



KANAZAWA
UNIVERSITY

Орог нуурын хүнцэл, ураны бохирдол: Ууршилтын үед
шүлтлэг, давслаг нууранд ураны консерватив хэлбэрийн
хуримтлал үүсэж буйн нотолгоо

Arsenic and uranium contamination in Orog Lake from Valley of the Gobi Lakes, Mongolia: Field evidence of conservative accumulation of U in alkaline closed-basin lake during evaporation

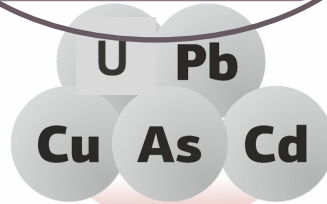
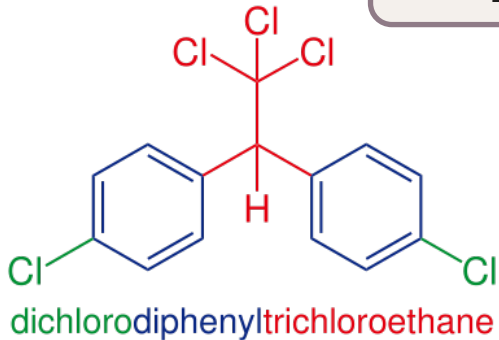
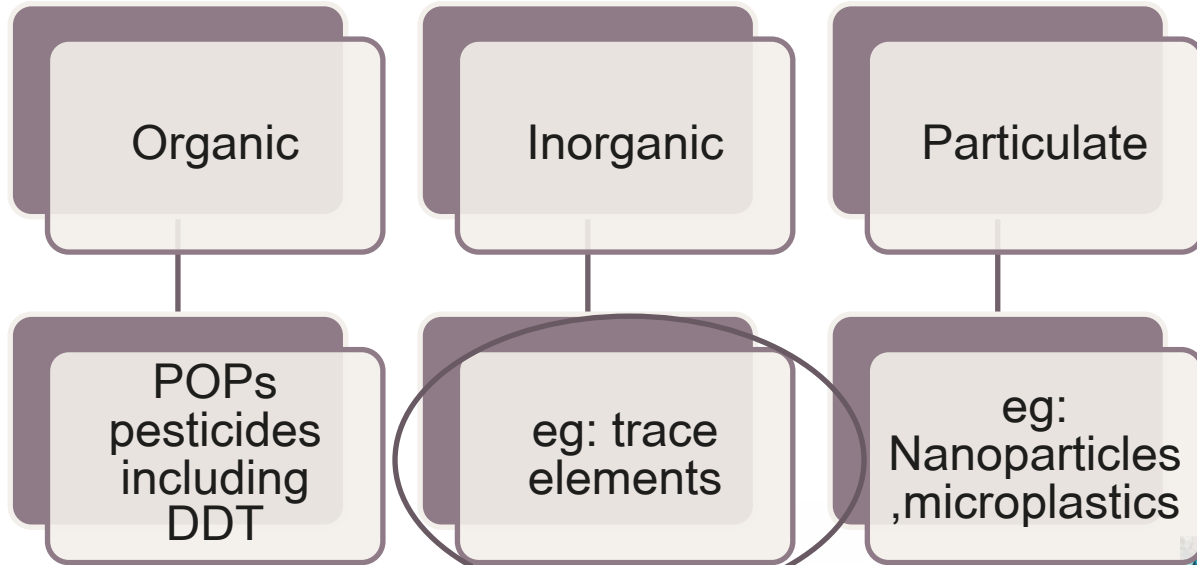
Baasansuren Gankhurel

Chief Supervisor: Keisuke Fukushi

Institute of Natural Science and Technology, Kanazawa University

MPTI/ Open Geoscience seminars 2022.10.06

• Types of pollutants in environment •

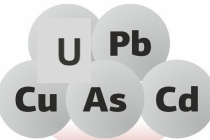


POP= persistent organic pollutants, DDT= Dichlorodiphenyltrichloroethane

• Sources of trace elements •



- Natural / Anthropogenic
- Rock weathering, mining, agriculture, industrial activities. Alloway (1995)



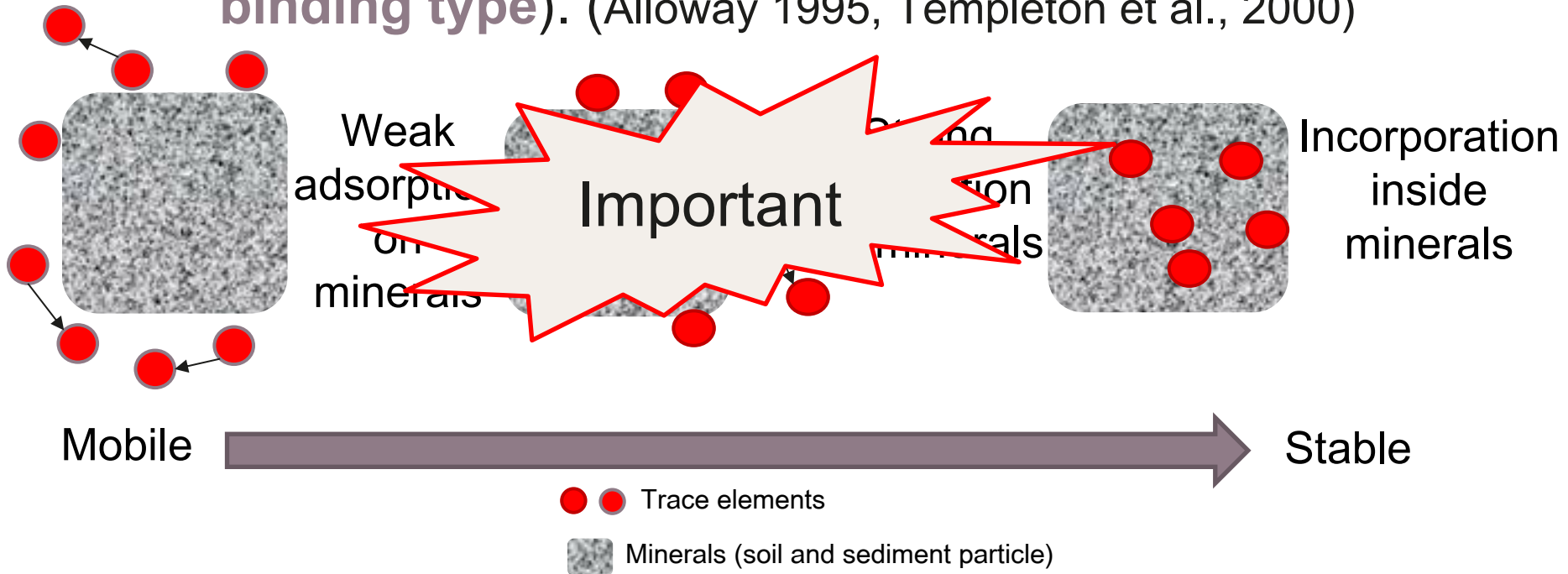
Concentrations of trace elements, mg/kg

		As	Cd	Cr	Cu	Ni	Pb	Zn	Hg
China (72 examined mines)	Mean	195.5	11.0	84.28	211.9	106.6	641.3	1163	3.82
Iran (3 examined mines)	Mean	146.2	1.49		88.40		1002	363.4	3.13
Spain (16 examined mines)	Mean	191.9	6.59	63.20	120.8	28.35	881.8	465.8	52.9
South Korea (70 examined mines)	Mean	70.08	1.00		70.00	22.00	111.1	182.2	1.12

High concentrations of trace elements harmful for environmental and human health

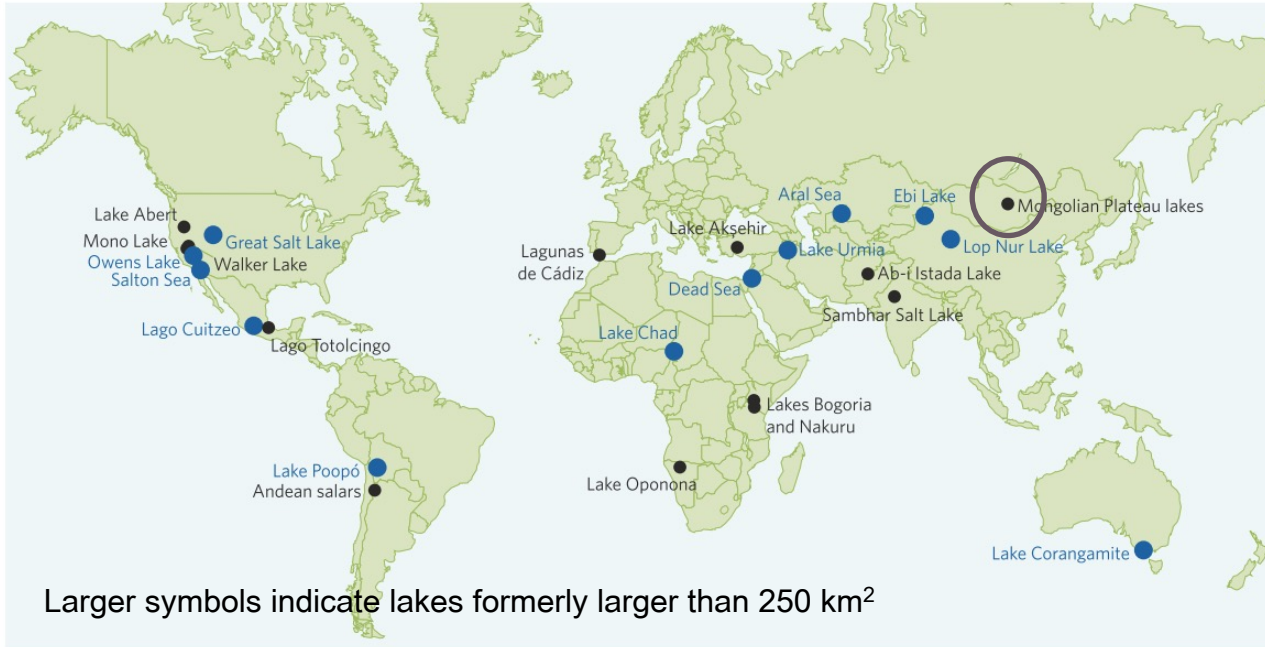
Chemical speciation

Mobility and toxicity of metals depends not only on their concentrations also chemical speciation (**chemical forms and binding type**). (Alloway 1995, Templeton et al., 2000)



Introduction

Mobility and solubility of trace elements in Saline lake of arid area

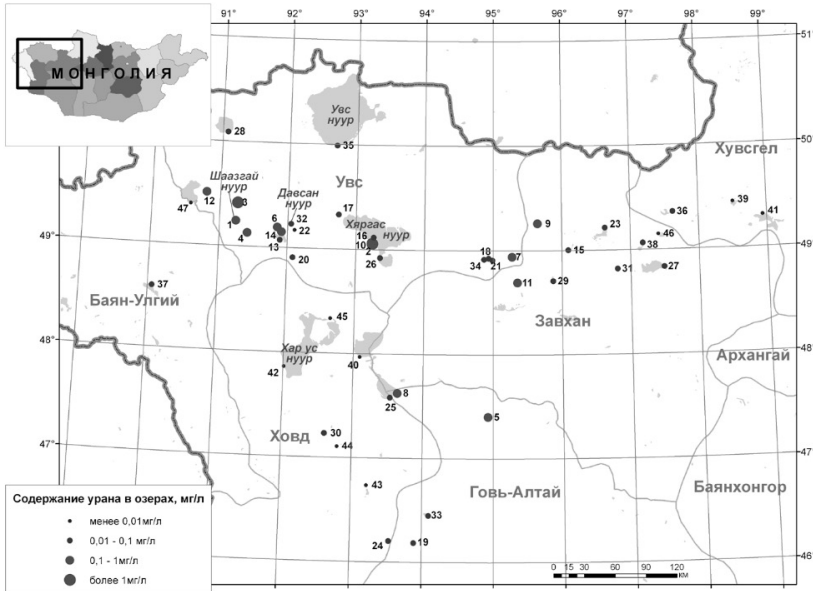


- 23% of the area of all lakes
- Located mostly in arid area

Wurtsbaugh et al.,
2017

INTRODUCTION

U concentration in studied lakes

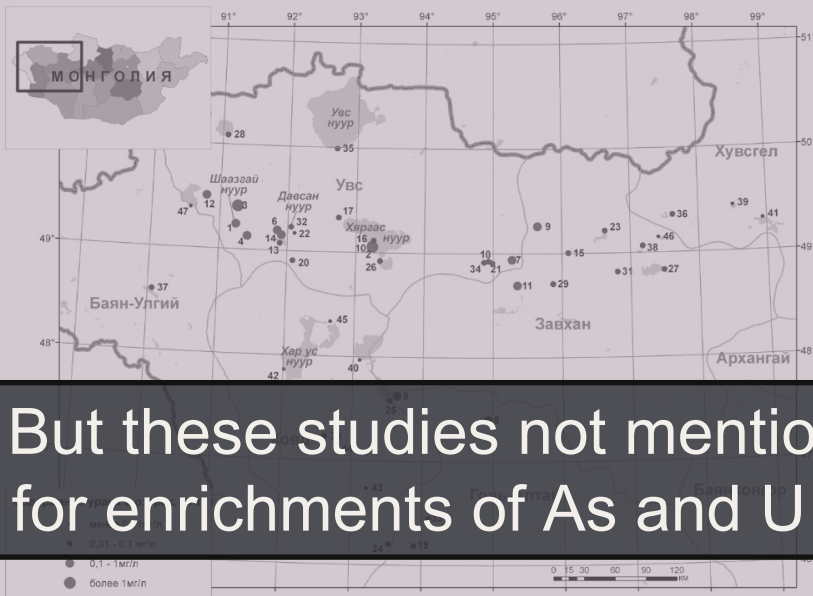


Ariunbileg et al., 2013

- Russian scientists studied saline lake in western and northwestern of Mongolia
- High concentrations of arsenic, uranium and several trace elements were found (Isupov et al., 2014, 2015, 2016, Shvarstev et al., 2014, Ariunbileg et al., 2013)
- Correlated higher degree of evaporation

INTRODUCTION

U concentration in studied lakes



But these studies not mentioned chemical reactions responsible for enrichments of As and U (is it adsorbed on minerals or not?)

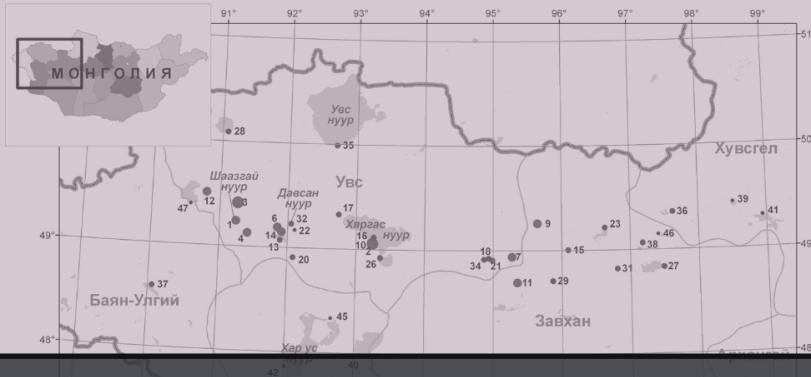
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Correlated higher degree of evaporation

Ariunbileg et al., 2013

INTRODUCTION

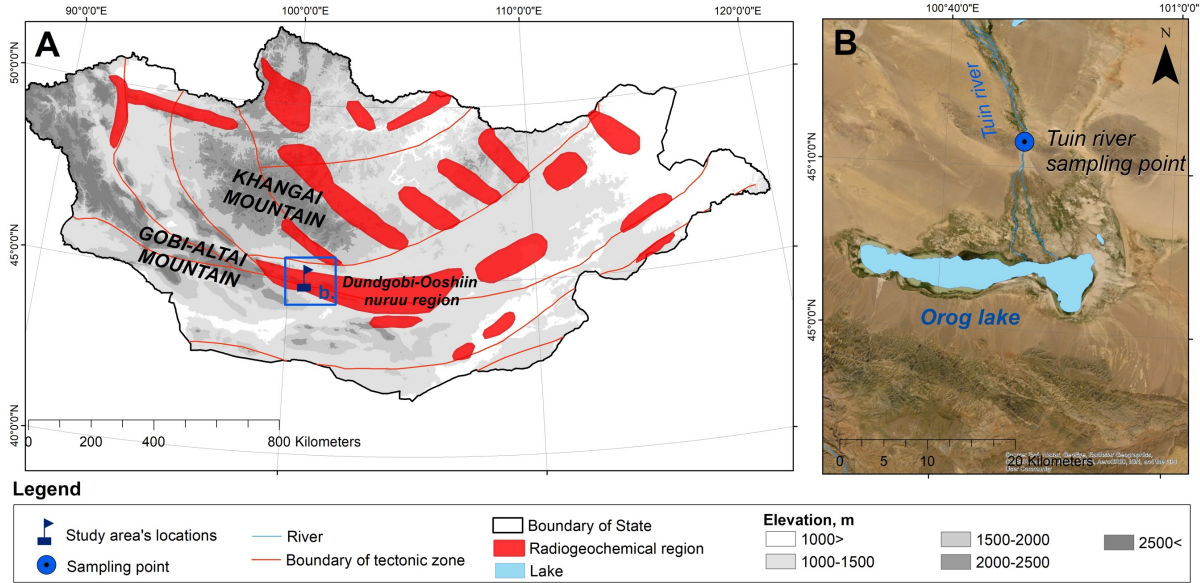
U concentration in studied lakes



- Russian scientists studied saline lake in western and northwestern of Mongolia
- High concentrations of arsenic, uranium and several trace elements

The purpose of this study is quantitatively understanding the dynamic chemical behaviors of As and U in alkaline saline lakes during evaporation based on 5-year monitoring of water chemistry of saline lake

Saline lakes- Valley of the Gobi lakes

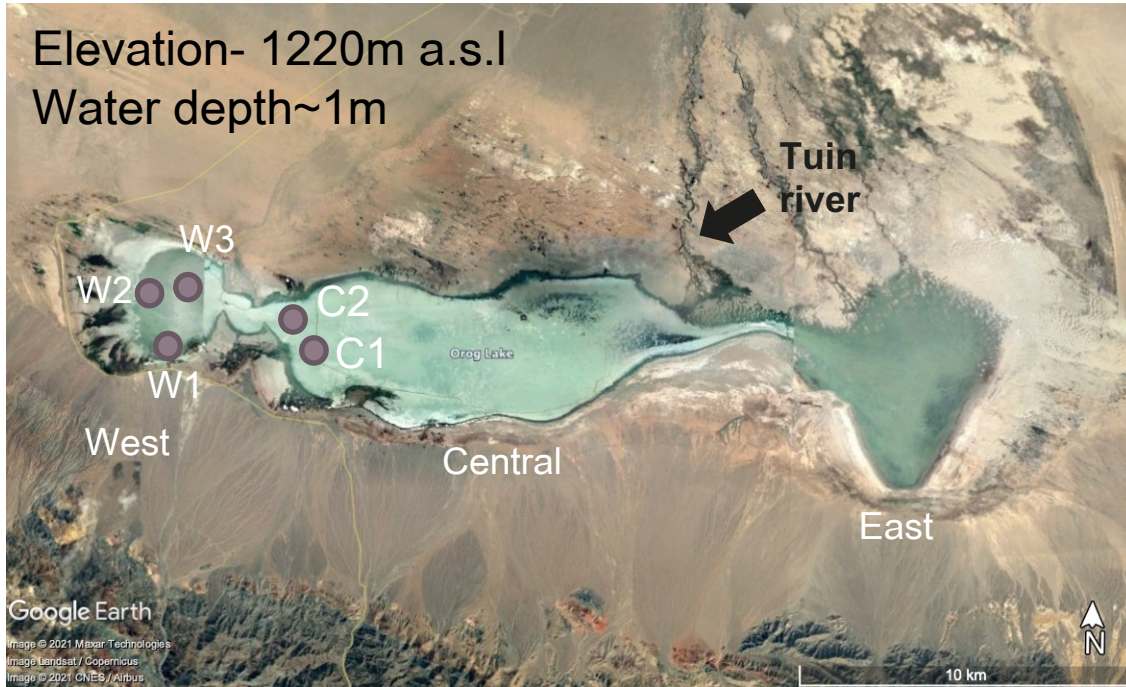


Orog lake -> the radiogeochemical region of Dundgobi-Ooshiin nuruu which has potential provinces of U-bearing rocks.

“Rock” -> U 8-16 mg/kg

Higher than the average in the world. Ariunbileg et al., 2020

Orog lake



2015 August 2016 August
2018 August 2020 July
and September- **C1**

2018 Aug- **C2**
2017 Oct- **W1**
2018 Aug - **W2**
2018 Aug - **W3**

**Orog lake- no outflow river, inflow- Tuin river
Lake (2015-2020) waters collected, sediments in 2018 collected**

MATERIALS AND METHODS

- Water and sediment samples (2018, freeze dried, sieved <2mm)

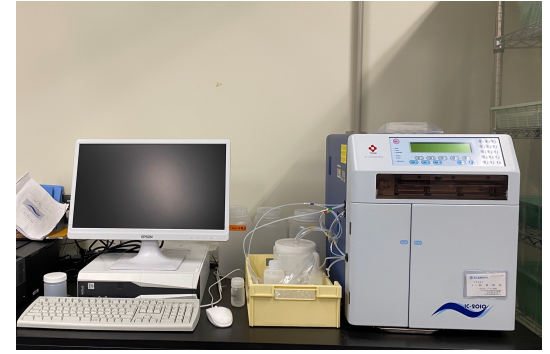


Water and sediment sampling

On site measurement (pH, DO, ORP, EC, alkalinity, and temperature)



HPLC (8020series, Tosoh)



Ion chromatography (IC2010, Tosoh)



ICP-OES (Varian 710- ES)




ICP-MS (iCAP RQ)

Laboratory measurement (major anions, cations, and trace elements) by HPLC, Ion chromatography, ICP-MS, ICP-OES

• MATERIALS AND METHODS •

- 6 step sequential extraction procedure (Orog **W2**,W3,C1)

Extraction steps	Reagent/ concentration/ pH	Soil phase	Mobile
1	MgCl_2 (1M)	Exchangeable, F1	
2	$\text{CH}_3\text{COONa} \times 3\text{H}_2\text{O}$ 1 mol l^{-1} , pH 5	Carbonates, F2	
3	$\text{C}_2\text{H}_2\text{O}_4$ (about 10 g / L) + $\text{C}_2\text{H}_8\text{N}_2\text{O}_4$ (16.1 g / L), pH3	Iron and manganese oxides (amorphous), F3	
4	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ (0.3 mol l^{-1}), NaHCO_3 (0.2 mol l^{-1}), $\text{Na}_2\text{S}_2\text{O}_4$ HCl, pH6.7	Reducible (e.g. iron and manganese oxides), F4	
5	H_2O_2 (8.8 mol l^{-1}) + $\text{CH}_3\text{COONH}_4$ (1 mol l^{-1}), pH2	Oxidizable (e.g. organic matter and sulfides), F5	
6	HNO_3 60% + HF 48%+ HCl 36%	Residual (non-silicate bound metals), F6	

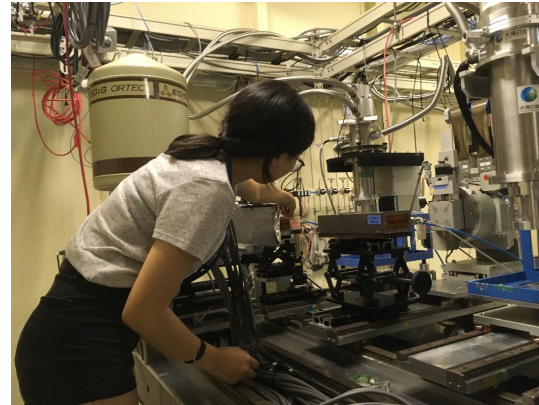
MATERIALS AND METHODS

- XRD and XAFS (Orog **W2**,W3,C1)

As and Fe

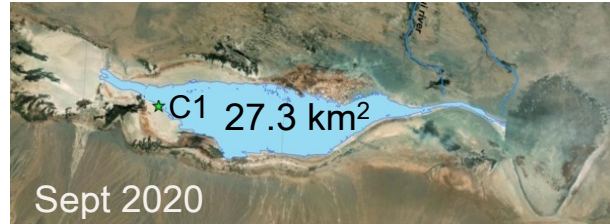
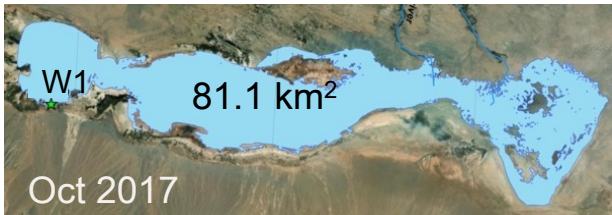
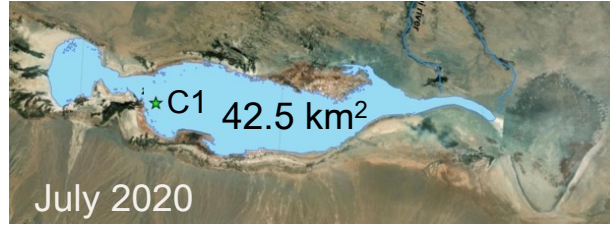
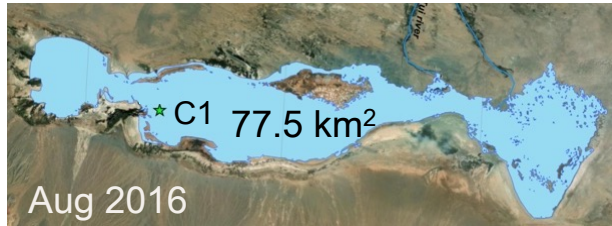
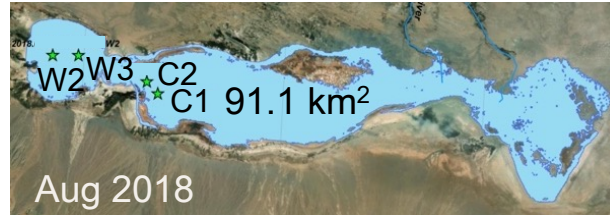
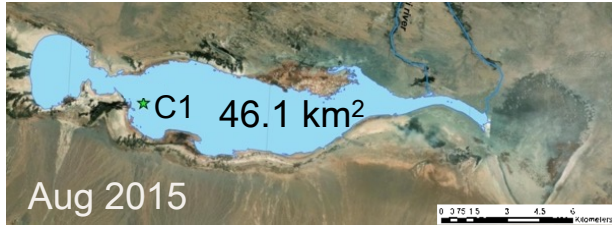


Mineralogical properties-
XRD (Ultima IV, Rigaku)



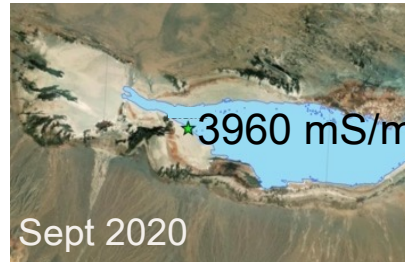
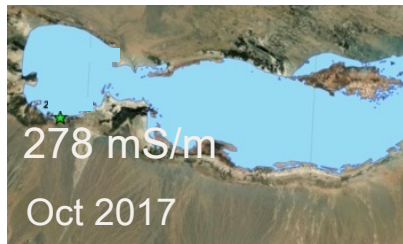
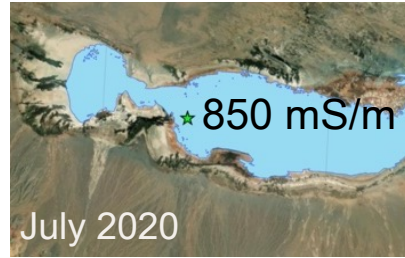
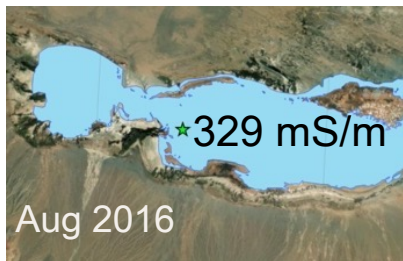
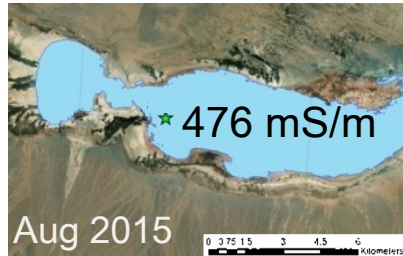
BL01B1 at SPring 8 (Hyogo, Japan)
BL-12C beamline of the Photon Factory
(Tsukuba, Japan)

Lake surface water area changes



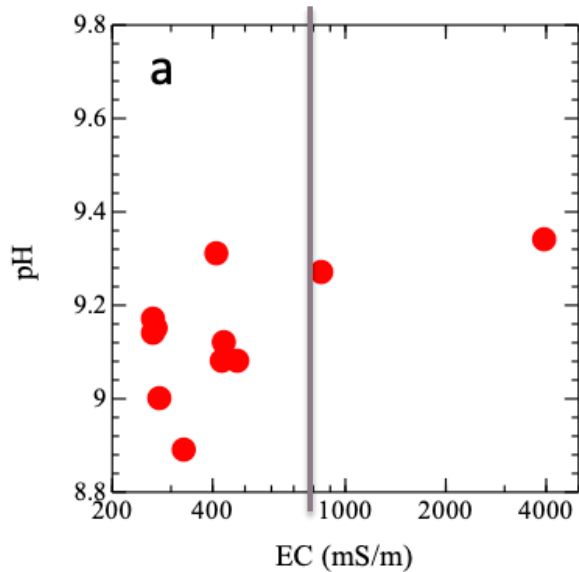
- Lake area differed throughout the sampling years
- Temporal: Highest in Aug 2018
- Lowest in 2020 September

Electric conductivity



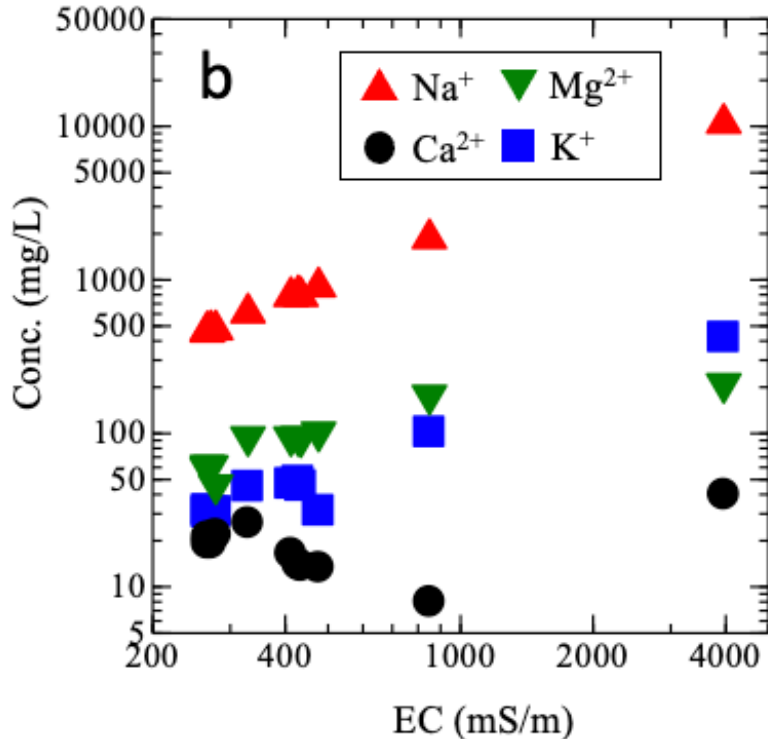
- EC is indicator of the concentrations of major ionic species in the solution -> indicator of evaporation
- Varied on sample locations and period
- When the lake water area has low -> value of EC is high (contrast)

pH of lake water



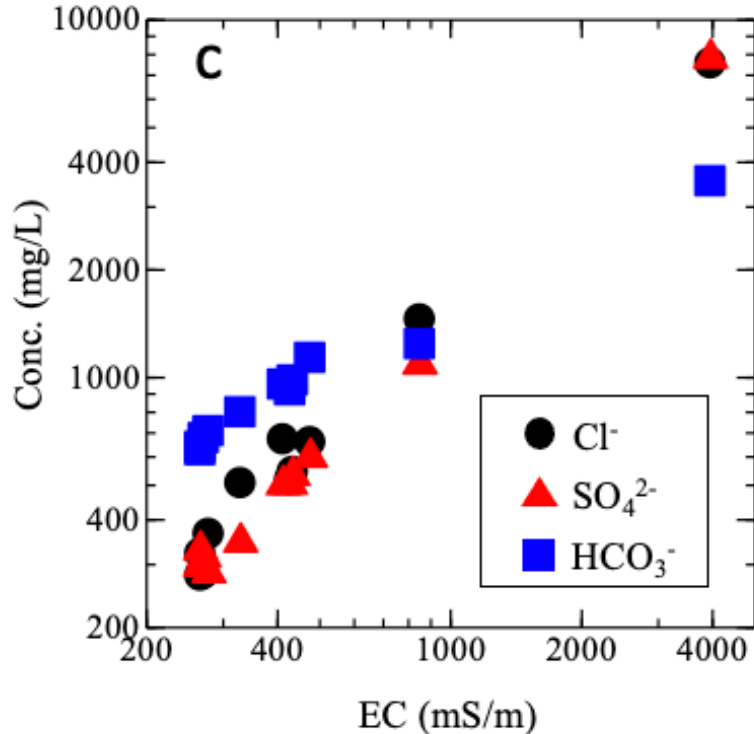
- pH → alkaline and slightly varied from 8.9 to 9.3
- The highest → at site C1 in Sep 2020
- The lowest → at site C1 in Aug 2016
- The pH of lake water under higher EC (>800 mS/m) was slightly higher than that those under lower EC (<800 mS/m)

Major cations



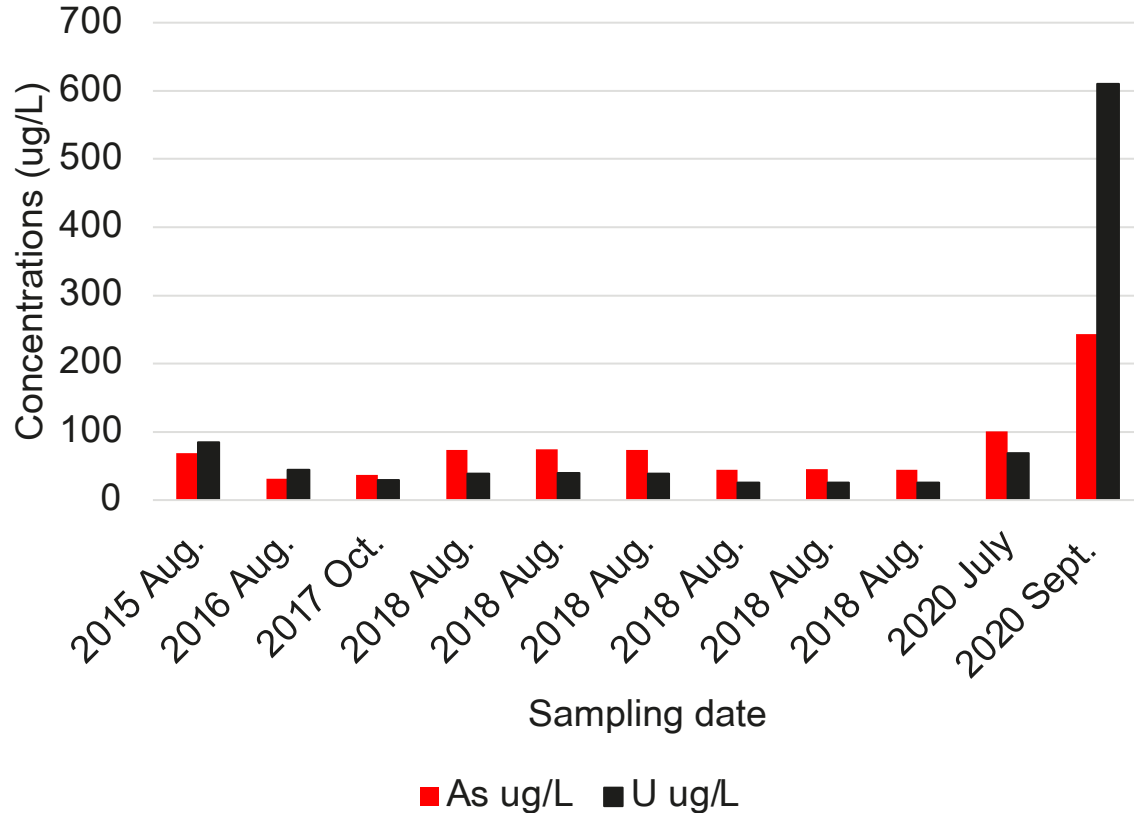
- Na⁺ predominant 458 to 10500 mg/L
- K⁺ 30.6 to 423 mg/L, Mg²⁺ 46 to 211 mg/L, Ca²⁺ lowest 8 to 40 mg/L
- Temporal: Highest in 2020 September
- Na⁺, K⁺ were linearly correlated with EC
- The Mg²⁺ concentration linearly increased with EC under EC < 800 mS/m but took similar level at the higher EC condition
- Ca²⁺ concentration decreased with the increase of EC under EC < 1000 mS/m but increased at the highest EC

Major anions



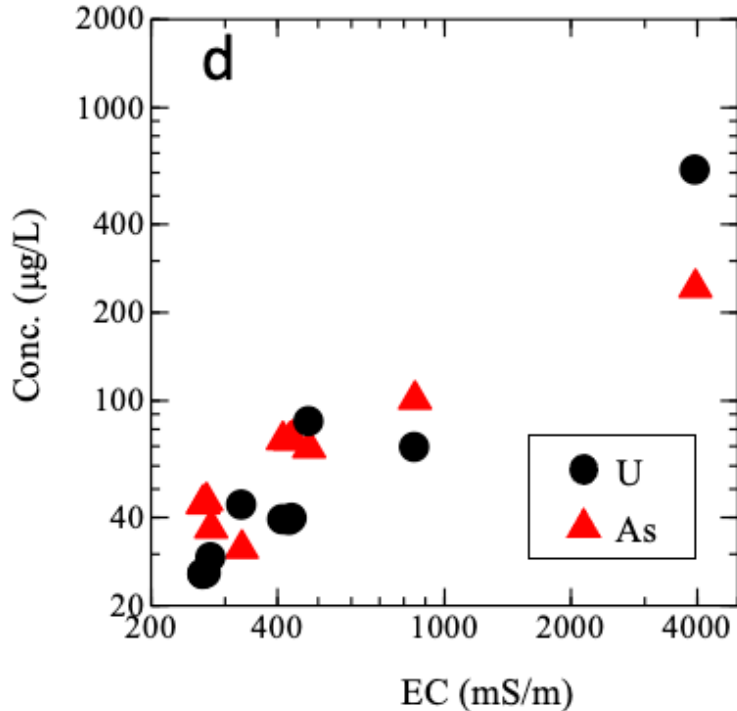
- Cl⁻, SO₄²⁻ highest
279 to 7552 mg/L, 283 to 7813 mg/L
- HCO₃⁻ 630 to 3500 mg/L
- Temporal: Highest in 2020
September
- Linearly correlated with EC
- HCO₃⁻ concentrations at highest
EC was lower than other anions

As and U in Orog lake



- U 25.5 to 610.6 ug/L
- As 31.3 to 243 ug/L
- Highest concentration of As and U -> lowest lake water surface area

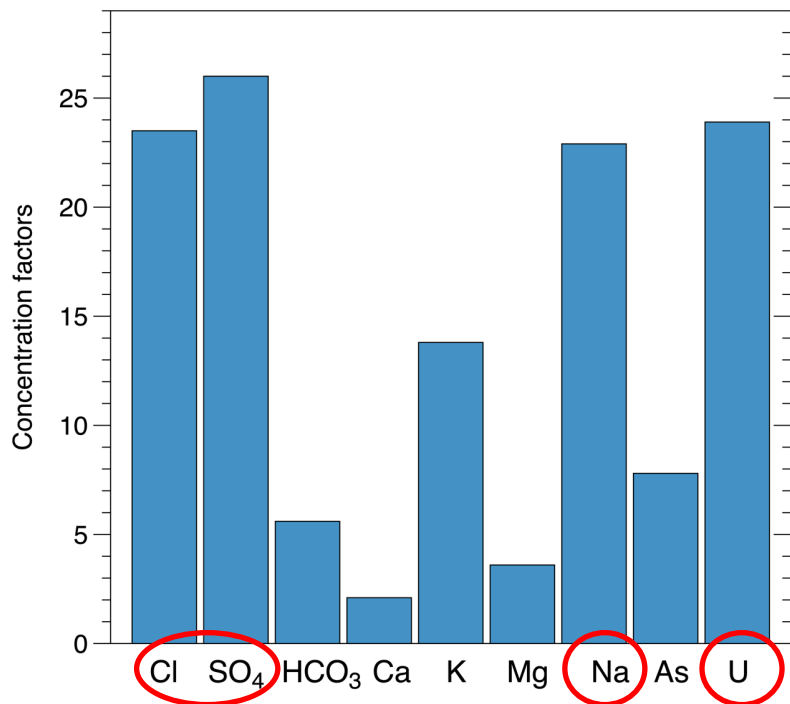
As and U in Orog lake



- U correlated with EC
- As were comparable to those U under lower EC
- As concentrations at highest EC was lower than U

Concentration factor

$$\text{Concentration factor} = \frac{\text{concentrations in the lake water Sep 2020 (lowest lake level)}}{\text{concentrations in the lake water Aug 2018 (highest lake level)}}$$

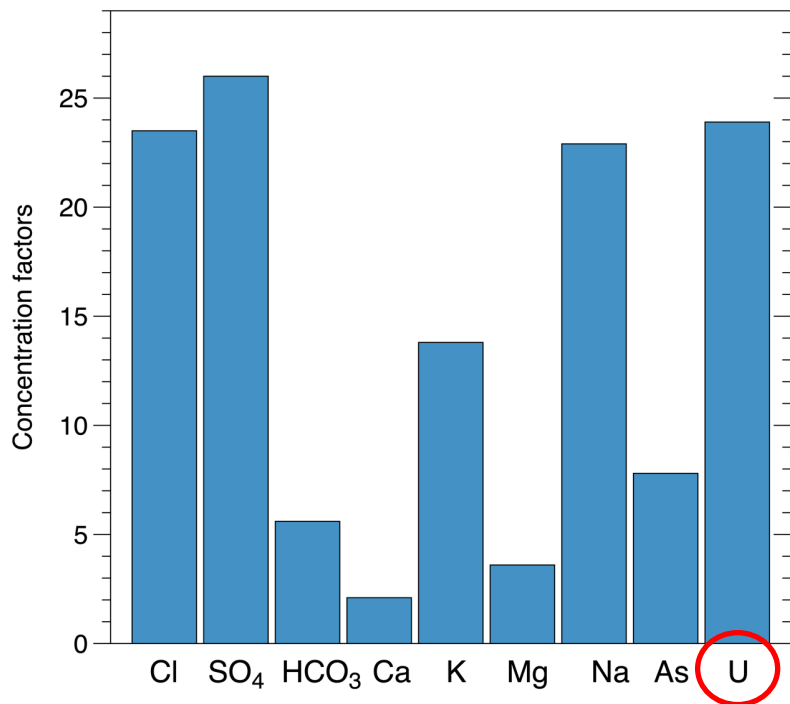


- The highest concentration factor → Cl⁻, SO₄²⁻, Na⁺, and U = conservatively
- The lowest → Ca²⁺

Cl⁻, Na⁺ in water is well known that do not take part in the chemical reaction SO₄²⁻ also behaves conservatively under neutral to high pH (Orog pH~9) (Fukushi et al., 2013, Berger et al., 2000)

Concentration factor

$$\text{Concentration factor} = \frac{\text{concentrations in the lake water Sep 2020 (lowest lake level)}}{\text{concentrations in the lake water Aug 2018 (highest lake level)}}$$



High concentration factor of U = conservatively

Conservative ions in lake water: Cl⁻, SO₄²⁻, Na⁺

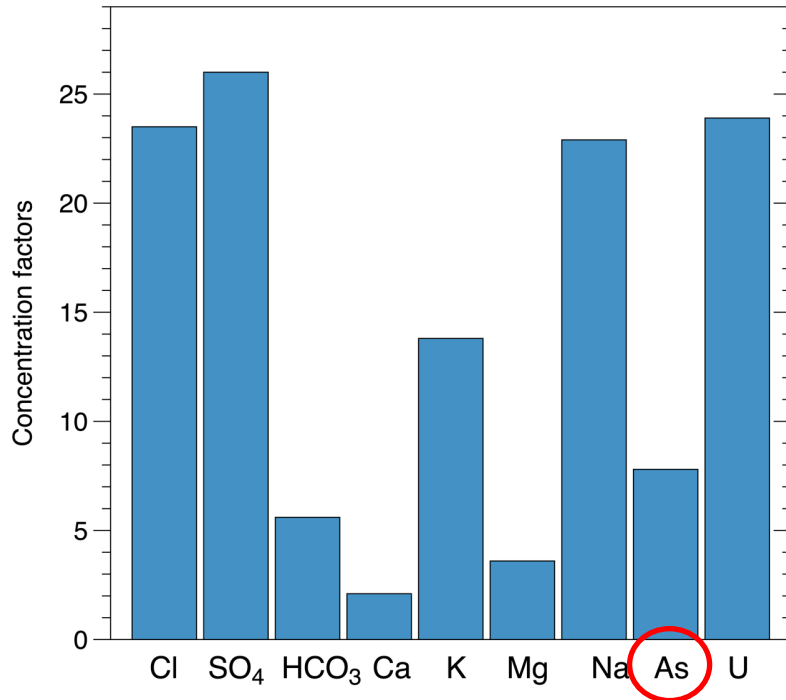
But trace elements are not accumulates like conservative ions in lake water

Not common

This study provide the field evidence of U conservative accumulation in lake water

Concentration factor

Concentration factor = $\frac{\text{concentrations in the lake water Sep 2020 (lowest lake level)}}{\text{concentrations in the lake water Aug 2018 (highest lake level)}}$

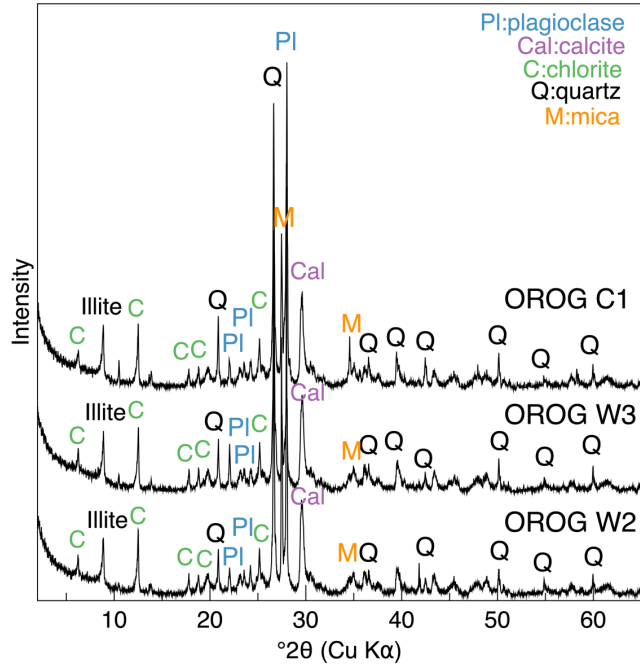


- The highest concentration factor -> Cl⁻, SO₄²⁻, Na⁺, and U = conservatively
- The lowest -> Ca²⁺
- As was lower than U

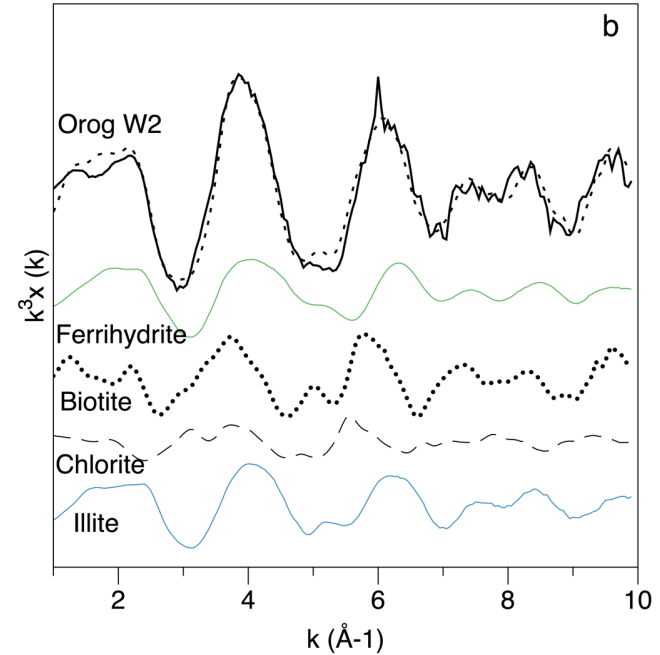
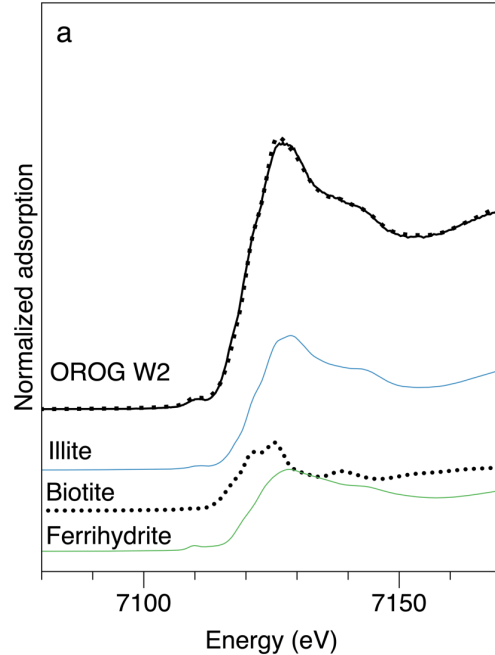
U behaves conservatively in lake water
In contrast to that, As in lake water
removed during evaporation

Results of sediment

Mineralogical properties



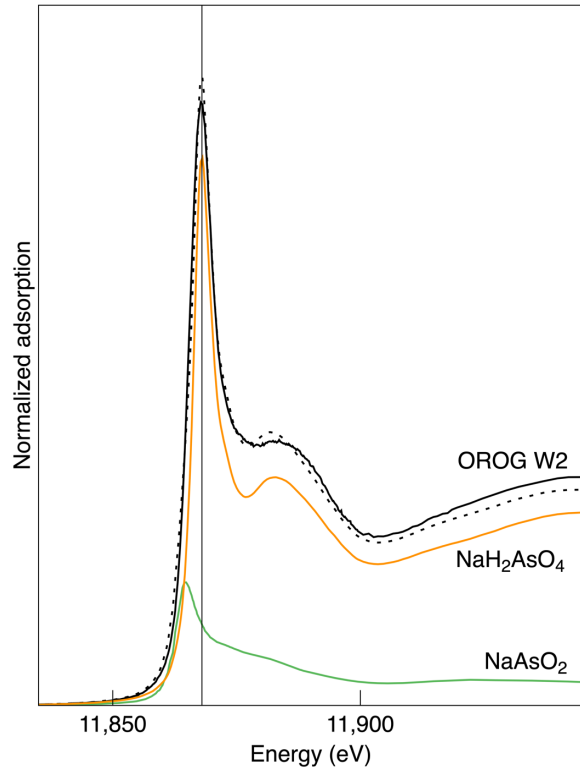
EXAFS results of Fe in sediment



Authigenic minerals (carbonates)

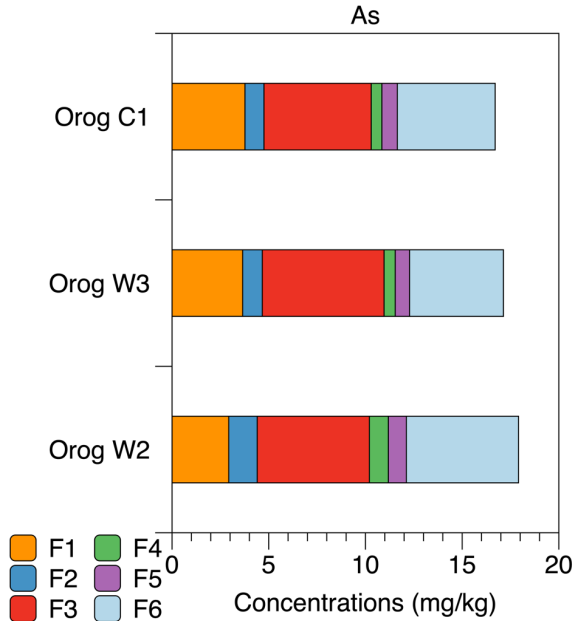
- Ferrihydrite, Biotite and illite
- Mica in XRD → biotite and illite

XANES results of As in sediment



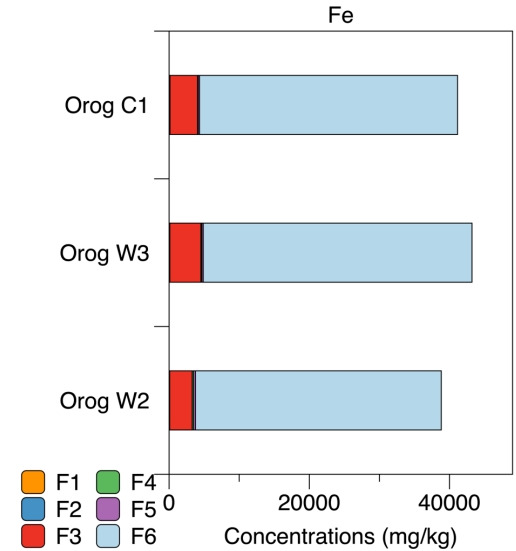
- As in Orog sediment (2018) – pentavalent oxidation state As (V)

Results and Discussion



Samples	As on ferrihydrite (mg/kg)
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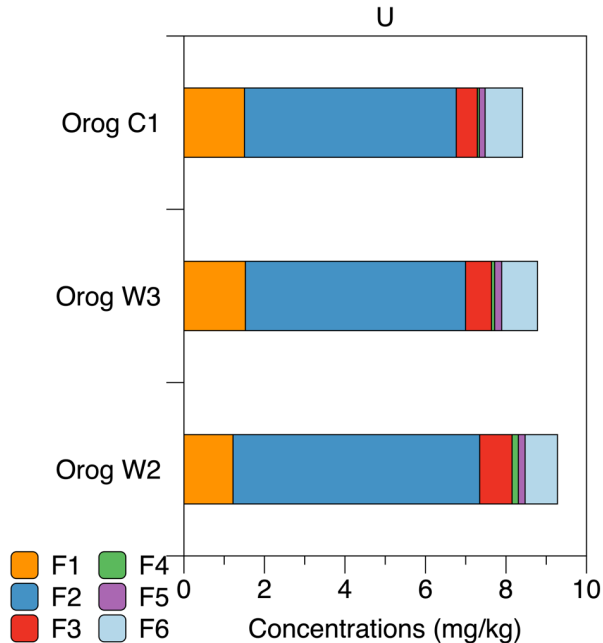
W2	1240.2
W3	973.6
C1	965.2



➤ **Ferrihydrite** is the main host of As

Results suggests that the significant amount of **As can be removed** from the lake water during evaporation

Results and Discussion

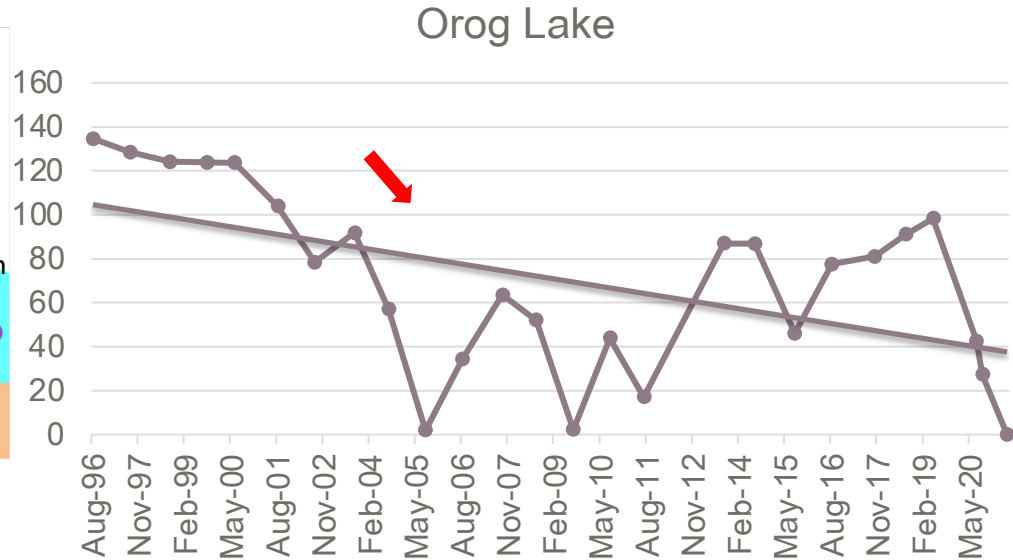
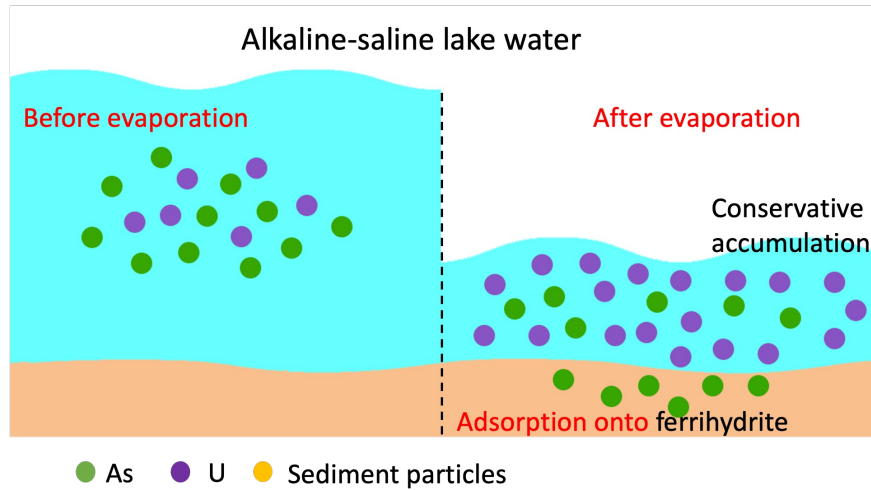


Samples	U on ferrihydrite (mg/kg)	U in calcite (mg/kg)
W2	172	43.0
W3	99.5	41.0
C1	91.2	42.8

- U removal by **calcite and ferrihydrite in the sediment almost negligible** compared to **U accumulation in lake water during evaporation**

Results suggests that **U accumulates conservatively** in lake water

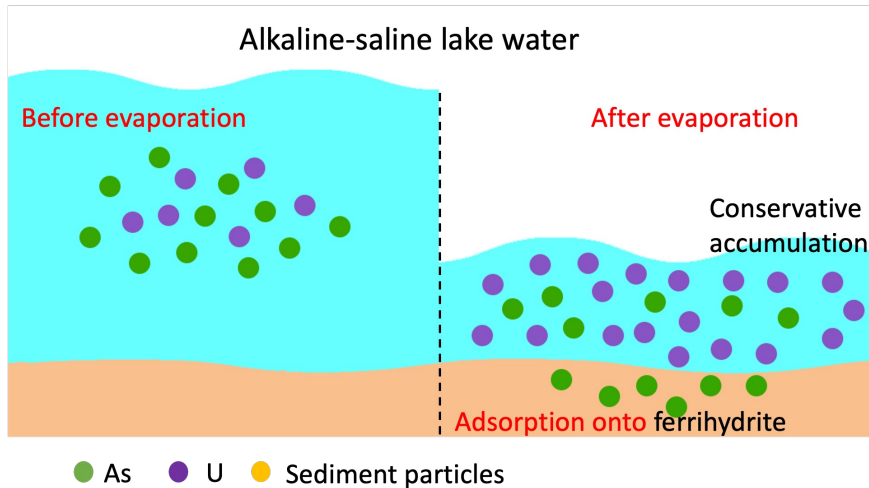
Environmental implication



- **As**-> adsorbed onto ferrihydrite
- **U**-> in water->in salt-> easily washed by water or transport by wind
- It is possible to transport into the environment by water or wind

Tuvshin 2020

Environmental implication



Tuvshin 2020

- **As**-> adsorbed onto ferrihydrite
- **U**-> in water-> soluble salt-> easily washed by water or transport by wind
- It is possible to transport into the environment by water or wind

CONCLUSION

- Major species, including Na^+ , Cl^- , and SO_4^{2-} , were accumulated in lake water conservatively.
- As in lake water can be removed from water during evaporation. The primary host of As (V) is the ferrihydrite in sediments.
- Uranium behaves conservatively during evaporation like Na^+ and Cl^- .
- Carbonate minerals (calcite) and low crystalline iron oxides (ferrihydrite) do not play a role in the effective sink of U.
- U is more soluble than As, and it can be transported into the environment by water or wind.

THANK YOU FOR YOUR ATTENTION

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Arsenic and uranium contamination of Orog Lake in the Valley of Gobi Lakes, Mongolia: Field evidence of conservative accumulation of U in an alkaline, closed-basin lake during evaporation

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