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Chemical Forms of Arsenic and Selenium Leached from Excavated Mudstones

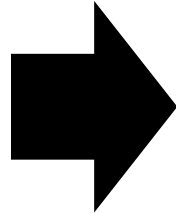
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tunnel construction



excavated rocks

heavy metals
(arsenic (As),
selenium (Se), etc.)

- ◆ **Heavy metals** and metalloids leach from excavated sedimentary rocks of marine origin.
 - ➔ Risk of contamination to the surrounding **soil** and **groundwater**
- ◆ Batch leaching and consecutive batch leaching experiments were conducted to evaluate the speciation of **arsenic (As)** and **selenium (Se)**.
 - ➔ The amount leached and **chemical forms** of **As** and **Se** were of primary concern.

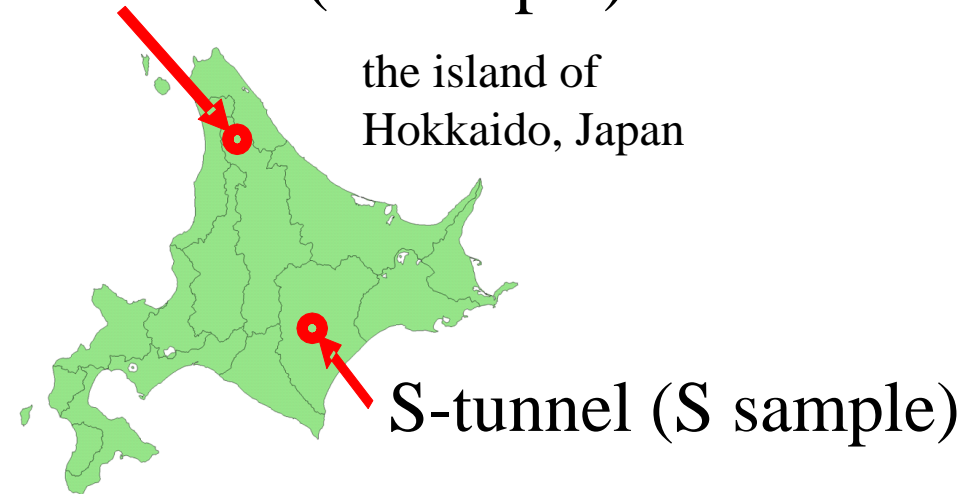
- ◆ Two mudstone samples (S-tunnel (S sample), O-tunnel (O sample)) were collected from different tunnel construction projects in the island of Hokkaido, Japan.

They were dried and crushed, and particles < 2 mm in diameter were used for experiment.

Results of XRF analysis

	S sample	O sample
SiO ₂ (wt.%)	61.8	33.7
TiO ₂ (wt.%)	0.67	0.44
Al ₂ O ₃ (wt.%)	15.90	9.07
Fe ₂ O ₃ (wt.%)	6.03	3.9
MnO (wt.%)	0.06	0.06
MgO (wt.%)	1.95	0.85
CaO (wt.%)	2.49	1.95
Na ₂ O (wt.%)	2.51	1.08
K ₂ O (wt.%)	2.92	2.72
P ₂ O ₅ (wt.%)	0.18	0.04
S (wt.%)	0.38	0.23
As (mg/kg)	10.0	21.3
Se (mg/kg)	0.59	0.40
LOI (wt.%)	5.09	8.19

O-tunnel (O sample)



Results of XRD analysis

	Quartz	Feldspar	Mica	Chlorite	Calcite	Kaolinite	Smectite	Pyrite
S sample	+++	++	+	+	+		+	-
O sample	+++	++	+			+		-

* +++: Strong, ++: Medium, +: Weak, -: Trace

◆ Batch leaching experiments



crushed sample



deionized water



120 rpm
shaking time:
0.5, 2, 6, 24 h



filtration after measurements
of temperature, pH, EC and
ORP



sample for
measurement

conducted in triplicates to calculate standard deviations and evaluate the statistical significance

◆ Consecutive batch leaching experiments

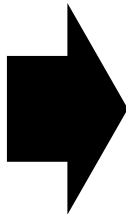
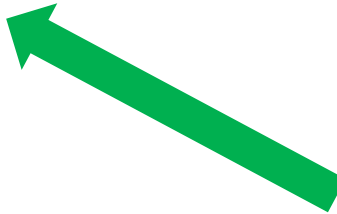
Crushed sample and deionized water were mixed in an erlenmeyer flask in the solid-liquid ratios of 1:5 and 1:10, and filter the solution with 0.45 μm membrane filters after 24 hours of shaking at 120 rpm



deionized water



residual sample

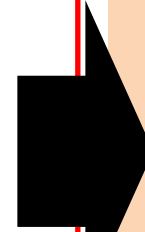


120 rpm
shaking
time 24 h



sample for
measurements

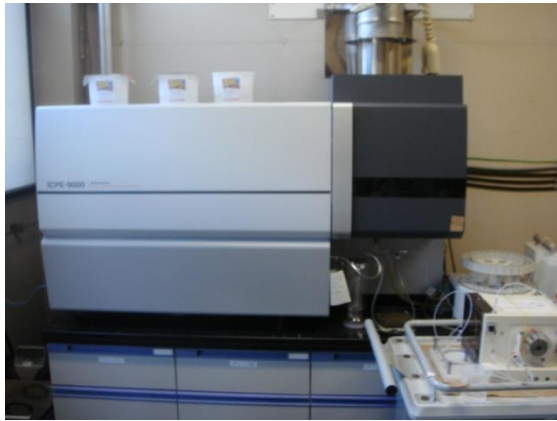
filtration with 0.45 μm
membrane filters



◆ repeat 6 times at mixing intervals of 24, 48, 72, 96, 120, 144 h for each solid-liquid ratio

◆ Measurements of major ions and trace elements in each filtrate

◆ Quantitative analysis of chemical constituents



ICP-AES

◆ hydride generation method ... Se(IV)



ICP-MS

◆ As(total), As(III),
Se(total)

- ◆ Analysis of As and Se with different chemical forms

- ◆ As and Se have different chemical forms (As(III) or As(V), Se(IV) or Se(VI)).

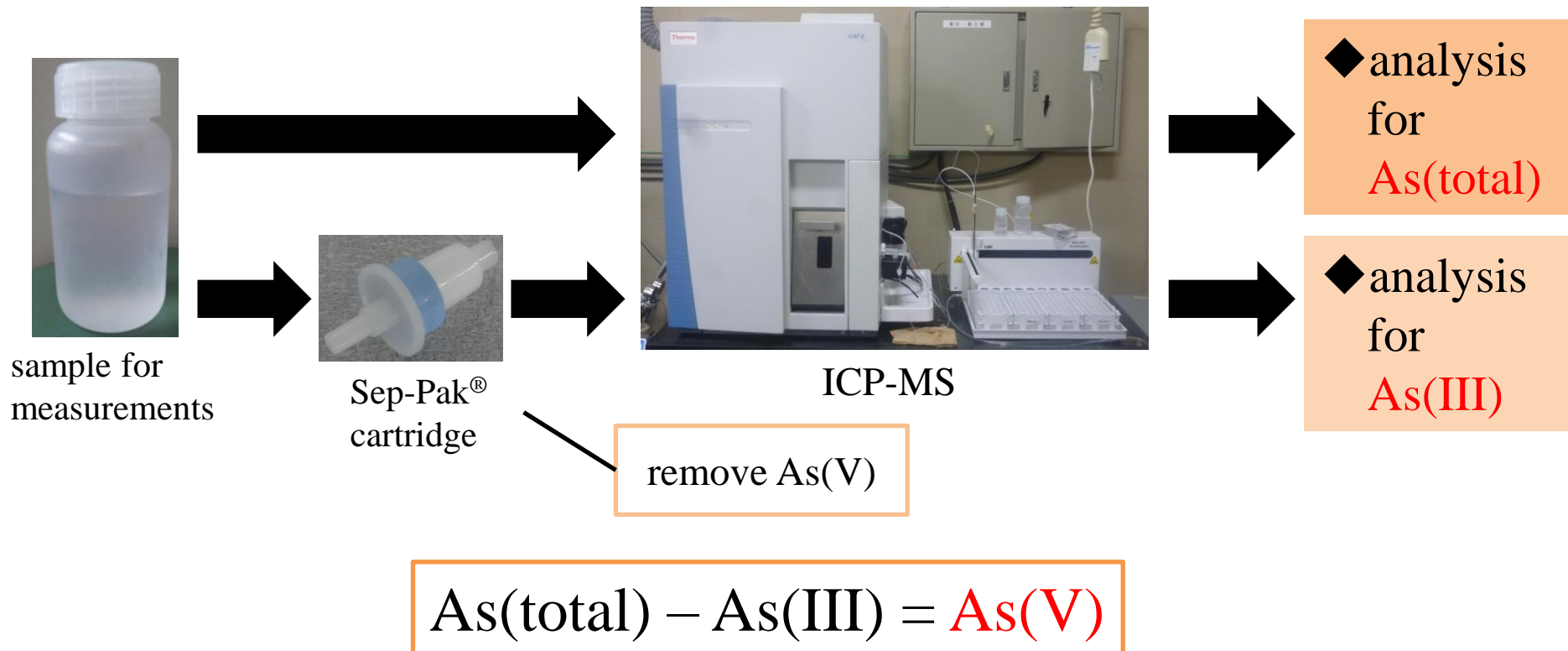
- ◆ Leachability and mobility are different depending on the chemical forms.

- ◆ Toxicity is also different.



Analysis of each chemical form is important.

◆ Analysis of each chemical form (As)



◆ Analysis of each chemical form (Se)



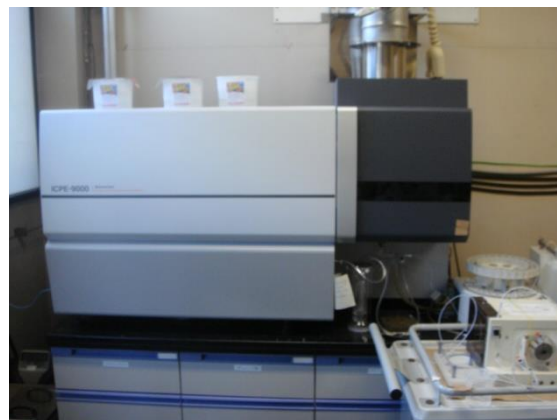
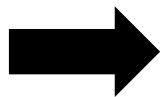
sample for measurements



ICP-MS



◆ analysis for **Se(total)**



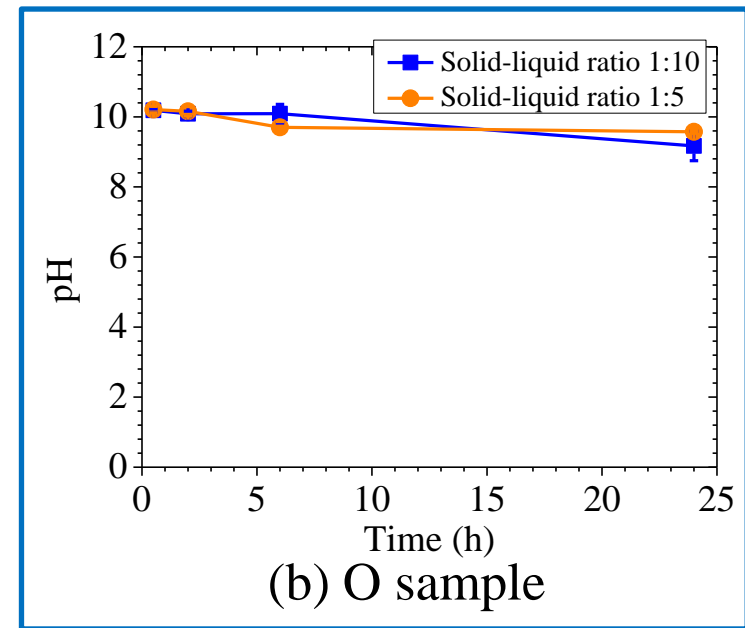
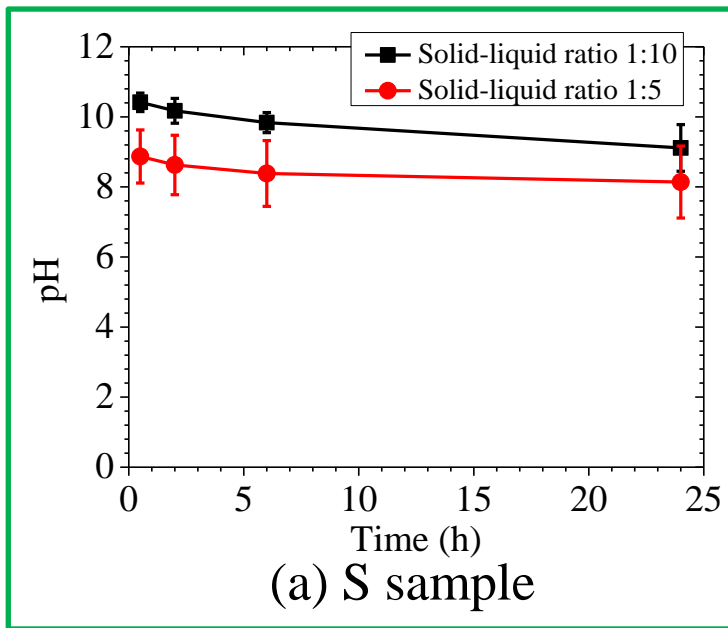
ICP-AES (hydride generation method)



◆ analysis for **Se(IV)**
(Se(VI) is not detected)

$$\text{Se(total)} - \text{Se(IV)} = \text{Se(VI)}$$

◆ Evolution of leachate pH (batch leaching experiments)



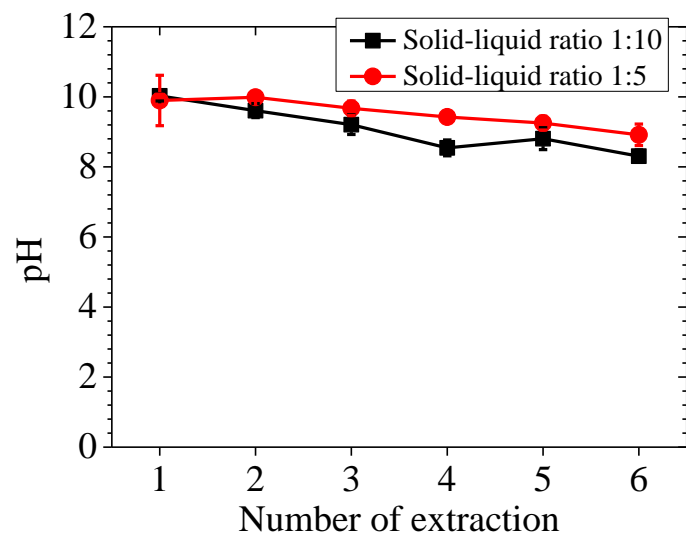
pH change with time in the batch leaching experiments. Each plot and error bar are average and standard deviation based on the values that we conducted three times, respectively.

- The pH decreased with the mixing time in both two solid-liquid ratios.
- The pH values were higher at 1:10 than those at 1:5 during the first 6 hours of mixing, but were nearly the same after 24h.

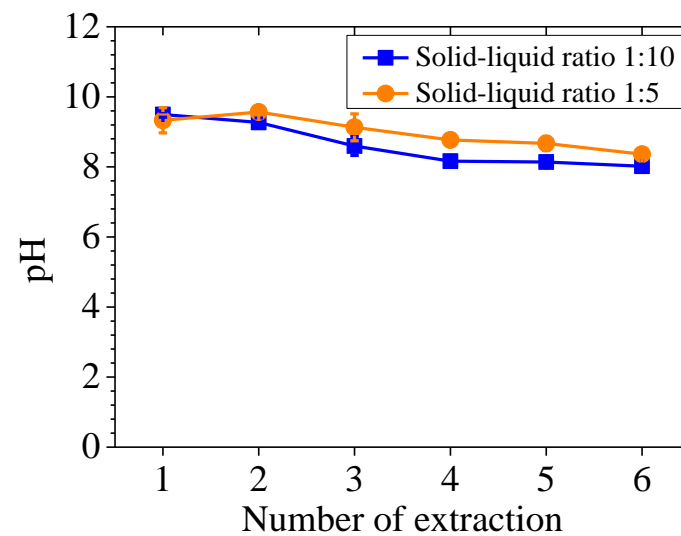
- The leachate pH was nearly constant from 0.5 to 24 h.

- Although both samples generated leachates with alkaline pH, those of S sample (8.1 - 10.3) were slightly lower than those of O sample (9.2 - 10.3).

◆ Evolution of leachate pH (consecutive batch leaching experiments)



(a) S sample



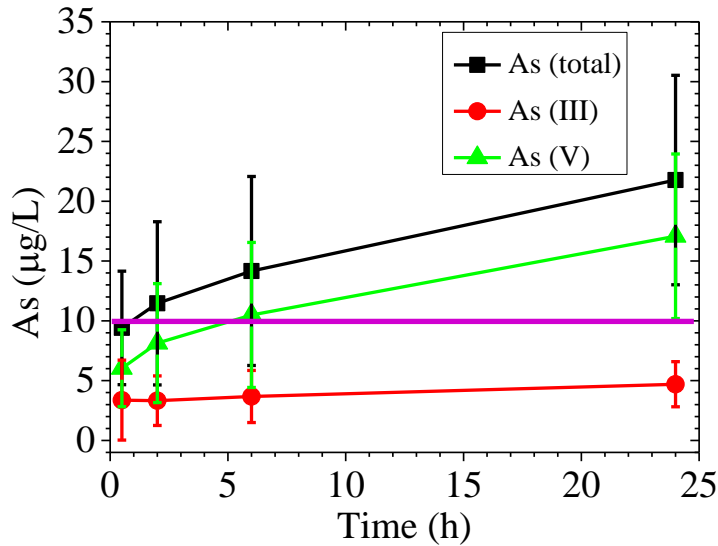
(b) O sample

pH change with time in the consecutive batch leaching experiments. Each plot and error bar are average and standard deviation based on the values that we conducted three times, respectively.

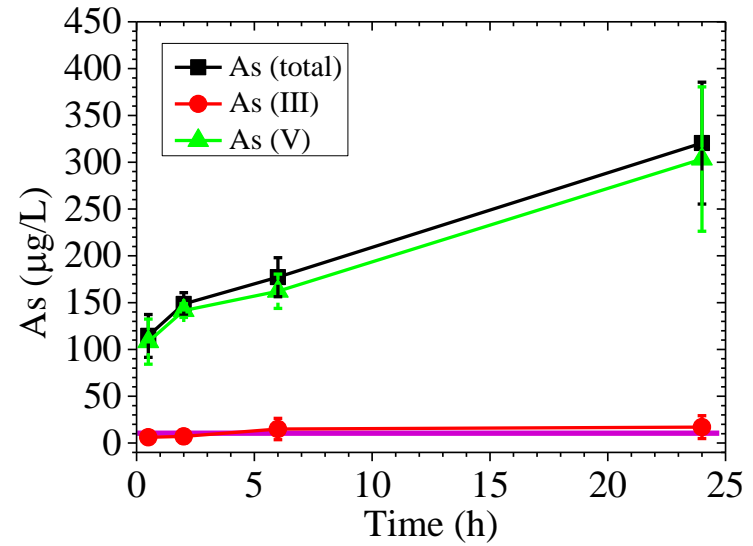
- Changes in the pH were slightly lower at lower solid-liquid ratio.
- The leachate pH in both rocks gradually decreased with time and approached similar pH values (8.5-9).

◆ Evolution of arsenic in batch leaching experiments

— : environmental standard



(a) S sample

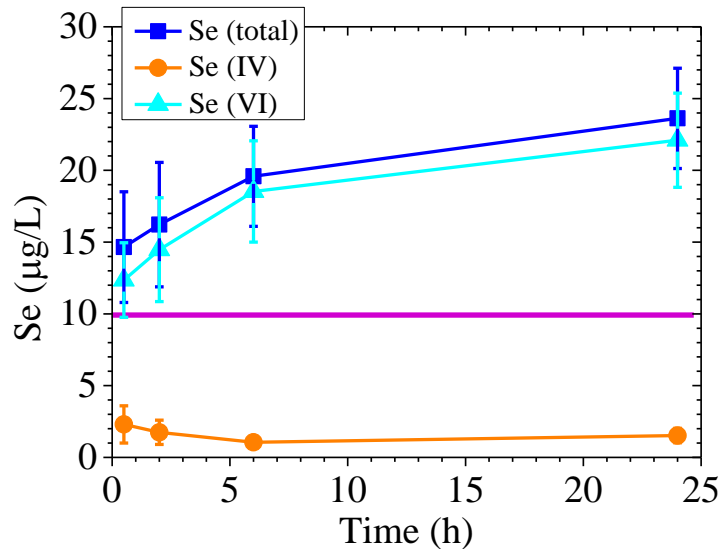


(b) O sample

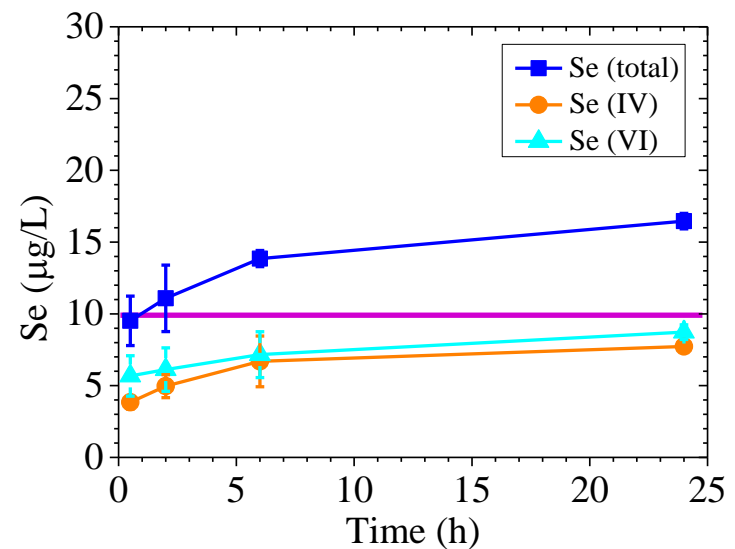
As concentration change with time in batch leaching experiments (solid-liquid ratio 1:5). Each plot and error bar are average and standard deviation based on the values that we conducted three times, respectively.

- The total As concentration increased with time and exceeded 10 µg/L only after 2 h of mixing for both samples.
- The total As leaching concentrations of O sample were 15-times higher than those of S sample.
- The major chemical forms of As was As(V) in both samples, but the concentrations of As(III) were also substantial.

◆ Evolution of selenium in batch leaching experiments



(a) S sample

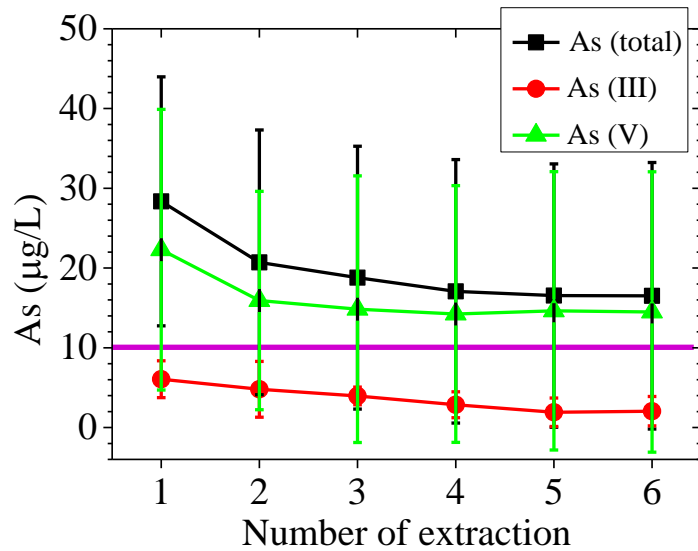


(b) O sample

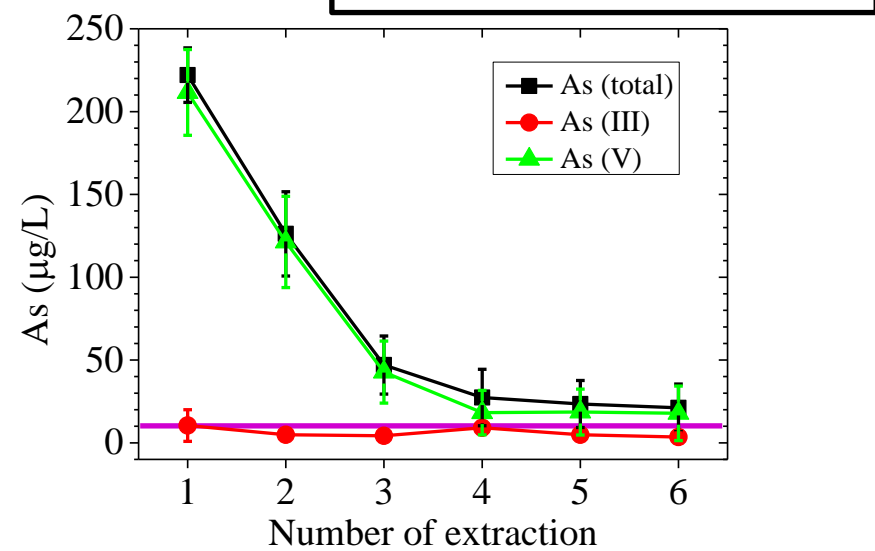
Se concentration change with time in batch leaching experiments (solid-liquid ratio 1:10). Each plot and error bar are average and standard deviation based on the values that we conducted three times, respectively.

- The total Se leaching increased with time and were higher than 10 µg/L after 0.5 and 2 h for samples S and O, respectively.
- The amount of Se leached from S sample were slightly higher than those from O sample.
- For S sample, the predominant Se species was Se(VI), but the concentrations of Se(IV) and Se(VI) in the leachates of O sample were almost equal.

◆ Evolution of arsenic in consecutive batch leaching experiments



(a) S sample

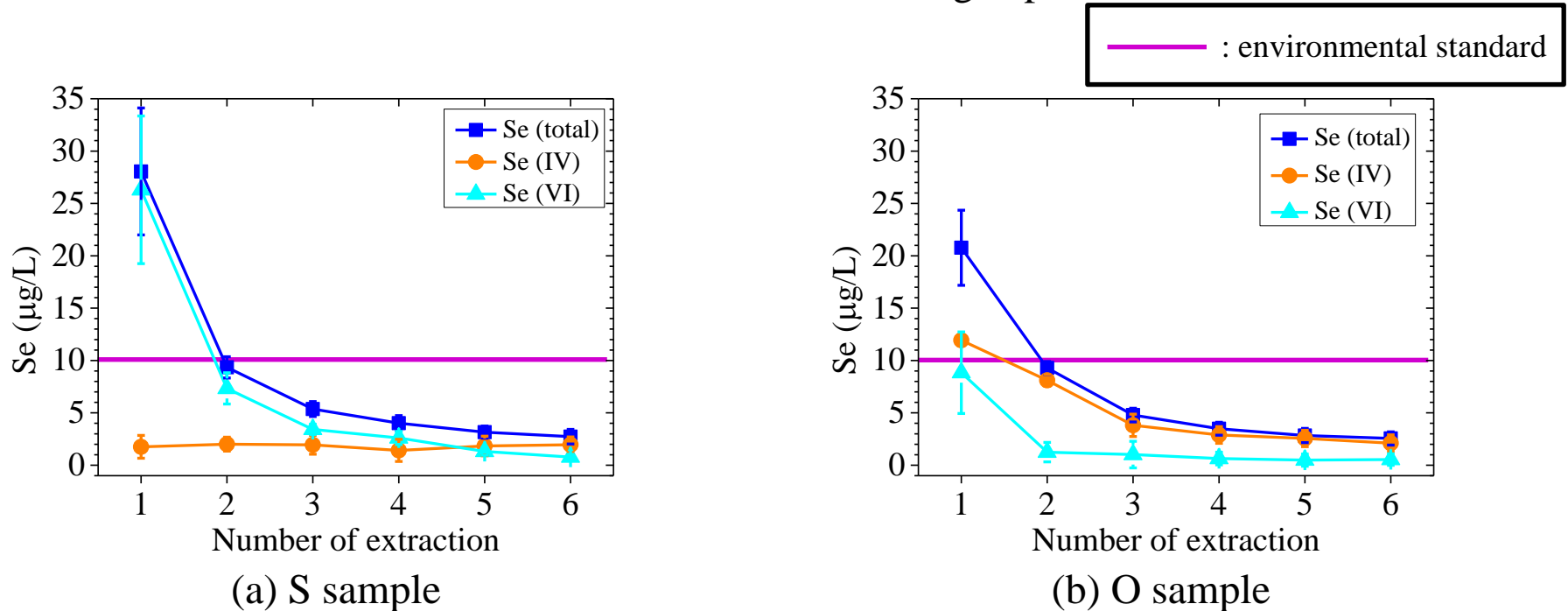


(b) O sample

As concentration change with time in consecutive batch leaching experiments (solid-liquid ratio 1:10). Each plot and error bar are average and standard deviation based on the values that we conducted three times, respectively.

- The leaching of As(III) was nearly constant while that of As(V) decreased with the number of extraction.
- Considerable amounts of As(III) ($< 20 \mu\text{g/L}$) were observed independent of the number of extraction.
- The total As concentrations were still higher than $10 \mu\text{g/L}$ even after six extractions for both samples.

◆ Evolution of selenium in consecutive batch leaching experiments

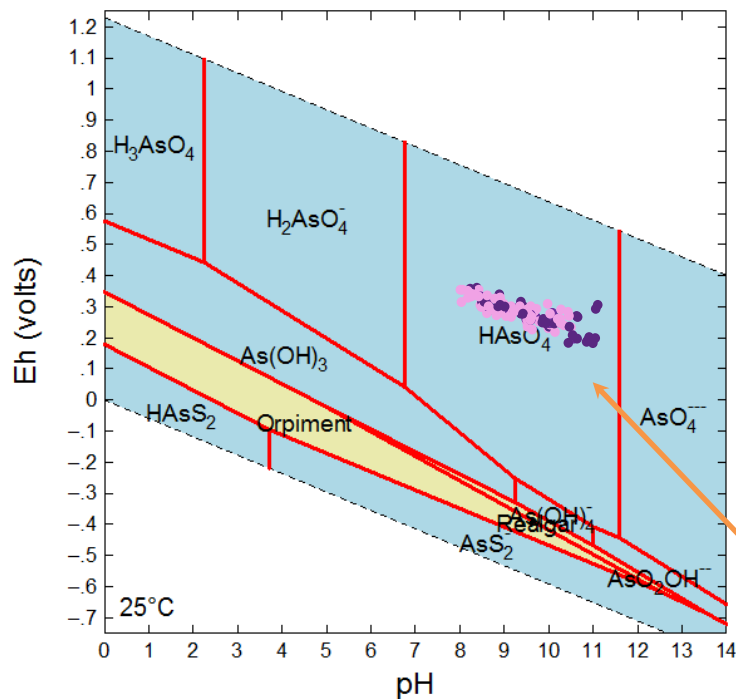


Se concentration change with time in consecutive batch leaching experiments (solid-liquid ratio 1:5). Each plot and error bar are average and standard deviation based on the values that we conducted three times, respectively.

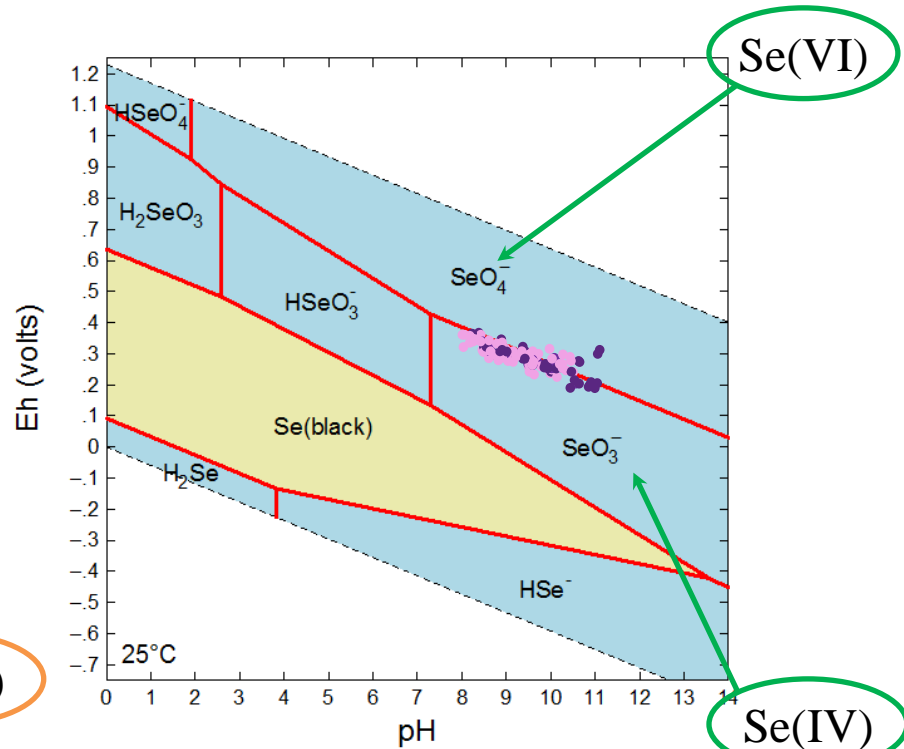
- The total Se concentration decreased with the number of extraction, and after the 2nd extraction, the total Se concentration decreased below 10 µg/L.
- The leachability or mobility of Se is higher than that of As.

◆ pH and redox potential dependence of arsenic and selenium speciation

●: S sample ●: O sample



Eh-pH diagram of As



Eh-pH diagram of Se

The measured chemical forms of As and Se agreed well with those predicted under equilibrium conditions.



The chemical forms of As and Se can be evaluated by equilibrium geochemical modeling.

The leaching behavior and speciation of As and Se leached from mudstones were evaluated by batch, consecutive leaching experiments and geochemical modeling.

1. Although the leaching concentrations of As and Se increased with time, they decreased with the number of extraction.
2. The major chemical form of As was As(V) regardless of the sample.
3. The major chemical form of Se changed from Se(VI) to Se(IV) with the number of extraction.
4. The measured chemical forms of As and Se agreed well with the calculated results under equilibrium conditions.



Thank you for your kind attention.