U.S. Department of Energy
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Np Incorporation into Uranyl Alteration Phases: A Quantum Mechanical Approach

Presented to:
Materials Research Society

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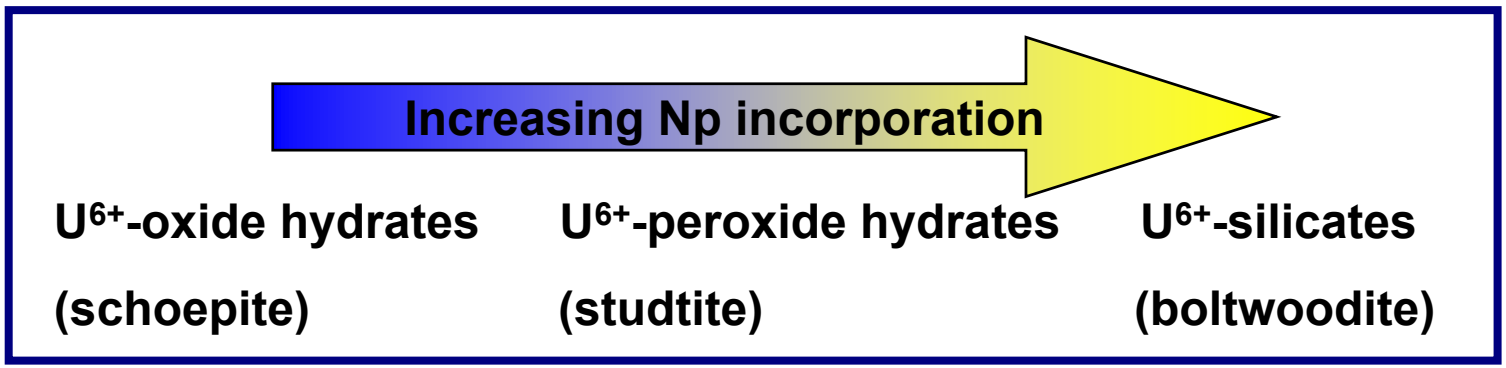
Significance and Background

- **Np - potential contributor to dose at long times**
  - **2.1 million year half-life**
  - **highly mobile in the 5+ oxidation state**

- **U^{6+} phases can limit the mobility of Np^{5+}**



Douglas *et al.* 2005, Burns *et al.* 2004 and *Elements* (in press)

Background

- **Potential Np barriers**
  - **studtite $UO_2O_2(H_2O)_2)(H_2O)_2$**
    - **only known U-peroxide phase**
    - **forms by radiolysis near SNF(UO_2) surfaces**
  - **boltwoodite $K(UO_2)(SiO_3OH)\cdot 1.5(H_2O)$**
    - **U-silicate observed in most UO_2/SNF dissolution studies**

QUESTIONS:

Is incorporation of Np^{5+} or Np^{6+} more favorable in studtite?

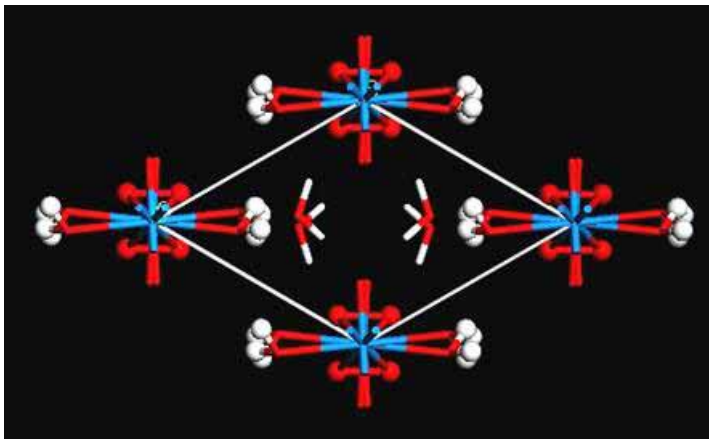
What is the energetically favorable Np^{5+} incorporation mechanism in boltwoodite?

Quantum Mechanics Glossary

- **CASTEP** – density functional theory-based code
- **Pseudopotentials (ultrasoft)** – describe core e^-'s
- **Plane waves** – describe valence e^-'s
  - generalized gradient approximation (**GGA**) w/ Purdew-Burke-Ernzerhof (**PBE**) functional
  - **$E_{cut\text{-}off}$** – determines # plane waves
  - **k-points** – points in Brillouin zone for which the wave function is evaluated
  - **unoccupied orbitals** – find most favorable spin configuration

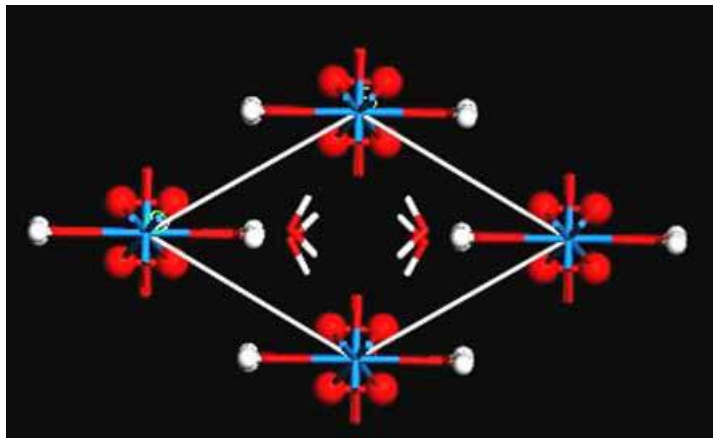
Determination of H^+ positions in studtite

- **Optimize H^+ positions ($\Delta E \sim 3eV$)**



(Burns and Hughes, 2003)

● = U^{6+}
● = O^{2-}
○ = H^+



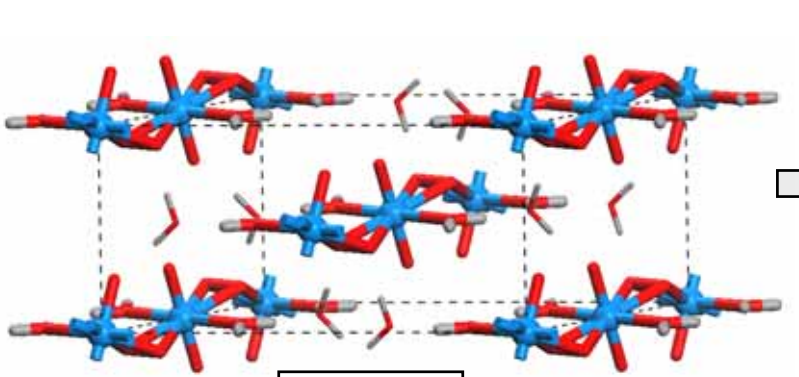
Geometry-optimized structure

- **Calculate incorporation energies**
  - **determine incorporation mechanisms**
  - **understand reference phases (Np source and U sink)**

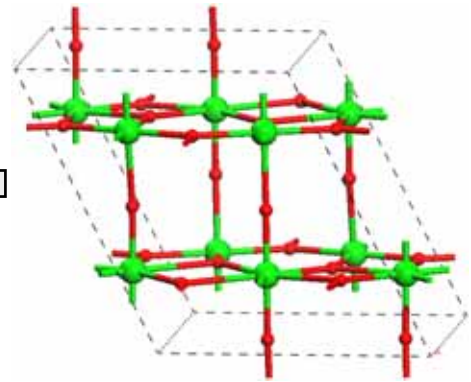
Studtite Incorporation (Case A)

studtite + ½Np_2O_5 + ½H_2O → (studtite–U^{6+} + Np^{5+} + H^+) + UO_3

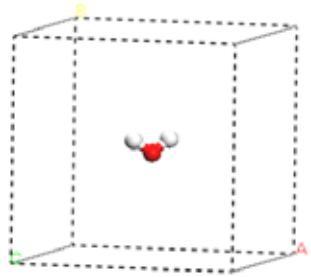
● = U^{6+} ● = Np^{5+} ● = O^{2-} ● = H^+ ● = H^+ (used for charge balance)



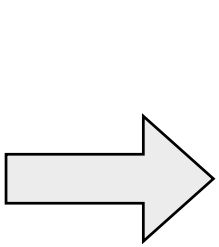
studtite

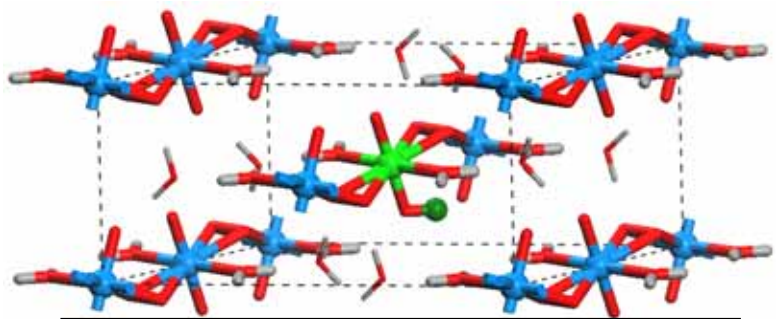


Np_2O_5

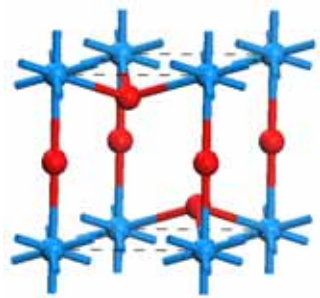


H_2O





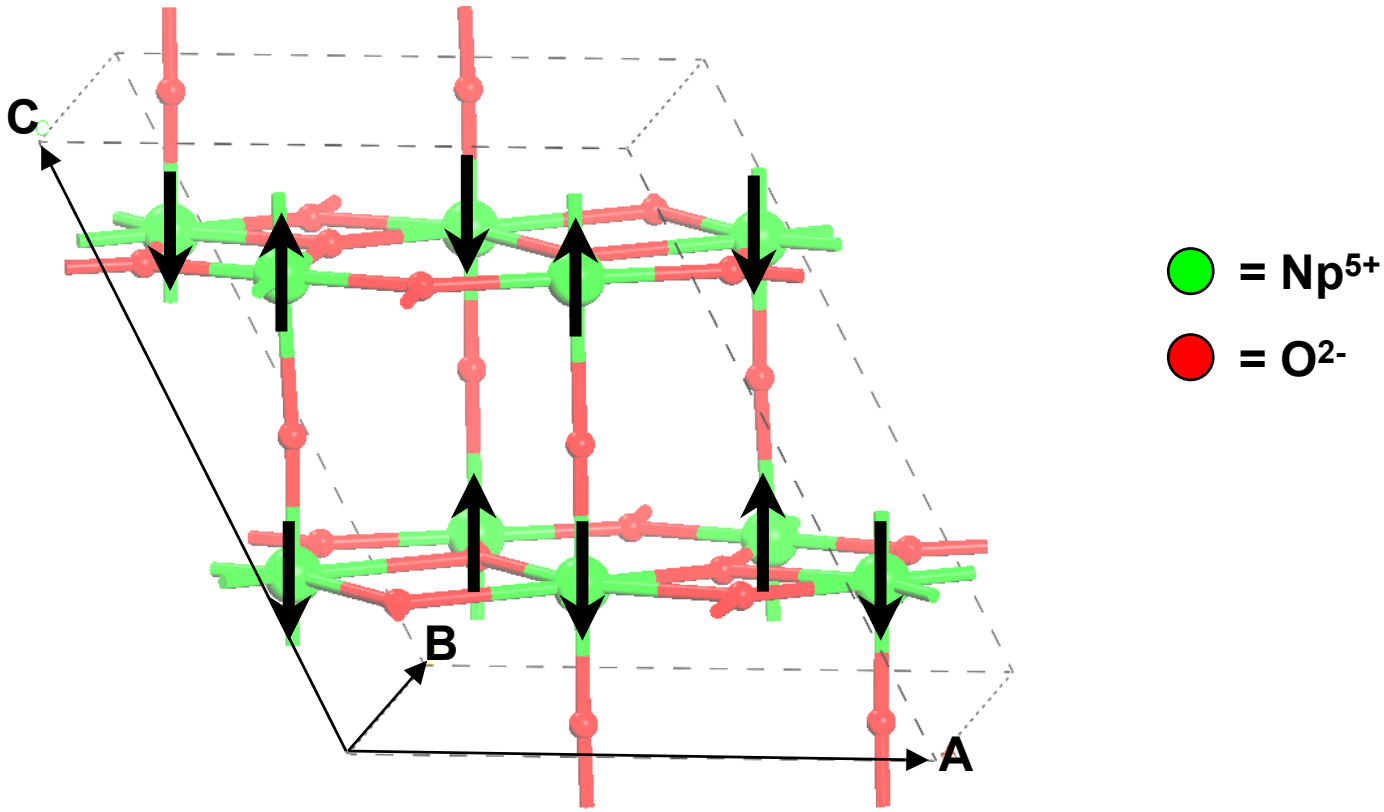
studtite (Np^{5+} + H^+ replacing U^{6+})



UO_3

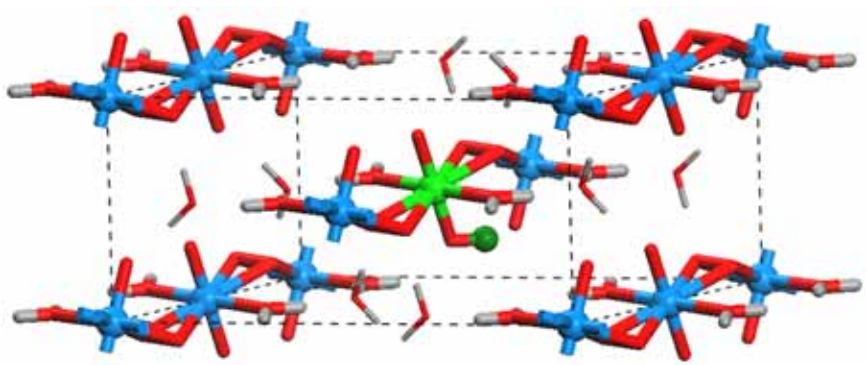
Np_2O_5

- **Antiferromagnetic (with *P2/c* symmetry)**
  - $E_{Ferromagnetic} > E_{Antiferromagnetic\ (P2/c)}$ **(ΔE = 0.11 eV)**

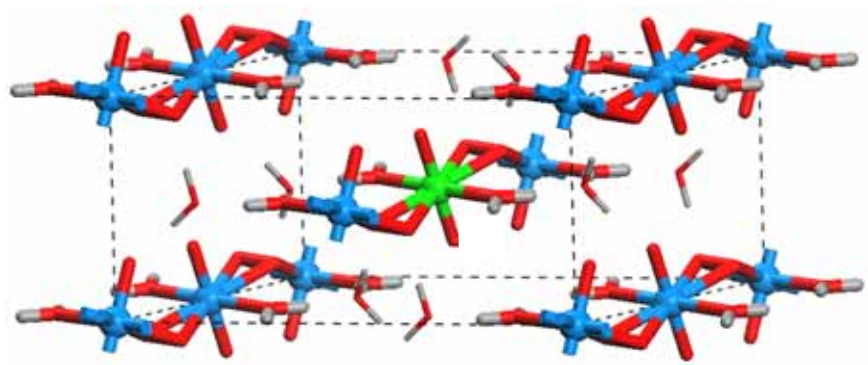


Studtite Results

Np^{5+}:	studtite + ½Np_2O_5 + ½H_2O → (studtite - U^{6+} + Np^{5+} + H^+) + UO_3
Np^{6+}:	studtite + ½Np_2O_5 + ¼O_2 → (studtite - U^{6+} + Np^{6+}) + UO_3



Np^{5+} + H^+ replacing U^{6+}

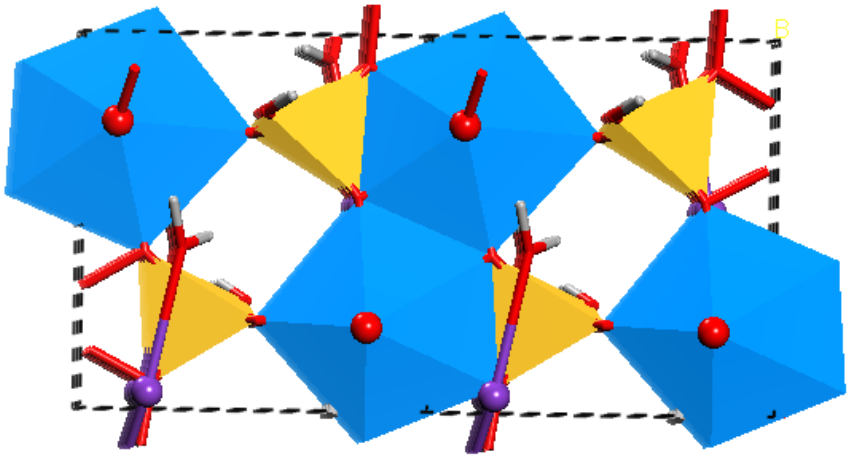


Np^{6+} replacing U^{6+}

Np^{6+} incorporation more favorable

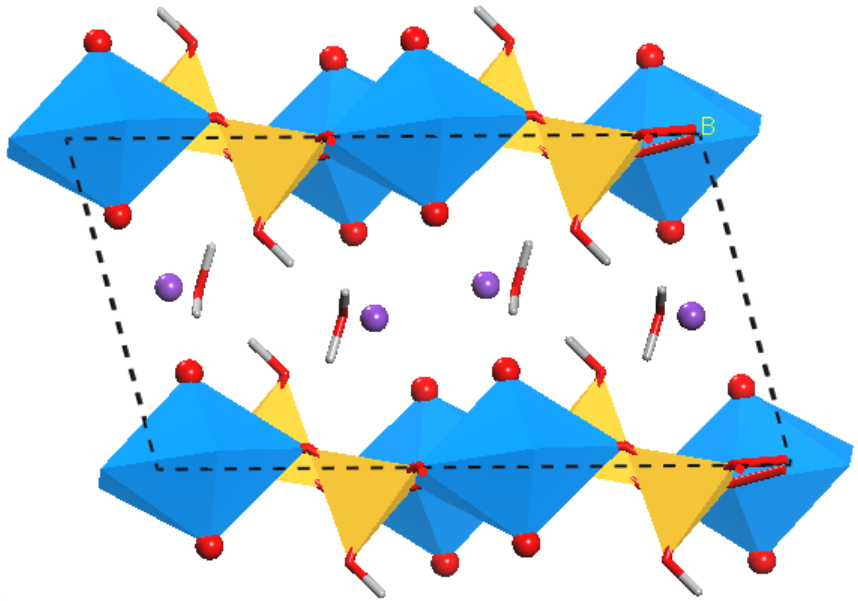
ΔE = 3.63 eV

Boltwoodite
$K(UO_2)(SiO_3OH)*1.5(H_2O)$; Z=2



● = U^{6+} ● = Si^{4+} ● = O^{2-}

● = H^+ ● = K^+



- $[SiO_4]$ tetrahedra
- Uranyl polyhedra

} Edge- and corner-sharing

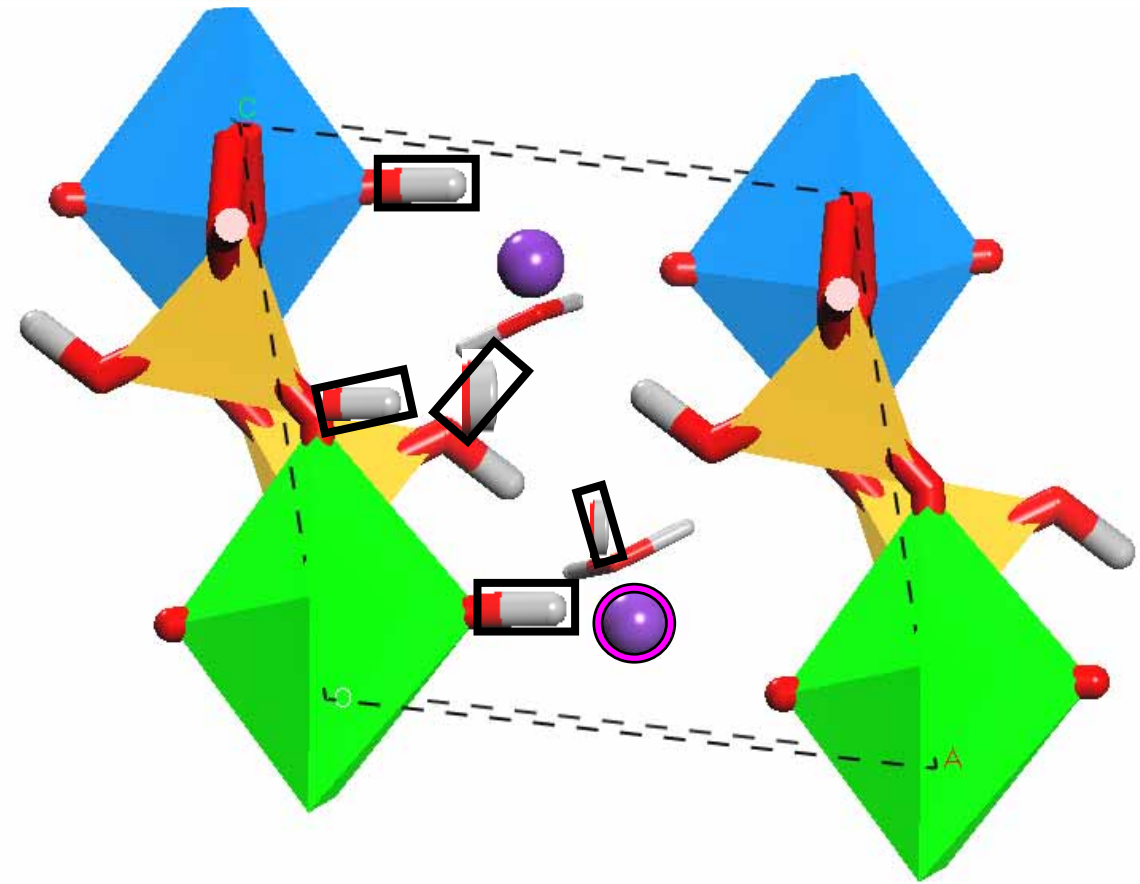
- Interlayer K^+ and H_2O

Incorporation mechanisms for boltwoodite

boltwoodite + ½Np_2O_5 + ½H_2O → (boltwoodite – U^{6+} + Np^{5+} + H^+) + UO_3

boltwoodite + ½Np_2O_5 + MgO → (boltwoodite - U^{6+} - K^+ + Np^{5+} + Mg^{2+}) + UO_3 + ½K_2O

boltwoodite + ½Np_2O_5 + CaO → (boltwoodite – U^{6+} - K^+ + Np^{5+} + Ca^{2+}) + UO_3 + ½K_2O



= U^{6+}

= Np^{5+}

= Si^{4+}

= O^{2-}

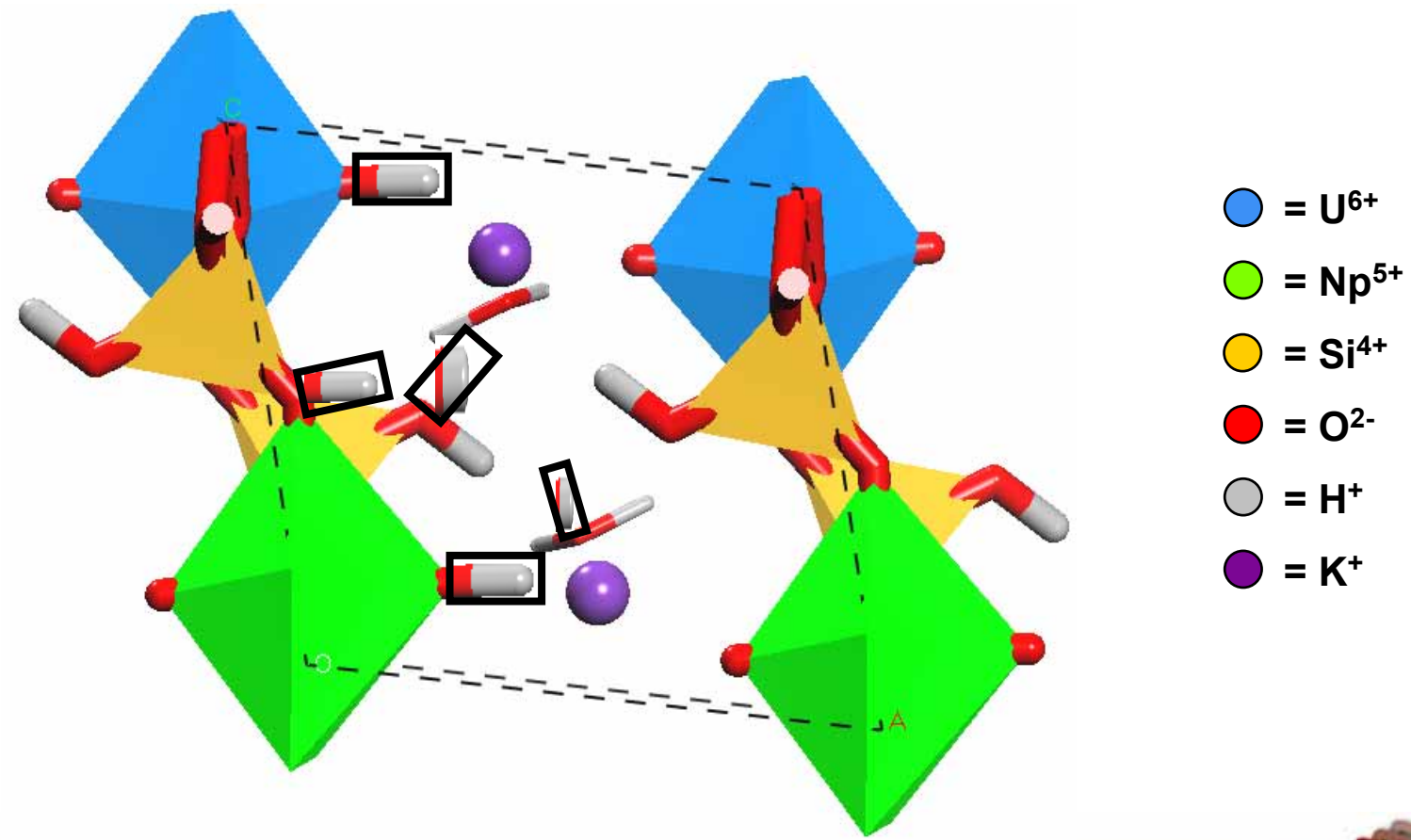
= H^+

= K^+

= Mg^{2+}/Ca^{2+}

H^+ location in Np-boltwoodite

boltwoodite + ½Np_2O_5 + ½H_2O → (boltwoodite – U^{6+} + Np^{5+} + H^+) + UO_3



Conclusions and Future Work

- **Reference phases play a significant role in determining incorporation energies**
- **Studtite**
  - **Np^{6+} substitution favored**
- **Boltwoodite**
  - **H^+ substitution location: on apical neptunyl oxygen**

Goal: determine the thermodynamically stable limit of Np^{5+} in various uranyl phases

QM results → empirical potential set → Monte-Carlo simulations

Acknowledgements

- **Funding source: DOE/OCRWM/OSC/S&T**
- **Research Group @ the University of Michigan**