

NAWG-17 workshop

8th-12th May 2023, Zadar, Croatia

Water-rock interactions of uranium deposits: a field study in the Okchoen Metamorphic Belt, Korea and laboratory batch experiments

Sung-Wook Jeon^{1,2*}, Hakyung Cho²

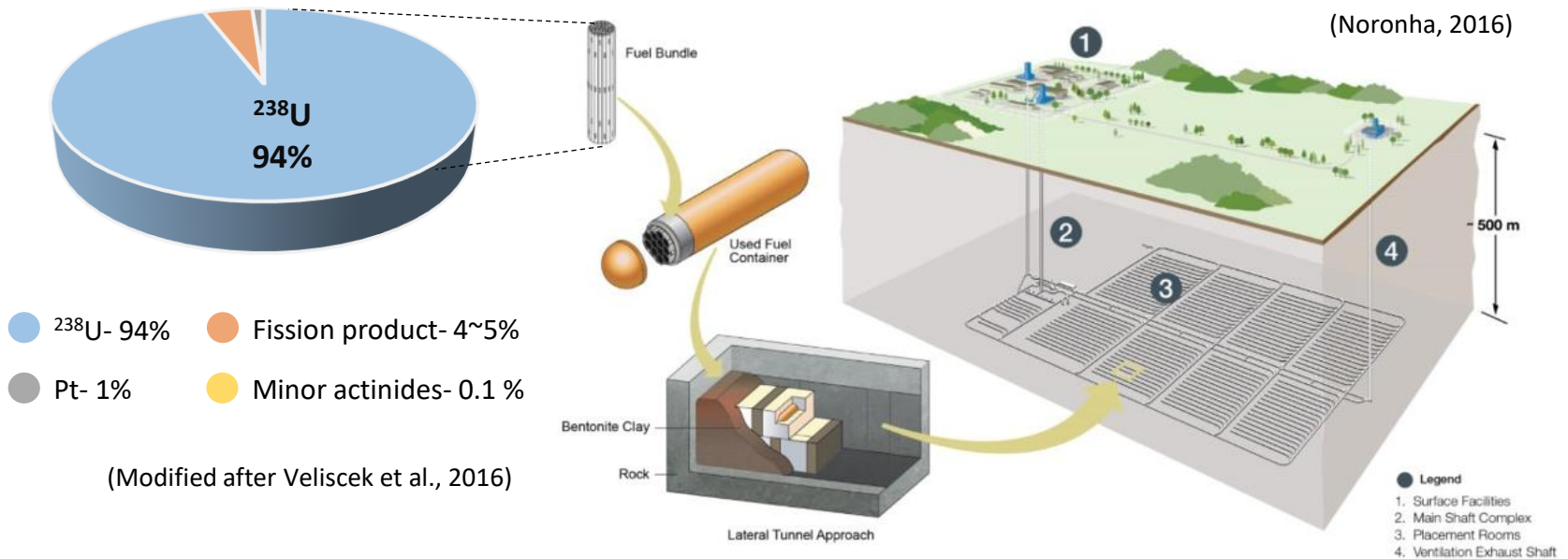
¹Department of Earth and Environmental Sciences, Jeonbuk National University, Korea

²Department of Environment and Energy, Jeonbuk National University, Korea

*sjeen@jbnu.ac.kr



< Deep Geological Repository (~500 m) for Spent Nuclear Fuel >

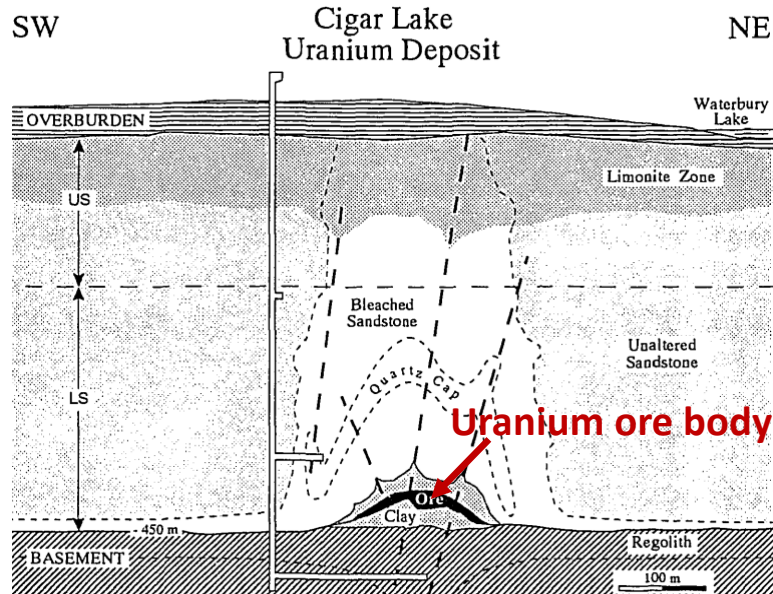


- The disposal method proposed and accepted in many countries (Smellie et al., 1986)
- In case uranium leaks out and gets into the groundwater



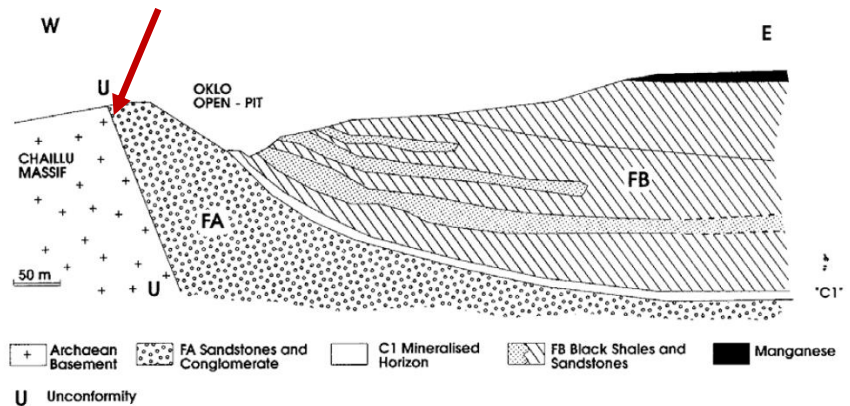
Geological formations in the far-fields are the final barriers

< Natural Analogue Study >



▲ Cigar lake in Canada (Cramer, 1995)

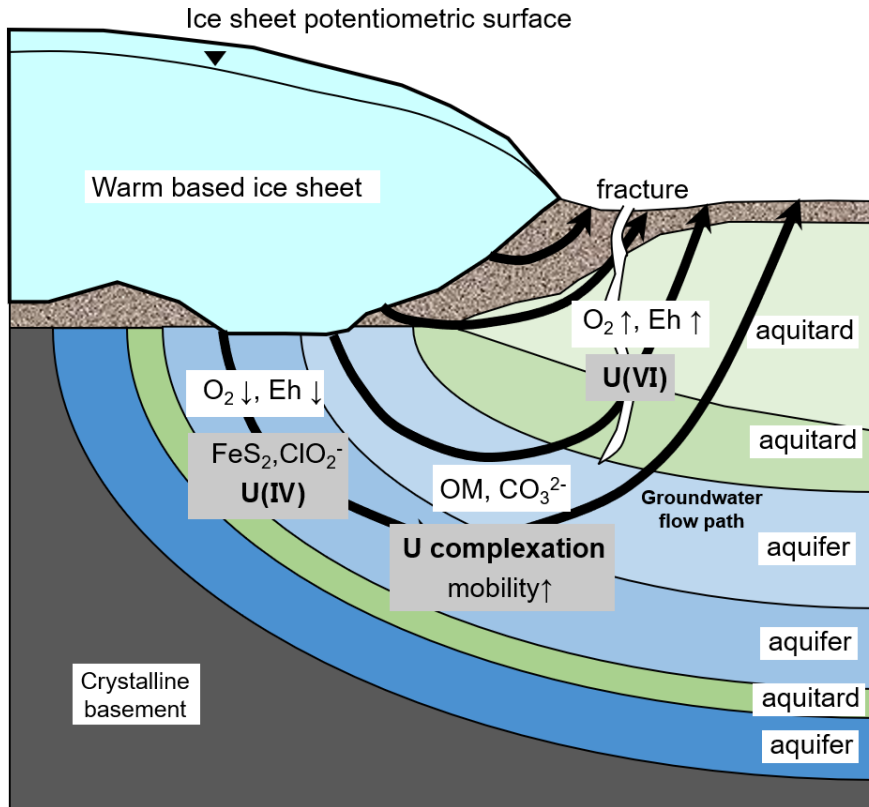
Unconformity of uranium



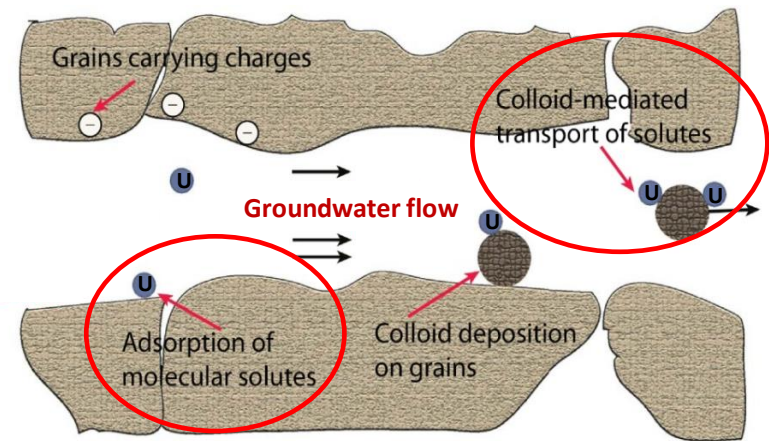
▲ Oklo, Republic of Gabon (Smellie, 2009)

- Modeling studies → Uncertainties related to parameter estimation
- Study of uranium mobility under natural conditions during geological time
 - Natural systems similar to the repository environment

< Mobility of Uranium in Groundwater >



(Modified after Mayer and MacQuarrie, 2007)



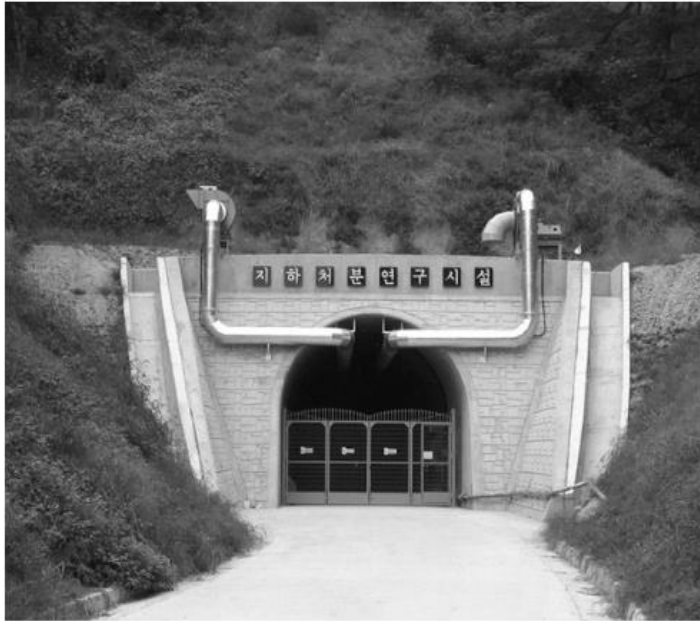
(Modified after Sharma, 2012)

- Under reduced conditions → **U(IV)** → precipitated
- Under oxidized conditions → **U(VI)** → solubility increased

- Uranium reactions through **water-rock interactions**
- Adsorption & precipitation
→ Limiting mobility
- Aqueous complexes & adsorption on colloids
→ Increasing mobility

01 Introduction - Purpose

< Previous Studies in Korea related to Underground Research and Uranium Deposits >



(a) KURT portal



(b) Access tunnel



(c) Research module

- KURT was constructed to conduct researches related to the disposal system of the underground repository
- **Okcheon Metamorphic Belt** contains **uranium ore bodies**
→ Origin of uranium deposits, geochemical characteristics of uranium ore bodies (Shin and Kim, 2011; Cho et al., 2013)

I To evaluate the **mobility of uranium** under the **redox conditions** of the Okcheon Metamorphic Belt

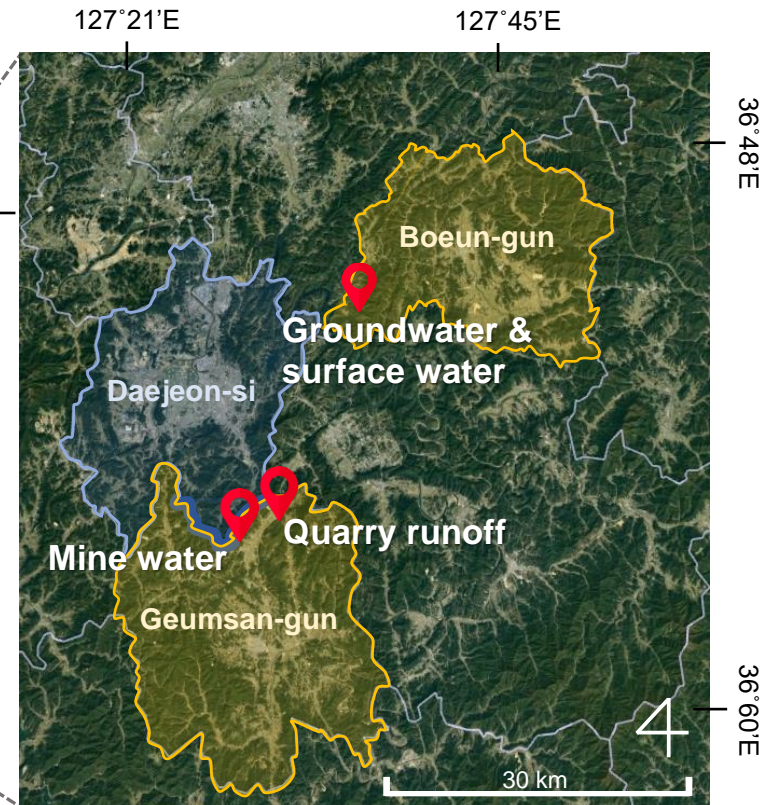
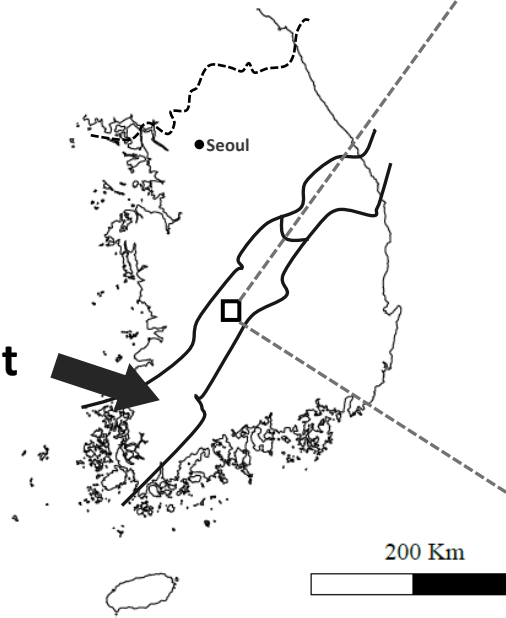
II To understand the **reaction processes of uranium** through batch (water-rock interaction) experiments

2.1 Methods – Field Study

< Study Site: Boeun-gun & Geumsan-gun >

Site	Redox conditions	Water sampling
53-5 Gwangpori mountain, Hoenam-myeon, Boeun-gun	Reduced condition	▪ Groundwater (+ Surface water)
873-16 Sinpyeong-ri, Chubu-myeon, Geumsan-gun (Quarry)	Oxidized condition (runoff)	▪ Quarry runoff
34-1 Birae-ri mountain, Geumsan-gun (Closed U mine)	Oxidized condition (infiltration)	▪ Mine water (infiltrated rain water)

**Okcheon
Metamorphic Belt**



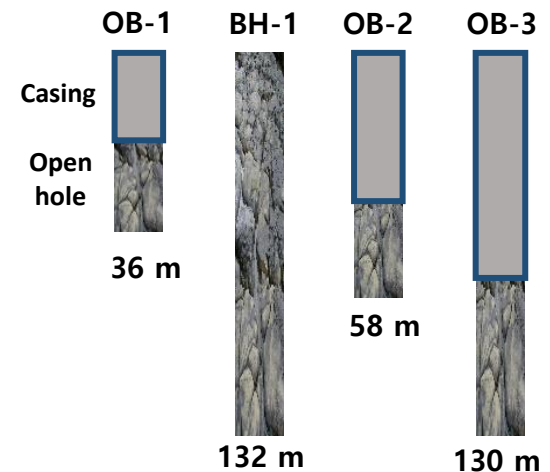
2.1 Methods – Field Study

< Natural Analogue Study in the Okcheon Metamorphic Belt >

- Study Site: Boeun-gun → **Reduced condition**



Boreholes



Coaly slate (CS)



- **Groundwater (GW) & surface water (SW) sampling**
 - From 4 wells installed in Boeun-gun
 - From Deacheong lake
- **Rock sampling**
 - Outcrop: quartz vein, black slate, and **coaly slate**
 - Radiation level: **800 cpm**

2.1 Methods – Field Study

< Natural Analogue Study in the Okcheon Metamorphic Belt >

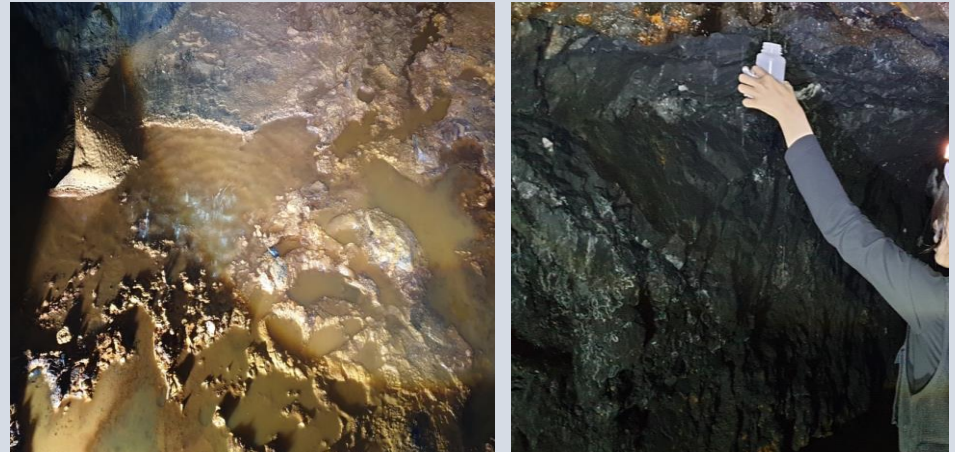
● Study Site: Geumsan-gun

Quarry runoff: **Oxidized condition**



- Sampling of quarry runoff
 - **Quarry**
- Sampling of sediment
 - **White sediment (WS)** under runoff

Mine water (infiltrated rain water): **Oxidized condition**



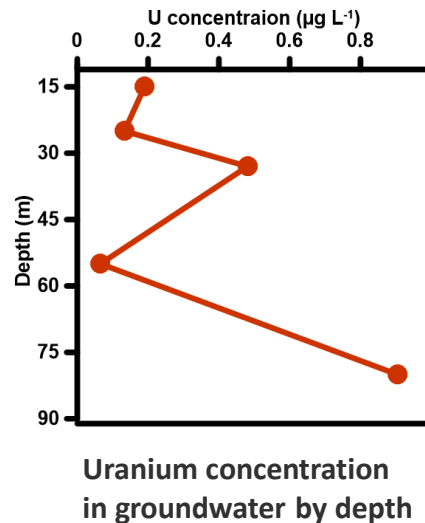
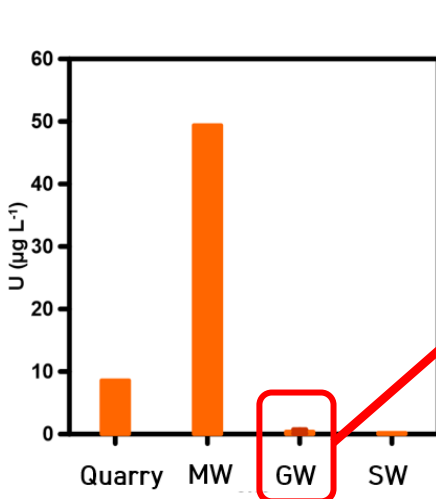
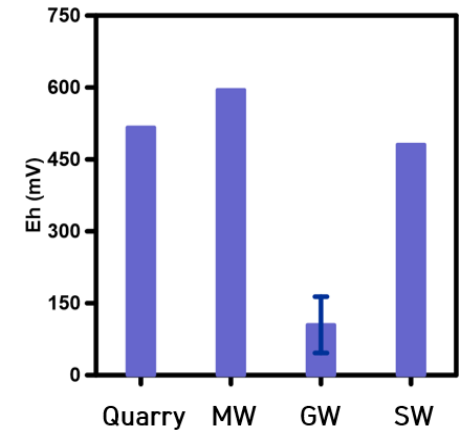
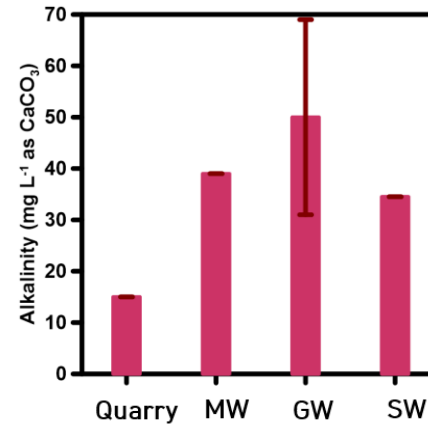
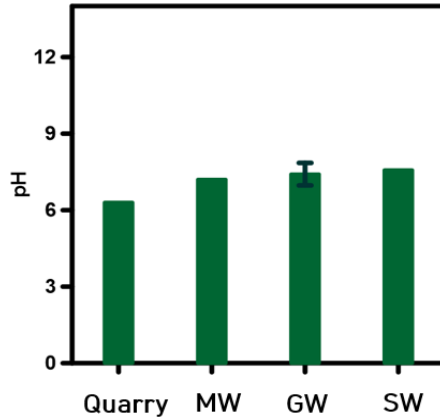
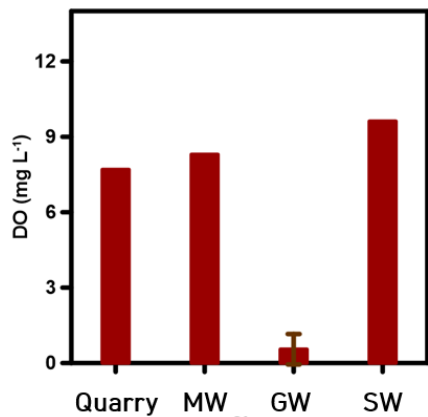
- Sampling of mine water
 - **Stagnant water on the floor (Mine 1)**
 - **Dripping water from the ceiling (Mine 2)**
- Sampling of sediment
 - **Floor sediment in the stagnant water (MS-1)**
 - **Sediment under the dripping water from the ceiling (MS-2)**

2.2

Results and Discussion - Field Study

< Comparison of Geochemical Conditions and Uranium Concentrations >

● Quarry: runoff, MW: mine water, GW: groundwater, SW: surface water

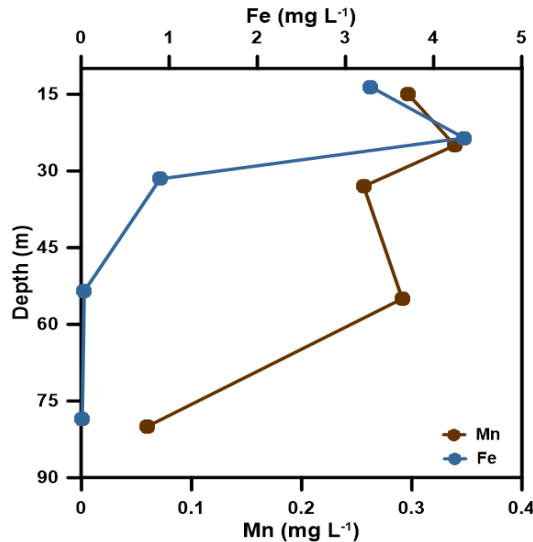


- DO
GW ≪ Quarry ≅ Mine ≅ SW
- Eh
GW ≪ Quarry ≅ Mine ≅ SW
- GW: slightly reduced condition
- Quarry, Mine, SW: oxidized condition
- Uranium concentration
- Mine ≫ Quarry > SW > GW (below 1 µg L⁻¹)

2.2

Results and Discussion - Field Study

< Concentrations of Fe & Mn and Water-Rock Interactions >



- **Mn**

- Dissolution of Mn-containing minerals

- **Fe**

- Slightly reduced condition / mixed Fe(II) & Fe(III)

- Relatively low concentrations at lower depths

- Fe(III) was precipitated as ferrihydrite and hematite

- Fe(II,III) was precipitated as magnetite

→ **Ferrihydrite causes co-precipitation of uranium** (del Villar et al., 2002)

Saturation Index (SI) of Mineral

	Ferrihydrite	Hematite	Magnetite	Siderite	Rhodochrosite	Pyrolusite
	Fe(OH) ₃	Fe ₂ O ₃	Fe ₃ O ₄	FeCO ₃	MnCO ₃	MnO ₂
BH-1 (15 m)	2.29	15.6	21.22	-1.71	-1.32	-10.82
OB-1a (25 m)	3.2	14.34	17.70	-1.55	-1.82	-12.33
OB-1b (33 m)	3.79	15.51	19.29	-2.05	-0.68	-9.87
OB-2 (55 m)	1.86	11.66	11.10	-5.79	-1.15	-6.87
OB-3 (80 m)	2.09	12.09	12.71	-5.13	-0.87	-7.16

2.2

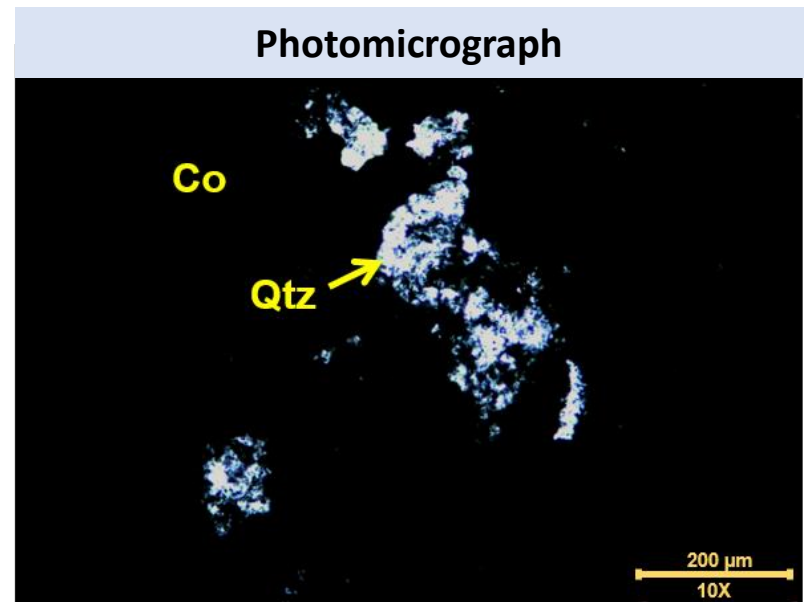
Results and Discussion - Field Study

< Mineralogy of Raw Rock: XRD & XRF >

XRD Mineral	wt.% Ratio
Muscovite ((KF) ₂ (Al ₂ O ₃) ₃ (SiO ₂) ₆)/illite	54
Quartz (SiO ₂)	46

XRF Composition	wt.% Ratio
SiO ₂	52.19
Al ₂ O ₃	11.59
Fe ₂ O ₃	6.28
CaO	0.27
MgO	1.15
K ₂ O	3.98
Na ₂ O	0.31
TiO ₂	0.86
U	0.01
lg. loss	17.51

About 100 ppm

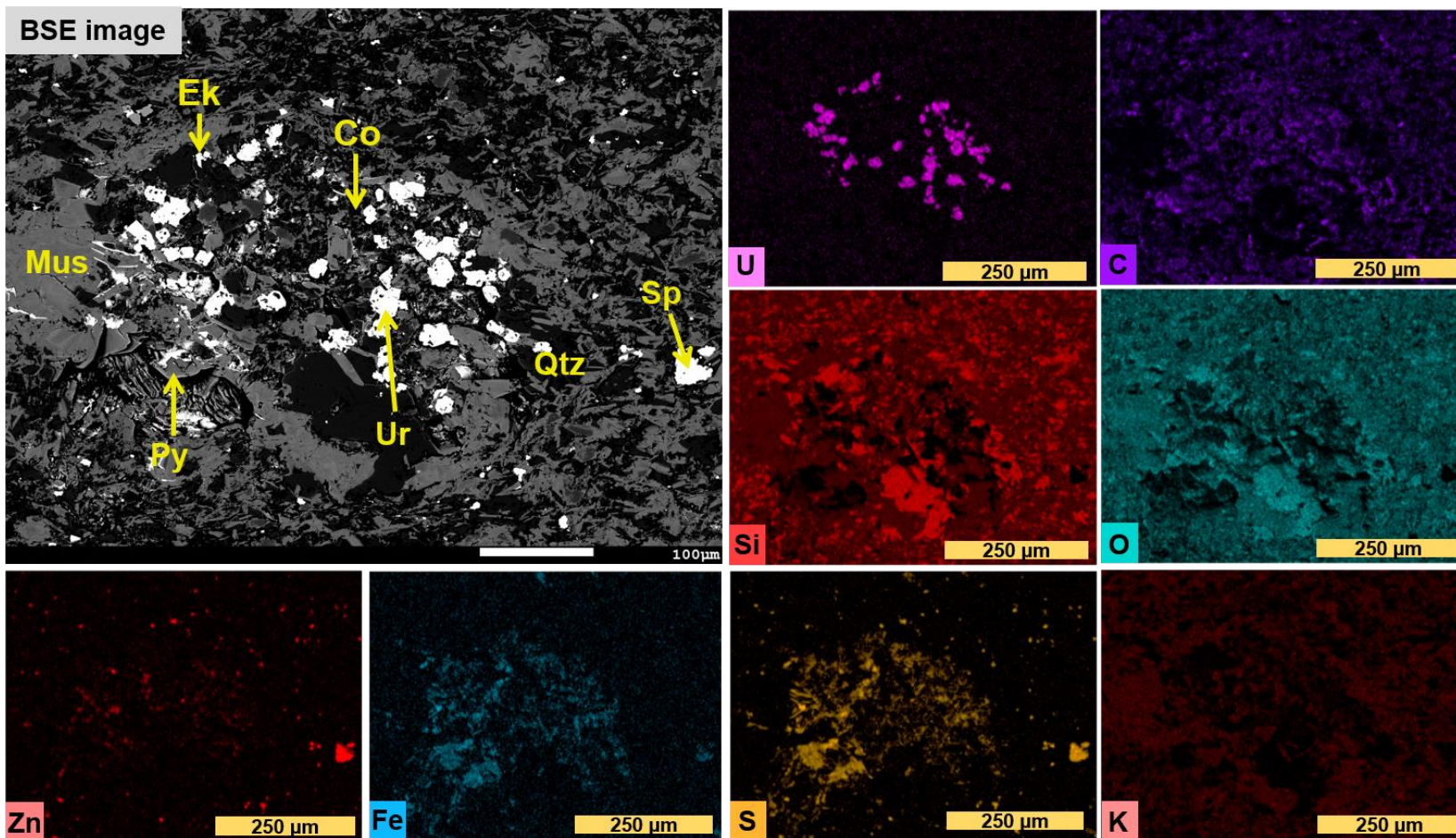


Coal material (Co), Quartz (Qtz)

2.2

Results and Discussion - Field Study

< Mineralogy of Raw Rock: FE-EPMA >



Ek: ekanite, $(Ca,Fe)_2(Th,U)(Si_8O_{22})$

Qtz: quartz, SiO_2

Pry: pyrite, FeS_2

Sp: sphalerite, $(Zn,Fe)S$

Ur: uraninite, UO_2

Co: coaly materials

Mus: muscovite, $(KF)_2(Al_2O_3)_3(SiO_2)_6$

2.2 Results and Discussion - Field Study

< Compositions of Coaly Slate and Sediments: Acid Digestion & ICP-MS >

- Coaly slate (CS)



Fe (57,300 ppm), S (18,750 ppm), U (97 ppm)

→ Contains a lot of **iron sulfide (FeS₂)**

- White sediment in the quarry (WS)



Fe (39,500 ppm), Al (32,100 ppm), U (58 ppm)

→ **Al(OH)₃** (Shand et al., 2006)

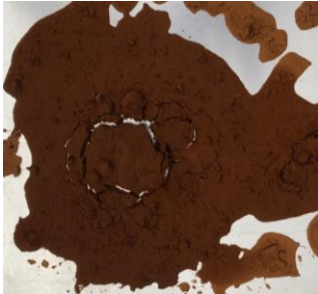
→ Secondary precipitates contain large amounts of **iron**
- **Co-precipitation with uranium**

2.2

Results and Discussion - Field Study

< Compositions of Coaly Slate and Sediments: Acid Digestion & ICP-MS >

● Floor sediment in the stagnant water (MS-1)



Fe (>300,000 ppm), Al (13,600 ppm), S (3,010 ppm), U (775 ppm)

→ Reddish brown color

→ **Ferrihydrite (Fe(OH)₃) and/or hematite (Fe₂O₃)** (Schwertmann and Cornell, 2008)

● Sediment under the dripping water from the ceiling (MS-2)

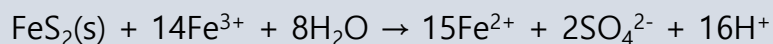
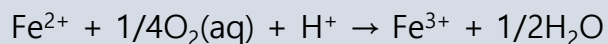


Fe (270,000 ppm), Al (8,700 ppm), S (3,530 ppm), U (1150 ppm)

→ Ochre color

→ **Oxidation products of iron sulfide (FeS₂)** (Murad and Rojik, 2003)

Oxidation of FeS₂/ Production of Fe(II) & Fe(III)



(Amos et al., 2015)

time lapse

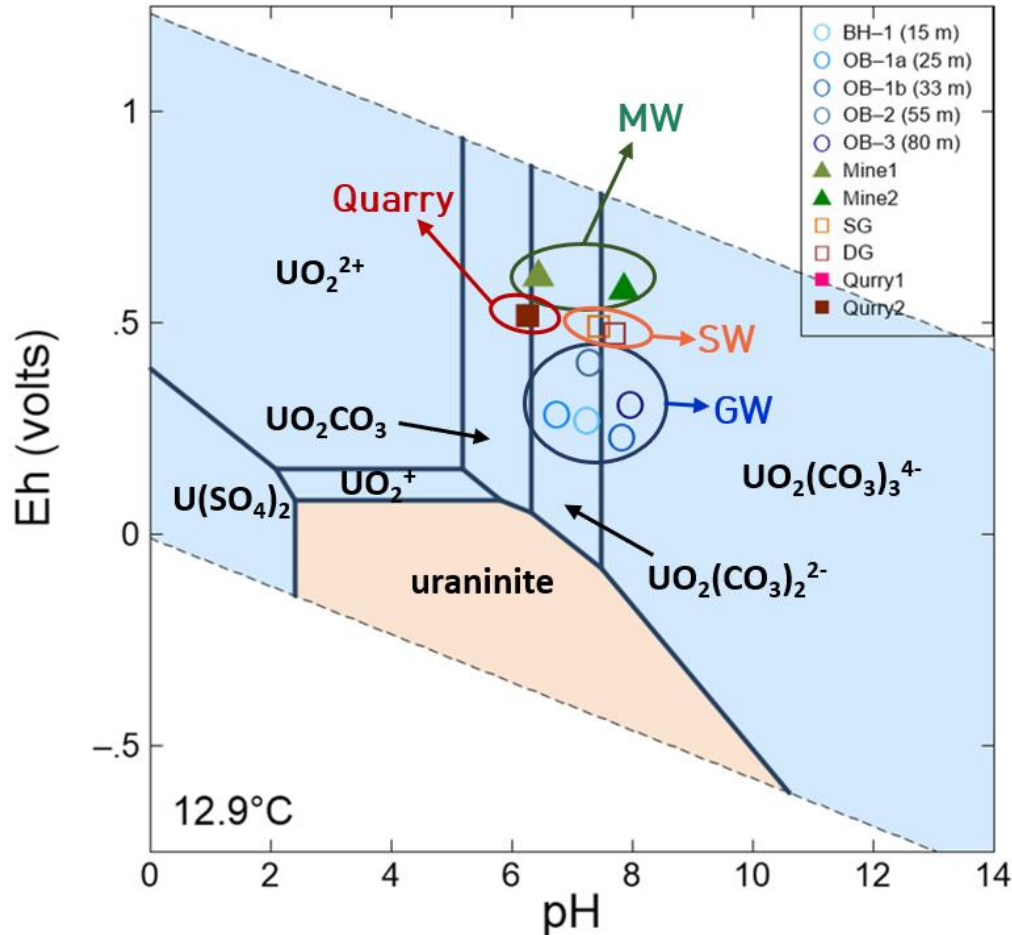
▪ Fe(II) & Fe(III) form secondary precipitates, **iron (hydr)oxides**

▪ Iron (hydr)oxides **co-precipitate with uranium** (Corchran, 1993)

2.2

Results and Discussion - Field Study

< Speciation of Uranium in Aqueous and Solid Phases >



- **Groundwater (GW) & Surface water (SW)**
 - UO₂(CO₃)₃⁴⁻, UO₂(CO₃)₂²⁻ complex
- **Quarry runoff (Quarry)**
 - UO₂CO₃, UO₂(CO₃)₃²⁻ complex
- **Mine water (MW)**
 - UO₂CO₃, UO₂(CO₃)₃²⁻, UO₂(CO₃)₃⁴⁻ complex

2.3 Summary – Field Study

Groundwater

- Slightly reduced condition
- **Uranium concentration is very low** (below $1 \mu\text{g L}^{-1}$)
- Reduced condition & adsorption/surface complexation

Quarry runoff

- Oxidized condition
- **$\text{Al}(\text{OH})_3$ contains a large amount of iron**
- Secondary precipitates containing **iron (hydr)oxides** can lead to co-precipitation of uranium

Mine water

- Infiltrated rainwater
 - More oxidized condition than quarry runoff
 - **Iron sulfide is oxidized** and **iron (hydr)oxide is formed**
-

- **Uranium concentration is very low under the reduced condition**
- **Mobility of uranium is limited by co-precipitation with iron (hydr)oxides under the oxidized condition**

3.1 Methods – Batch Experiment

< Setting of Batch Experiments >

❖ Rock sample

Coaly slate



❖ Artificial groundwater

Recipe

Composition	Concentration (mg L ⁻¹)	Composition	Concentration (mg L ⁻¹)
Ca ²⁺	49.3	HCO ₃ ⁻	50.0
Mg ²⁺	20.0	Cl ⁻	6.8
Na ⁺	18.8	SO ₄ ²⁻	189.8
K ⁺	1.5		

- Dissolved oxygen (DO) < 1 mg L⁻¹ (Ar purging)

→ Reflecting the environment of groundwater with little dissolved oxygen

❖ Setup

- Weight ratio
artificial groundwater:rock
= 20:1 (100 mL:5g)
- Temperature → 15 °C
- Rotation rate → 140 rpm

❖ Sampling

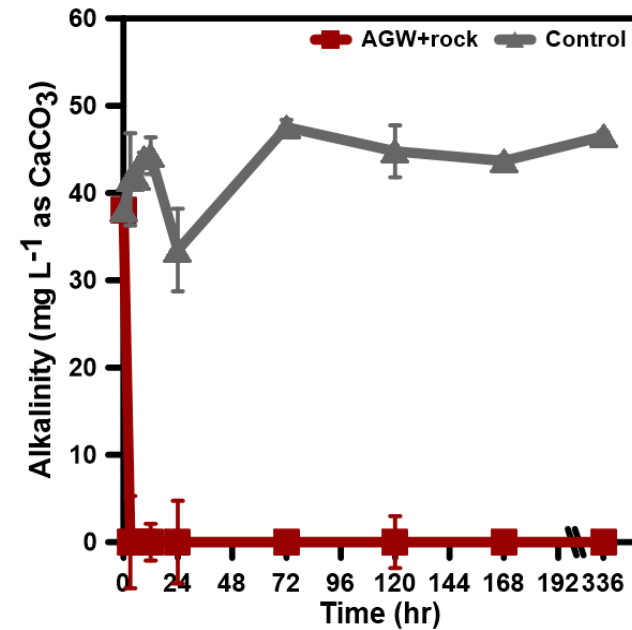
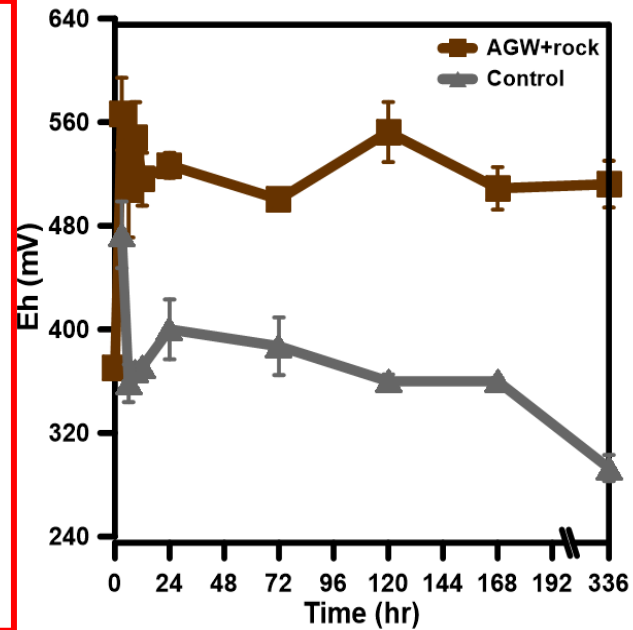
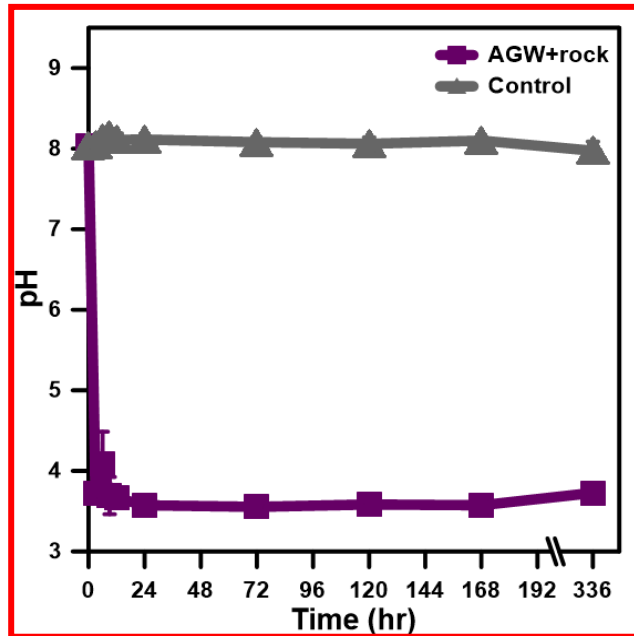
- Sampling time
- for 14 days (3, 6, 9, 12, 24, 72, 120, 168, 336 hr)
- DO & Eh measurements were conducted in a glove box filled with Ar gas



3.2

Results and Discussion – Batch Experiment

< Changes in Geochemical Parameters with Reaction Time >

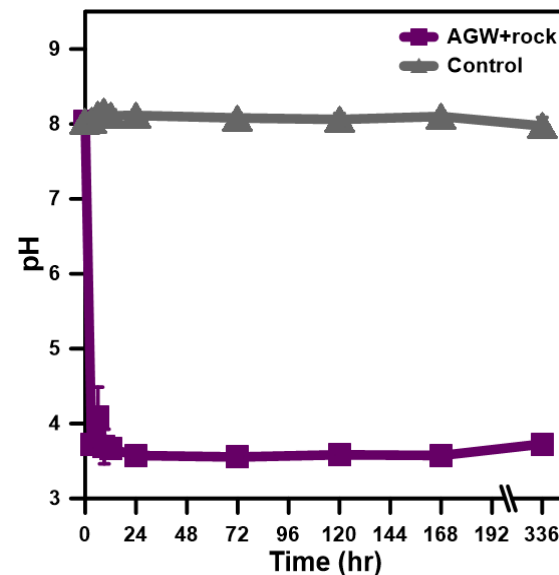
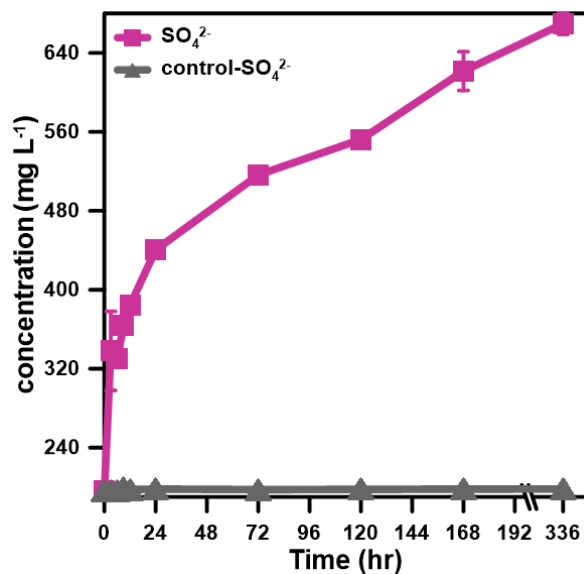
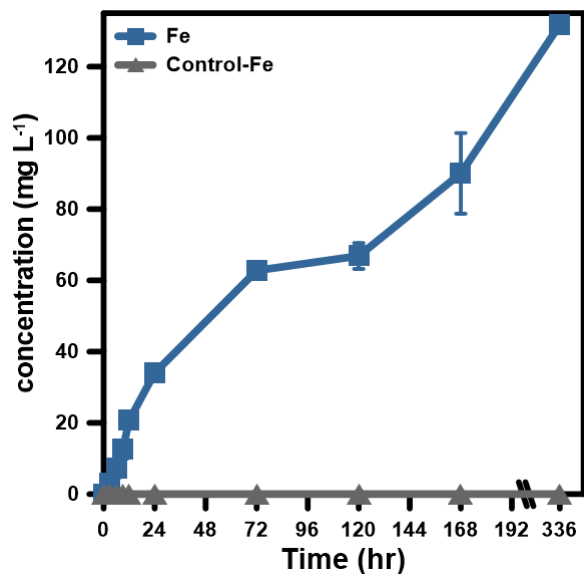


- pH: Decreased to below 4.5 → Due to **no carbonate buffer**
- Eh: Increased to about 500 mV → Inversely correlated to pH
- Alkalinity: Not existed → Because of the **very low pH**

3.2

Results and Discussion – Batch Experiment

< Changes in Fe and SO₄ Concentrations >



❖ Oxidation of iron sulfide

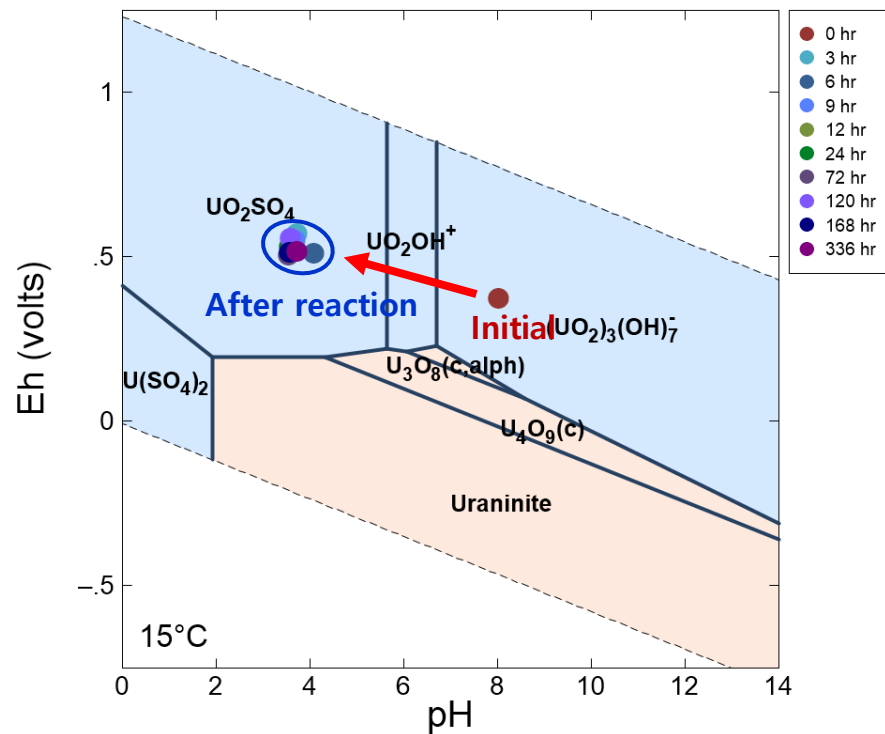
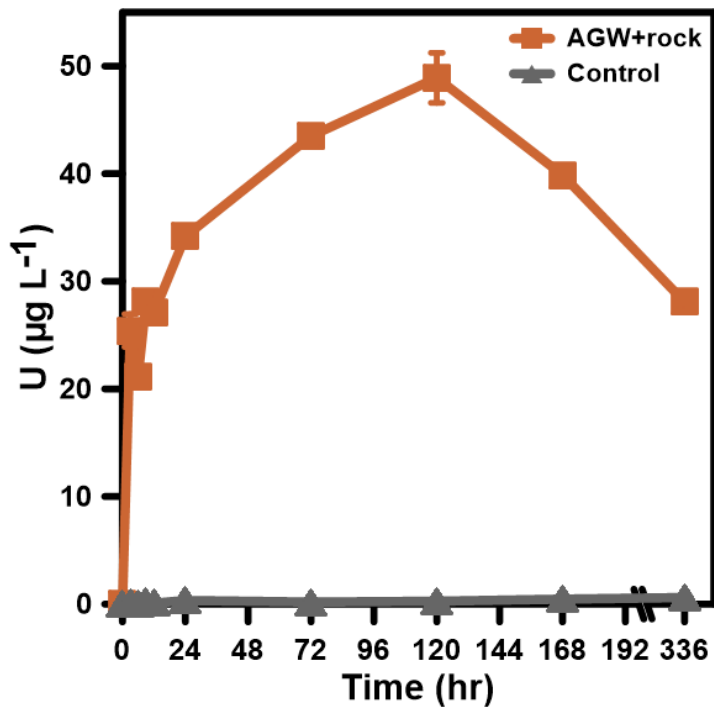
- $2\text{FeS}_2(\text{s}) + 7\text{O}_2(\text{aq}) + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+$
- $\text{Fe}^{2+} + 1/4\text{O}_2(\text{aq}) + \text{H}^+ \rightarrow \text{Fe}^{3+} + 1/2\text{H}_2\text{O}$
- $\text{FeS}_2(\text{s}) + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$

(Amos et al., 2015)

3.2

Results and Discussion – Batch Experiment

< Changes in Uranium Concentrations and Uranium Speciation >



- Increase up to 120 hr → **Dissolution of uraninite & ekanite**
- Decrease after 120 hr → **Adsorption or surface complexation on iron oxide & SiO₂**

- Before reaction: **(UO₂)₃(OH)₇⁻ complex**
- ↓
- After reaction: **UO₂SO₄ complex**

(Read et al., 1991; Sylwester et al., 2000)

3.3 Summary – Batch experiment

-
- **Decrease in pH**
 - Due to the absence of carbonate buffer and production of hydrogen ion by oxidation of iron sulfide
 - Increased uranium concentration
 - **Dissolution of uraninite & ekanite**
 - Decreased uranium concentration
 - **Co-precipitation, adsorption & surface complexation with iron (hydr)oxides** produced by oxidation of iron sulfide
-

- Evaluation of uranium mobility under the chemical condition similar to that in the Okcheon Metamorphic Belt through the water-rock interaction experiment
- Differences were mainly due to the absence of carbonate buffer

- **Evaluation of uranium mobility resulting from water-rock interactions** between uranium-bearing rock and groundwater in the Okcheon Metamorphic Belt
- **Uranium limits its mobility** through **co-precipitation, adsorption** and/or **surface complexation** with iron (hydr)oxides



Establishing a 'natural analogue study' from a hydrogeochemical point of view

Contributing to the safety assessment of the high-level radioactive waste repository



IGC
2024
the 37th International Geological
Congress 2024



IUGS
International Union of Geological Sciences



IGC 2024

The 37th International Geological Congress

Busan, Korea

25-31 August 2024



Contact:
Sung-Wook Jeen
(sjeen@jbnu.ac.kr)

Thank you!