Pacific Northwest NATIONAL LABORATORY

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Effect of Co-Contaminants on Ammonia Gas Treatment of Uranium in Vadose Zone Sediments

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2023 Global Summit on Environmental Remediation
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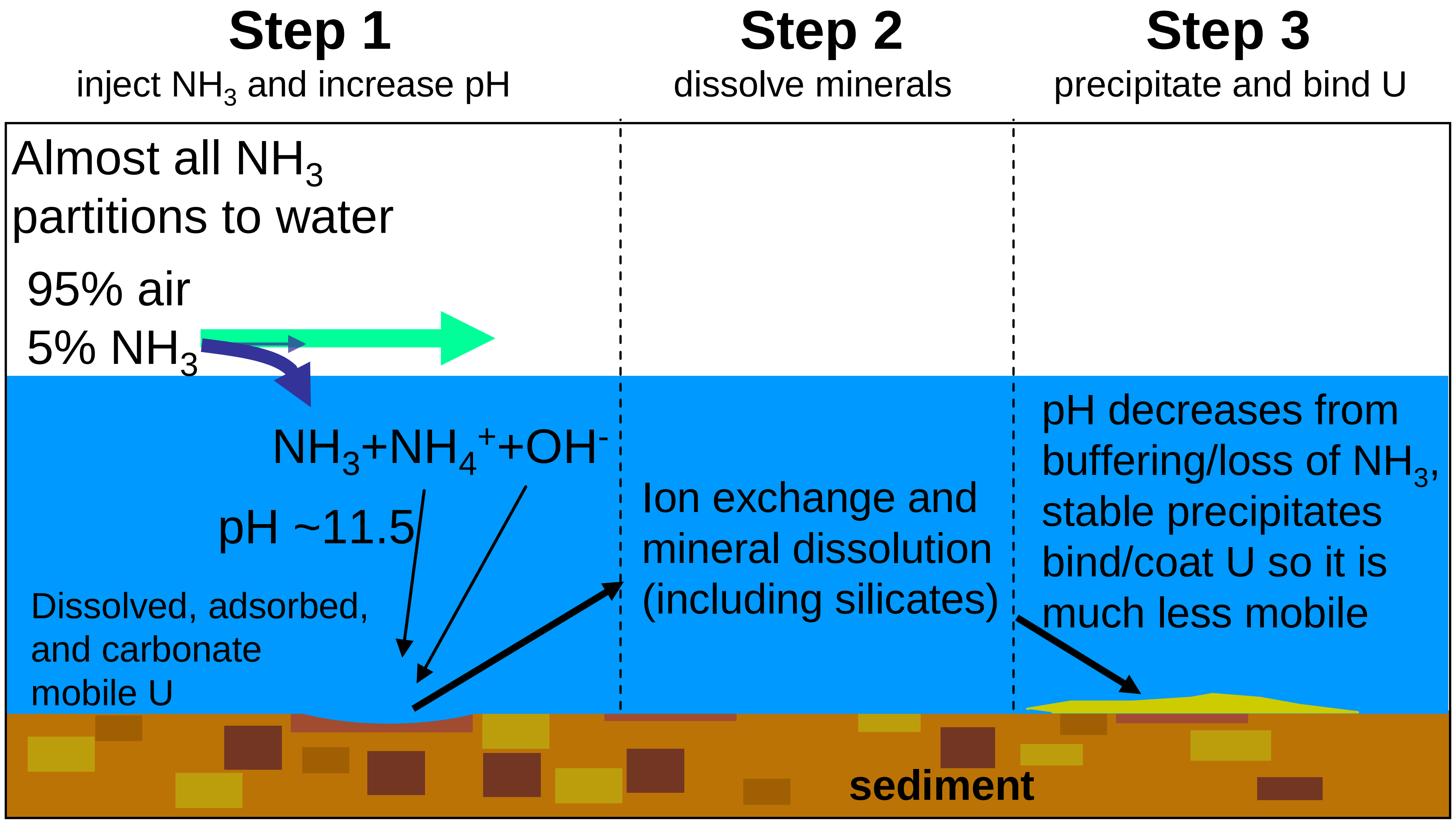
Outline

- concept: uranium immobilization using NH_3 gas

- ammonia gas:
  - gas transport and partitioning
  - sediment mineralogy changes

- uranium mobility change in field-contaminated sediments
  - few co-contaminants
  - acidic co-contaminants

Uranium Immobilization using NH_3 gas



- **some aqueous, adsorbed, and carbonate-U minerals are precipitated as U-silicates (Na-boltwoodite)**
- **some U precipitates are coated by aluminosilicate precipitates (cancrinite, sodalite, brucite, goethite)**

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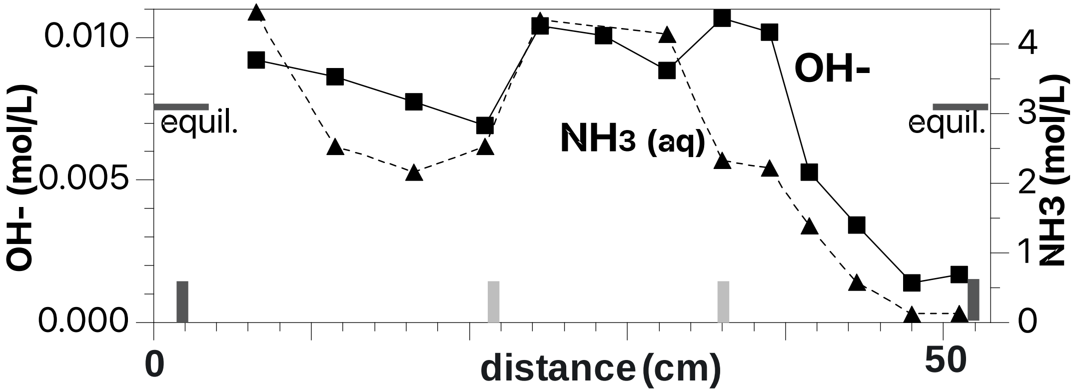
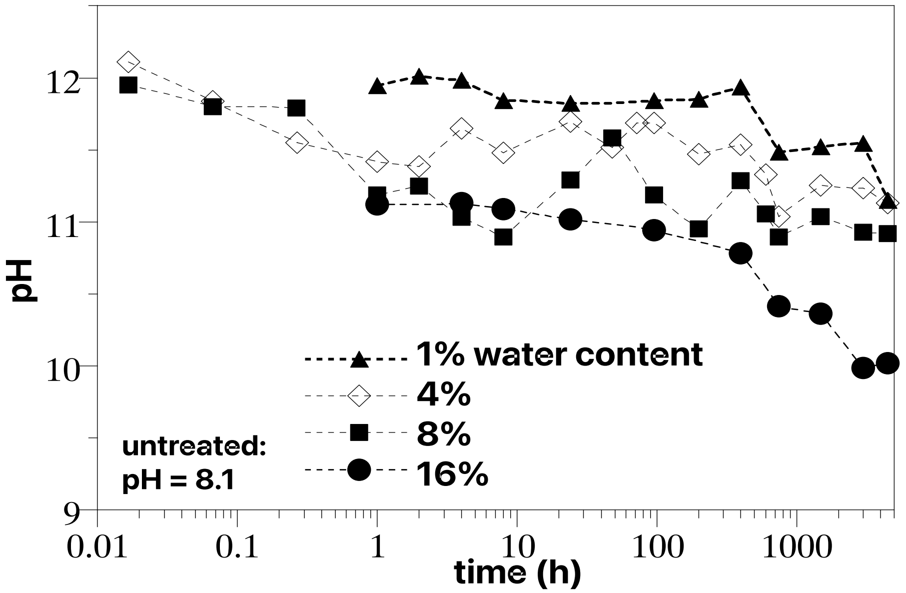
NH_3 Gas Injection into Unsaturated Sediments





during NH_3 injection

- pH increase
- heat (exothermic)
- sharp front

over time or air injection

- pH slowly neutralizes
- aluminosilicate precipitates form

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NH_3 Gas Injection into Heterogeneous Sediment

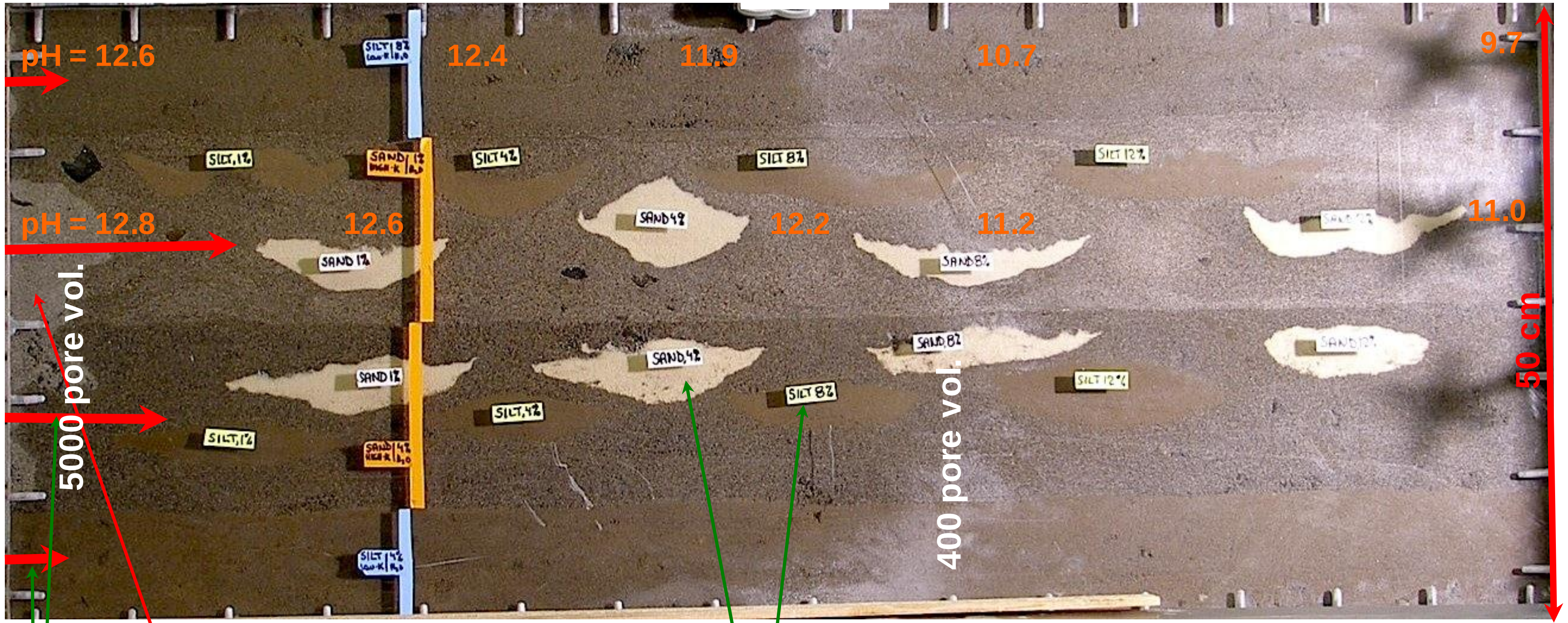
122 cm

silt 8% WC

sand 1% WC

sand 2% WC

silt 4% WC



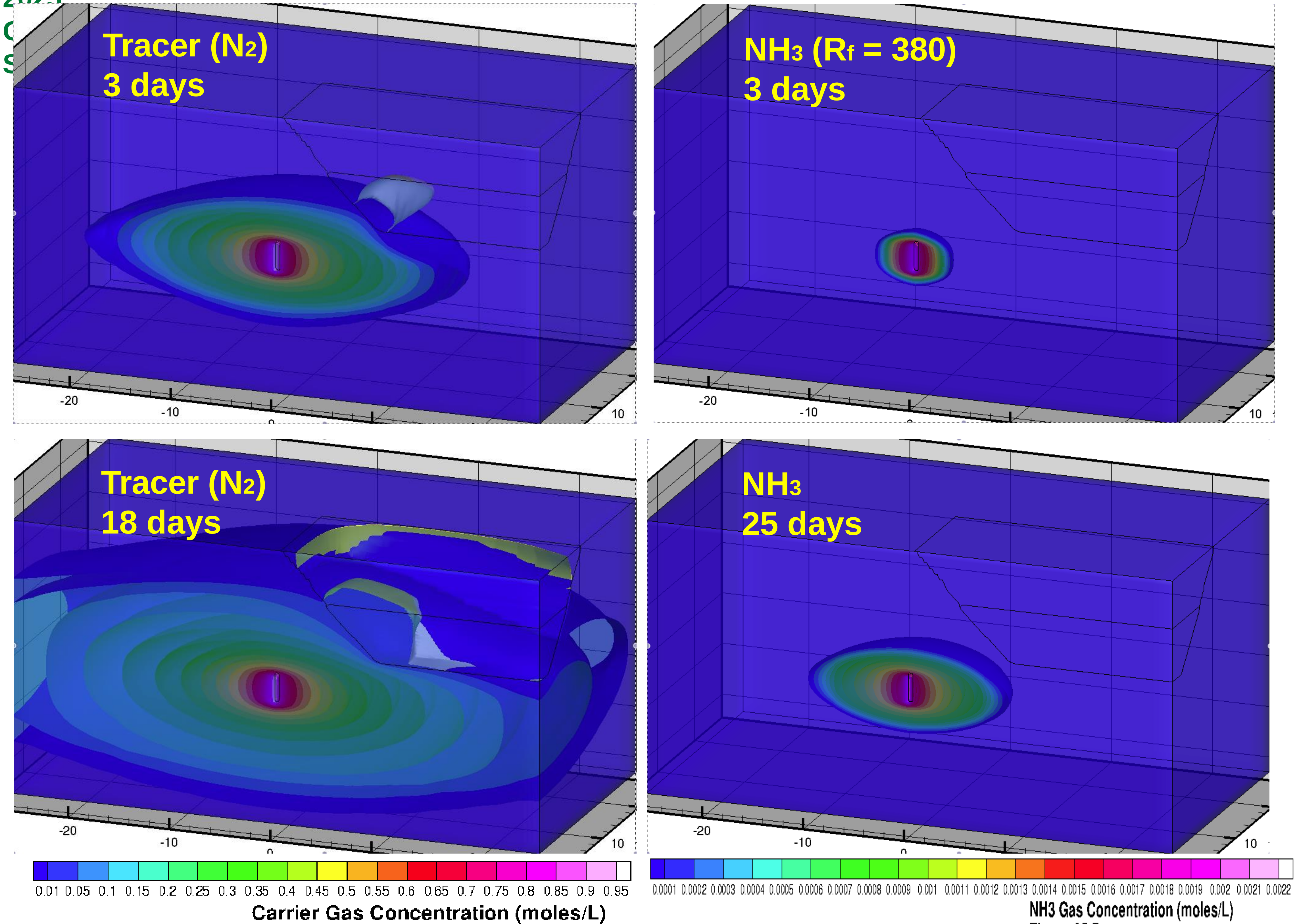
- higher pH, electrical conductivity, more fluid, lower surface tension
- NH_3 reaction front: higher temperature

desiccation

diffusion, slower advection into low-K, high WC zones

slower advection in low-K and/or higher water content layers
significantly more pore volumes needed at higher water content

Field Scale Simulation: 5% NH_3 Injection at 1400 Liters/Minute



NH_3 and Mineralogy Change

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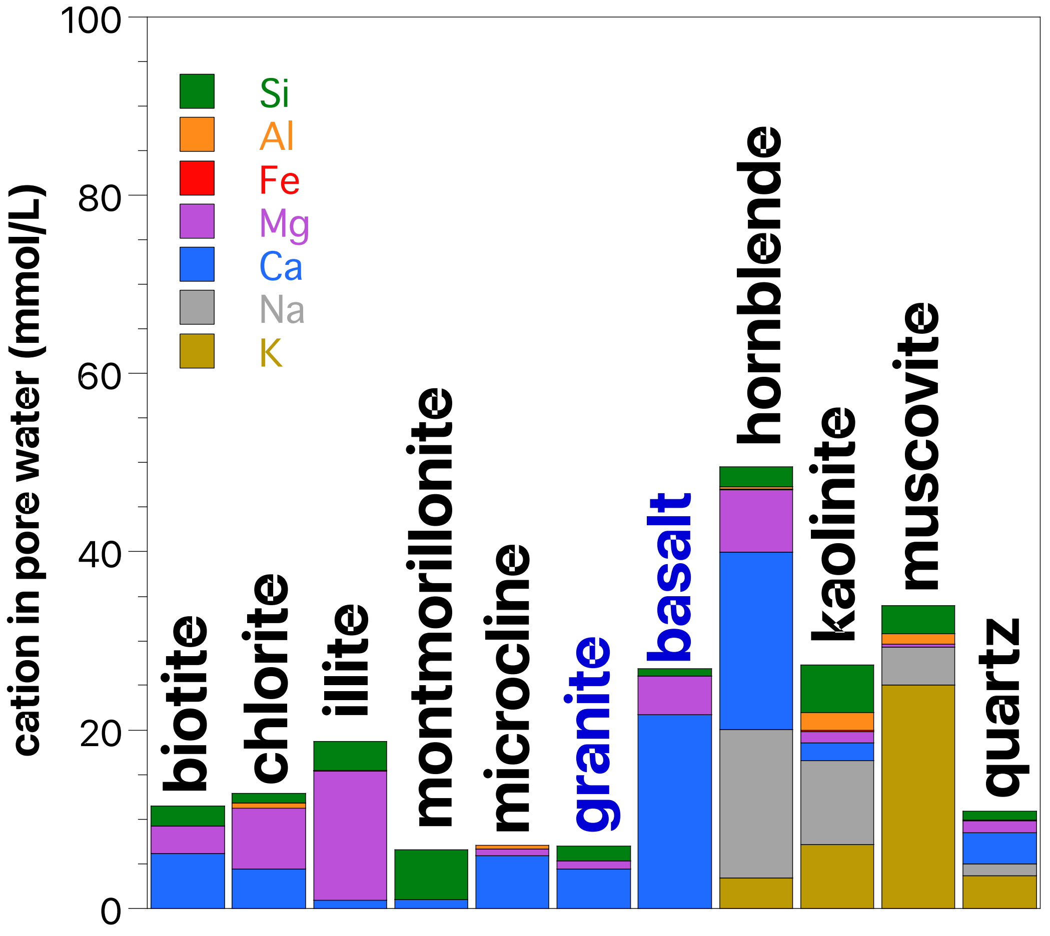
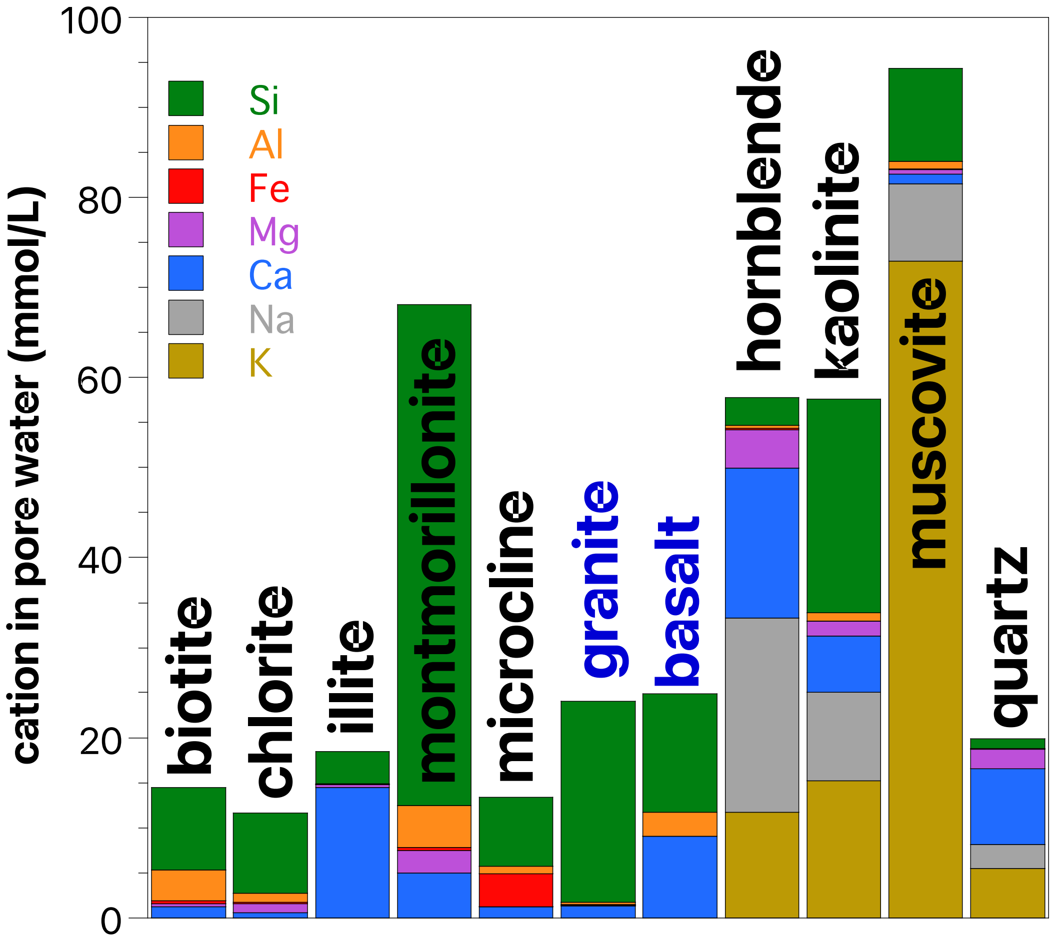
Untreated Minerals

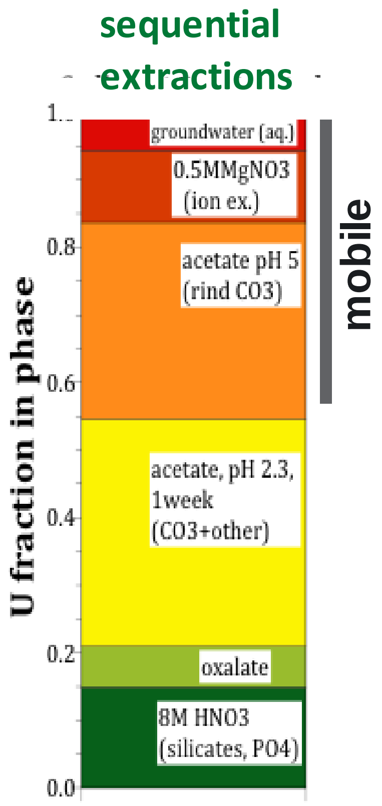


NH_3 Treated Minerals (200 h)

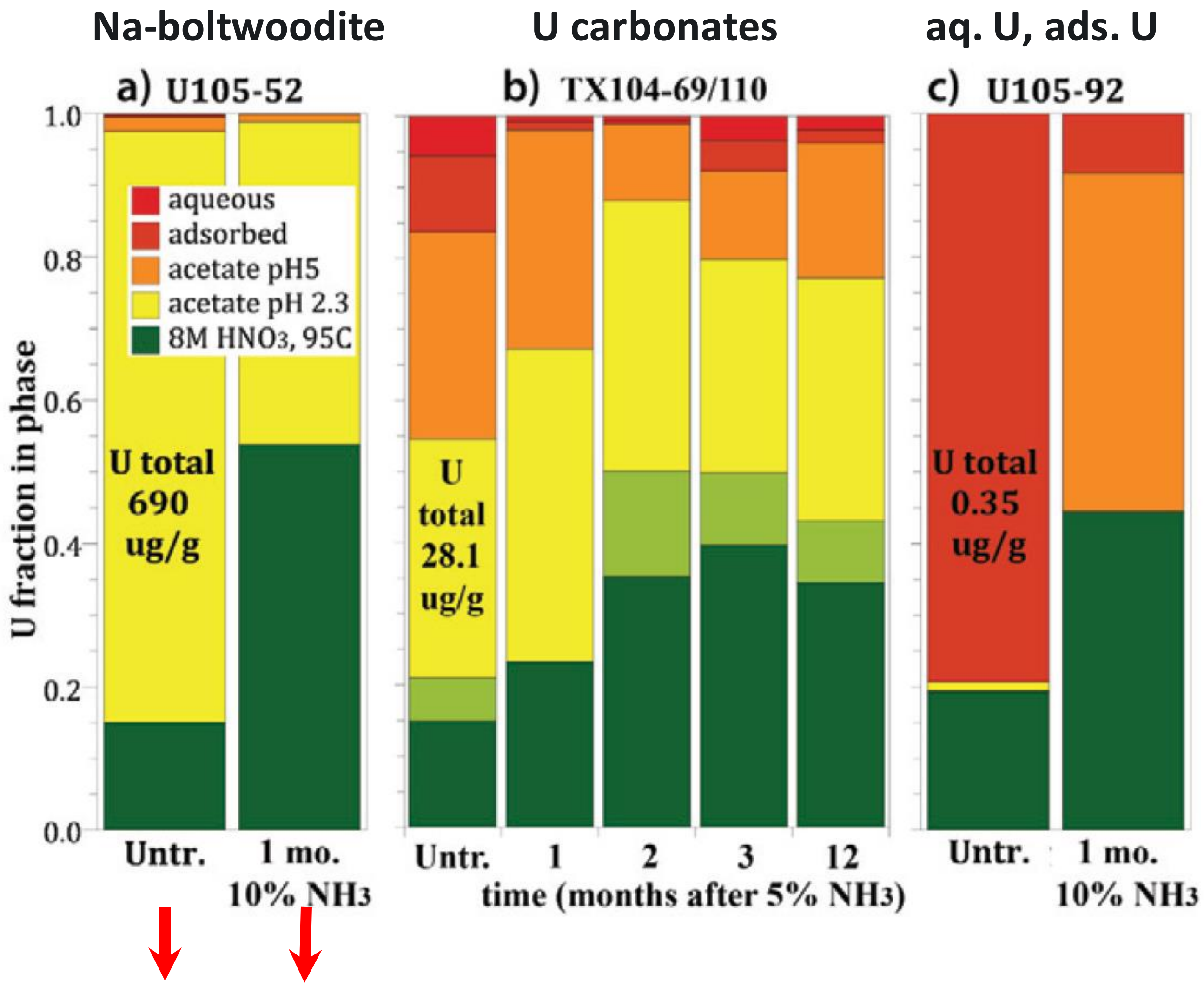


- montmorillonite, muscovite, and kaolinite show significant dissolution with NH_3 treatment

Uranium Mineralogy and Mobilization Change

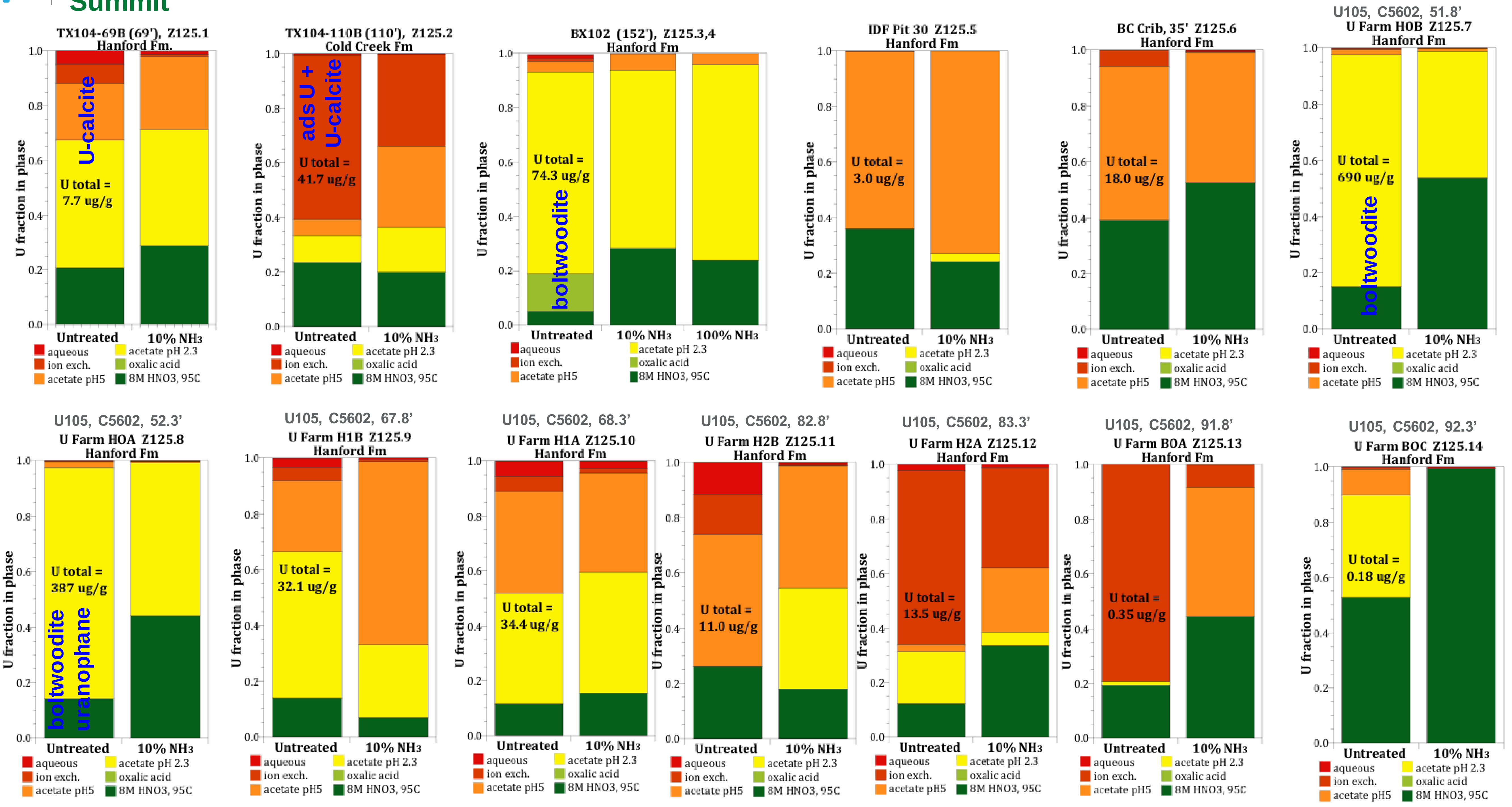


U in different waste sites



- EXAFS after NH_3 treatment shows no change in local molecular structure around U. Changes in U release rate may be from coating by other precipitates.

Uranium Treatment at Different Waste Sites



- likely influence of co-contaminants on NH_3 treatment of uranium

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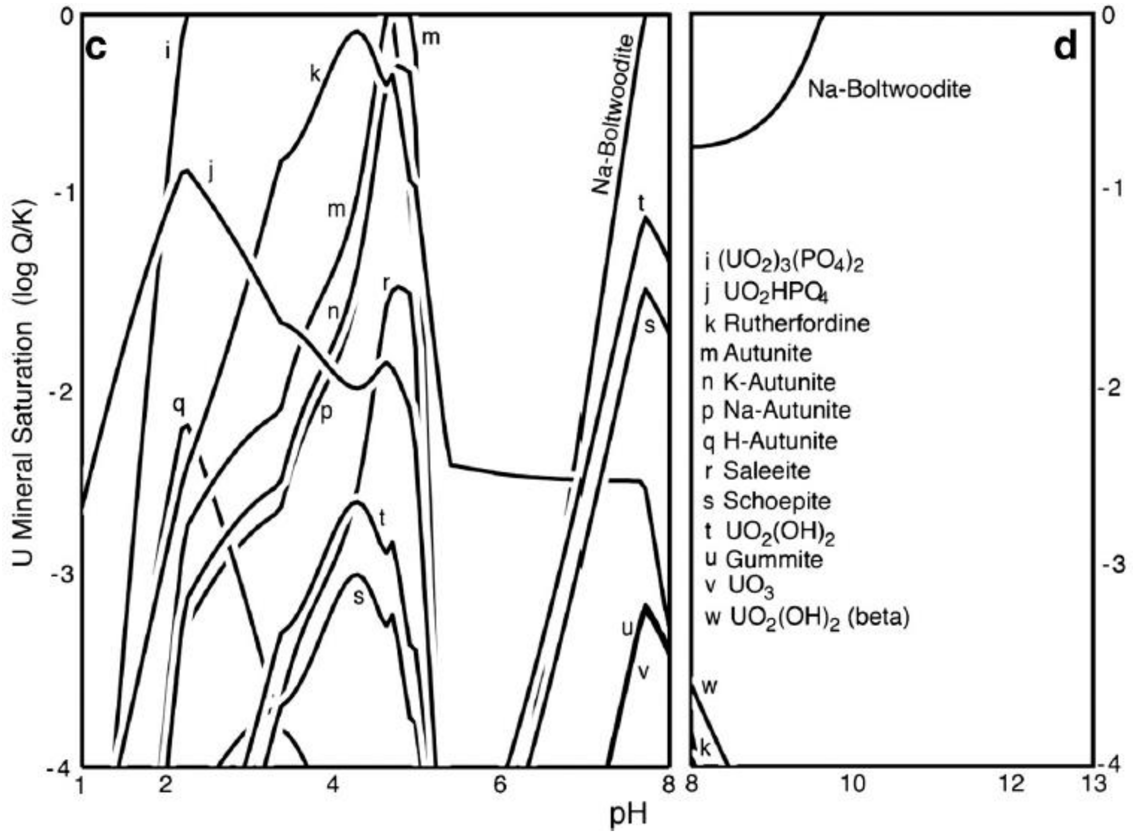
Mechanisms: Uranium Mobilization Change

Uranium precipitates:

- U more mobile at pH 11.5 (less U(ads), dissolve some ppts)
- Na-boltwoodite [$Na(UO_2)(SiO_3OH)\cdot 1.5H_2O$] should precipitate as the pH neutralizes (Ca, Mg-CO_3 water, no co-contam.)

Coating by non-U precipitates:

- clay dissolution releasing Si, K, Na
- incongruent dissolution; Al precipitates rapidly (Di Pietro et al, 2020)
- chrysotile, diaspore, cancrinite, hematite precipitate coating U precipitates (decreasing mobility), but not coating U(aq) or U(ads)



Uranium Leaching in Sediment

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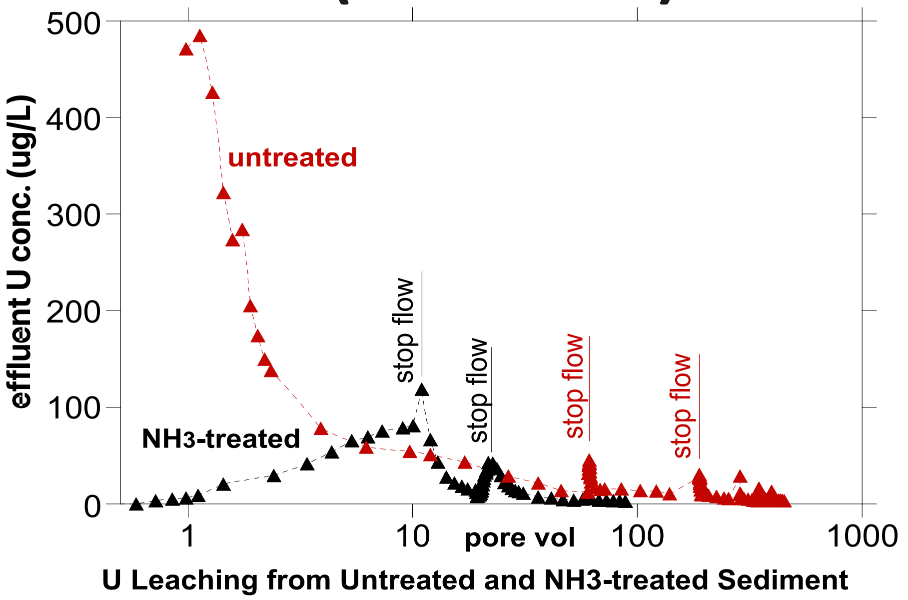
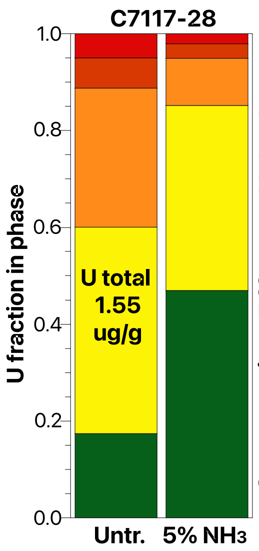
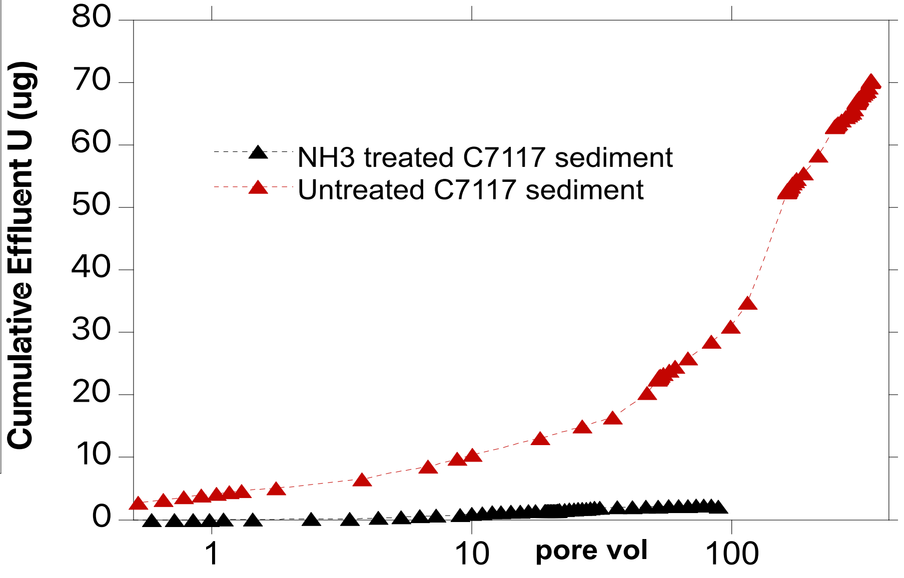
4 weeks of NH_3 treatment (acidic site)

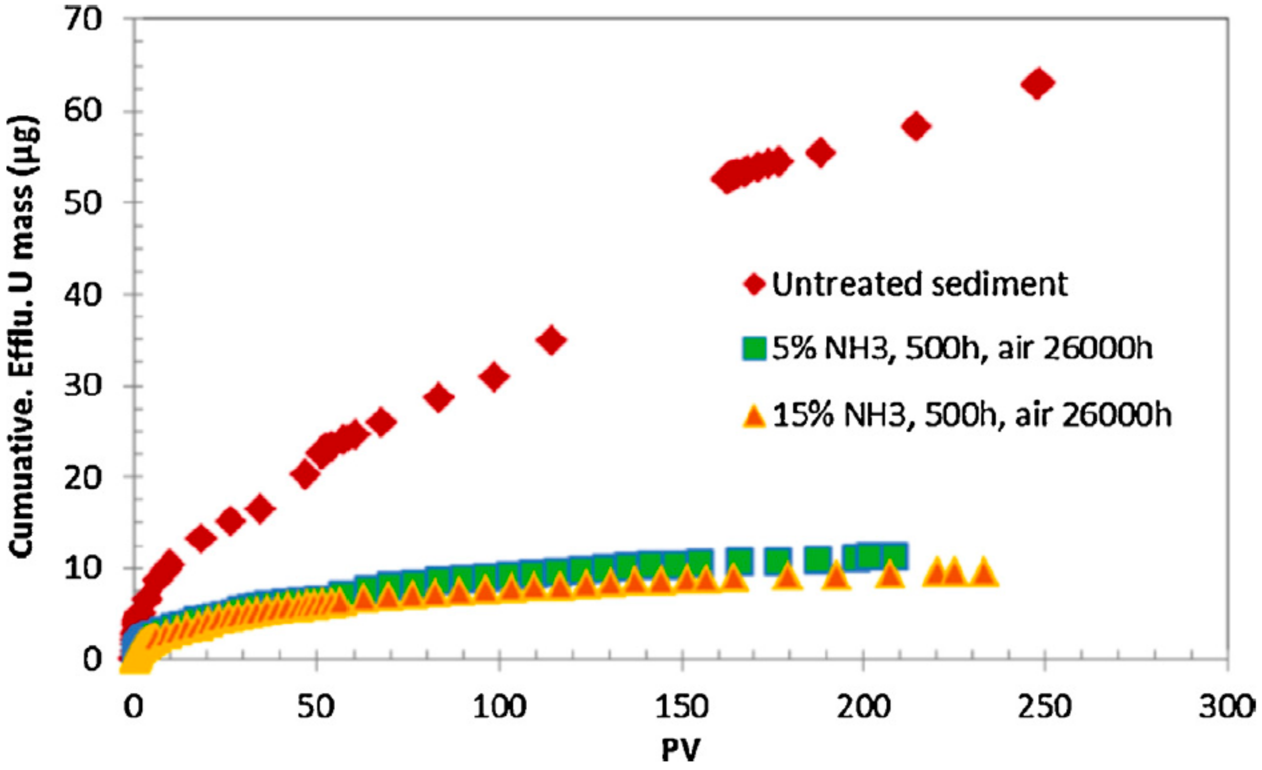






93% less U leached

3 years of NH_3 treatment (pH 8 sediment)



80% less U leached

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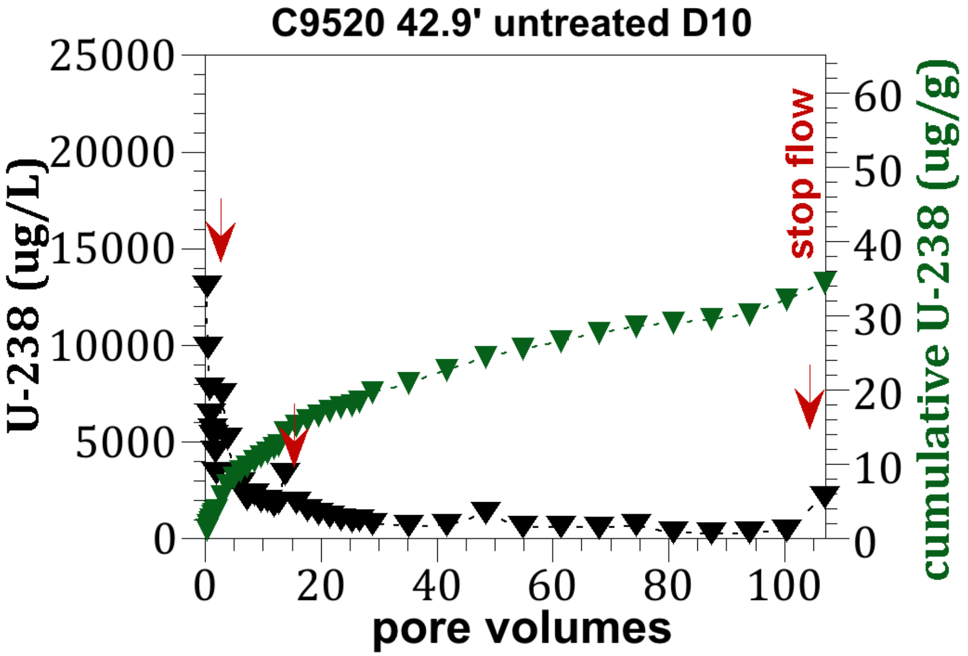
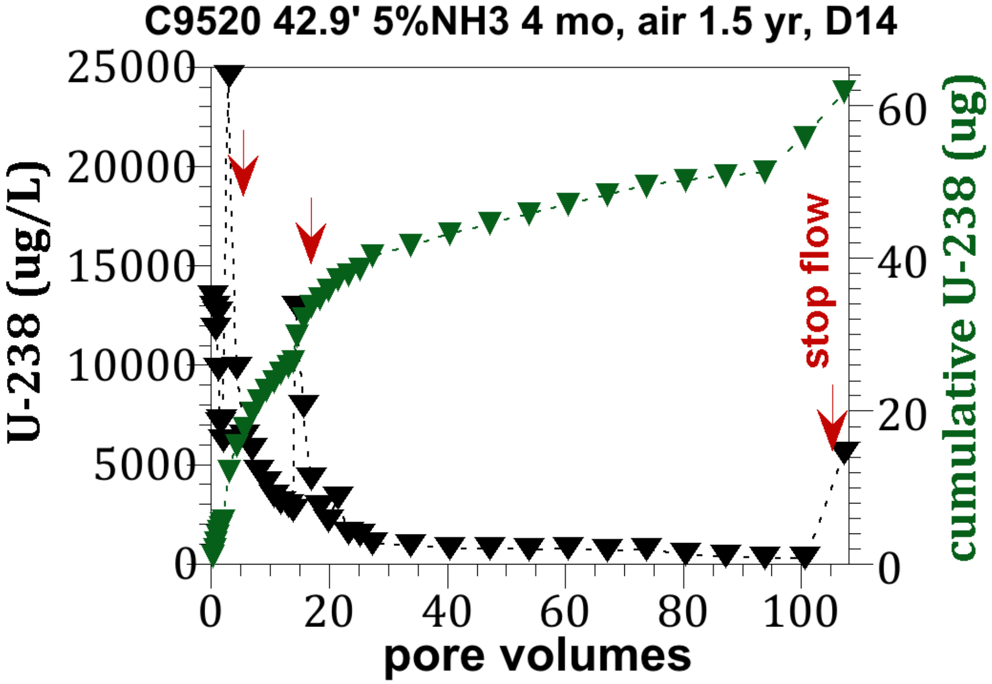
Uranium Leaching at Acidic U-8 Crib Site

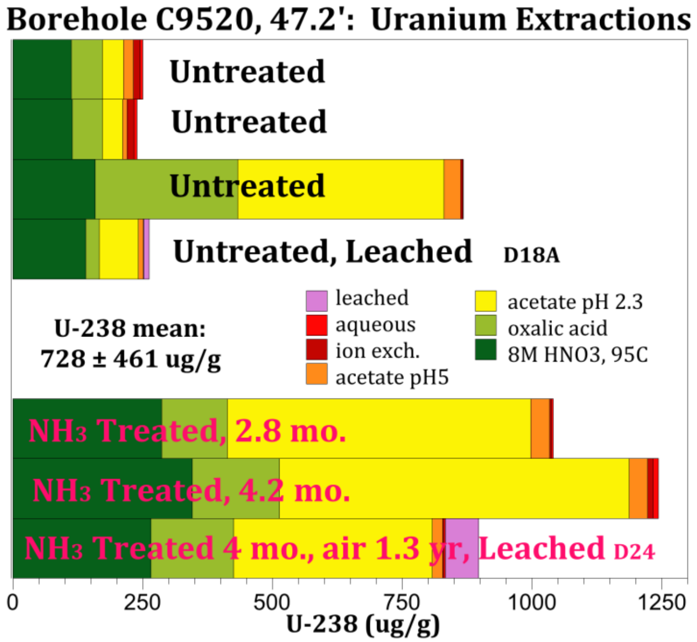
Untreated Sediment



NH_3 treated (4 mo.), air (1.5 yr)



extractions



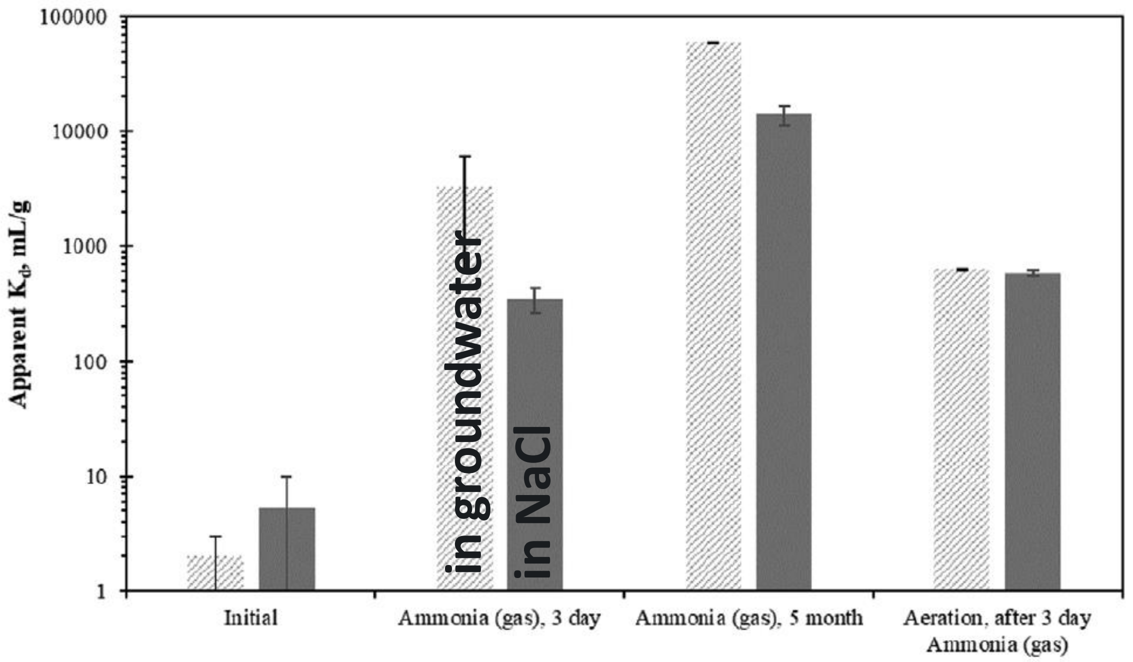
- most NH_3-treated sediments leach more U than untreated sediments (11 pairs of leach columns)
- U mass leached in NH_3/untreated sediments: 1.7 ± 1.2 (range 0.70 to 4.8)
- U peak concentration leached in NH_3/untreated sediments: 5.8 ± 8.3 (range 0.57 to 25)

Why is there Increased U Mobility in U-8 Site?

Hypotheses: fewer U precipitates formed; coating less effective, U-organic complexes kept U mobile

If sediments pH < 7.5 after NH_3 treatment, U will remain aqueous

- pH of NH_3 treated sediments = 11.6 to 9.5 (1000 h)
- acidic leaching did not remove Si (5-20 mg/L Si)
- Na-boltwoodite should still precipitate X
- LIFS showed no change in U precipitates



U apparent partitioning (K_d) in artificial groundwater or NaCl water with NH_3 treatment (Emerson et al, 2018)

Coating less effective (less U present as a precipitate):

- 16/19 sediments had low inorganic carbon (< 0.03%)
- lack of aqueous carbonate results in more mobile U upon NH_3 treatment

Organic complexants:

- 240 to 500 ug/g TOC, GC-MS/MS showed some organics
- inventory: U-8 not in top 35 sites with organic waste X (Simpson et al., 2006)

Key Points

- NH_3 gas partitions into pore water creating alkaline conditions that promotes clay dissolution and upon pH neutralization, silicate precipitation

- decreased uranium mobility results from precipitation of U silicates and non-U precipitates coating U precipitates

- some co-contaminants (NO_3, SO_4, Cl, Na, alkaline pH, one acidic pH site) have little influence on U precipitation/coating

- one acidic site (U-8) showed 70% increased U mobility with NH_3 treatment, geochemistry poorly understood but low carbonate contributes to increased U mobility in alkaline conditions

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Questions?

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