

# Spectroscopy and Microscopy Study of Abandoned Uranium Mine Wastes on Navajo Nation in Northeastern Arizona, USA

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# *Abandoned Uranium Mine Wastes*



- More than 1,000 abandoned mine waste sites on the Navajo Nation, many with only interim reclamation or no remedial actions.
- Rural communities, particularly Native American, live in close proximity of these sites.
- Human health risks associated with metal exposure in these sites remain poorly understood.
- Fundamental understanding about the fate and transport of metals is necessary.

# Blue Gap-Tachee Site, Northeastern AZ



Navajo Nation Blue Gap-Tachee mines

- 16779.7 tons
- 4181 tons (Claim 28)
- **Uranium and Vanadium mining (1950s-1980s)**
- **Several families still live at base of cliff next to Claim 28 wastes**



# Research Objective

Determine the co-occurrence of U and other metals in abandoned mine wastes using spectroscopy and microscopy.

## Research Questions

- In what chemical species are U and co-occurring metals present in abandoned mine wastes in Blue Gap-Tachee Chapter of the Navajo Nation in northeastern Arizona?
- How do these metals move in the environment?

# Materials: Field Samples in Blue Gap-Tachee

- Soil (solid/**dirt**) from surface:

Sample name	Gamma Rad (uR/hr)	Sampling Date
Undisturbed soil	13	January, 2014
Mine Waste 1	320	January 2014
Mine Waste 2	401	June 2014

- Water (sampling date: June 2014):
  - **Seep** in Claim 28 site
  - **Spring** (~0.3 miles away from mine waste).



# Water Quality Analyses

Metals analyzed with ICP-MS\*

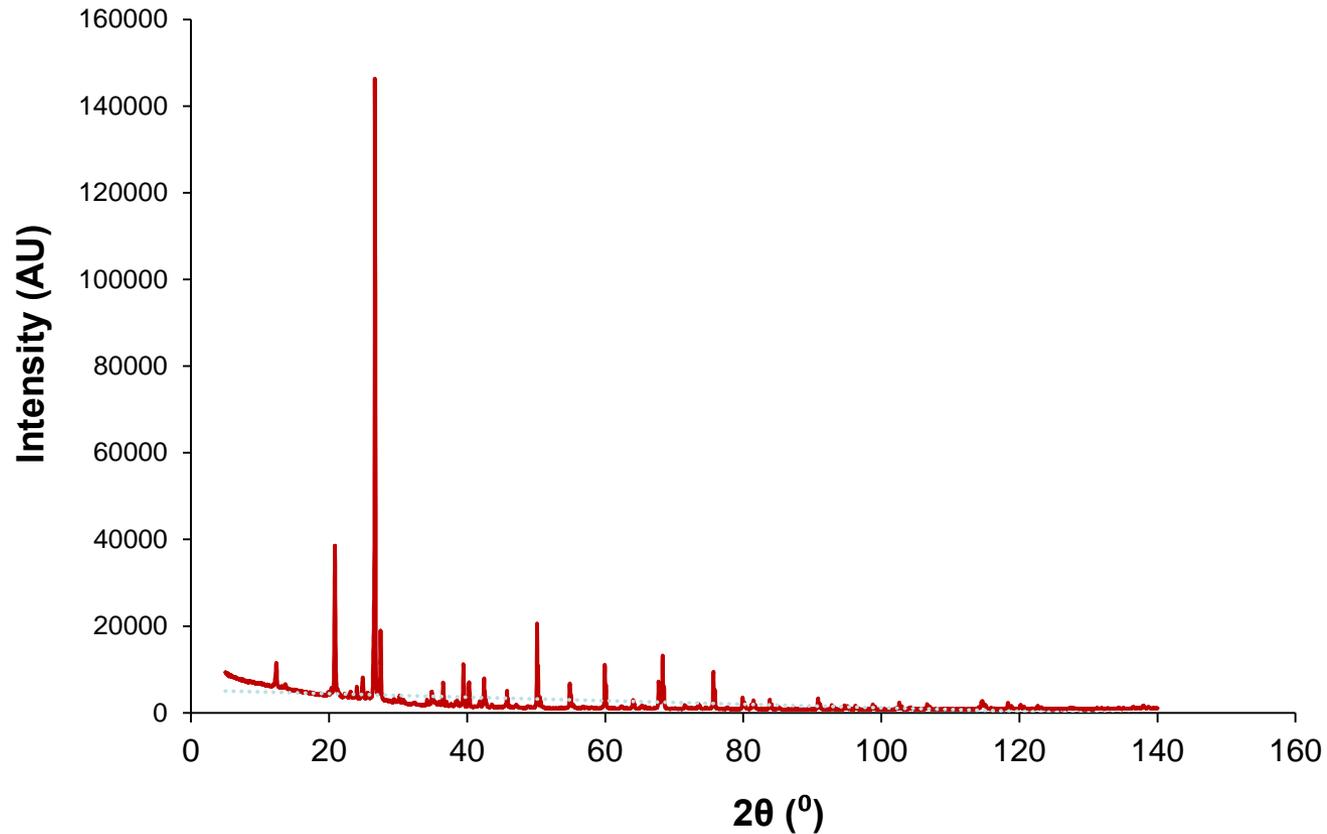
Sample	Parameter		
	<b>U (<math>\mu\text{g/L}</math>)</b>	<b>As (<math>\mu\text{g/L}</math>)</b>	<b>pH</b>
Spring	163.2	5.7	7.4
Seep	135.4	9.6	3.8
MCL**	30	10	6.5-8.5



\*ICP-MS = Inductively coupled plasma mass spectrometry

\*\*MCL = Maximum Contaminant Level, or drinking water standard

# X-ray Diffraction (XRD)



Semi-quantitative analyses indicate that:

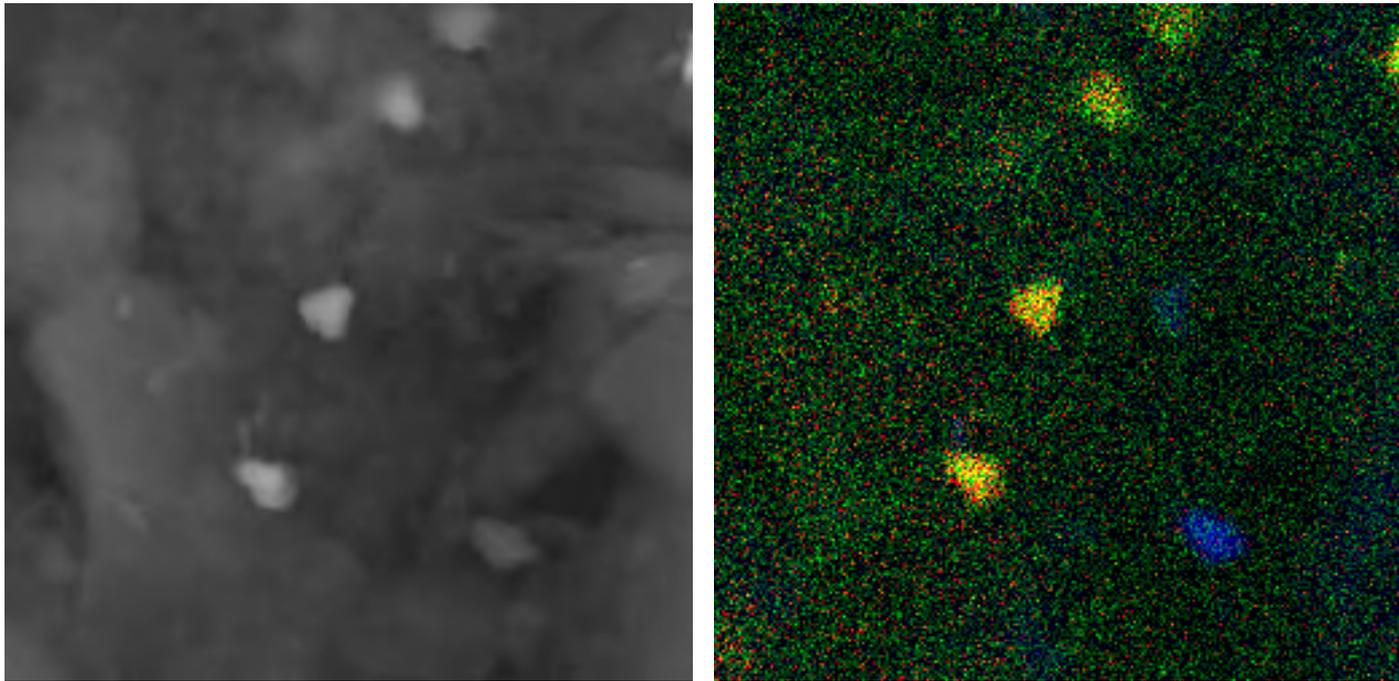
- 59 % quartz
- 34% potassium feldspar
- 7% kaolinite

# X-ray Fluorescence (XRF) on Mine Wastes

	Elemental Content, $\mu\text{g g}^{-1}$							
	Si	S	Al	Fe	Mg	U	V	Ca
<b>Undisturbed Soil</b>	241,950	1,339	52,129	26,739	3,068	BDL*	BDL*	16,441
<b>Mine waste1</b>	235,563	223	69,533	15,259	181	2,248	15,814	855
<b>Mine waste2</b>	243,703	1,834	59,730	3,511	405	6,614	4,328	3,293

- Abandoned mine waste solid samples were acid digested (HCl + HF + HNO<sub>3</sub>) determine elemental content of 20-40  $\mu\text{g g}^{-1}$  As.
- $\mu\text{g g}^{-1}$  = part per million

# Scanning Electron Microscopy (SEM)



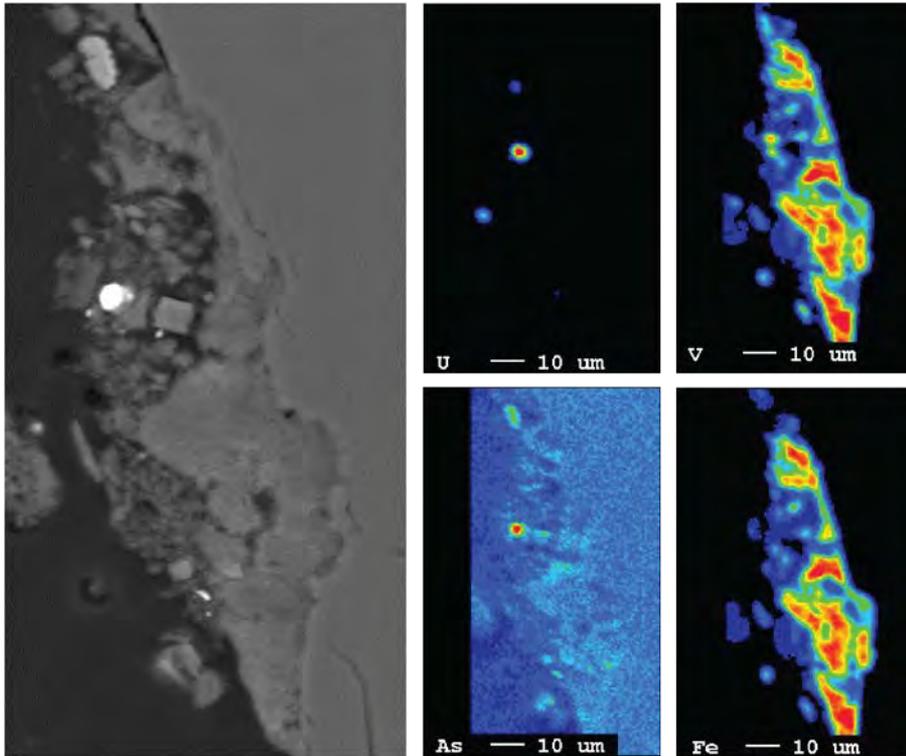
a) Back scattered-electron (BSE) SEM image.

b) Uranium(red) - Vanadium(green) - Iron(blue) composite BSE map. Yellow reflects combined U and V.

# Microprobe Blue Gap Tachee

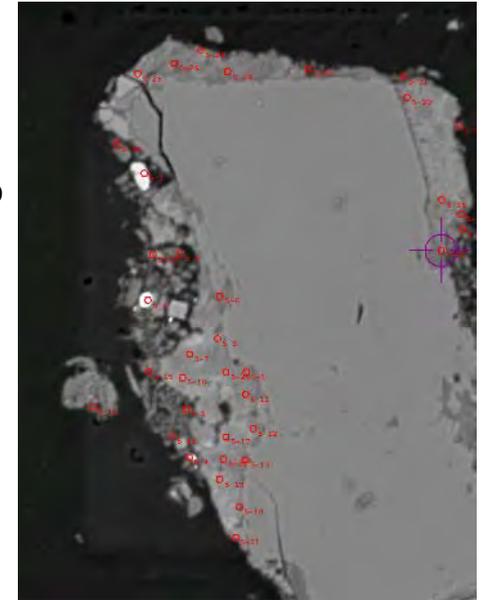
Surface elements of interest

## Qualitative Results

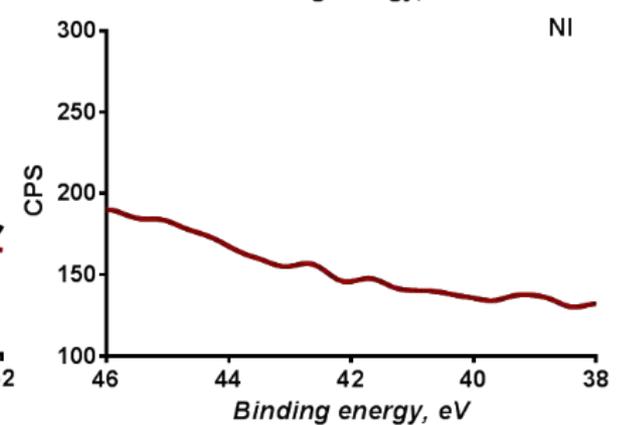
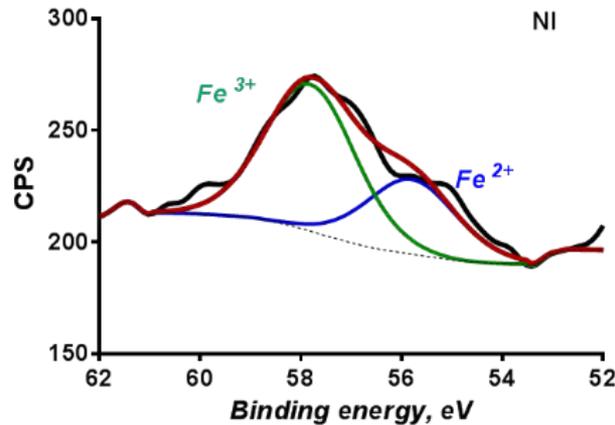
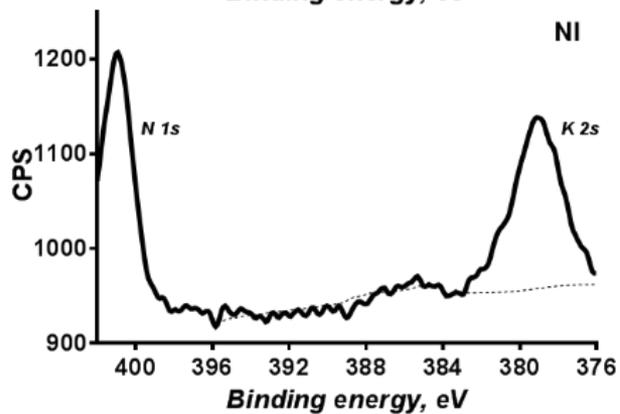
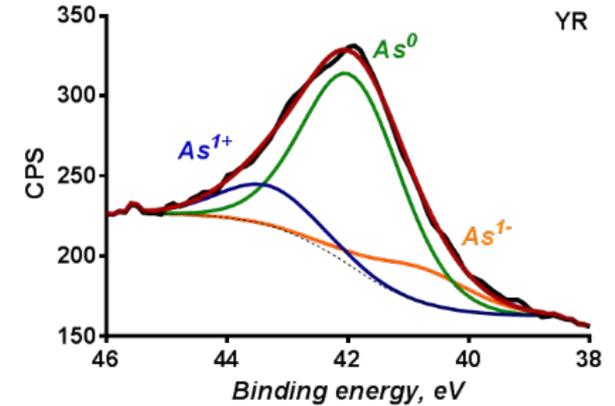
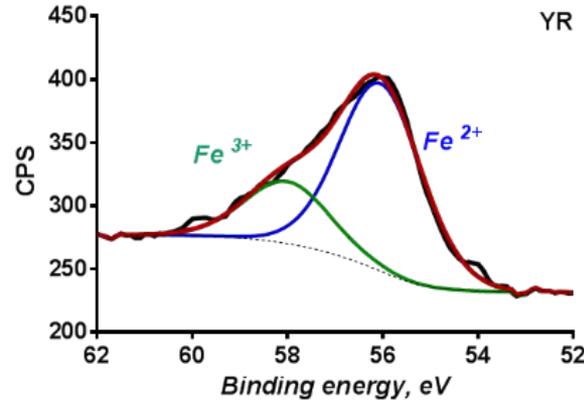
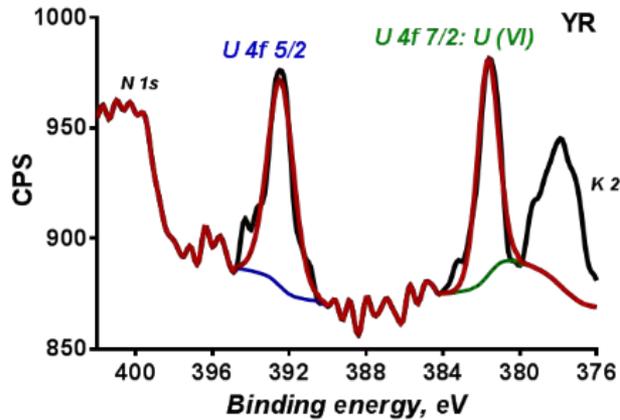


## Quantitative Results

U avg= 0.01%  
As avg= 0.012%  
V avg= 3.82%  
Fe avg= 3.63%



# X-ray Photoelectron Spectroscopy (XPS)



- ~74% Fe(III) and 26% Fe(II) in undisturbed soils
- ~26% Fe(III) and 74% Fe(II) when U(VI), V(V), and As (0,I) are present.

# Batch Chemical Extraction Experiments

## Water Quality Data

Sample	Parameter		
	U ( $\mu\text{g/L}$ )	As ( $\mu\text{g/L}$ )	pH
Spring	163.2	5.7	7.4
Seep	135.4	9.6	3.8

In 50 mL plastic vials loaded with 1g of sediment:

- 10mM  $\text{HCO}_3^-$  (~pH 8.3)
- 10 mM ascorbic acid,  $\text{C}_6\text{H}_8\text{O}_6$  (~pH 3.8).

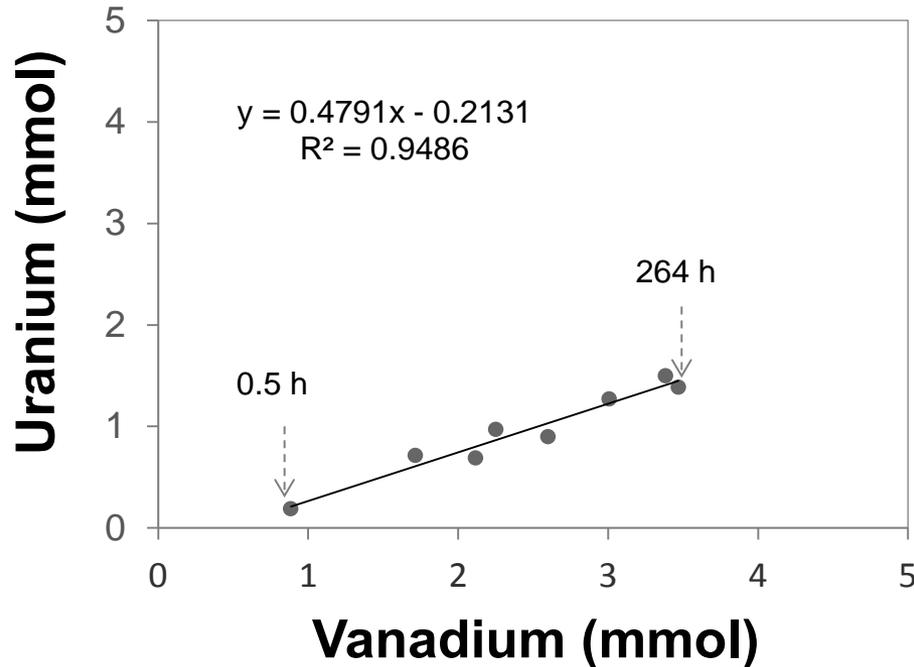
Total Reaction Time = 264 hours. Samples collected at:  
0.5, 1, 1.5, 2, 6, 24, 48, 96, 264 hours.

Filtered through 0.22  $\mu\text{m}$  filter membrane, acidified (2%  $\text{HNO}_3$ ).

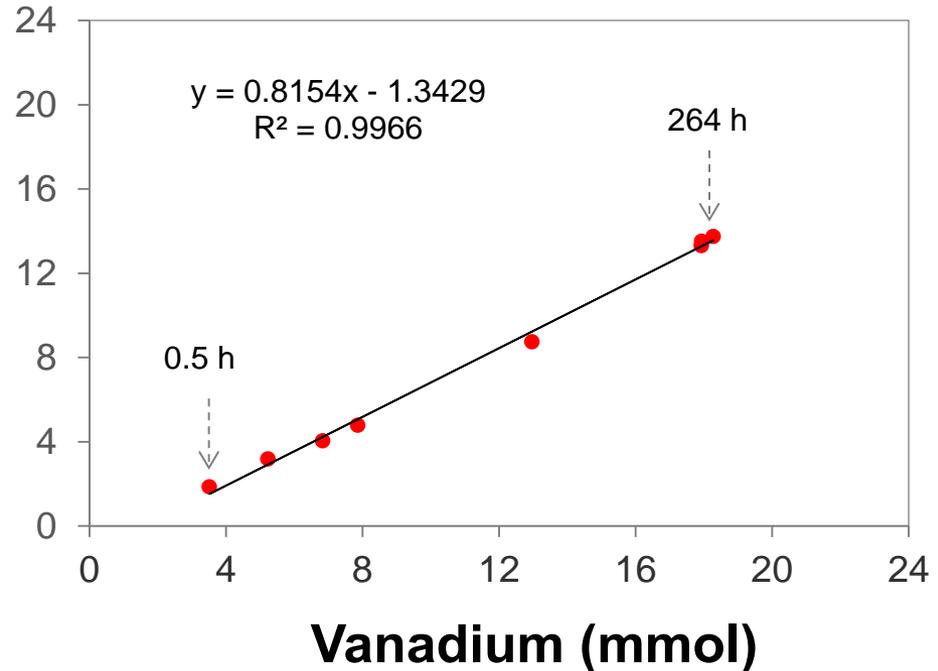
Measurements of aqueous concentrations with ICP-MS.

# Batch Experiments: U vs. V

10 mM  $\text{HCO}_3^-$  (~pH 8.3)



10 mM  $\text{C}_6\text{H}_8\text{O}_6$  (~pH 3.8)



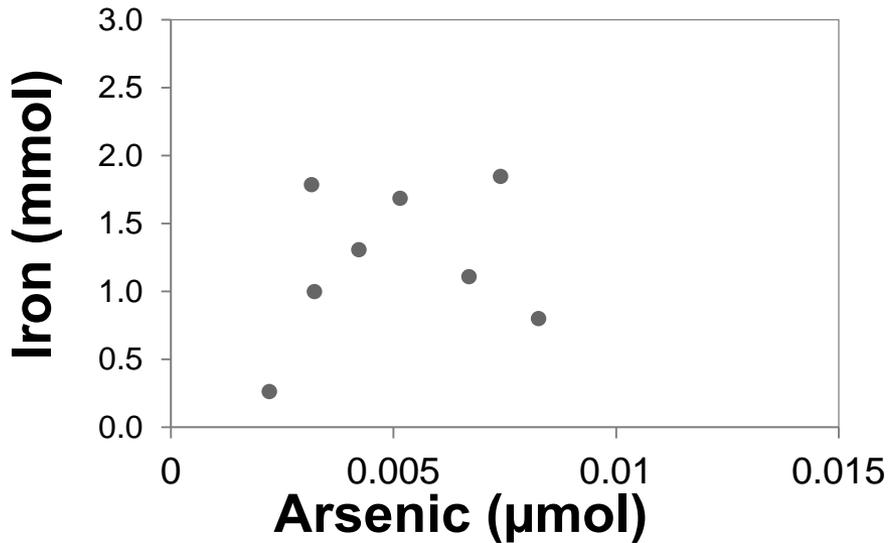
- Release of U was ~ 10 times lower with  $\text{HCO}_3^-$  than with  $\text{C}_6\text{H}_8\text{O}_6$ .
- Release of V was ~ 5 times lower with  $\text{HCO}_3^-$  than with  $\text{C}_6\text{H}_8\text{O}_6$ .
- Linear relationship between U and V release.

Reference:

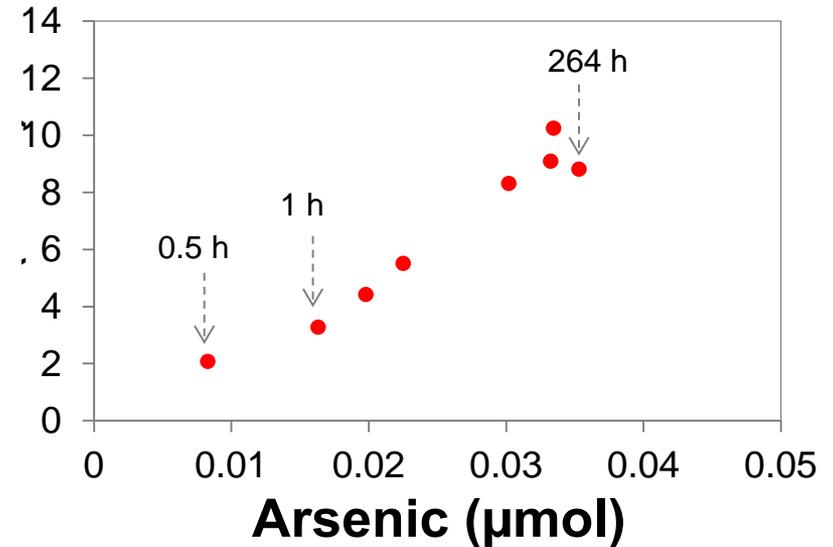
carnotite  $[\text{K}_2(\text{UO}_2)_2\text{V}_2\text{O}_8]$

# Batch Experiments: As vs. Fe

10 mM  $\text{HCO}_3^-$  (~pH 8.3)



10 mM  $\text{C}_6\text{H}_8\text{O}_6$  (~pH 3.8)

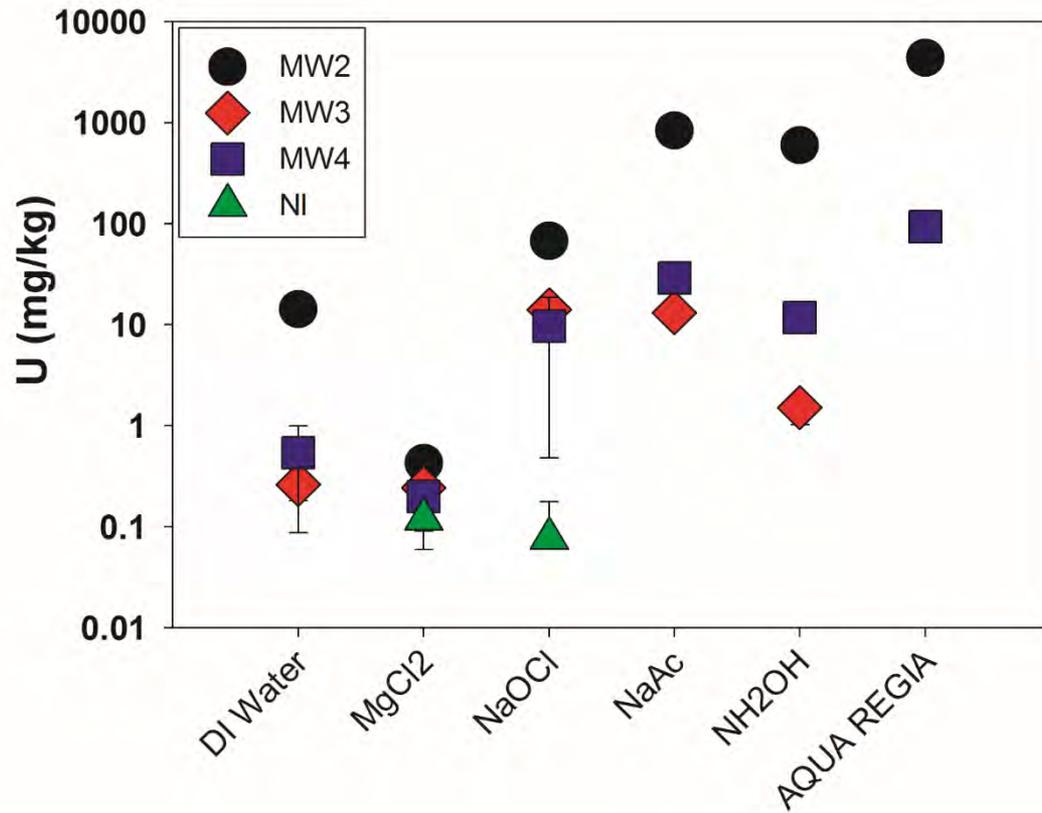


- ~ 25% of As is released at pH 8.3 (no clear correlation with Fe).
- ~ 46% of As released at pH 3.8 in 1 hours.
- Some correlation is observed between As and Fe release after 1 hour of reaction of mine waste with 10 mM  $\text{C}_6\text{H}_8\text{O}_6$  (pH 3.8).

# Sequential Extraction Blue Gap Tachee

Are As and U Mobile?

Under what chemical conditions are these U and As species mobilized?



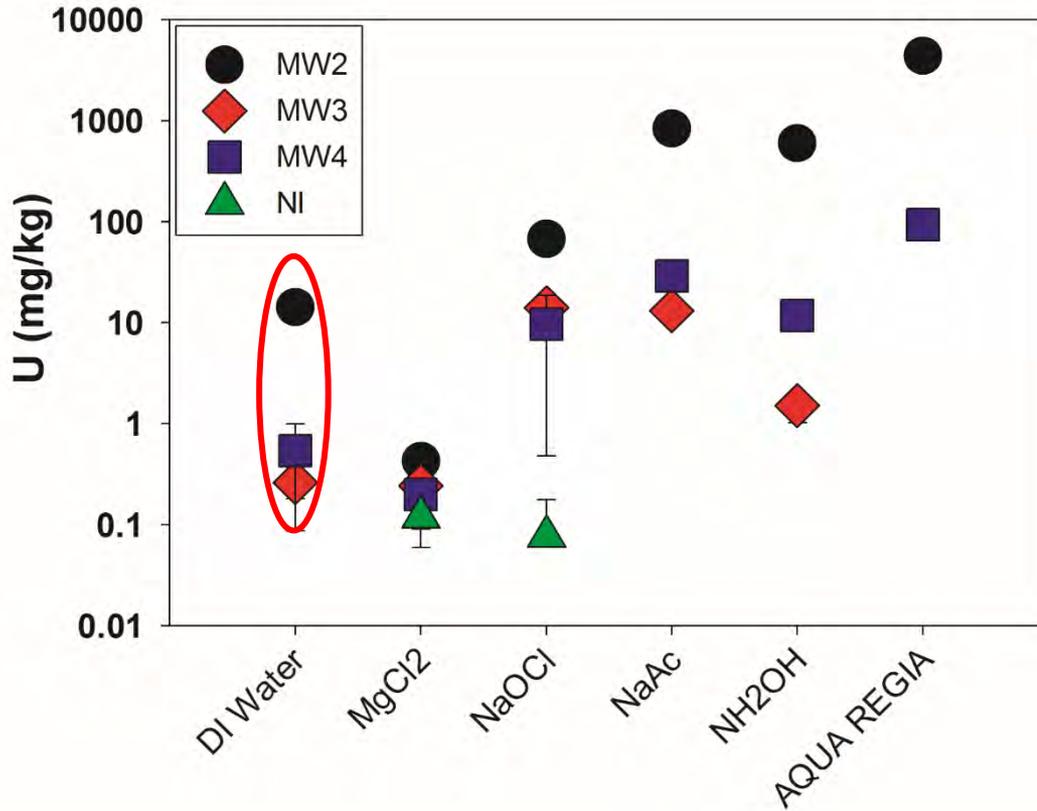
Uranium is desorbed or dissolved from the mine waste samples  
XRF: U = 6,614 mg/kg

sequential extractions:  
U = 5,895 mg/kg

# Sequential Extraction Blue Gap Tachee

Are As and U Mobile?

Under what chemical conditions are these U and As species mobilized?

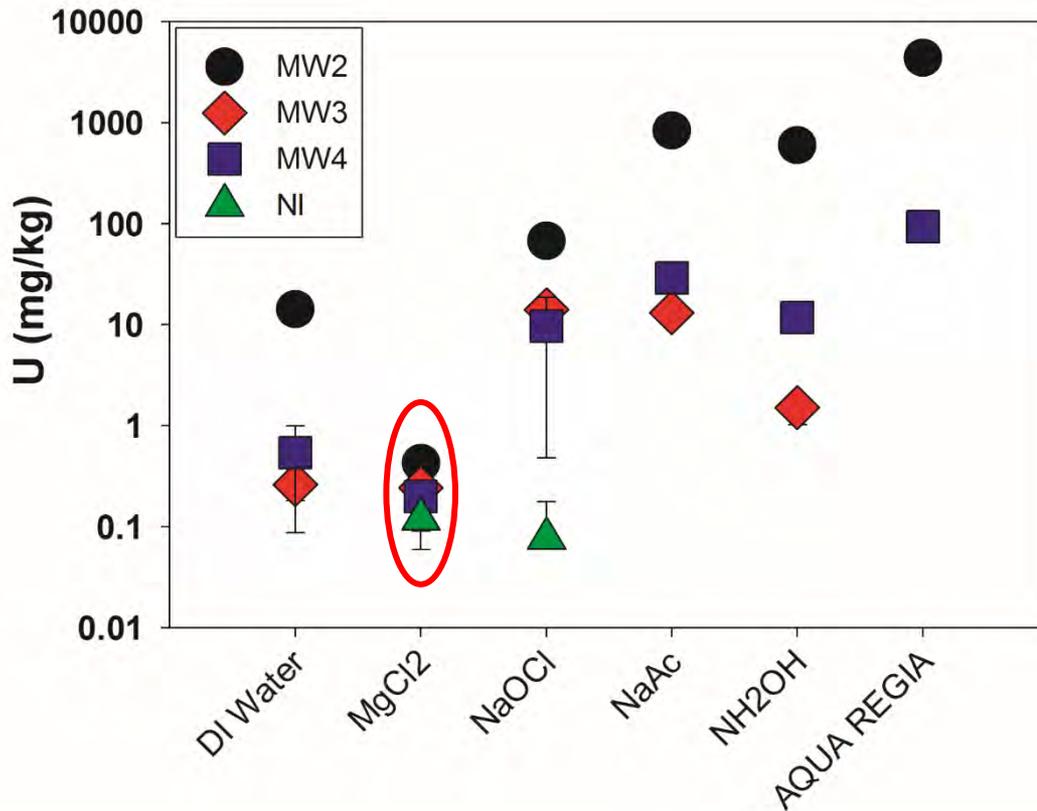


**DI Water**  
**pH=7**  
**Room Temp**  
**Easily Labile**

# Sequential Extraction Blue Gap Tachee

Are As and U Mobile?

Under what chemical conditions are these U and As species mobilized?



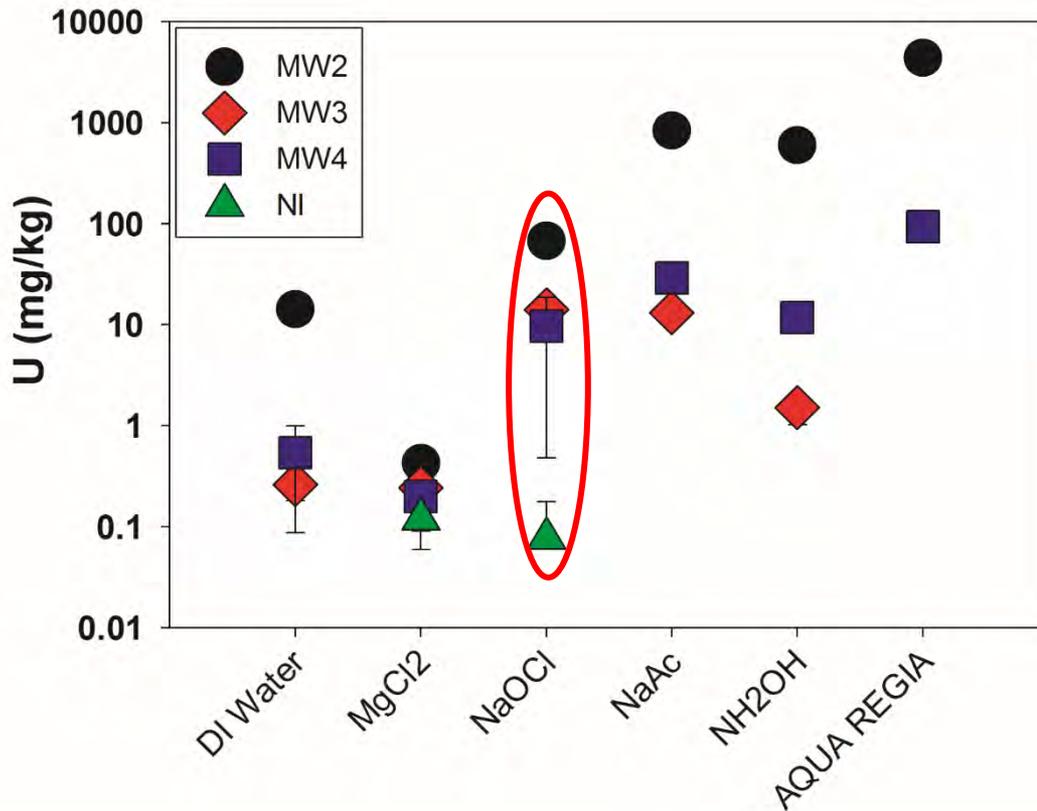
## MgCl<sub>2</sub>

- pH=5
- Room Temp
- Pulls off outer sphere complexes (cation exchange)

# Sequential Extraction Blue Gap Tachee

Are As and U Mobile?

Under what chemical conditions are these U and As species mobilized?



**NaOCl**

- pH=7.5
- 90°C
- Oxidizer-

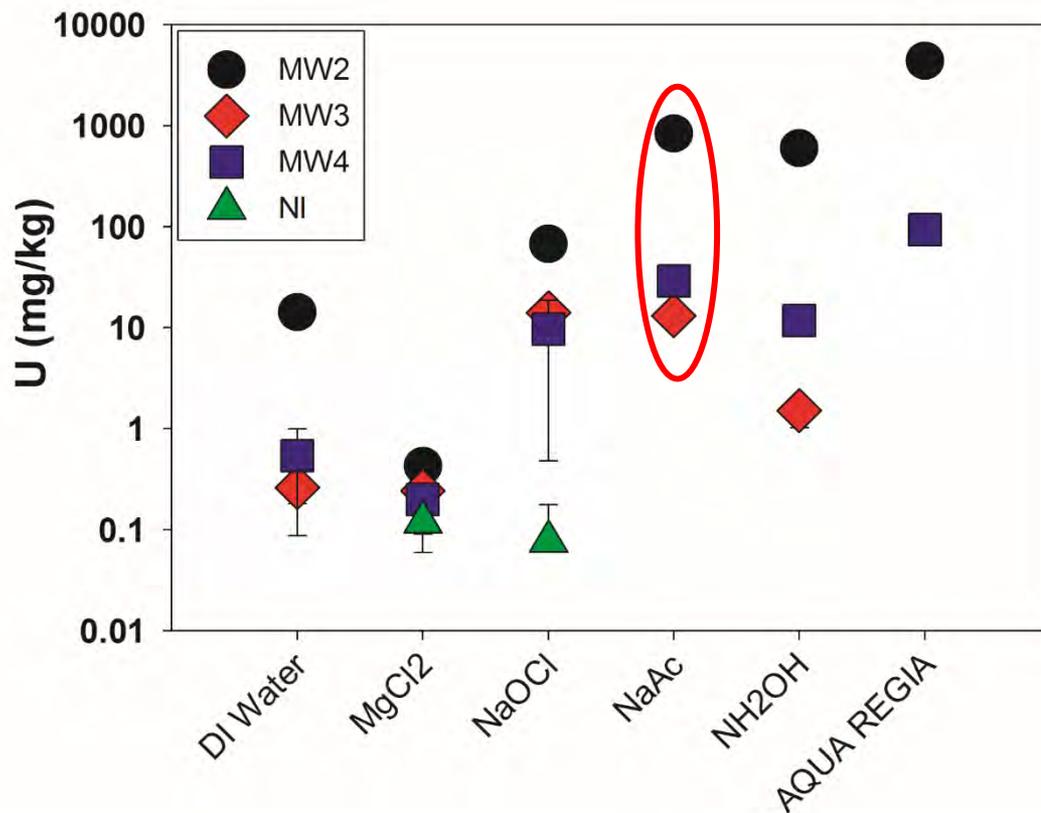
**kick                      Oxidize Fe and  
off U**



# Sequential Extraction Blue Gap Tachee

Are As and U Mobile?

Under what chemical conditions are these U and As species mobilized?



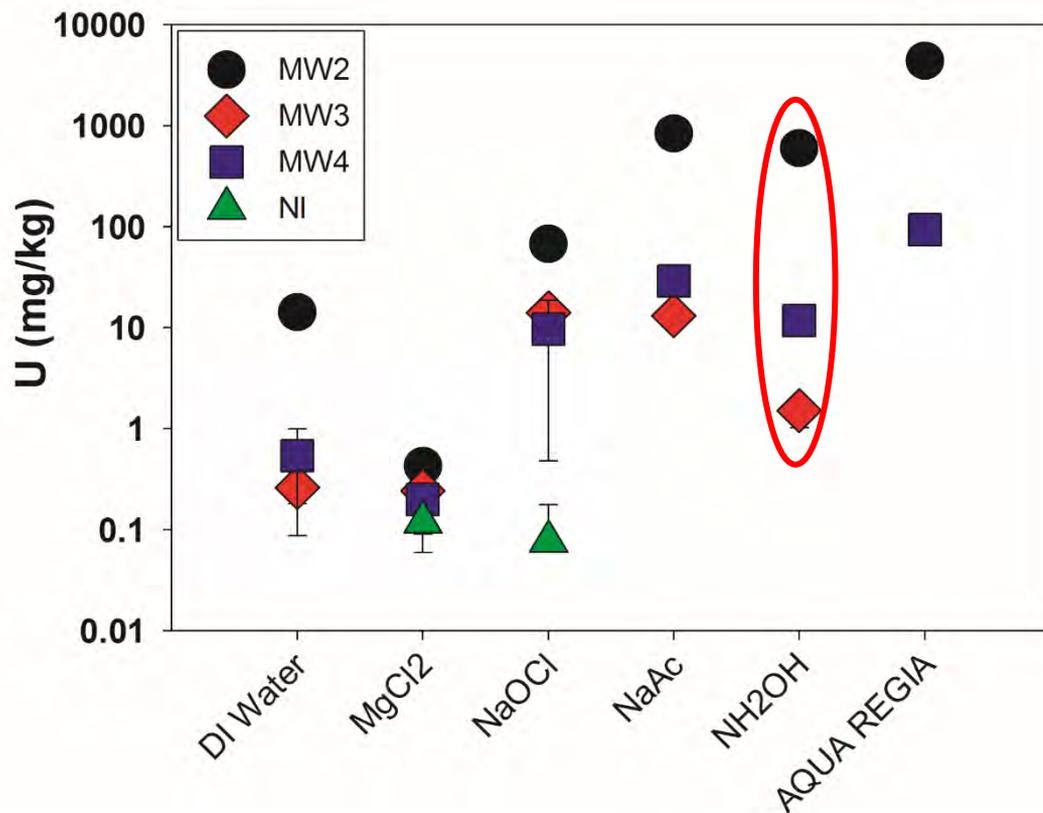
## NaAc

- pH=4
- Room Temp
- Mild Base

# Sequential Extraction Blue Gap Tachee

Are As and U Mobile?

Under what chemical conditions are these U and As species mobilized?



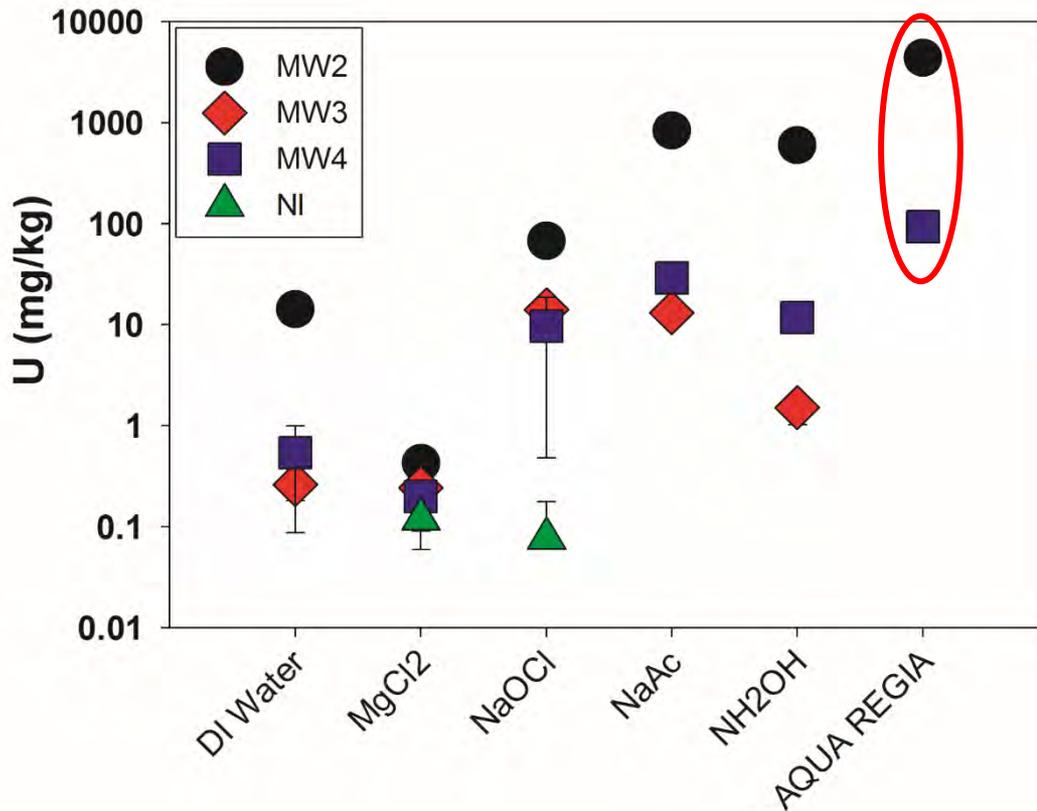
**NH<sub>2</sub>OH·HCl**

- pH=2
- Room Temp
- Reducer

# Sequential Extraction Blue Gap Tachee

Are As and U Mobile?

Under what chemical conditions are these U and As species mobilized?



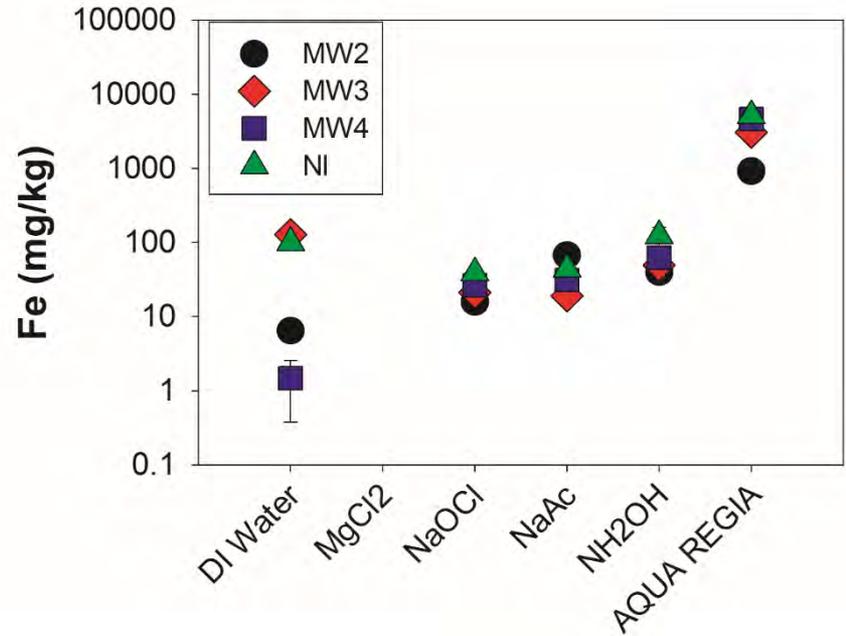
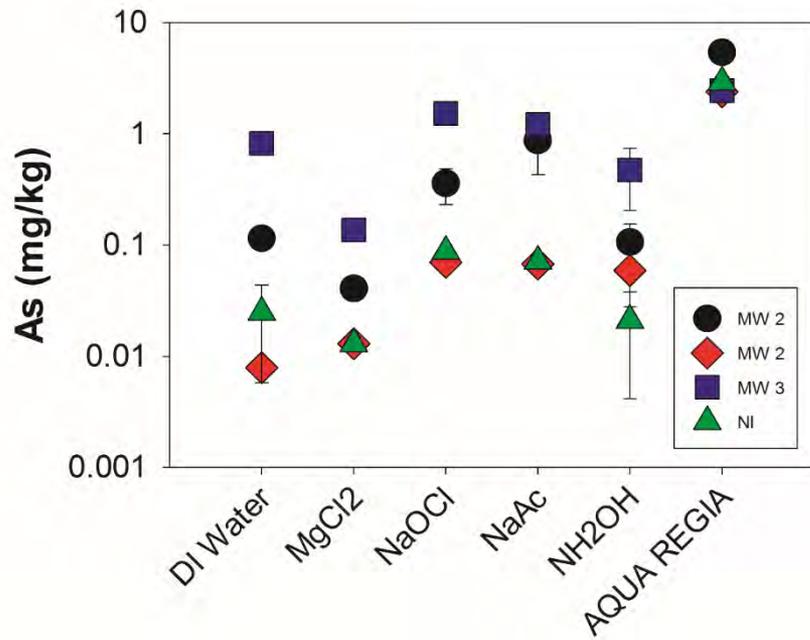
**Aqua Regia**  
**pH<2**

- **Room Temp**
- **Corrosive- Attacks residuals**

# Sequential Extraction Blue Gap Tachee

Are As and U Mobile?

Under what chemical conditions are these U and As species mobilized?



# Conclusions

- U-V phase present in abandoned mine wastes.
- U and As in mine waste can be released into water under environmentally relevant conditions.
- Release of U is 10 times higher at pH 3.8 compared with 7.4.
- U, As, and Fe are mobile across multiple chemical conditions

# Acknowledgements

## Co-Authors

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# Questions?



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