STUDTITE STABILITY IN AQUEOUS SUSPENSION: EFFECTS OF BORON SPECIES AND BICARBONATE ON DISSOLUTION

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Work Package 8: Release of safety relevant radionuclides from spent nuclear fuel under deep disposal conditions (SAREC)

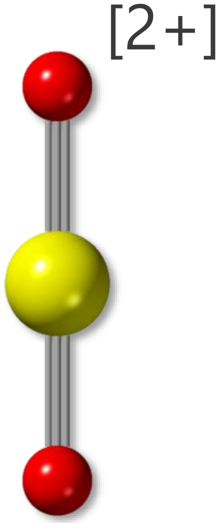
Quantify and understand mechanisms governing matrix dissolution and release of radionuclides; This presentation focuses on the stability and kinetics of secondary phase dissolution

Tasks 5 & 6

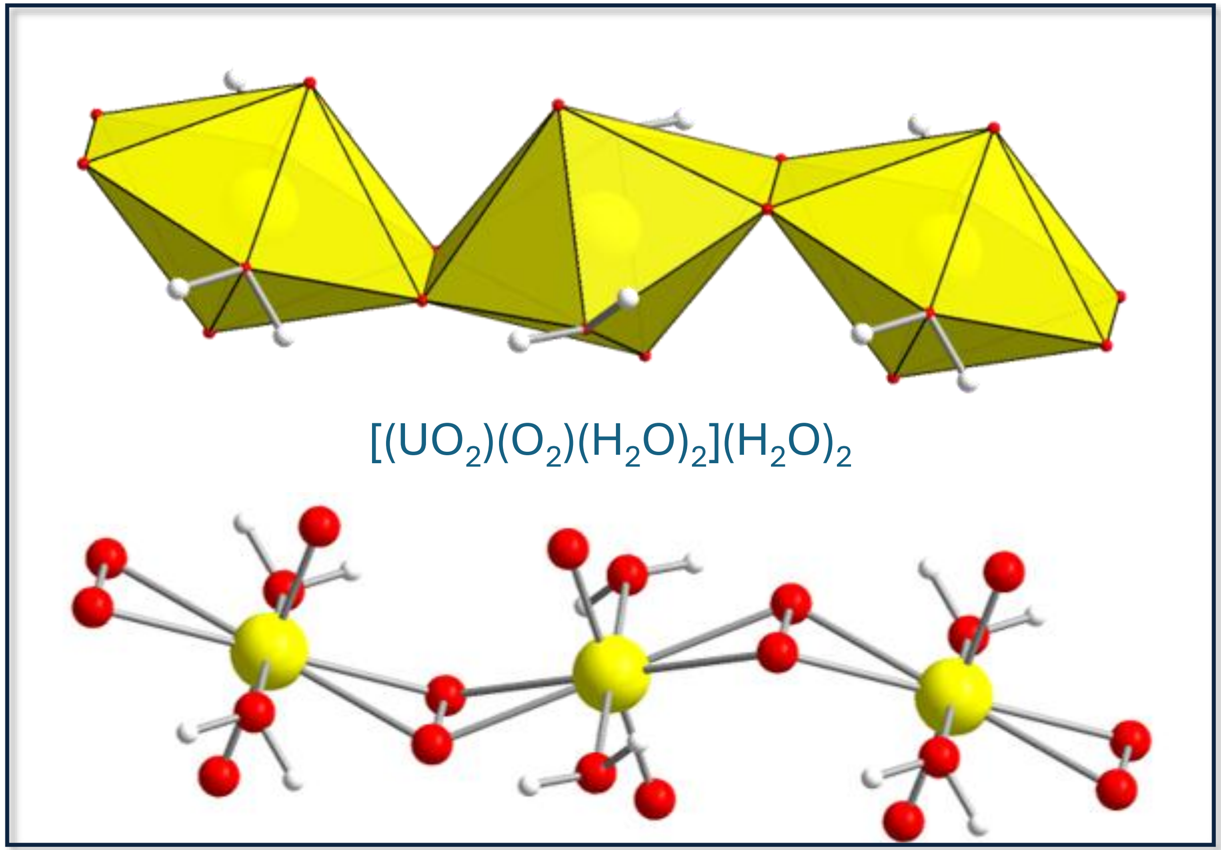
Results can inform reaction mechanisms for radionuclide release model development and improvement in Task 6

SECONDARY PHASES – URANYL PEROXIDES

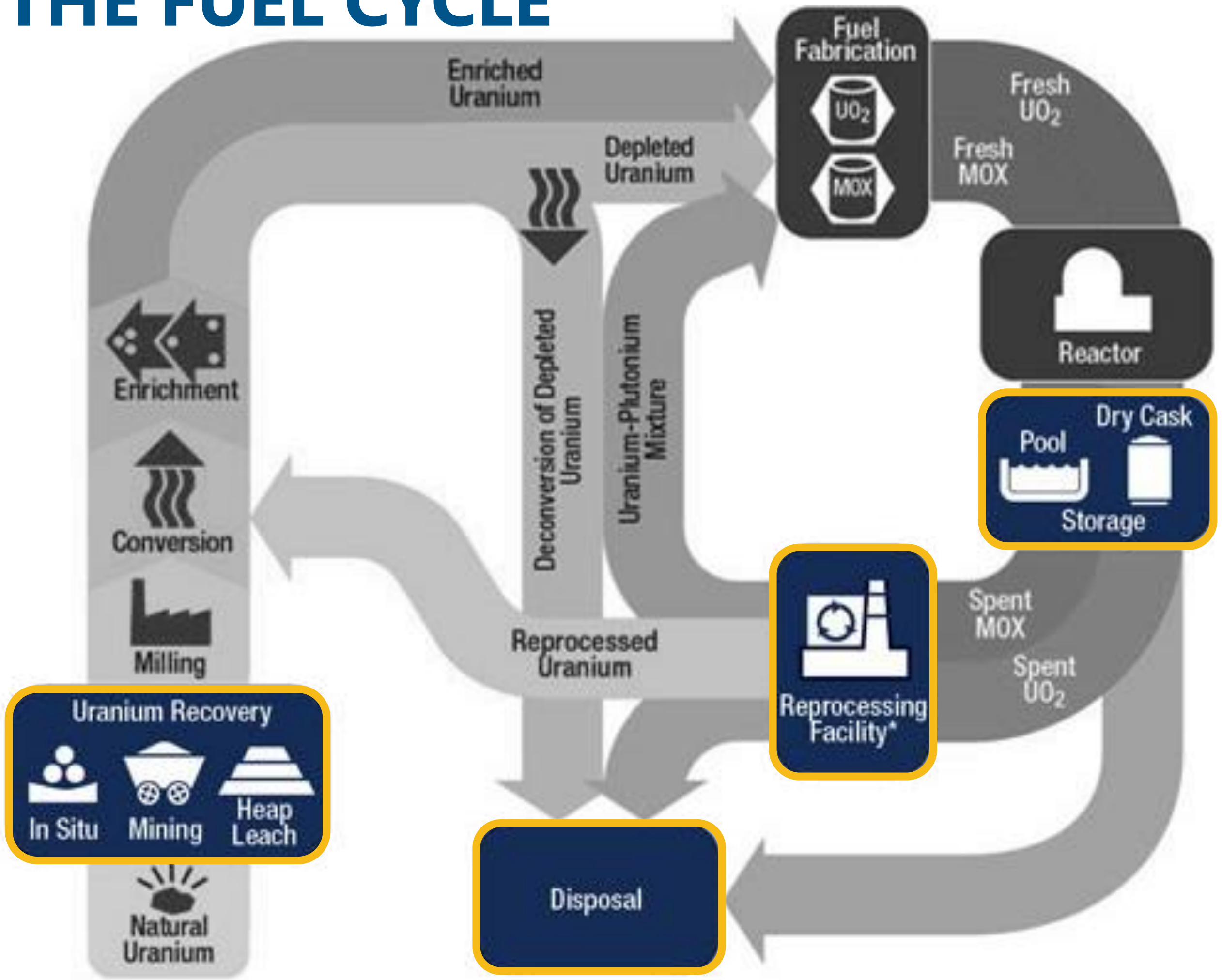
- U(VI)
- $[UO_2^{2+}]$



- Naturally occurring uranyl peroxide
- Insoluble in water ~ neutral pH



STUDTITE & THE FUEL CYCLE



* Reprocessing of spent nuclear fuel, including mixed-oxide (MOX) fuel, is not practiced in the United States.
Note: The NRC has no regulatory role in mining uranium.

As of January 2019

U.S.NRC
United States Nuclear Regulatory Commission
Protecting People and the Environment

STUDTITE & THE FUEL CYCLE

Image: https://world-nuclear.org/nuclear-essentials/how-is-uranium-made-into-nuclear-fuel

Image: https://www.mindat.org/min-3815.html

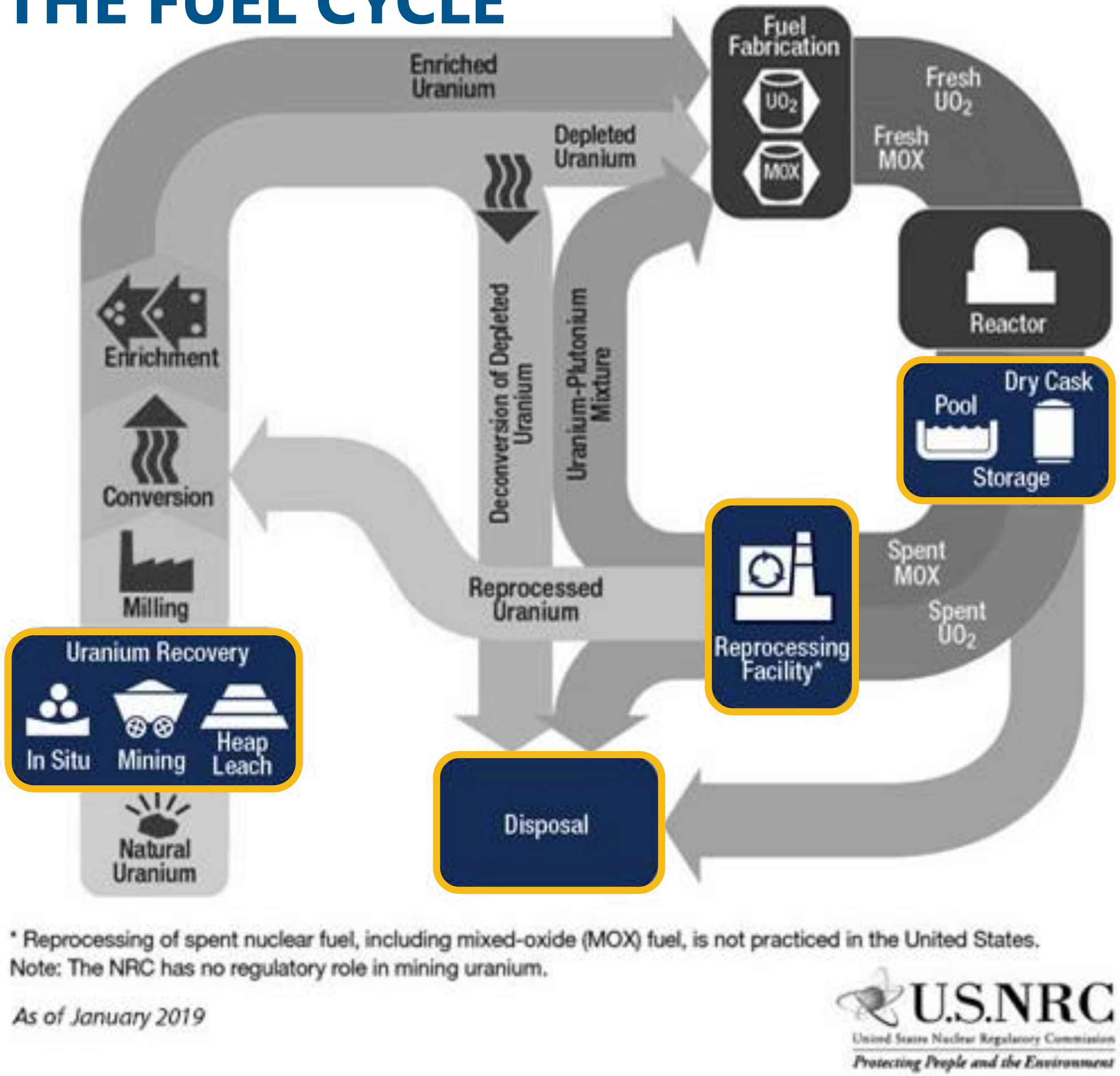
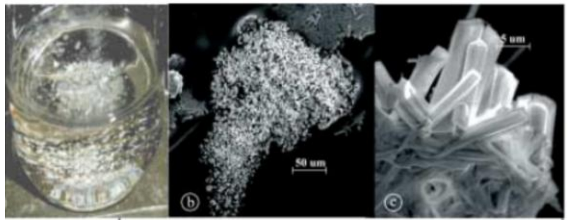


Image: https://www.atlasobscura.com/articles/elephants-foot-chernobyl



Hanson et al. (2005), *Radiochim Acta*, 93, 159-168

Image: https://www.sciencehistory.org/stories/magazine/leaking-legacy/

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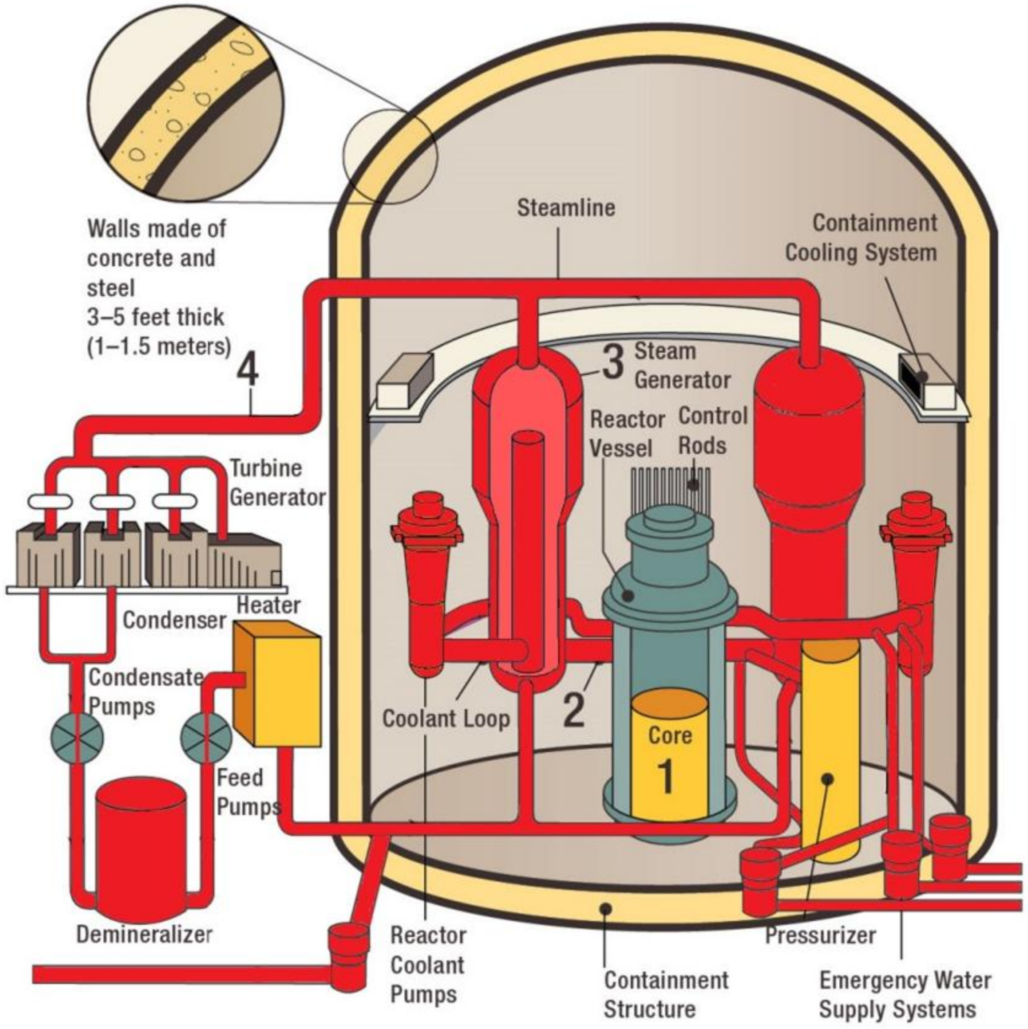
BORIC ACID AND BORATE & THE FUEL CYCLE

- ^{10}B – reaction moderation by neutron absorption
- Primary cooling circuit
- Emergency reactor coolant
- Spent fuel ponds
- High concentrations ~2,000 ppm $^{10}B/^{11}B$
- pH ranges between 4-10 in various uses



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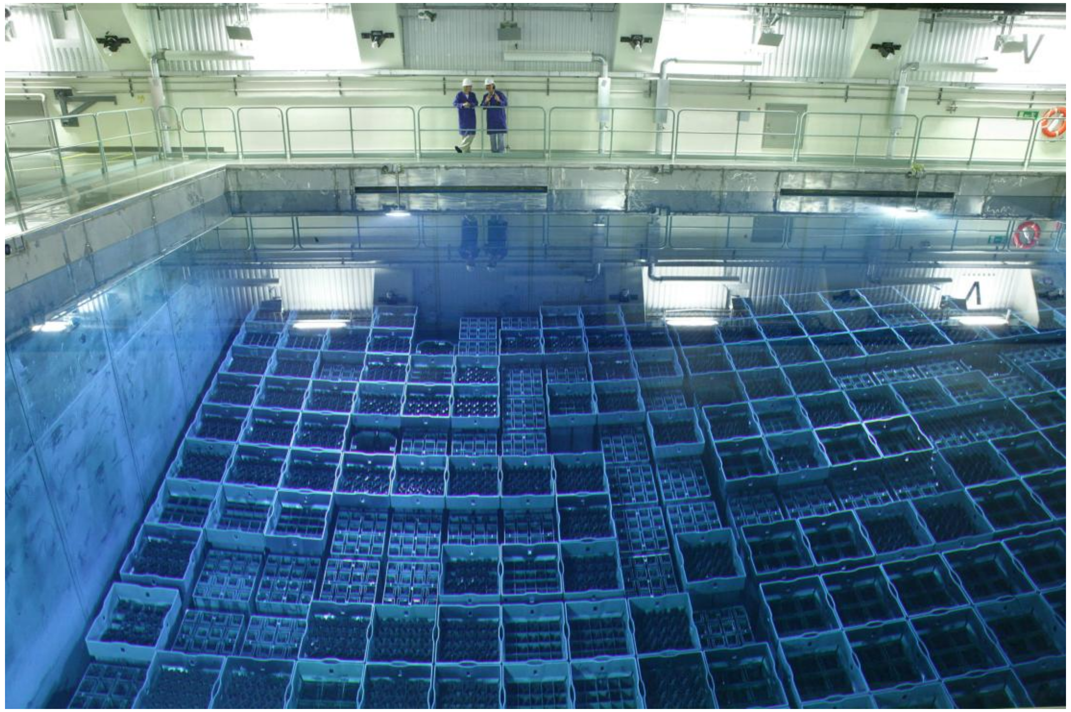


Photo: SKB

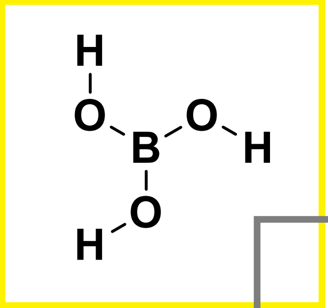
BORIC ACID SPECIATION

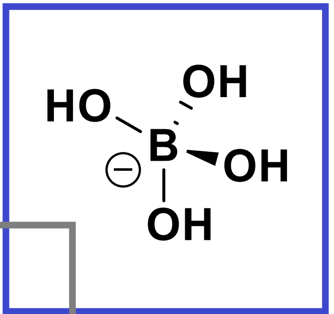
$$\boldsymbol{B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+}$$

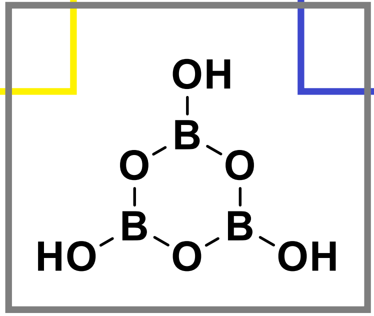
$$2B(OH)_3 \rightleftharpoons B_2O(OH)_5^- + H^+$$

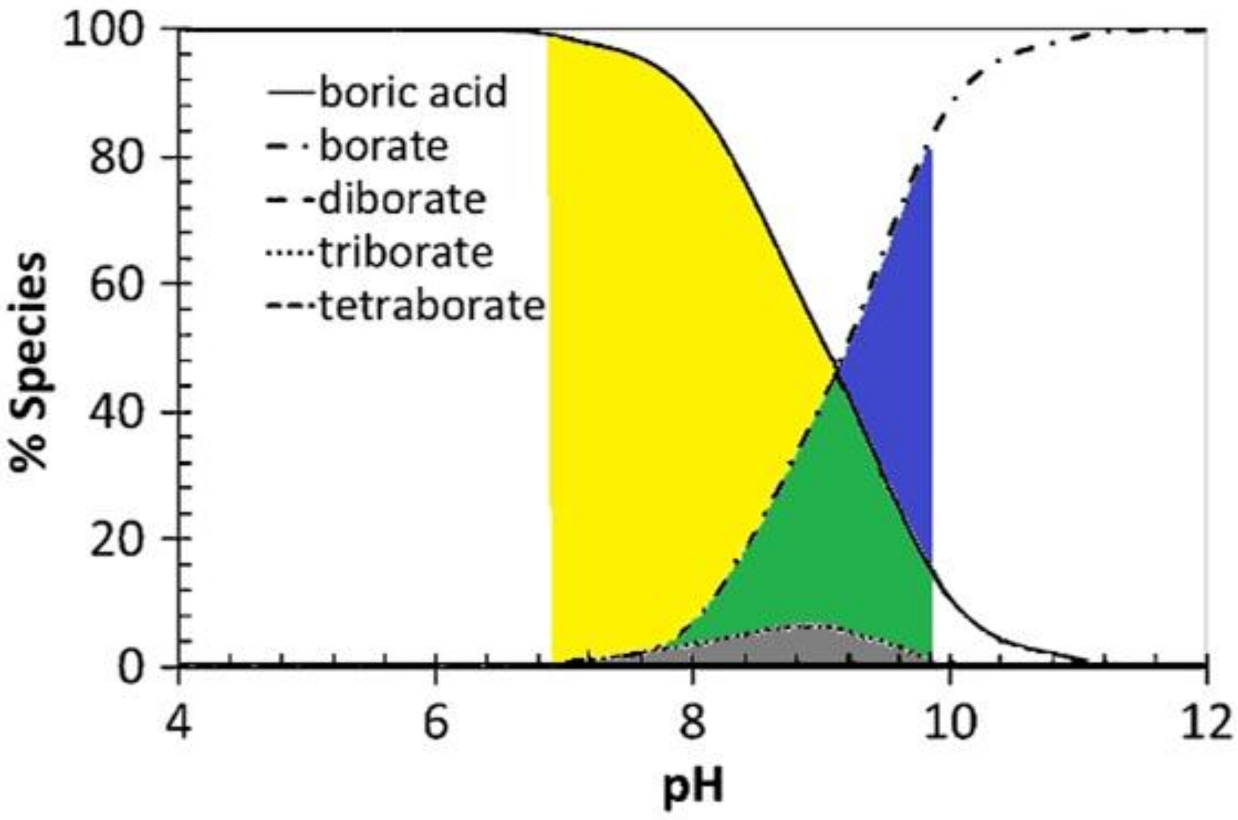
$$\boldsymbol{3B(OH)_3 \rightleftharpoons B_3O_3(OH)_4^- + H^+ + 2H_2O}$$

$$4B(OH)_3 \rightleftharpoons B_4O_5(OH)_4^{2-} + 2H^+ + 3H_2O$$







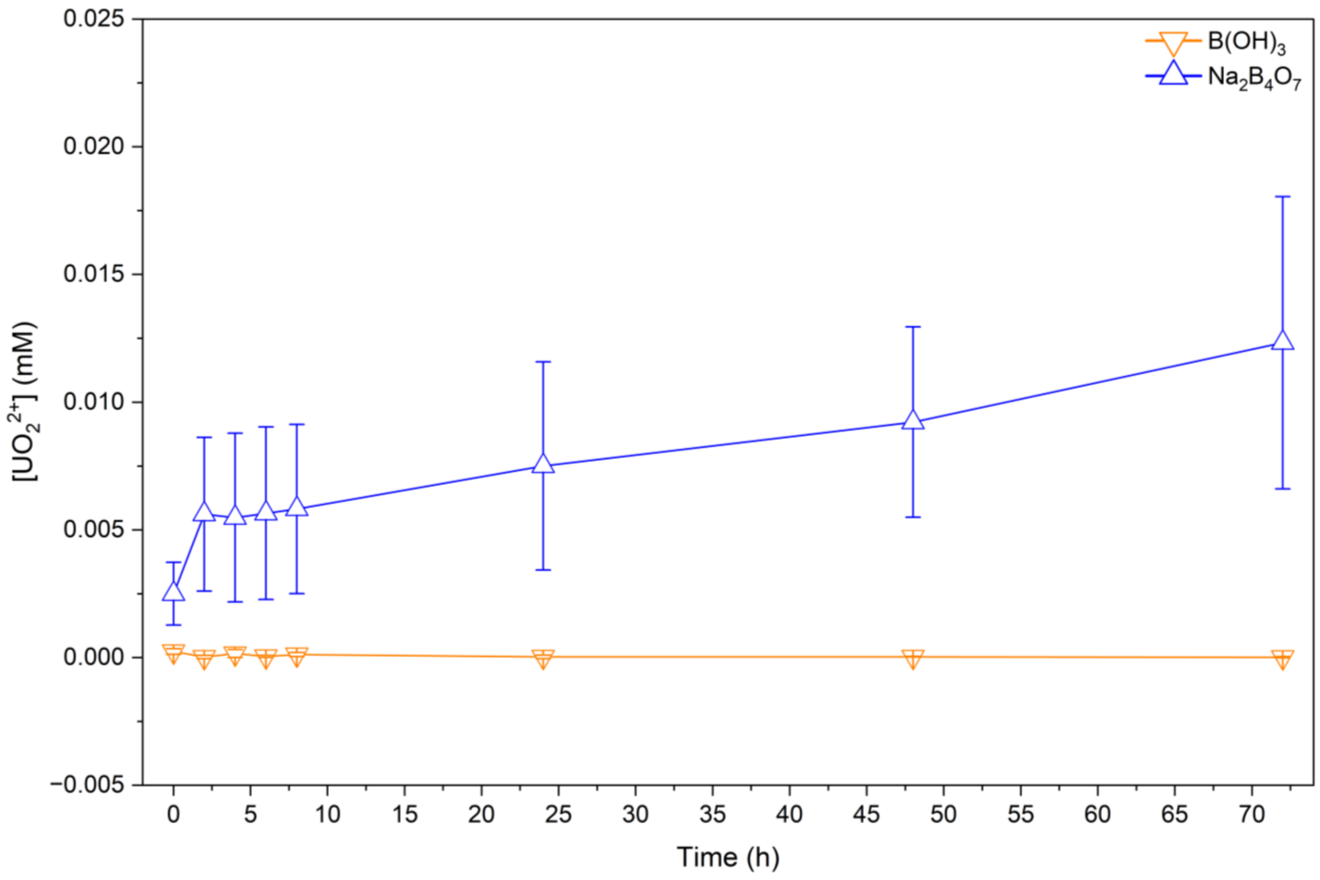


Graff, A. et al. J Solution Chem (2017).

STUDTITE DISSOLUTION OVER 72 HOURS: UO_2^{2+} CONCENTRATIONS

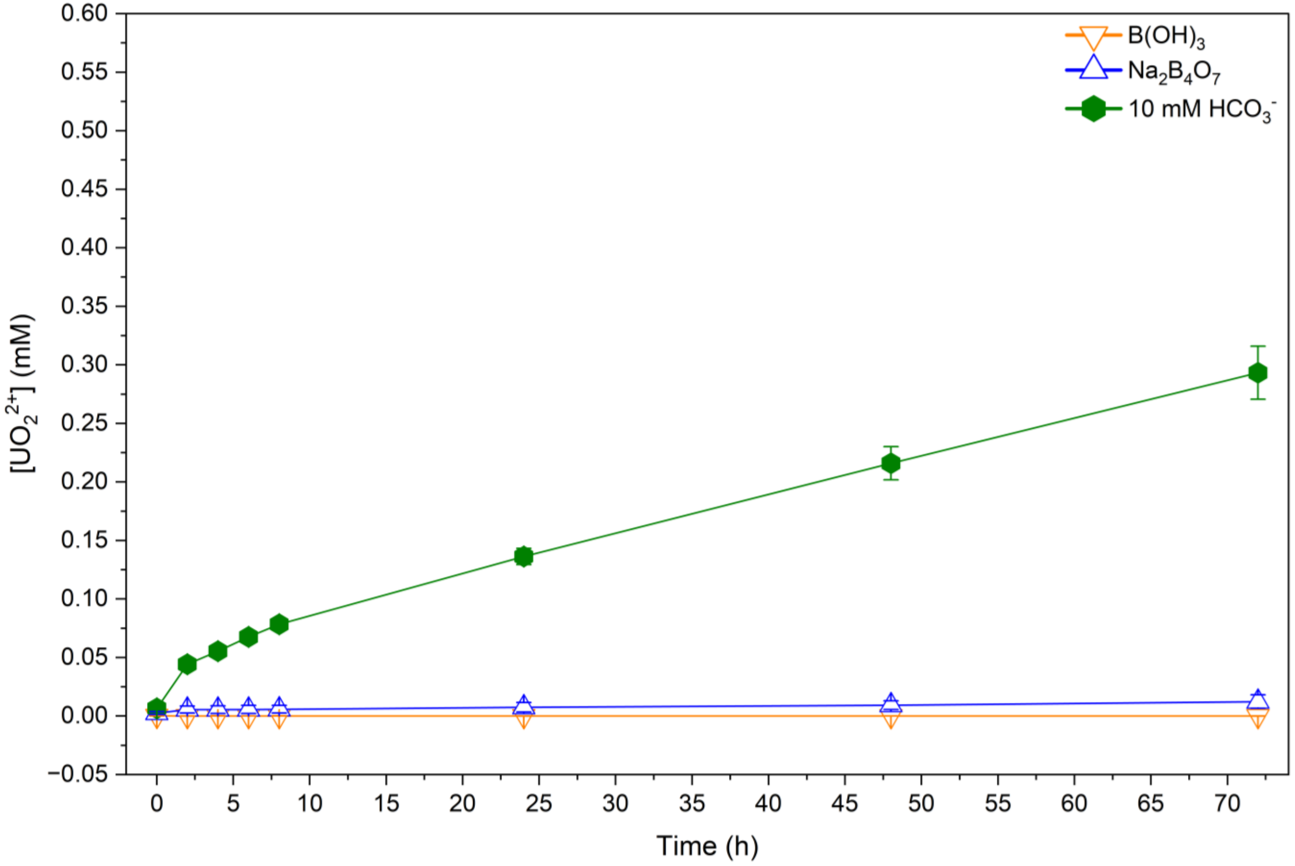
- **No dissolution in Boric Acid solution**
  - Likely due to lower pH, and unreactive nature of boric acid
- **Dissolution occurs in Borate solution**

~0.012 mM (12 µM)



STUDTITE DISSOLUTION OVER 72 HOURS: UO_2^{2+} CONCENTRATIONS

- **Studtite exposed to 10 mM HCO_3^- has significantly more dissolution**
- **~0.30 mM UO_2^{2+} after 72 hours**
- **Forms soluble uranyl carbonate complexes, driving the dissolution**

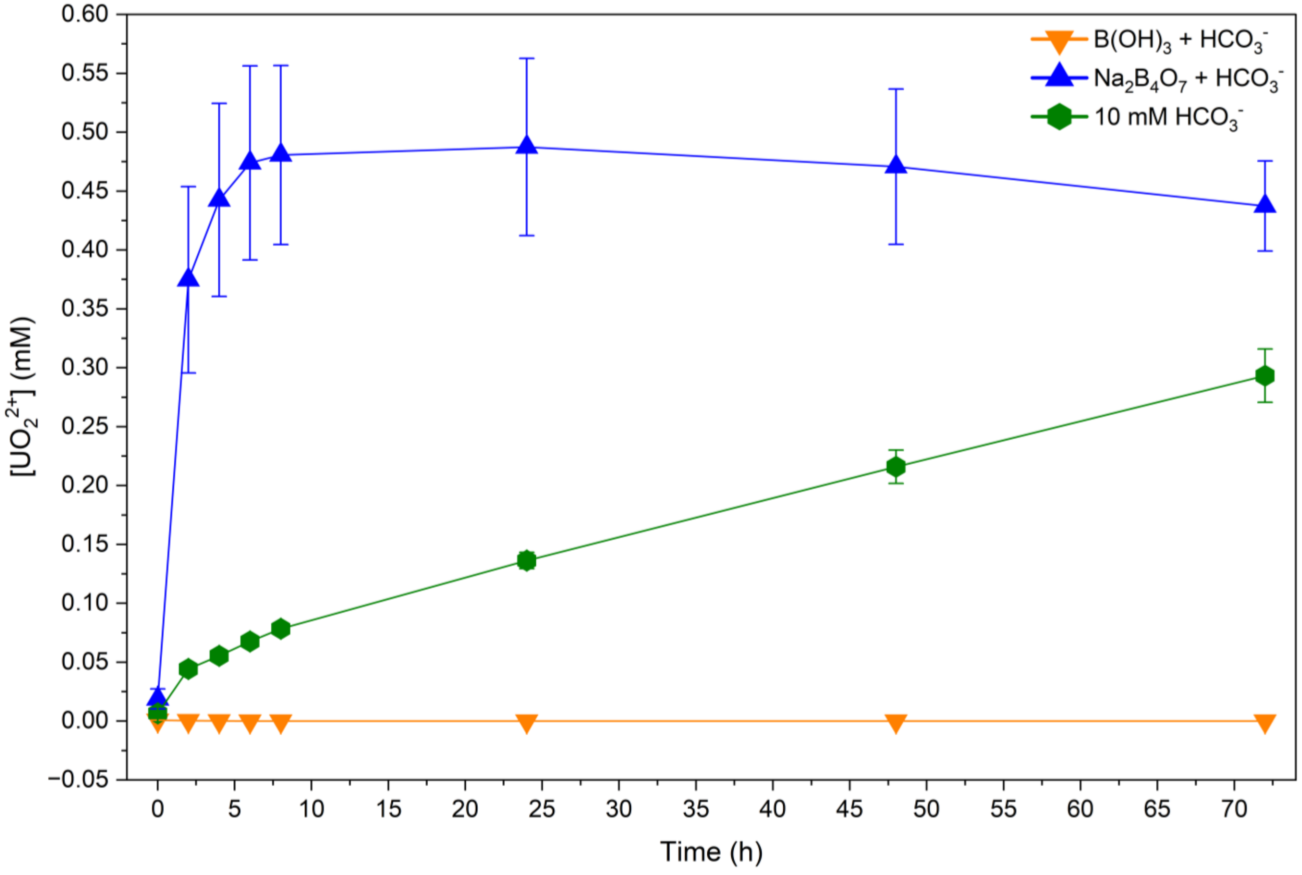


STUDTITE DISSOLUTION OVER 72 HOURS: UO_2^{2+} CONCENTRATIONS

- $B(OH)_3$ + 10 mM HCO_3^-
- Suppresses dissolution completely

- $Na_2B_4O_7$ + 10 mM HCO_3^-
- Promotes studtite dissolution

- 10 mM HCO_3^-



PH EFFECT?

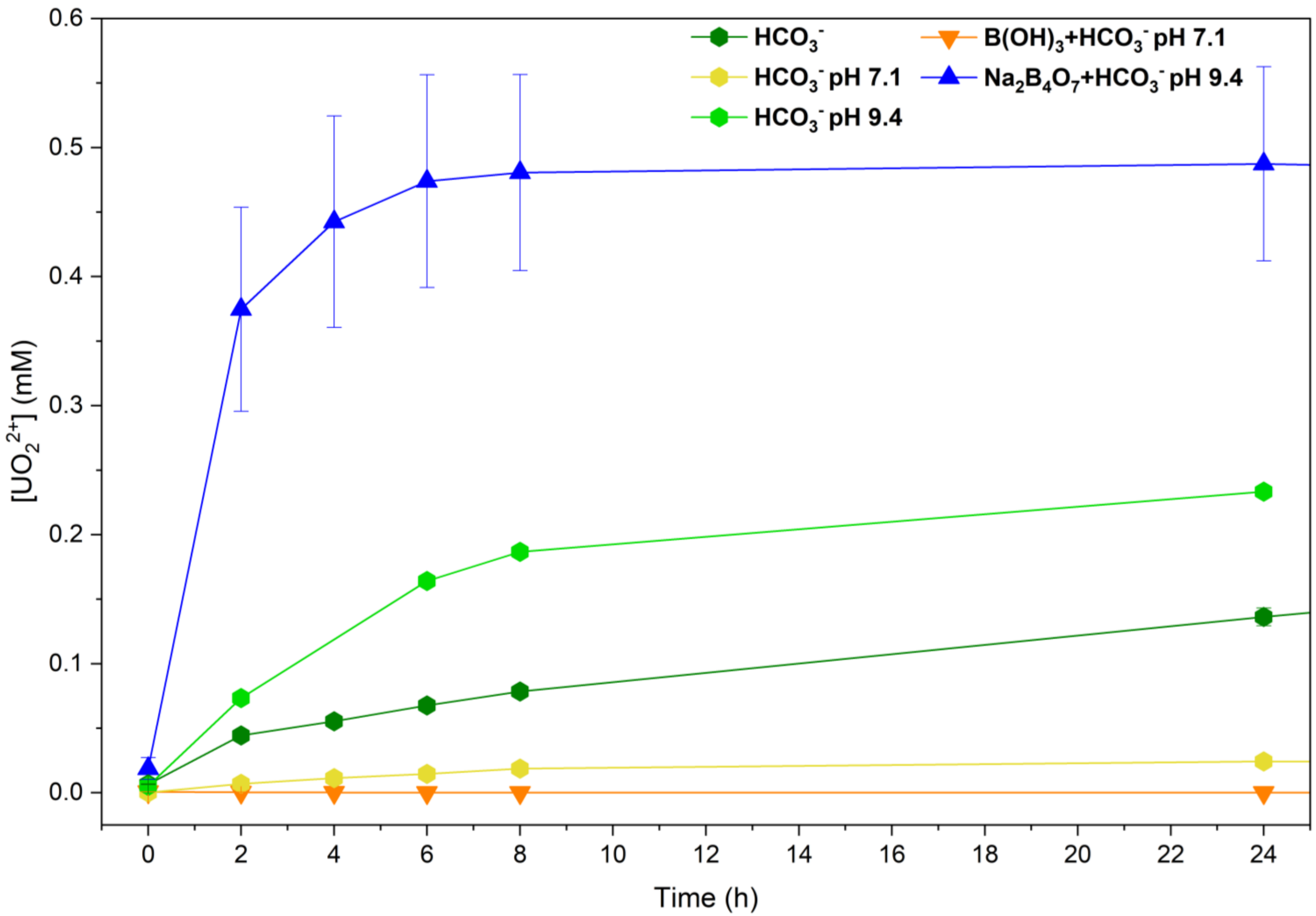
- pH impacts speciation of bicarbonate

$$HCO_3^- \leftrightarrow CO_3^{2-}$$

- Studtite stability impacted by pH, particularly high pH >8

What is the role of H_2O_2 in studtite dissolution?

Does ionic strength influence dissolution?



Thank You for Listening

Questions?

ACKNOWLEDGEMENTS

Professor Mats Jonsson

European Partnership
on Radioactive Waste Management

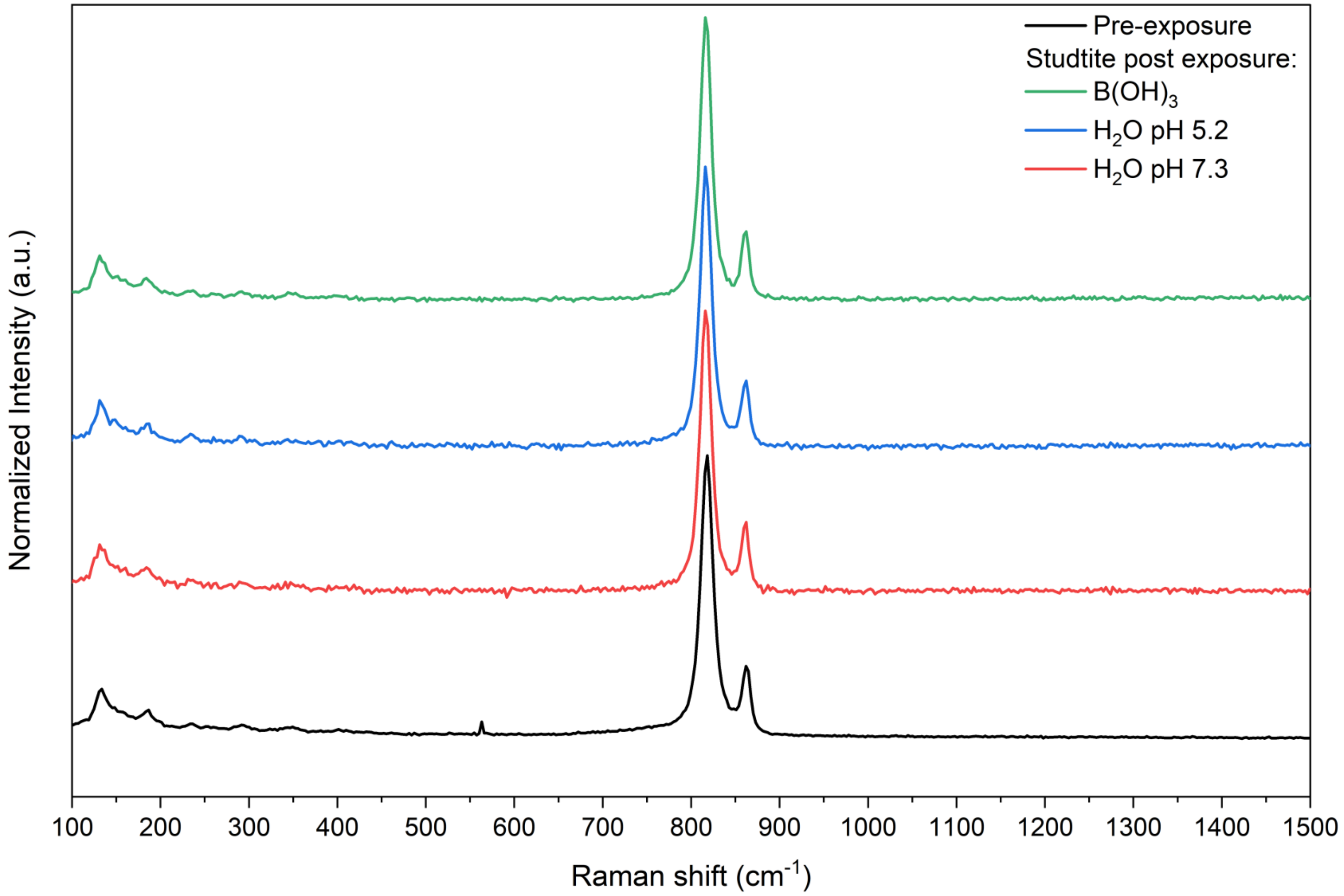
KTH
VETENSKAP
OCH KONST

SKB

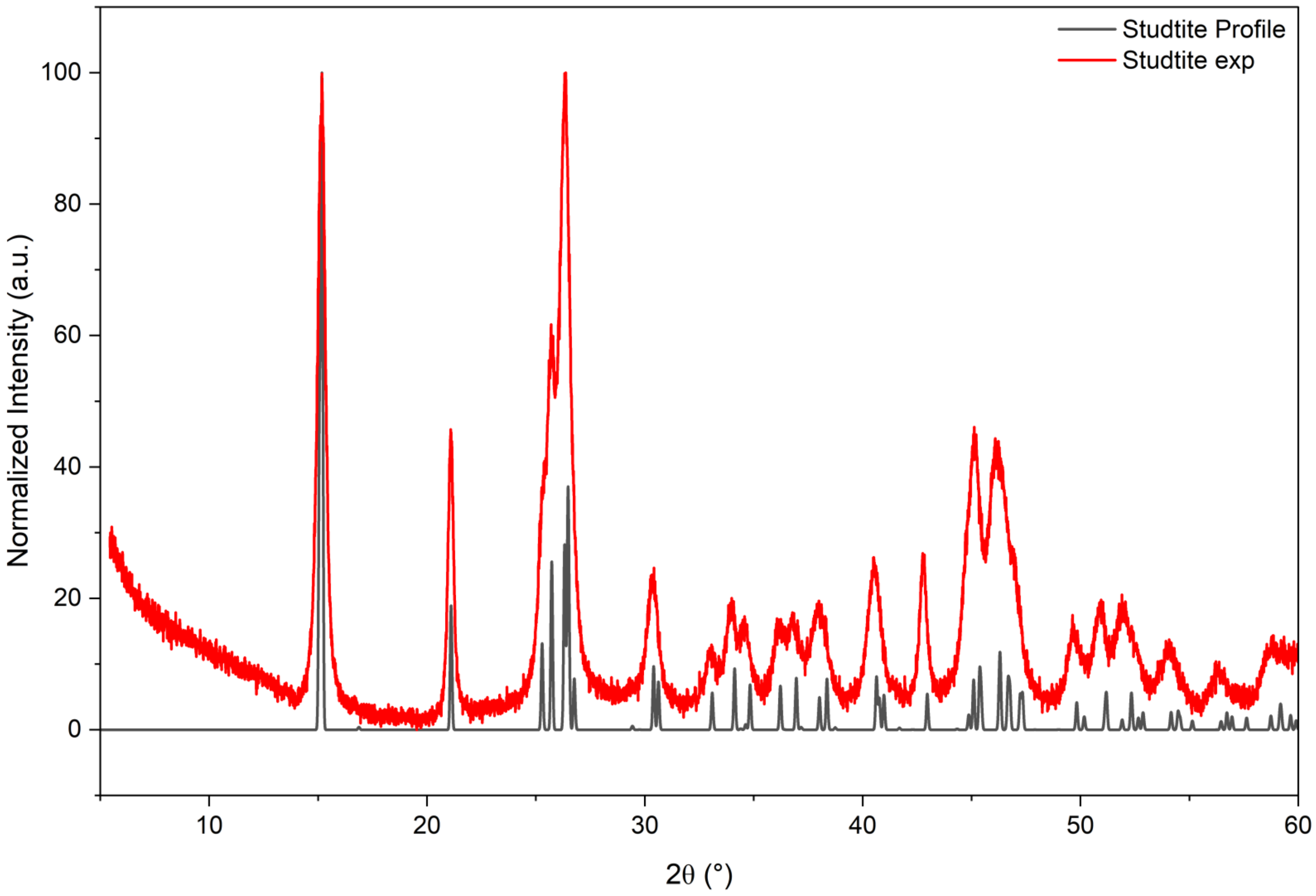
METHODOLOGY

- **40.0 mg Studtite + 25 mL solution**
- **2,000 ppm Boron (reactor relevant concentration)**
  - **0.185 H_3BO_3**
  - **0.046 $Na_2B_4O_7$**
  - **0.010 M HCO_3^-**
- **0.185 H_3BO_3 + 0.010 M HCO_3^-**
- **0.046 $Na_2B_4O_7$ + 0.010 M HCO_3^-**
- **Measure U(VI) by Arsenazo III method (UV-Vis)**

RAMAN SPECTRA OF MATERIAL PRE AND POST DISSOLUTION EXPERIMENT



POWDER X-RAY DIFFRACTION STUDTITE PHASE CONFIRMATION



STUDTITE FORMATION STUDIES