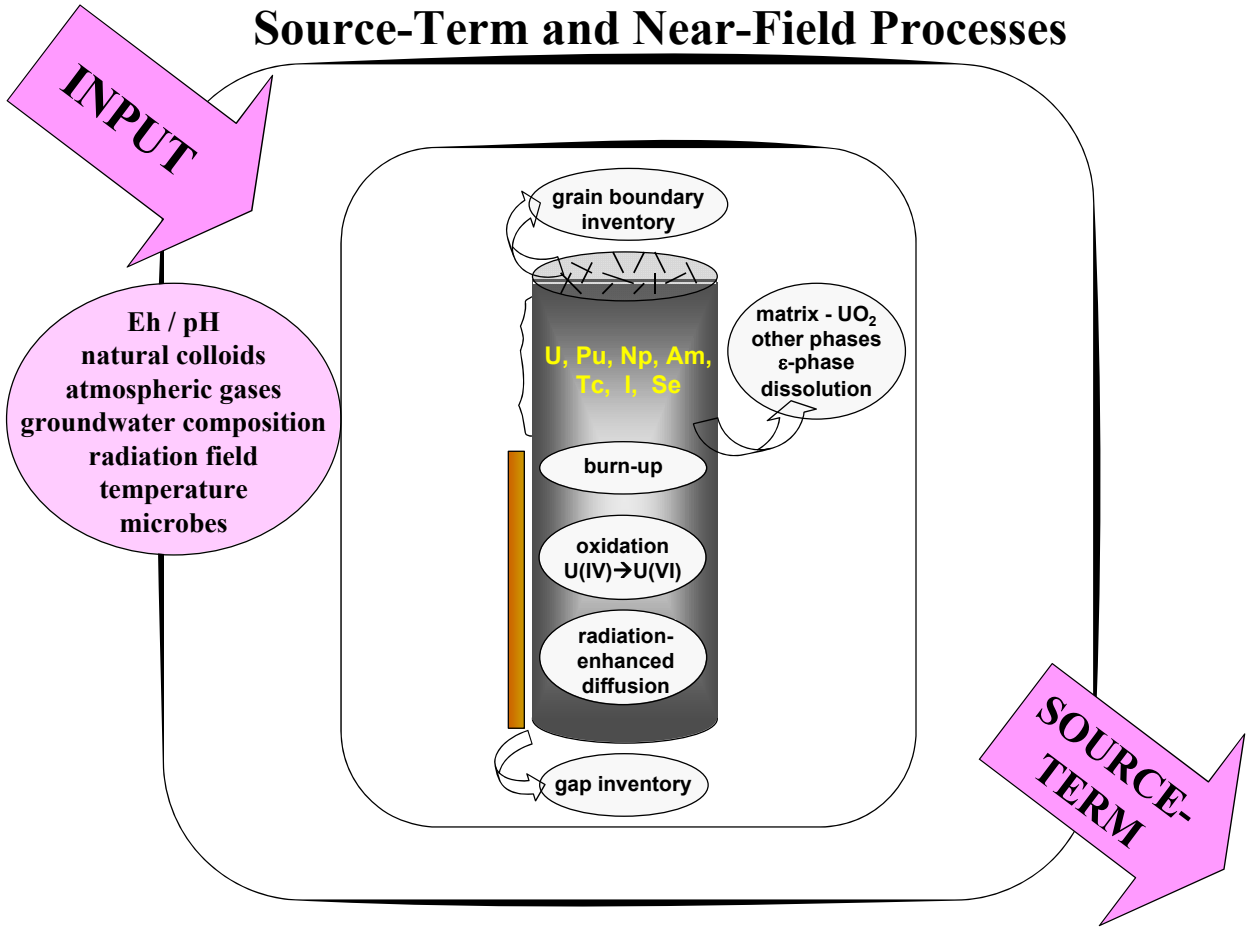
Radionuclides of Interest

^{238}U, ^{234}U, ^{233}U,

^{239}Pu, ^{237}Np, ^{241}Am,

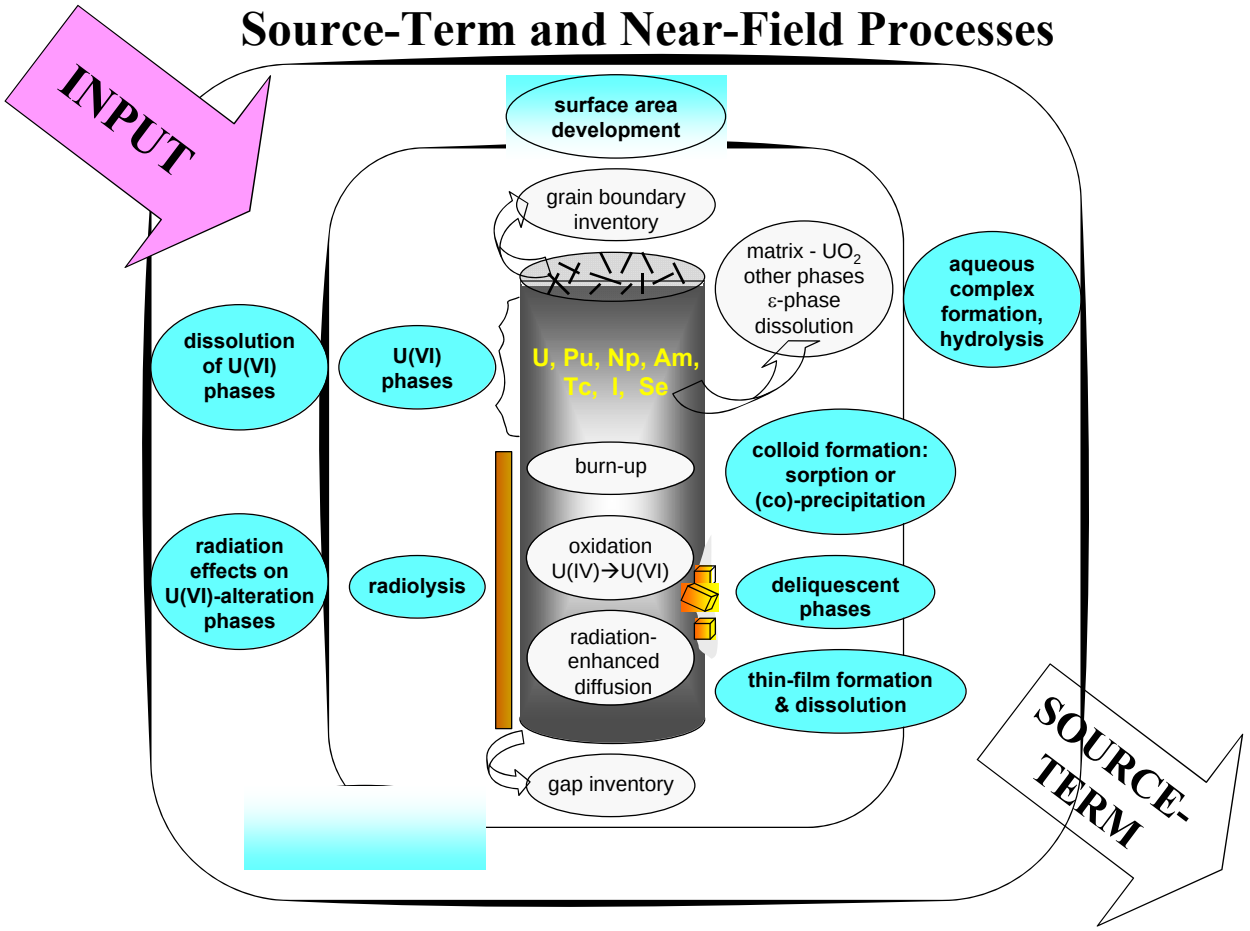
^{226}Ra, ^{129}I, ^{99}Tc, ^{79}Se, and ^{36}Cl

Source Term Targeted Thrust
(prior to breach of waste package)



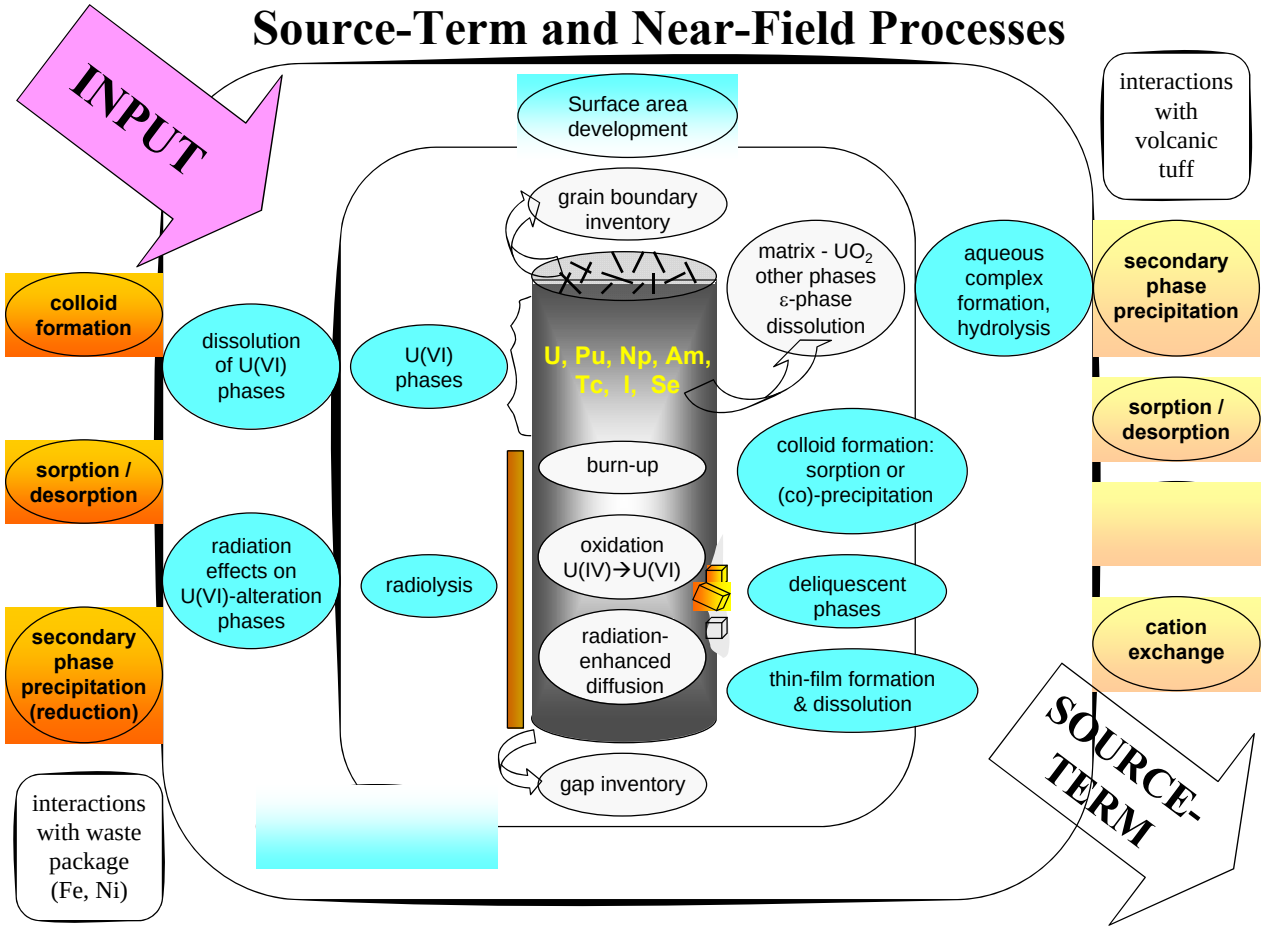
Source Term Targeted Thrust

(early waste package failure)



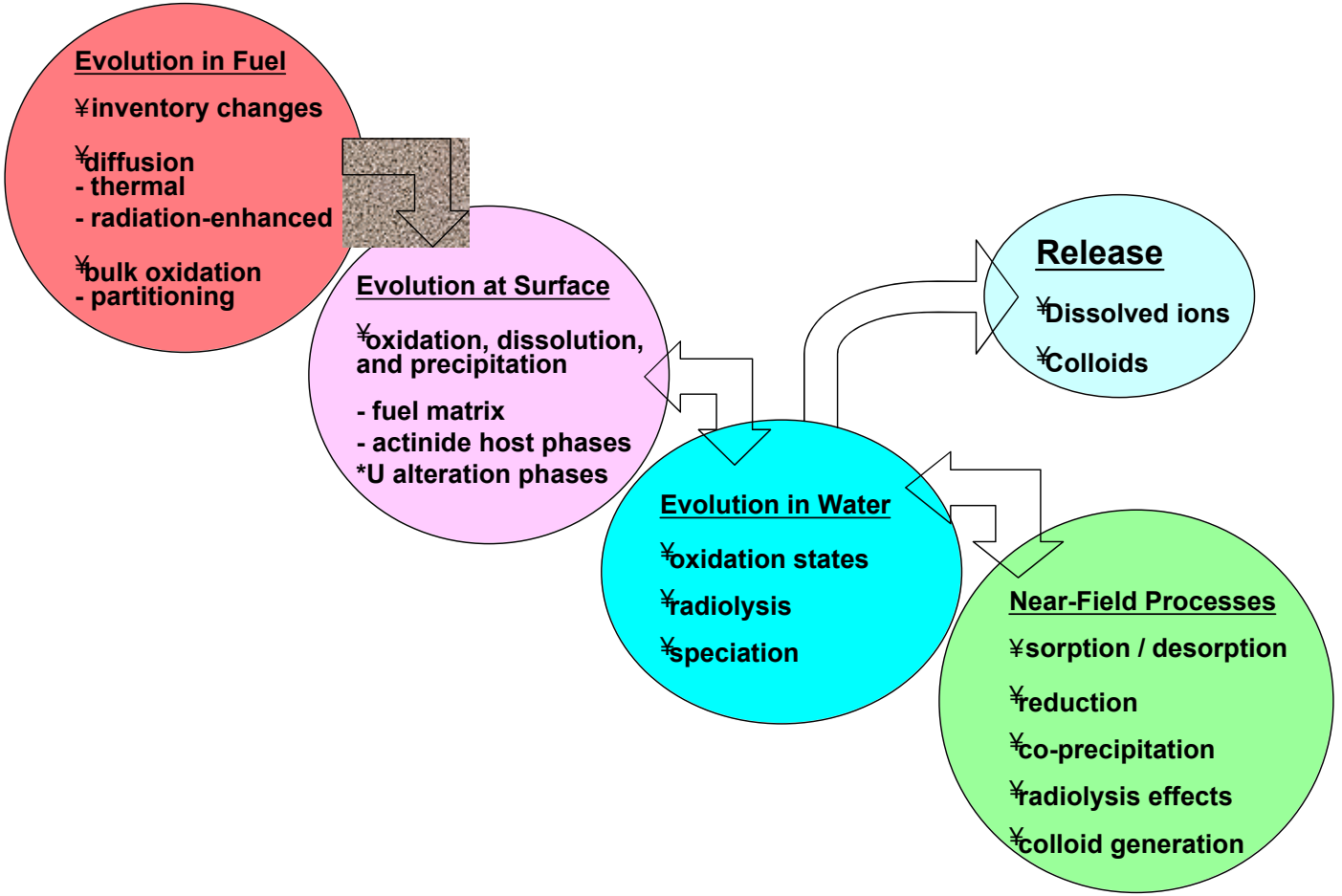
Source Term Targeted Thrust

(waste package failure at longer times)



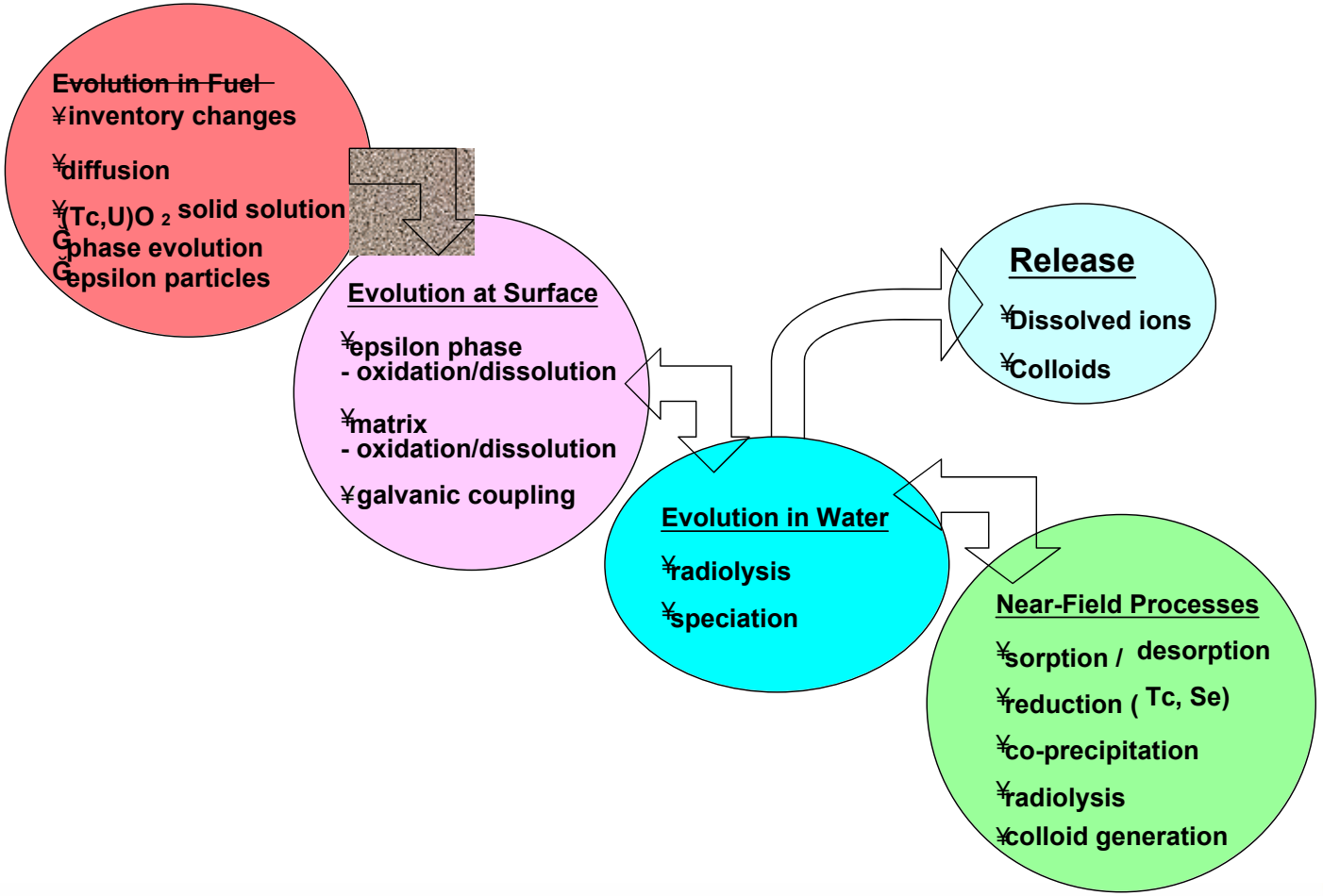
Source Term Targeted Thrust

Pathway to Release for Actinides (^{237}Np, ^{239}Pu, ^{241}Am)



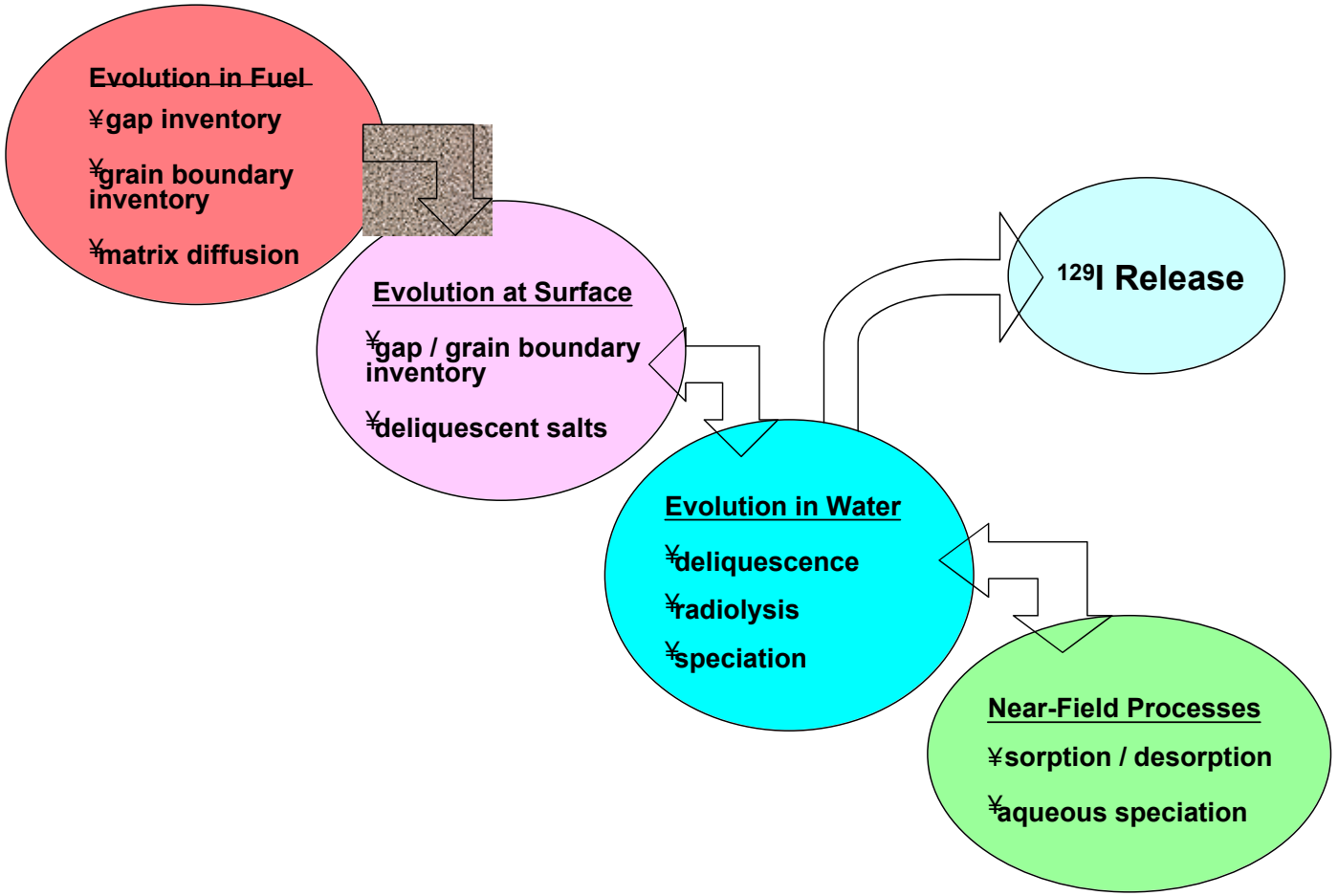
Source Term Targeted Thrust

Pathway to Release for Fission Products (^{99}Tc)



Source Term Targeted Thrust

Pathway to Release for Fission Products (^{129}I)



Source Term Targeted Thrust Research Areas

- **Objective - enhance the understanding of the release mechanisms of key radionuclides from spent nuclear fuel (SNF) and explore technical enhancements**
- **Engineered materials and radionuclide sequestration**
  - **Corrosion effects on chemistry and radionuclide release processes**
- **Secondary alteration phases**
  - **Effects of environment on the formation, evolution, and radionuclide incorporation**
- **Matrix dissolution**
  - **Oxidation and dissolution of SNF and evolution of surface conditions**

Source Term Targeted Thrust
Present Research Areas

- Sequestration of radionuclides (SNL, ANL, PNNL)
- Impact of secondary alteration phases of SNF on mobility of Np and Pu (Notre Dame)
- Deliquescence and decay heat effects on source term (ANL)
- Dissolution mechanisms and rates (PNNL)
- Chemistry and coordination structure of radionuclides (ANL)
- Corrosion of SNF: The long-term assessment (University of Michigan)

Source Term Targeted Thrust

Solicitation for Proposals 2005

- **Secondary alteration phases and radionuclide release**
  - **stability and thermochemistry**
  - **solubility**
  - **energetics of radionuclide incorporation**
  - **structural studies**
  - **sorption/desorption mechanisms**
  - **kinetics of precipitation and dissolution**
- **International source term programs for collaboration on understanding release of key radionuclides**

Recent Results

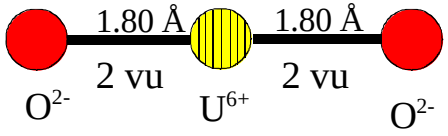
Source Term Targeted Thrust

Recent Advances

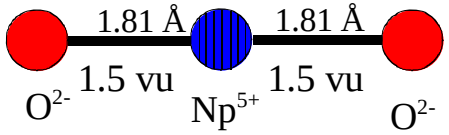
- **Crystal-chemistry and structure of Np-compounds (P. Burns at Notre Dame)**
- **Radiation effects in U^{6+}-phases (S. Utsunomiya at University of Michigan)**

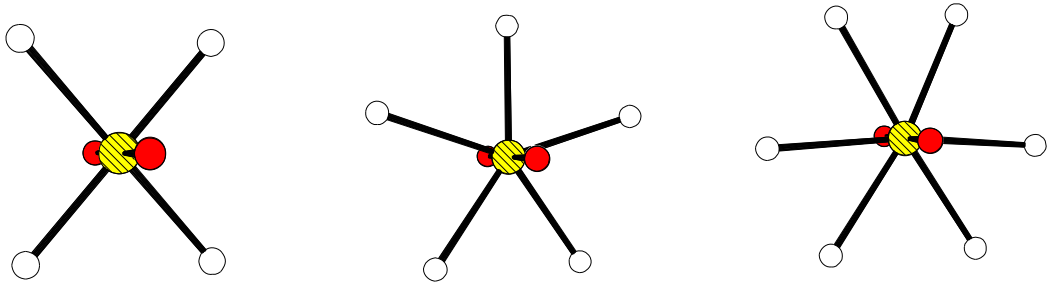
Np^{5+} Crystal Chemistry

$(U^{6+}O_2)^{2+}$ Uranyl Ion



$(Np^{5+}O_2)^{+}$ Neptunyl Ion

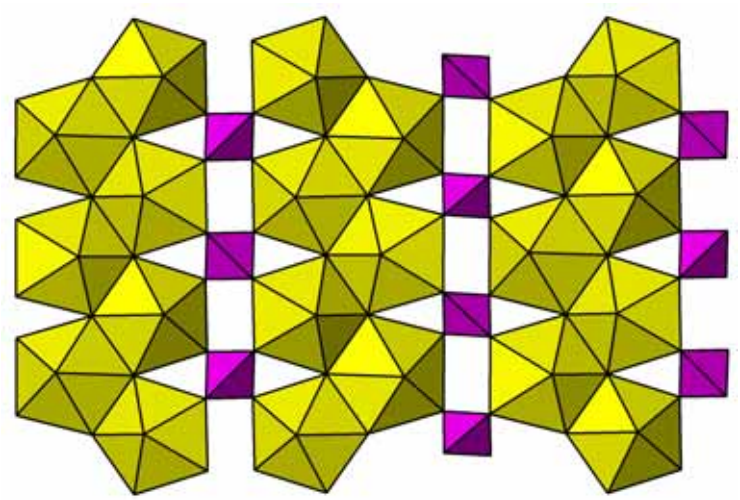




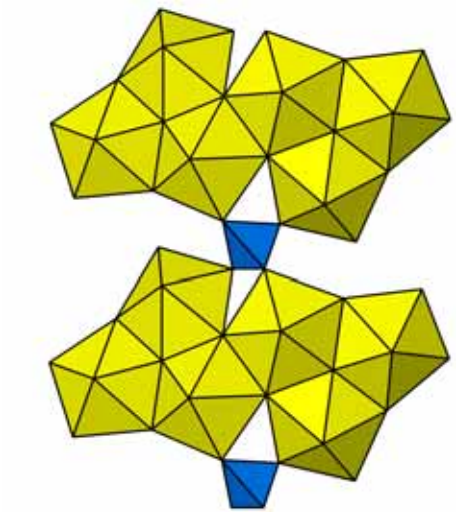
Uranyl			2.46 Å
Neptunyl	2.26 2.39	2.34 2.45	2.56 Å

Burns et al. (1997): Journal of Nuclear Materials

U^{6+} Crystal Chemistry

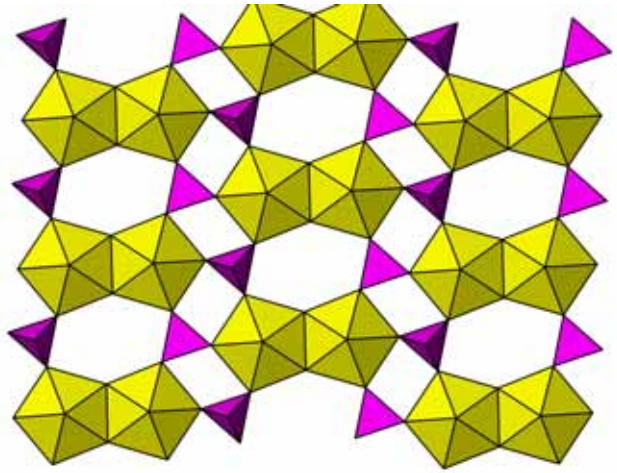


Zippeite Group: Hydrous monovalent and divalent-cation uranyl sulfates



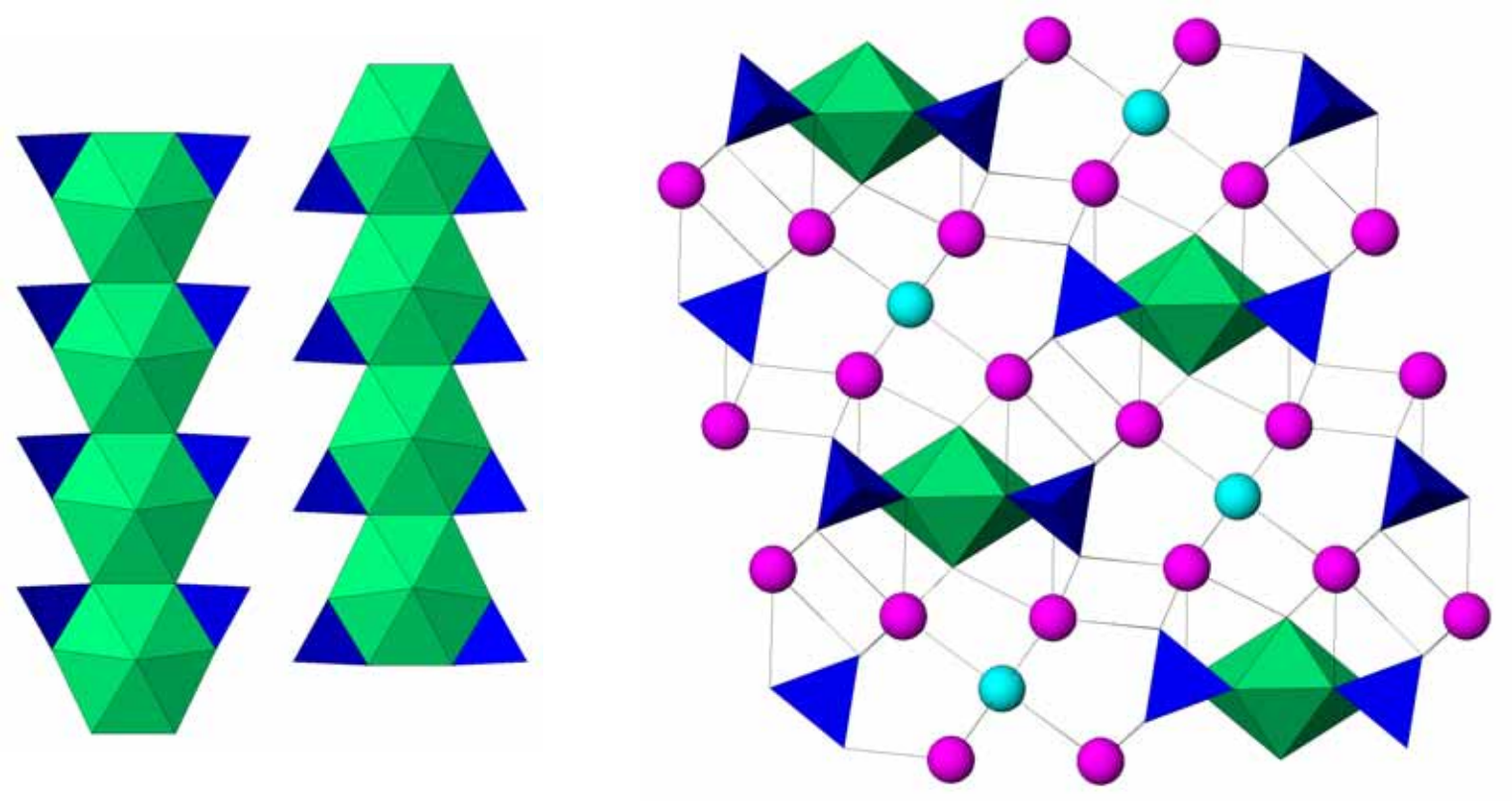
Uranopilite
$[(UO_2)_6(SO_4)O_2(OH)_6(H_2O)_6]$

Johannite
$Cu[(UO_2)_2(SO_4)_2(OH)_2](H_2O)_8$



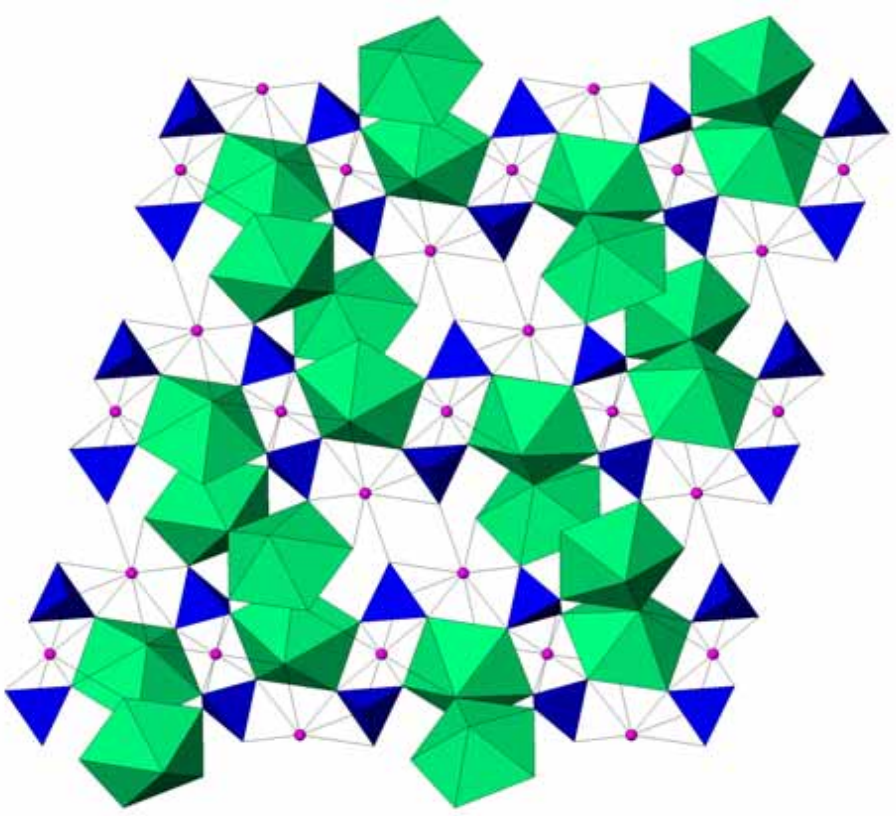
Crystal Chemistry of Np^{5+}

$K_4[(NpO_2)(SO_4)_2]Cl$

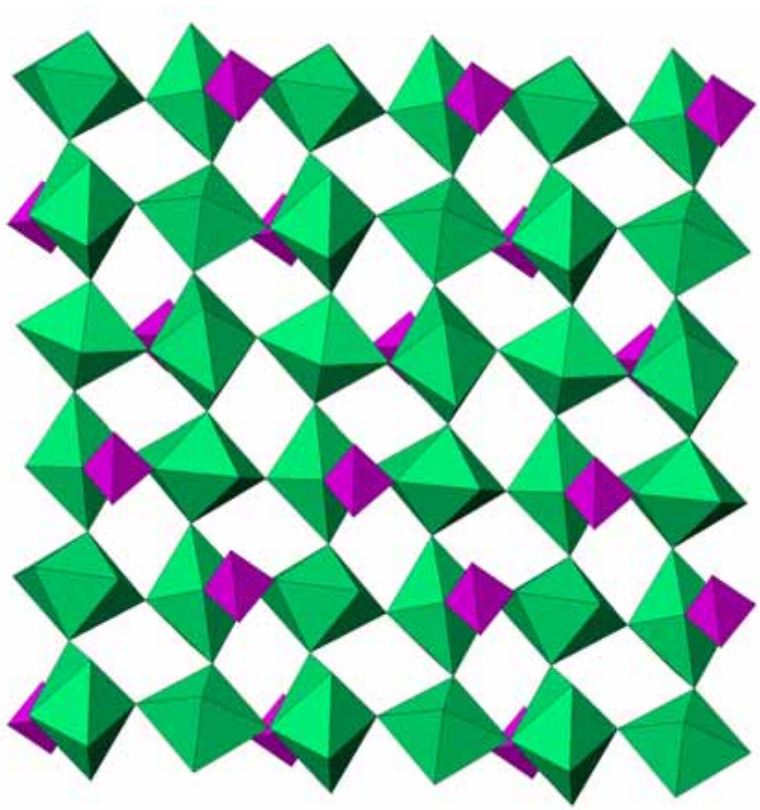


Np^{5+} Crystal Chemistry

$K_2(NpO_2)_2(SO_4)_2(H_2O)$

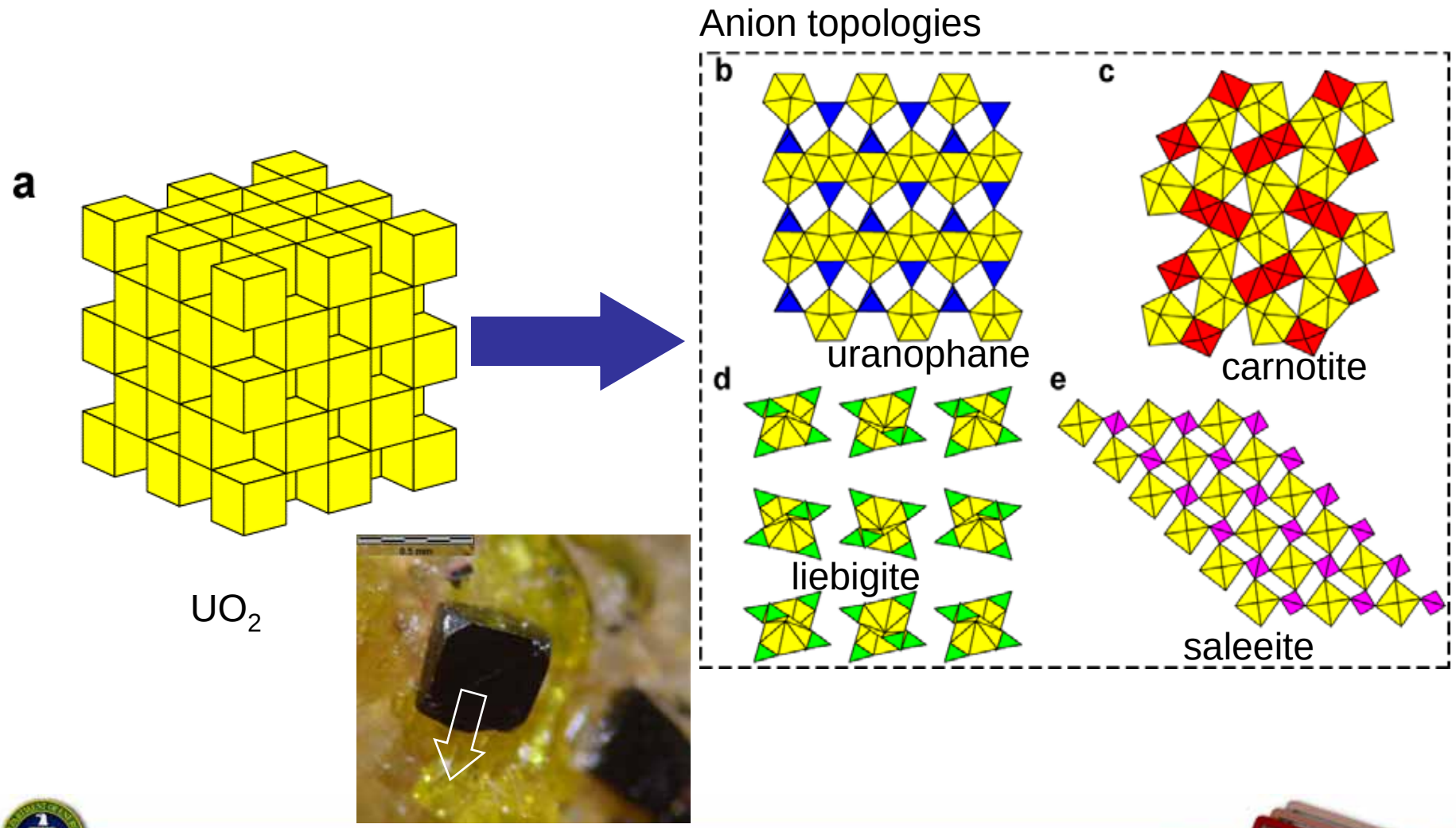


$[(NpO_2)_8(SO_4)_4(H_2O)_{16}]$

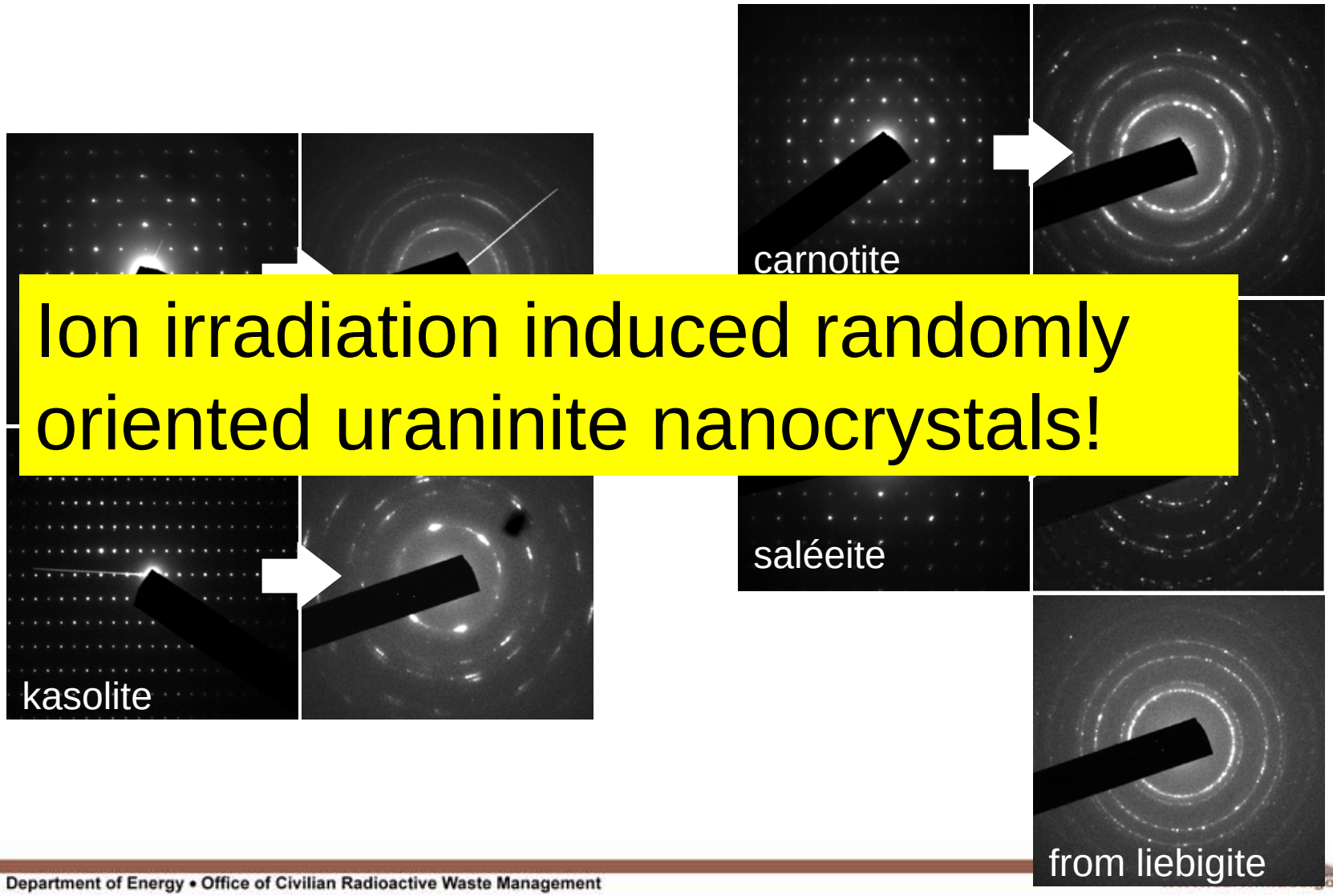


Unpublished

Alteration and oxidation of UO_2

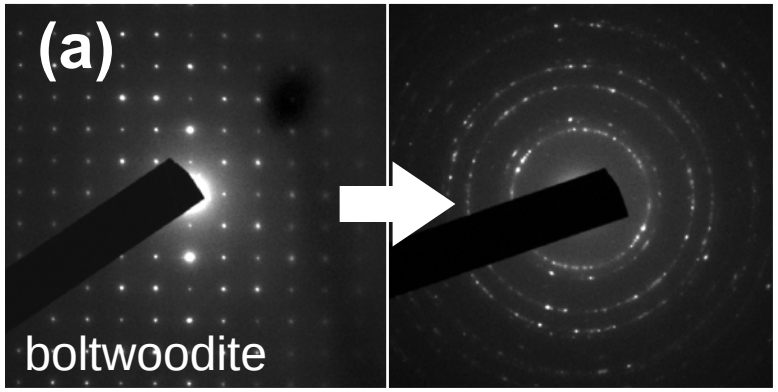


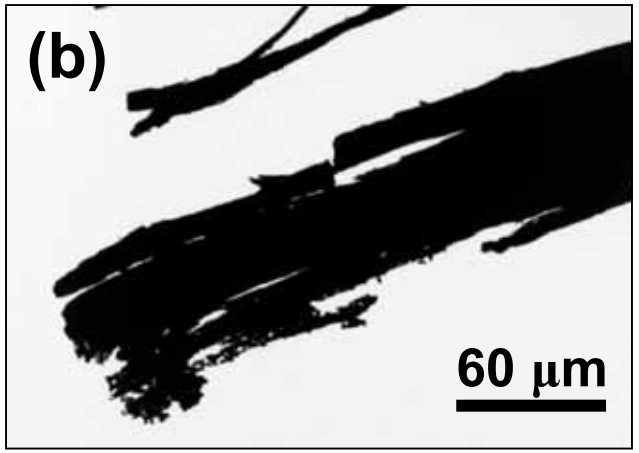
SAED of the transition in various U^{6+}-phases during Kr^{2+}- irradiation at 25 °C

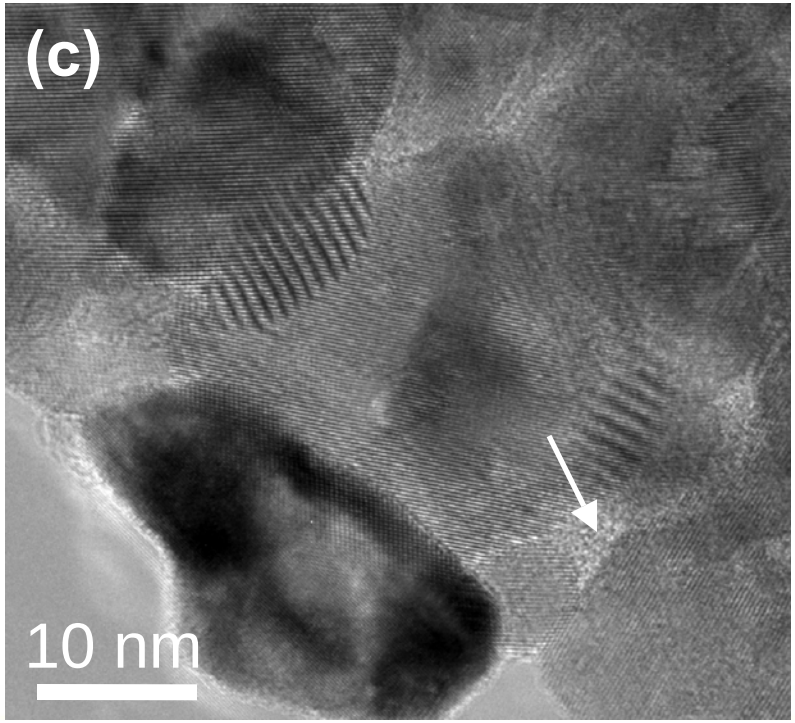


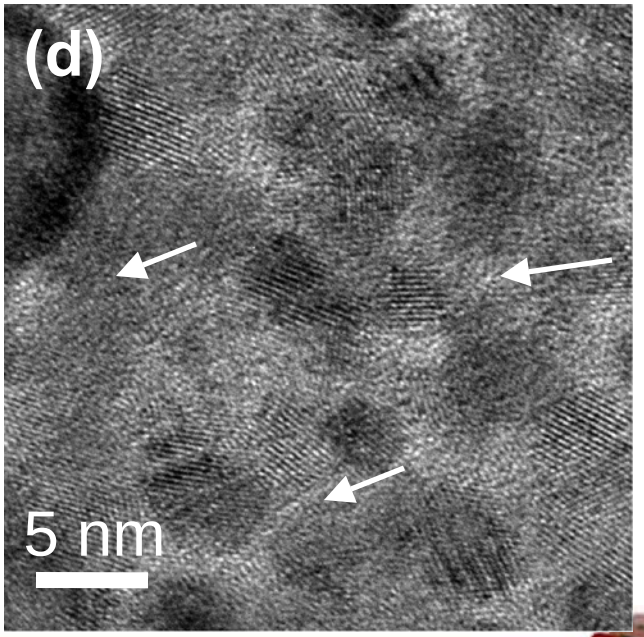
Ion irradiation induced randomly oriented uraninite nanocrystals!

Boltwoodite under Kr^{2+} irradiation (1.4 dpa)

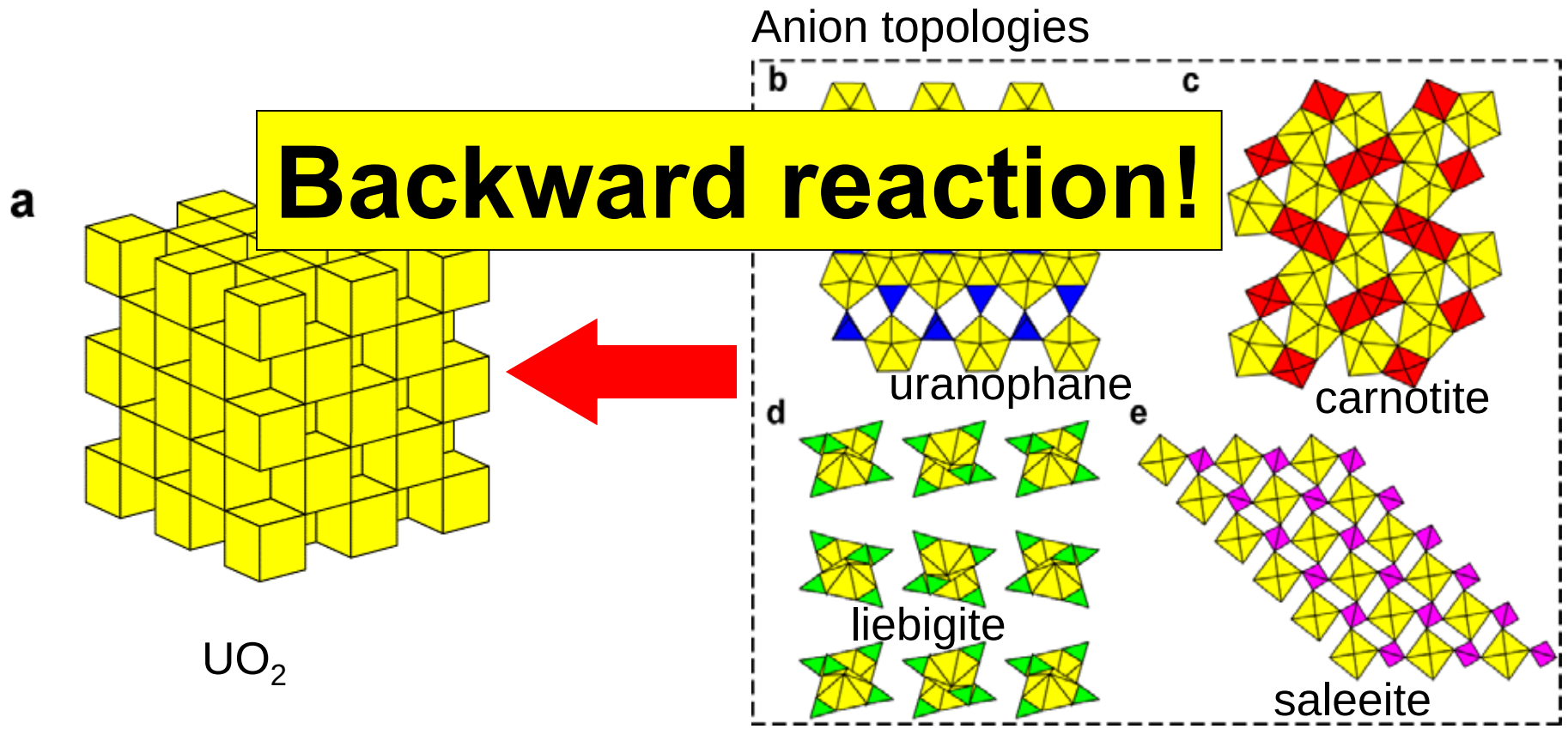








Radiation effects of U^{6+}-phases



Cumulative dose in uranophane

T (year)	D_α (α-decay events/mg)	dpa
10,000	1.80E+13	0.00090
100,000	1.80E+14	0.0090
1,000,000	1.80E+15	0.090

Dose contribution by 1 wt% of ^{239}Pu (Pu/U=0.018)

T (year)	D_α (α-decay events/mg)	dpa
10,000	6.30E+15	0.27
100,000	2.38E+16	1.01
1,000,000	2.54E+16	1.08

Dose contribution by 0.02 wt% of Np (Np/U=0.00036)

T (year)	D_α (α-decay events/mg)	dpa
10,000	1.00E+13	0.00050
100,000	9.88E+13	0.0050
1,000,000	8.73E+14	0.044

Conclusions

U^{6+}-phases with ^{239}Pu (1 wt.%) may accumulate substantial radiation doses (~1.0 displacement per atom) during 100,000 years.

Under oxidizing conditions, multiple cycles of radiation-induced decomposition to UO_2 followed by alteration to U^{6+}-phases may lead to the loss of incorporated radionuclides.

Extra Slides

Source Term Targeted Thrust
(present activities)