金属イオンを含む亜臨界水による汚染土壌からのCs回収
――水熱条件下での粘土鉱物からのCs脱離促進――

東京工業大学科学技術創成研究院

原子燃料サイクル研究ユニット

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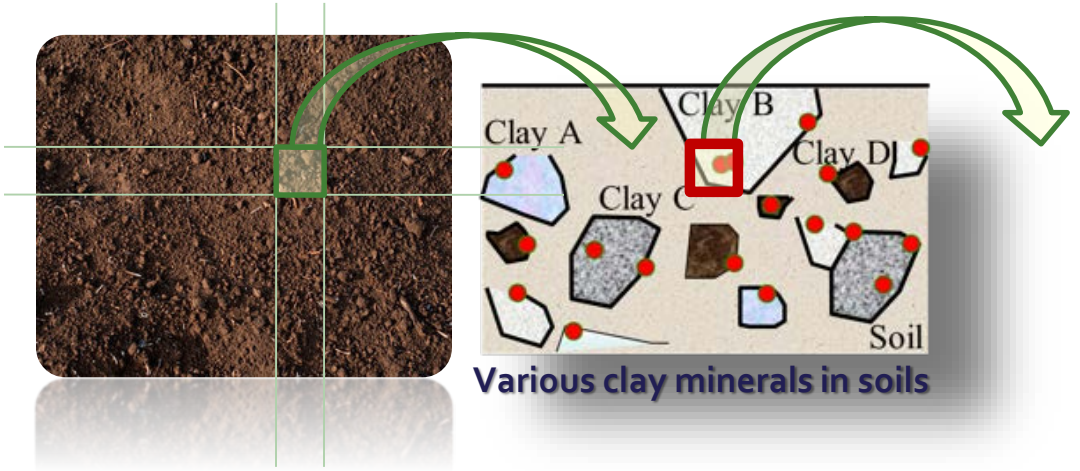
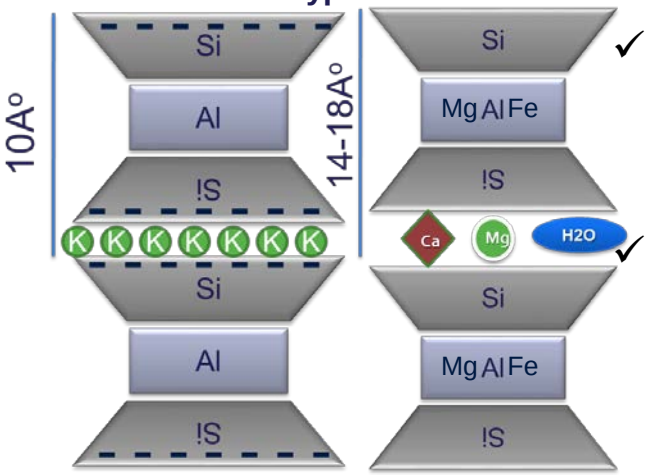
Cs Adsorption on Clay Minerals in Contaminated Soil



Various clay minerals in soils

2:1 dioctahedral type

2:1 trioctahedral type



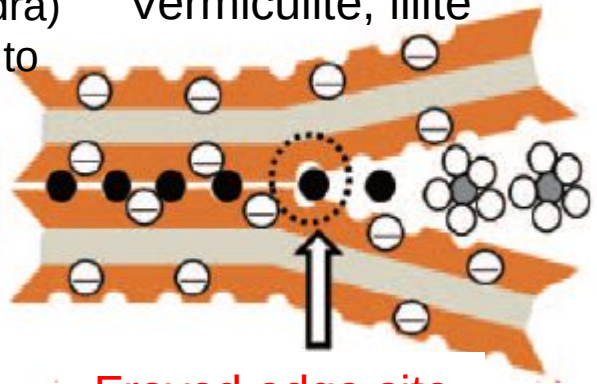
- ✓ **Important clay minerals in Fukushima**
- ✓ **Dominant adsorptive clay minerals**

Illite/muscovite/biotite vermiculite/smectite

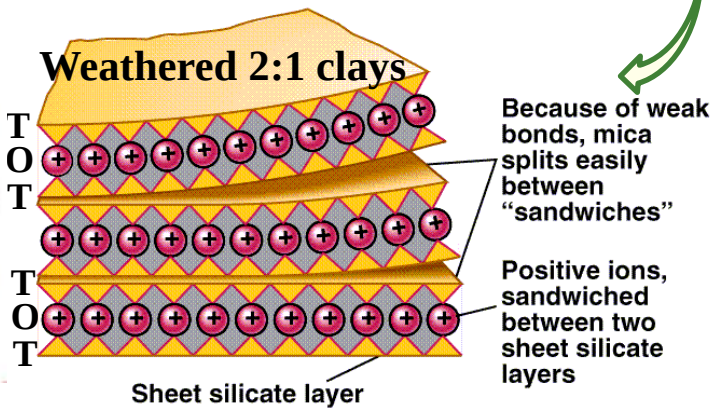
Phyllosilicate (Sheet of SiO_4 tetrahydra) has siloxane ditrigonal cavity similar to the size of Cs

- •Takes long time to access
- •Once Cs is trapped, no escape
- •Small ratio to whole charge
- •Main cause of Cs entrapment

Vermiculite, illite



Frayed edge site (10.7 Å)

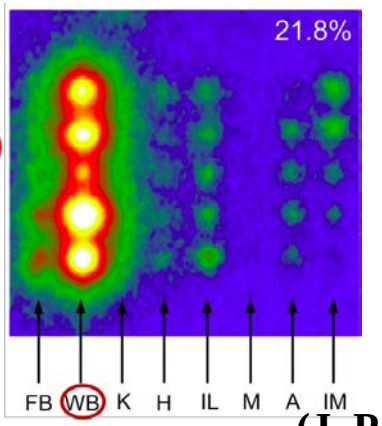


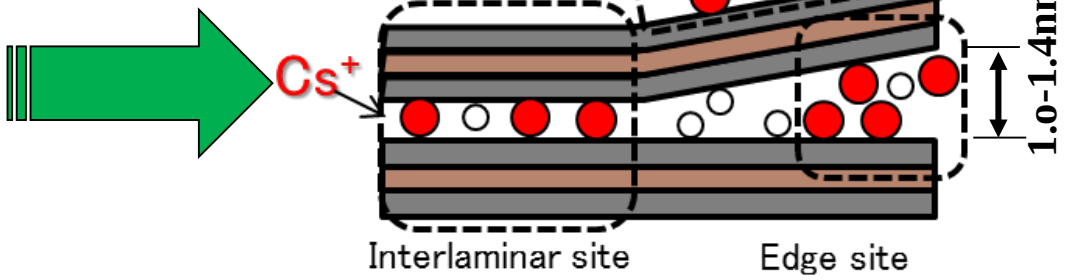
T: tetrahedral sheet O: octahedral sheet

Cs adsorption in soil and distribution on clay particles

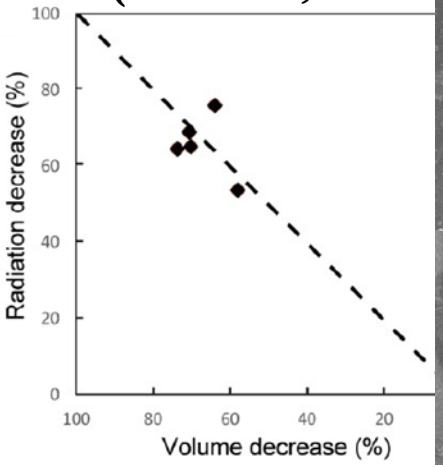
(H. Mukai, et al. 2016)

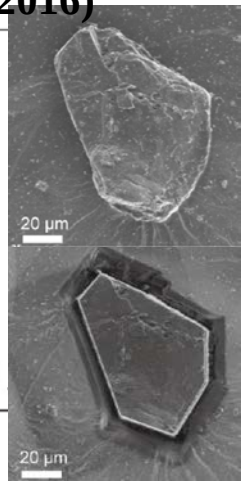
FB: fresh biotite
WB: weathered biotite (Vermiculite)
K: kaolinite
H: halloysite
IL: illite
M: montmorillonite
A: allophane
IM: imogolite





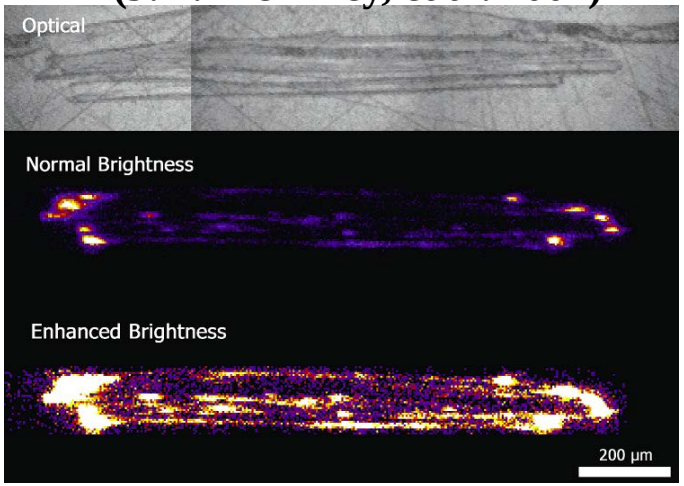
(H. Mukai, et al. 2016)





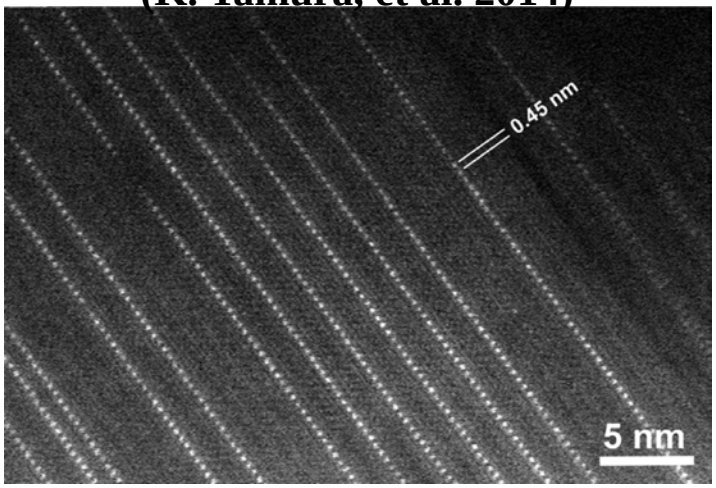
Edge-removal for radioactive Cs-biotite

(J. P. Mckinley, et al. 2004)



Cs adsorbed muscovite

(K. Tamura, et al. 2014)



HAADF-STEM image of Cs treated phlogopite

Cs is selectively sorbed by **vermiculite-like clay minerals** and fixed on various binding sites such as **planar/frayed edge/interlayer sites**.

Hiroki Mukai, etc. *Environ. Sci. Technology.* 2014, 48, 13053-13059. James P. Mckinley, etc. *Environ. Sci. Technology.* 2004, 38, 1017-1023. Kenji Tamura, etc. *Environ. Sci. Technology.* 2014, 48, 5808-5815.

Recent studies about Cs removal from clay/soil

Research Groups	Year	Clay/soil	Extraction Agent	Condition	Removal Ratio
K. Morimoto, et al.	2012	Vermiculite	3 M Mg^{2+}	25℃	70~90%
H. Mukai, et al.	2015	Fukushima biotite	1M NH_4^+, Cs^+, Mg^{2+}, 0.1M H^+	25℃	Mg^{2+}:58 % NH_4^+:5.1%
M. Yanaga, et al.	2015	Soil	2M K^+	25℃	75%
K. Murota, et al.	2016	Soil	0.001~0.1M K^+	25℃, 140d	60%
L. Dzene, et al.	2015	Vermiculite	1M NH_4^+	25℃	30%
D. Parajuli, et al.	2015	Soil	0.5M H^+	95~200℃	50~95%
C. Liu, et al.	2003	Sediments	3M Na^+, K^+, Rb^+, 0.5M NH_4^+	25℃,134d	27~80%
N. Kozai, et al.	2012	[illegible]	1M NH_4^+,1M H_2SO_4	25℃	40%
A. De Koning, et al.	2004		M NH_4^+	25℃	56%
C. Willms, et al.	2004		lkylammonium salt	25℃	45%
I. Shimoyama, et al.	2014	Vermiculite	Mixed NaCl-$CaCl_2$	620~800℃	40% (3min)

Sublimation

Problems/under discussion

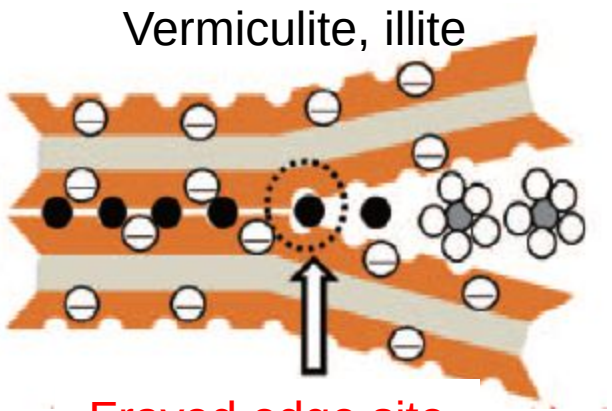
1. Cs was **poorly and partially** removed
2. **Mono/divalent ions** have varied roles
3. **High ion strength/temp** were used
4. **Desorption kinetics** were very slow

Objectives

Reversibility of Cs^+ on clay minerals

Adsorption

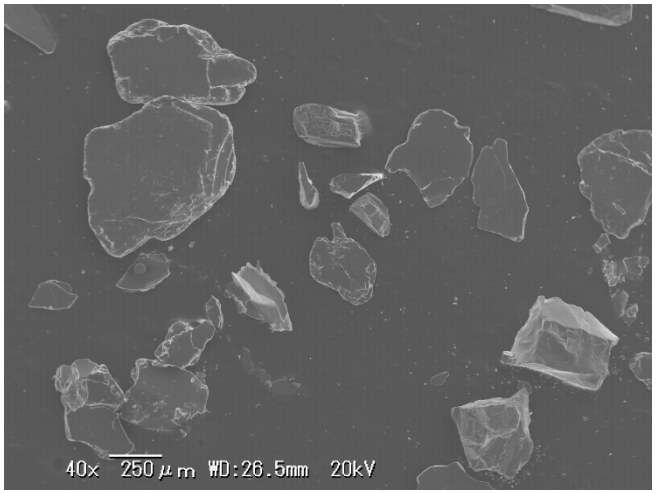
- ✓To clarify Cs sorption behavior on clays
- ✓To prepare samples similar with Cs simulated soil



Desorption

- ✓To improve the Cs desorption ratio.
- ✓To clarify the mechanism of Cs desorption.

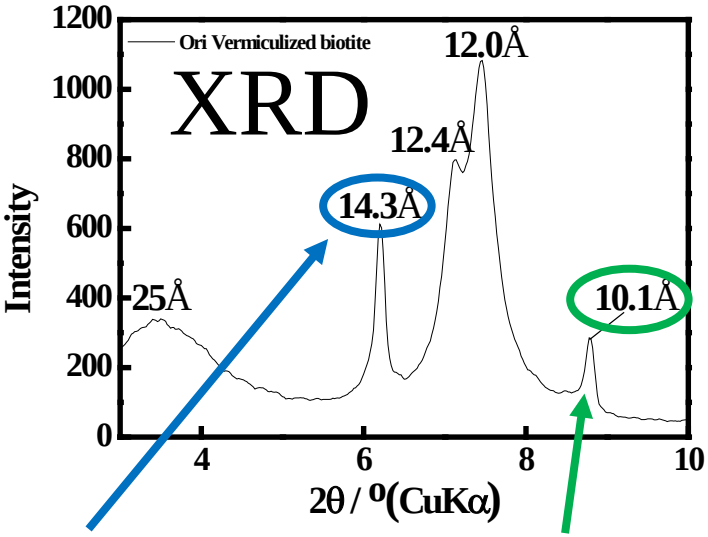
Characterizations of used Sample - Vermiculitized Biotite



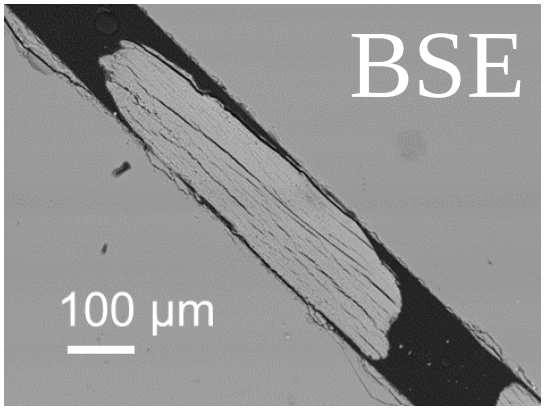
SEM

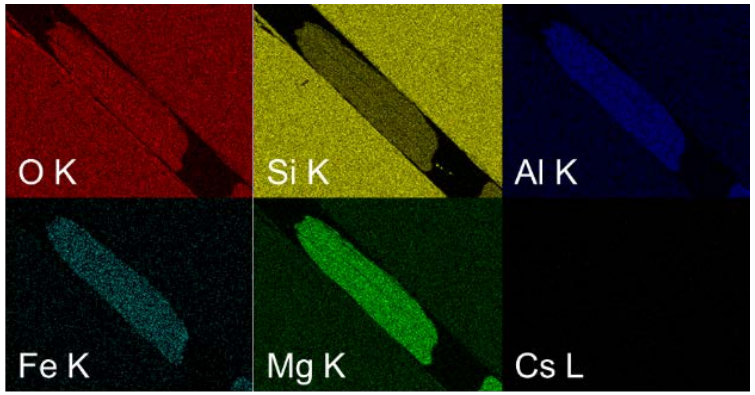
Compositions	(wt. %)
SiO_2	46.1
MgO	24.9
Fe_2O_3	8.61
Al_2O_3	13.0
K_2O	5.55
CaO	0.57
TiO_2	1.25

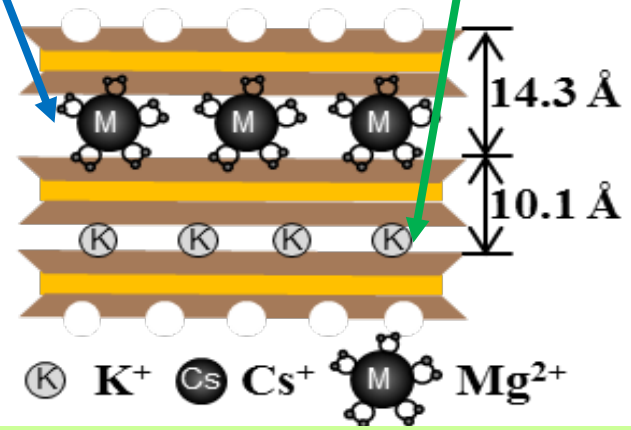
XRF



Mg-vermiculite layer K-biotite layer

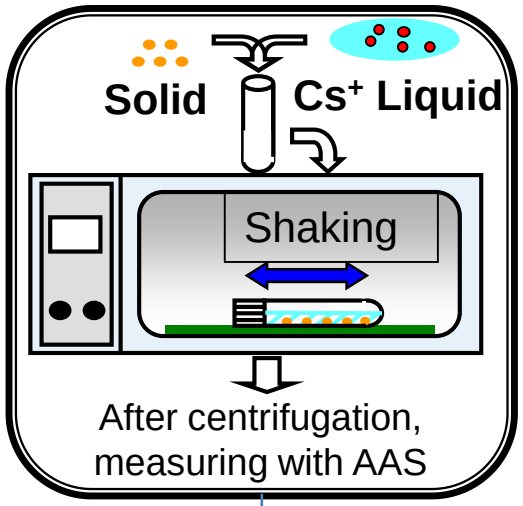






- ✓ Structure formula is $(Si_{3.14}Al_{0.86})O_{10}(Al_{0.18}Ti_{0.06}Fe_{0.15}Mg_{2.53})(OH)_2(K_{0.48}Ca_{0.04})$.
- ✓ VB occurs interstratificated structure with Mg-layers and K-layers.

Cs Adsorption Experiment



Vermiculitized biotite (VB)

Wash and sieve

Cs Con: 10ppm -2000ppm; S/L: 0.1g/10ml;
T: 25℃; t:2 d

Batch adsorption (25 ℃)

Solid-liquid Separate

Drying (85℃, 24h)

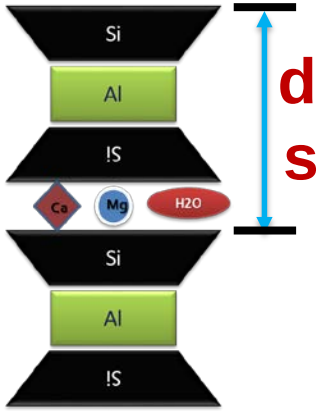
AAS

Adsorption capacity, *Q*

$$Q = \frac{C_i - C_e}{(S/L)}$$

Where:
C_o is the initial Cs concentration
C_e is the equilibrium Cs concentration
S/L is the solid-to-liquid ratio.

SEM-EDX



d: basal spacing

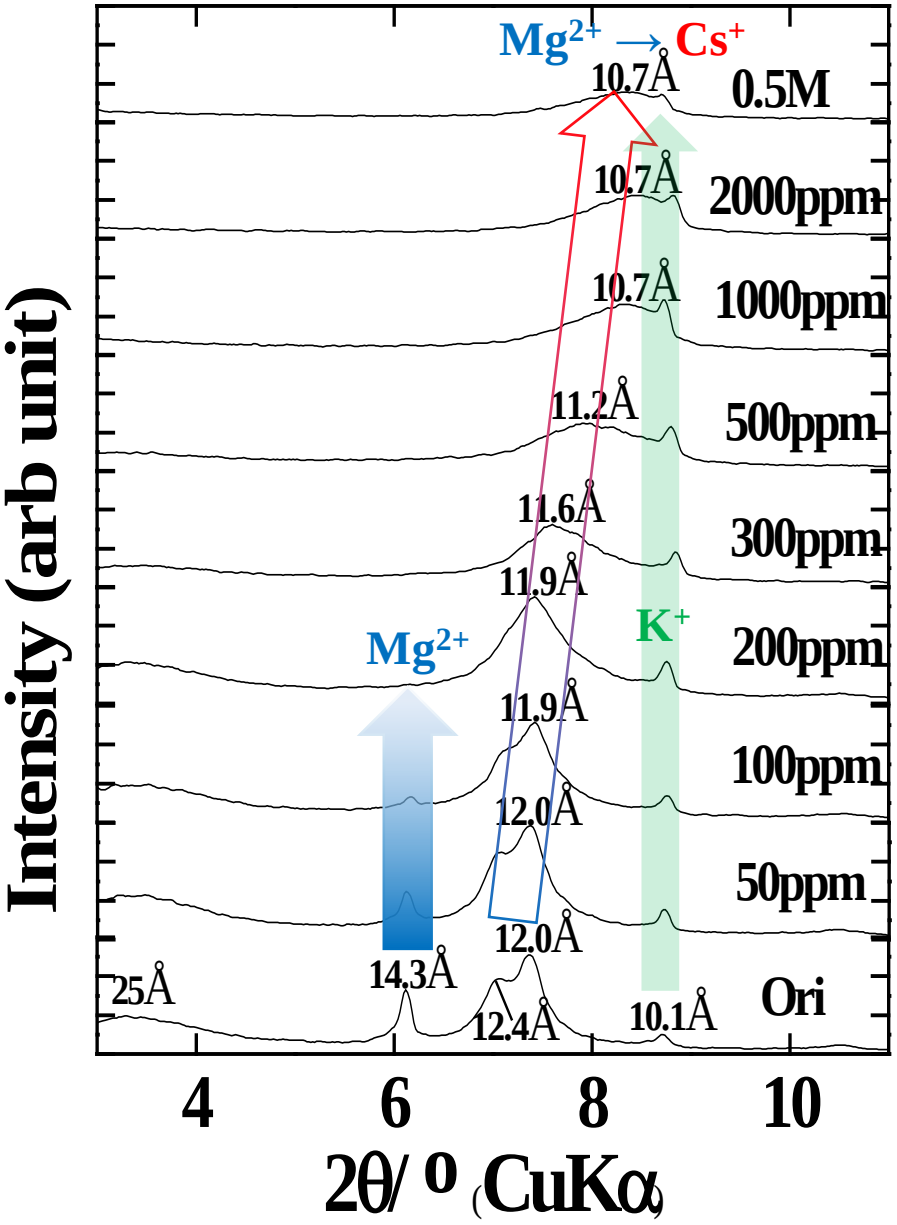
XRD

BRAGG LAW

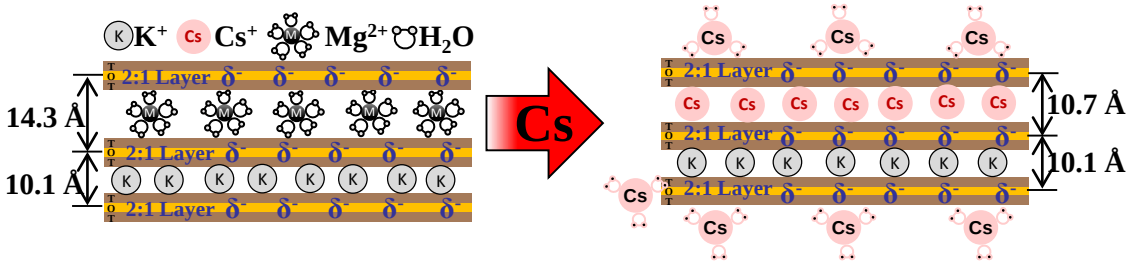
$$2d(\sin\theta) = \lambda_o$$

where:
d = lattice interplanar spacing of the crystal
θ = x-ray incidence angle (Bragg angle)
λ = wavelength of the characteristic x-rays

Cs Adsorption on VB

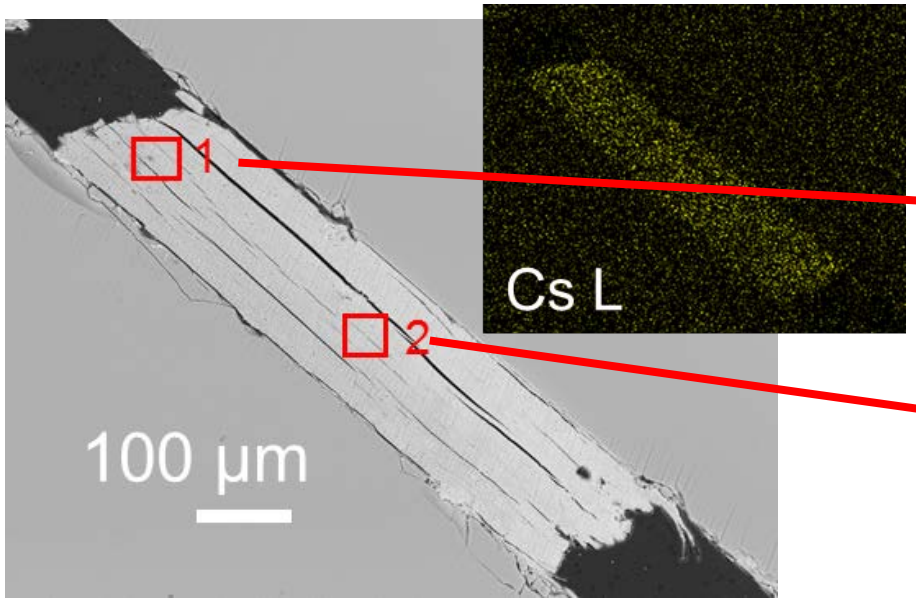


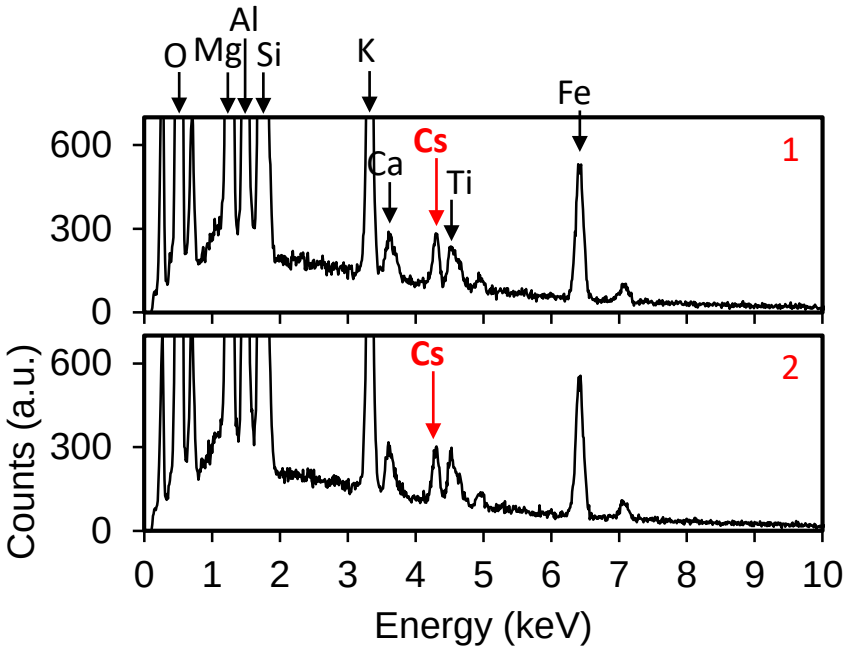
- **25 Å:** Regular interstratification of Mg and K layer
- **14.3 Å:** Hydrous Mg^{2+} layer
- **12.4 Å:** Partial hydrous Mg^{2+} layer
- **12.0 Å:** Random interstratification of Mg and K layer
- **10.6 Å:** Cs collapsed layer
- **10.1 Å:** Biotite K^+ layer



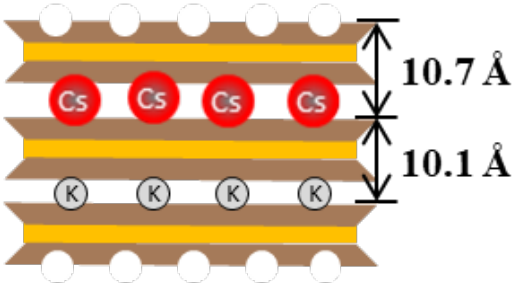
- ✓ The peak for **Mg** layer gradually **disappears** with Cs sorption increase.
- ✓ The peak for **K** layer shows **no change**.
- ✓ The disappearance is attributed to the transition from **Mg-vermiculite layers** to **Cs-substituting layers**.

Usage of Cs Saturated VB as Contaminated Soil

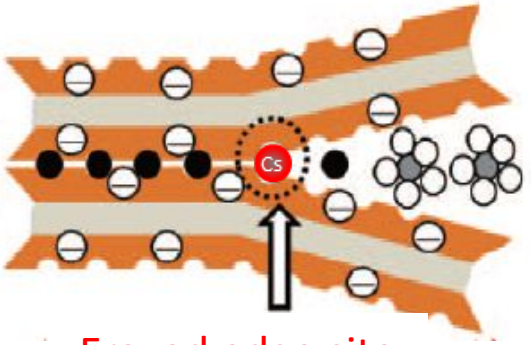




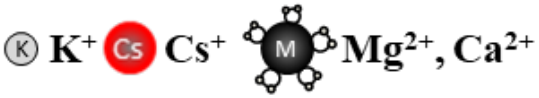
Cs collapsed VB



Trace amount of Cs in FES



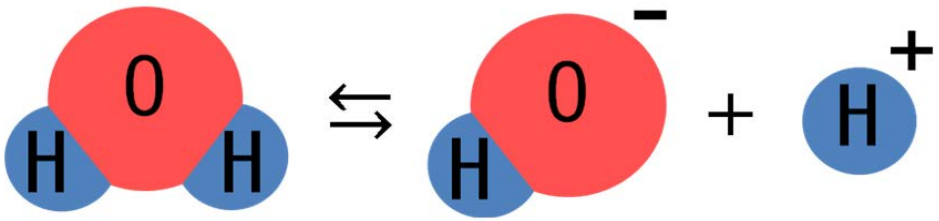
Frayed edge site
(10.7 Å)

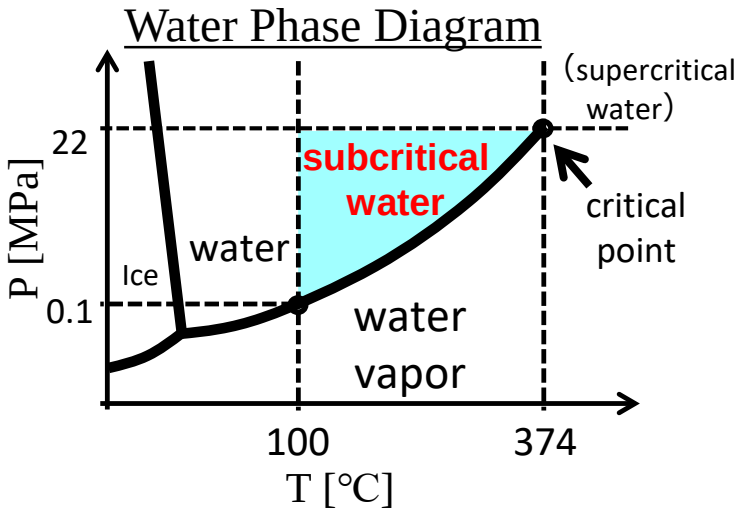


- ✓ VB used in the present study is capable of adsorbing **2.44 wt. %** of CsO (35.8 mg/g).
- ✓ Sorbed Cs is almost **homogeneously** distributed within collapsed interlayers.

Hydrothermal Treatment (HTT) using Subcritical Water

Ionic product of water becomes larger in subcritical state under high temperature (200-280℃) and high pressure (3-4 MPa).





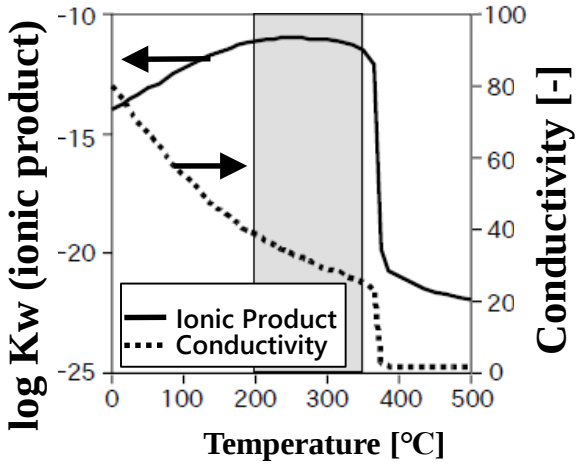
Specific Chemical Properties of Subcritical Water

① High-speed Hydrolysis Effect

→ Cs adsorbed in organic materials can be recovered to water phase by the decomposition of organic materials.

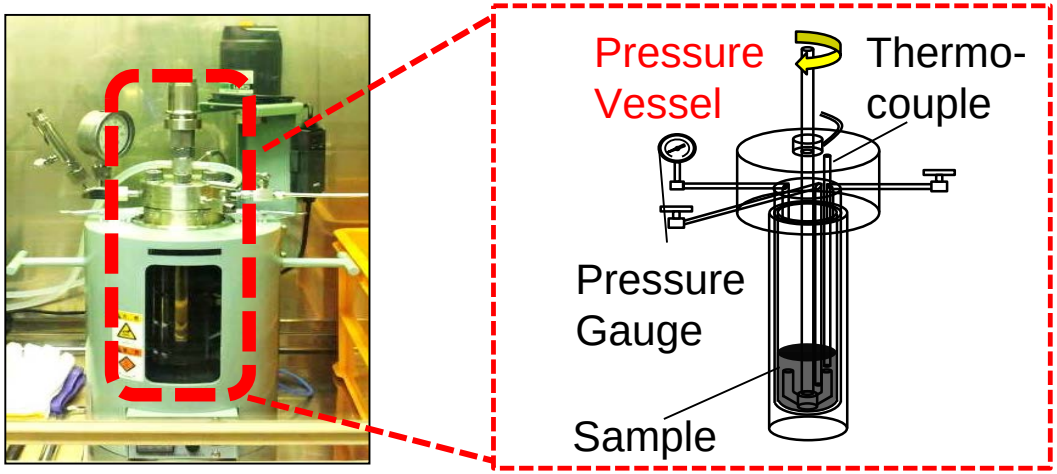
② High-speed Ion Exchange Effect

→ Cs adsorbed in inorganic materials can be recovered to aqueous phase by promoted ion exchange with various cations in subcritical water.

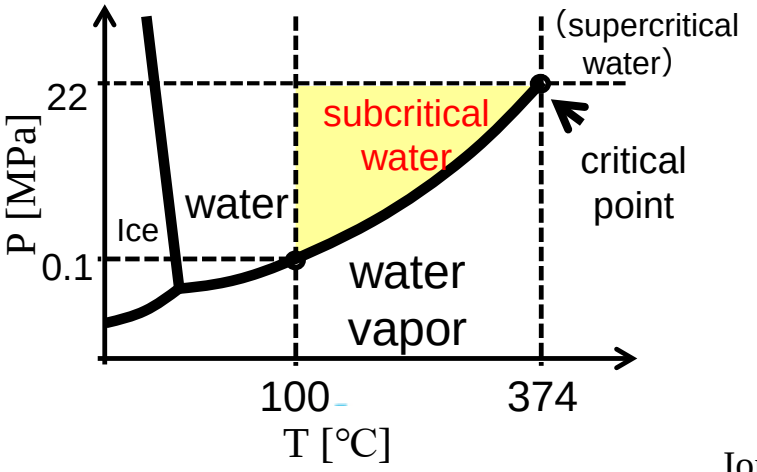


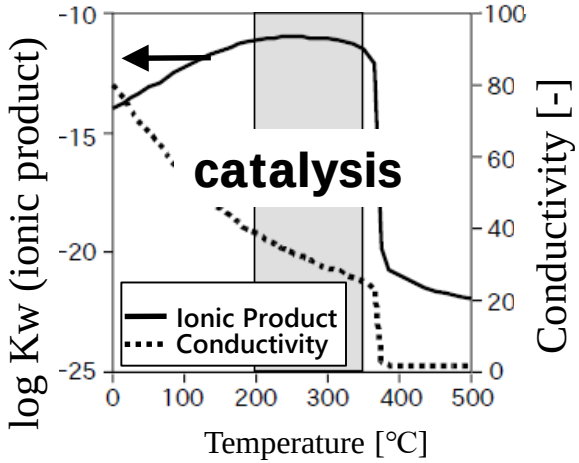
Ionic Product and Conductivity of Water

Cs Desorption by Hydrothermal Treatment (HTT)

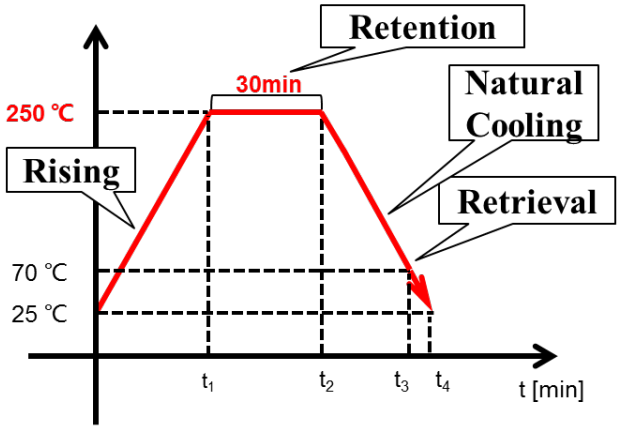


HTT Desorption (100-250 ºC, <4 Mpa)



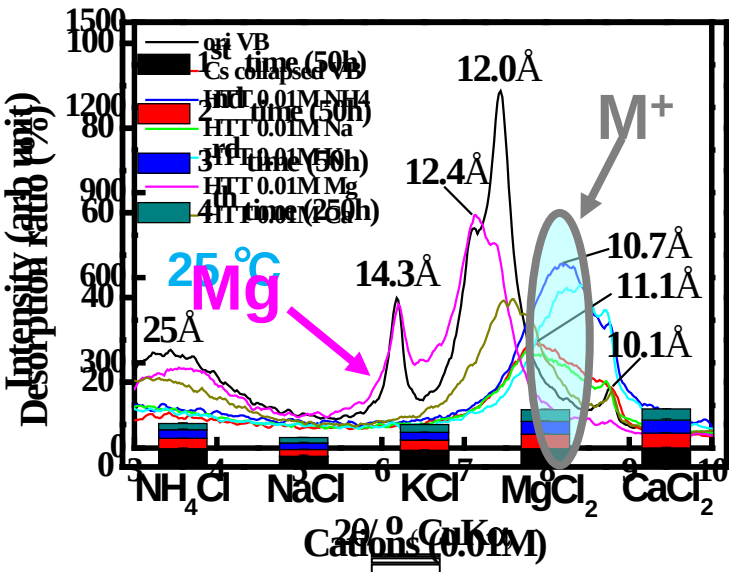


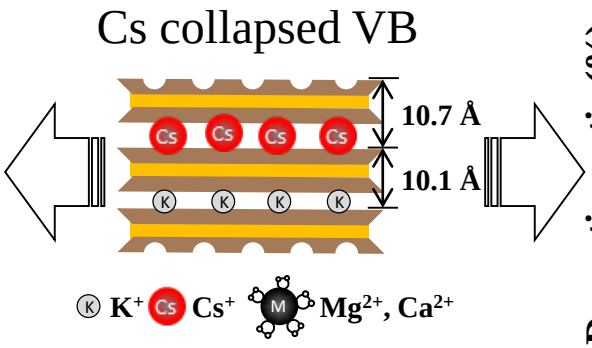
Ionic Product and Conductivity of Water

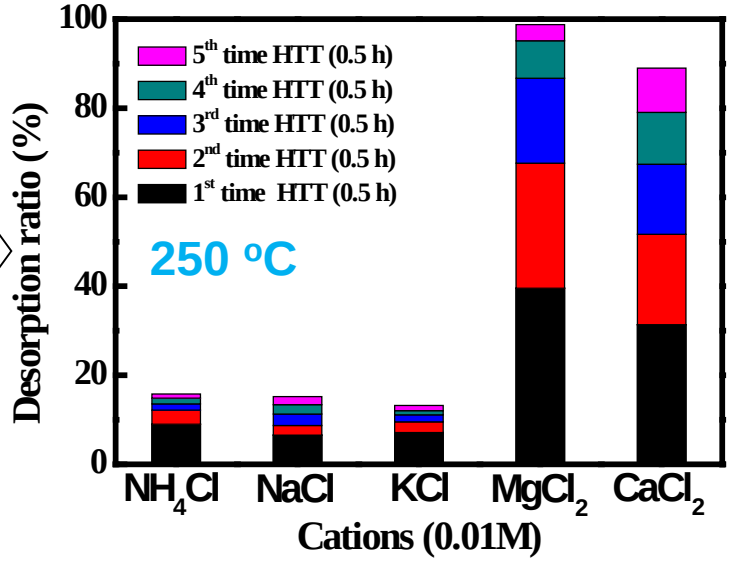


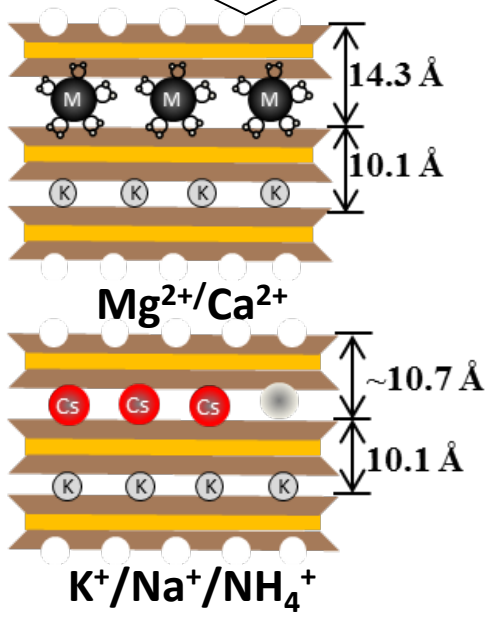
Relations of time and temperature

Enhanced Cs desorption by HTT with M^{2+} Cation





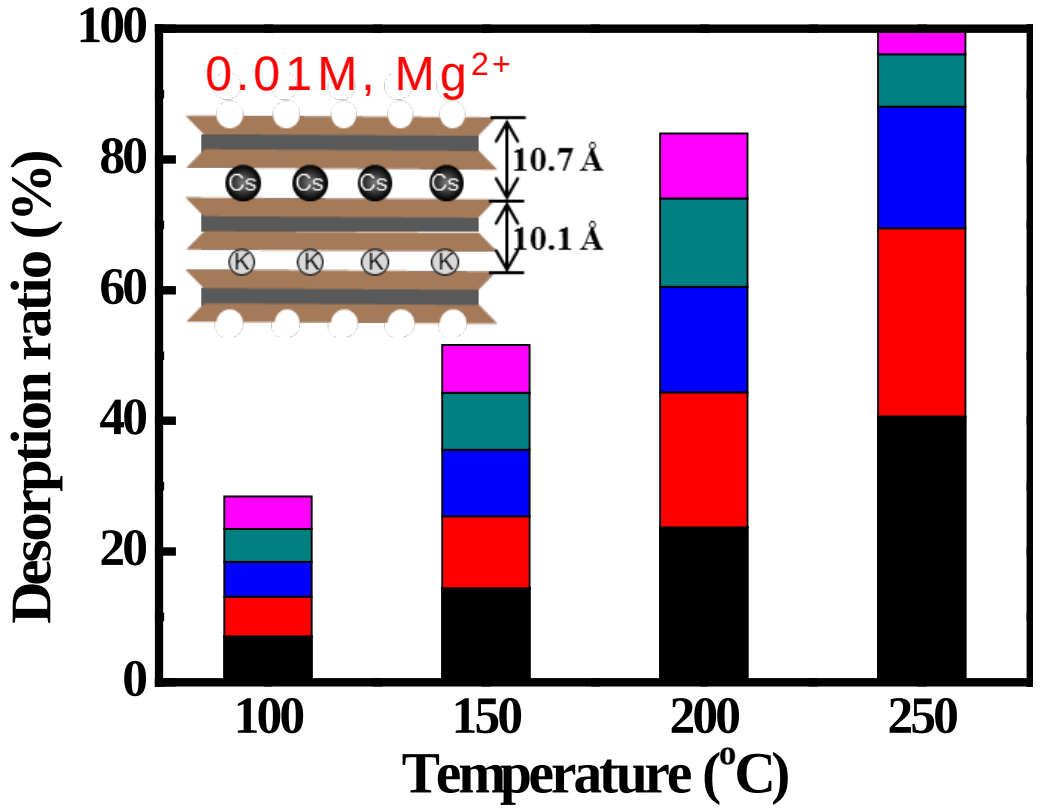


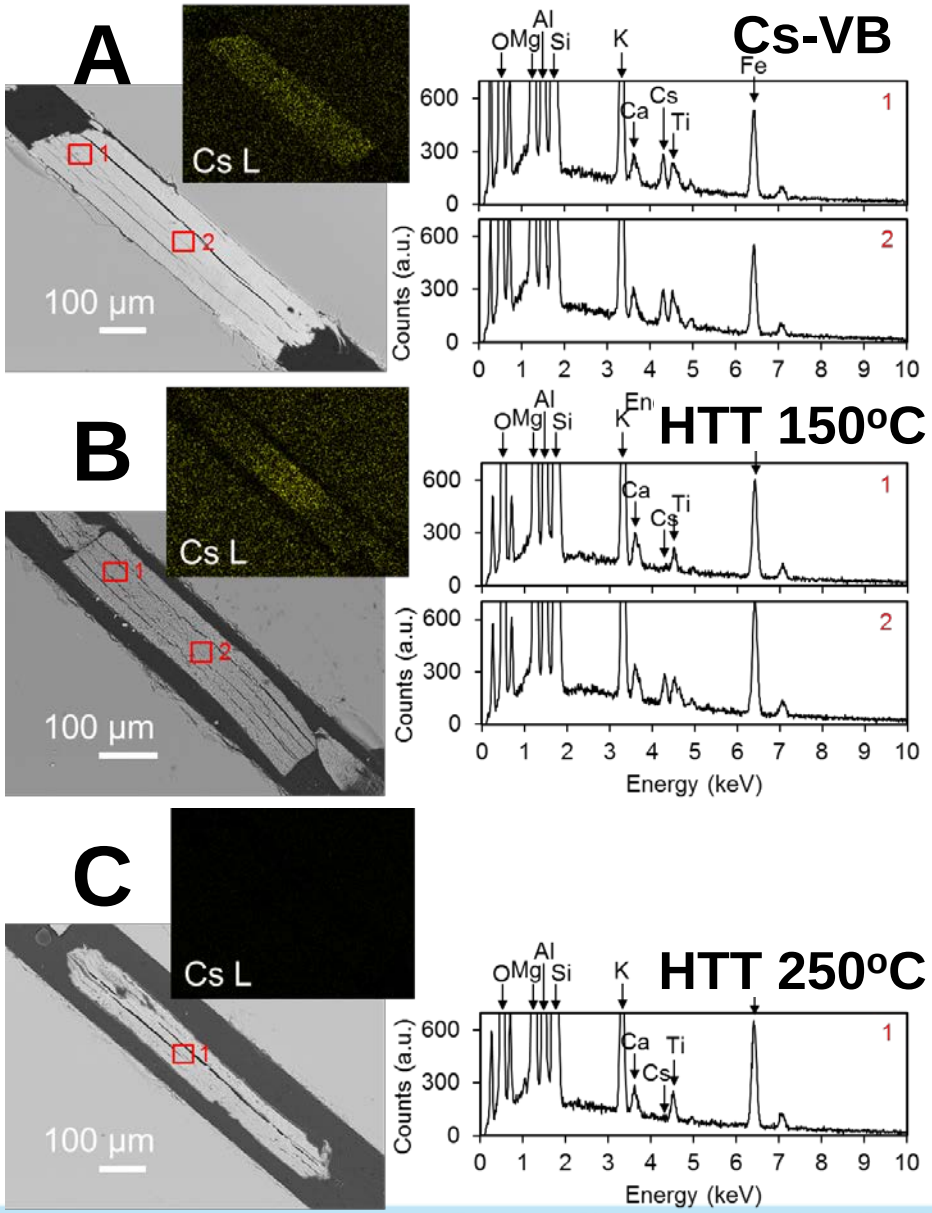


- ✓ Cs is still rarely desorbed by **monovalent cations**.
- ✓ High temperature greatly enhances the Cs desorption by **divalent cations**.
- ✓ XRD results confirms that **Mg^{2+}** indeed substitutes Cs^{+} from its collapsed interlayer.
- ✓ Mg^{2+}/Ca^{2+} **expands** the collapsed interlayer.

X.Yin et al., *J Hazard Mate*, Vol. 326, pp. 47-53, 2017

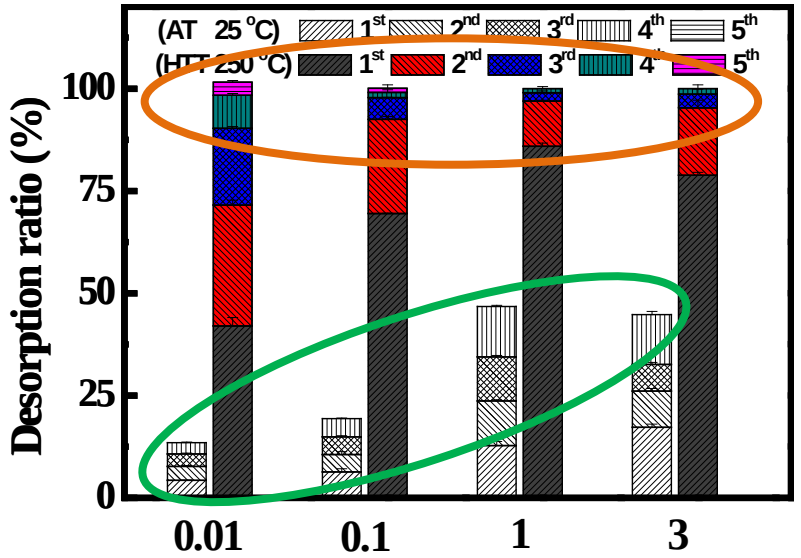
Cs Desorption from Cs-VB at Varied Temp

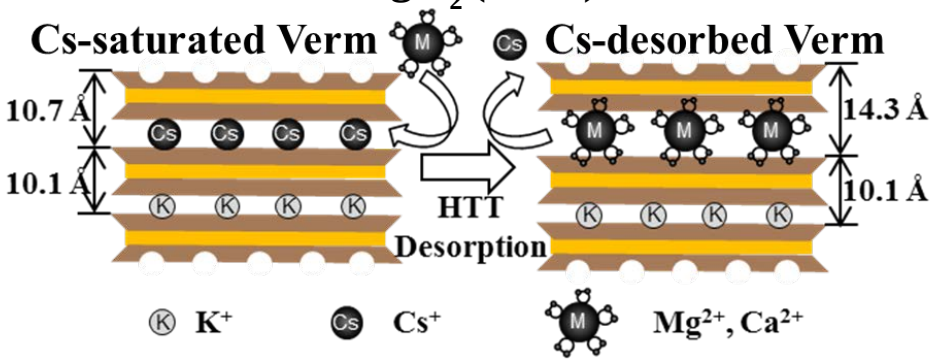


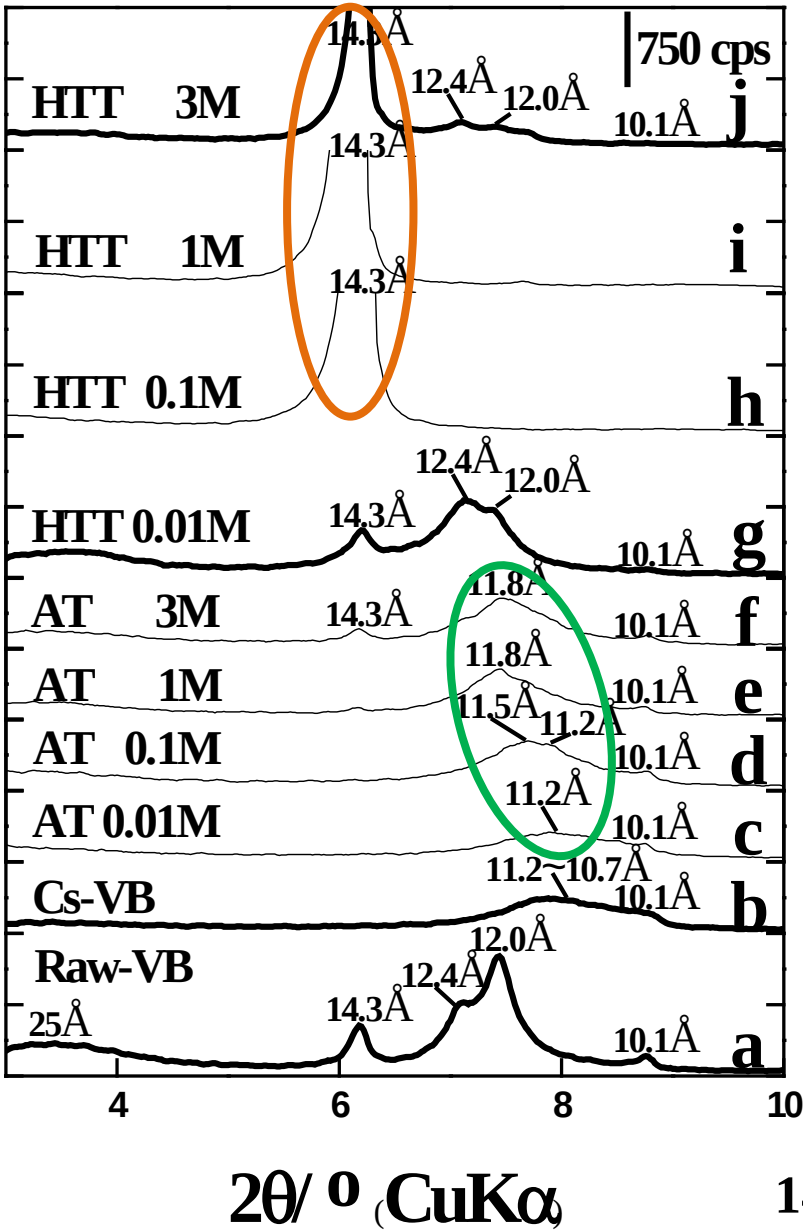


- Cs desorbed amount was dependent on the **treating temperature**.
- Higher temp enhanced **Mg^{2+} diffusion** within collapsed interlayers, resulting desorption of more Cs^{+} from center region.

Cs Desorption from Cs-VB by Mg^{2+} at different Conc.

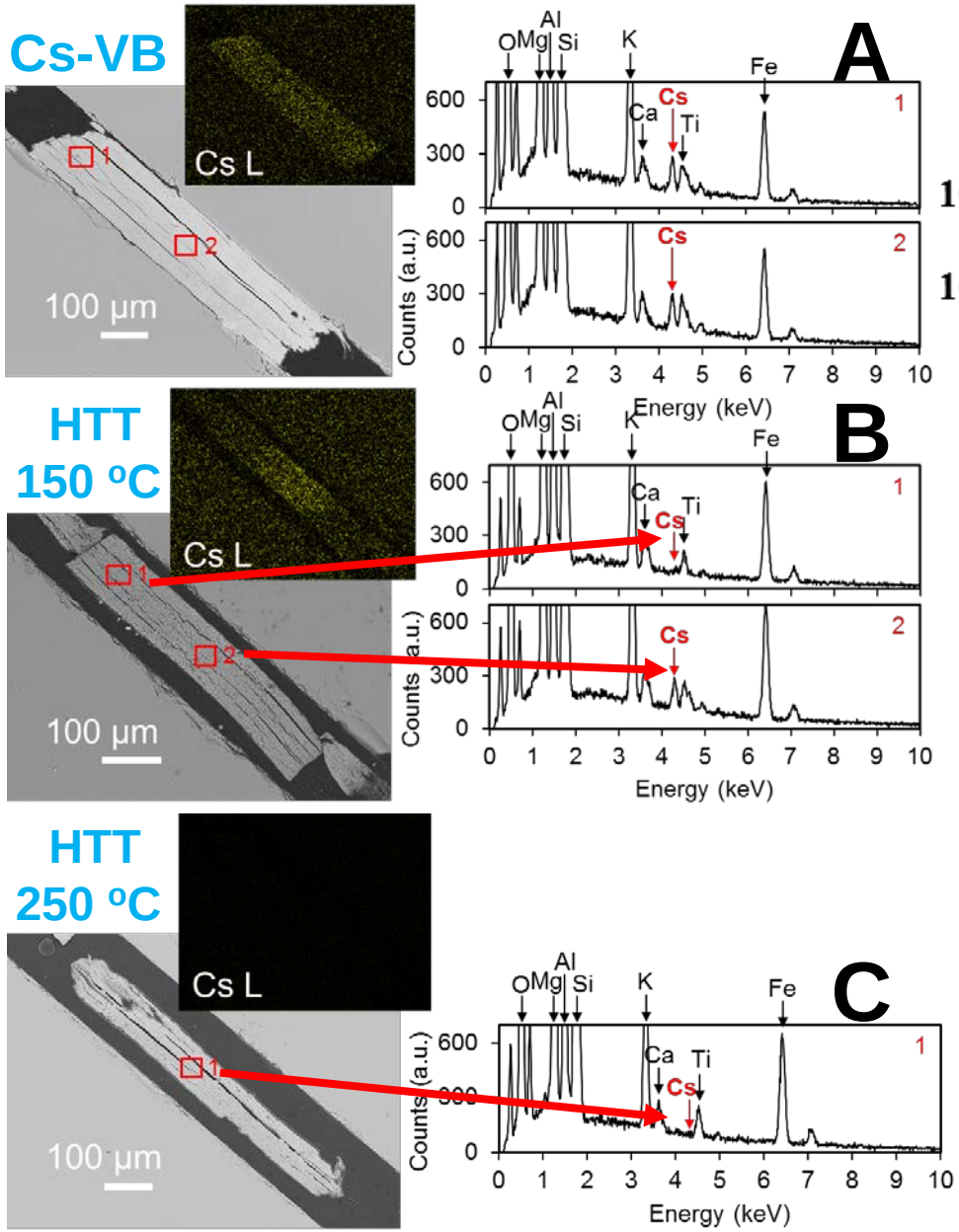


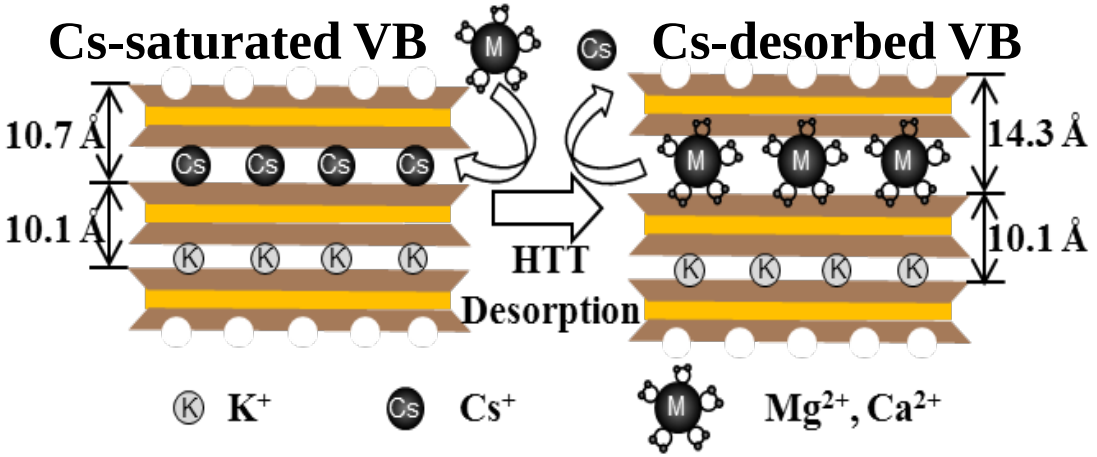




✓ Total desorption ratios improves with the increase of **concentration of Mg^{2+}.**

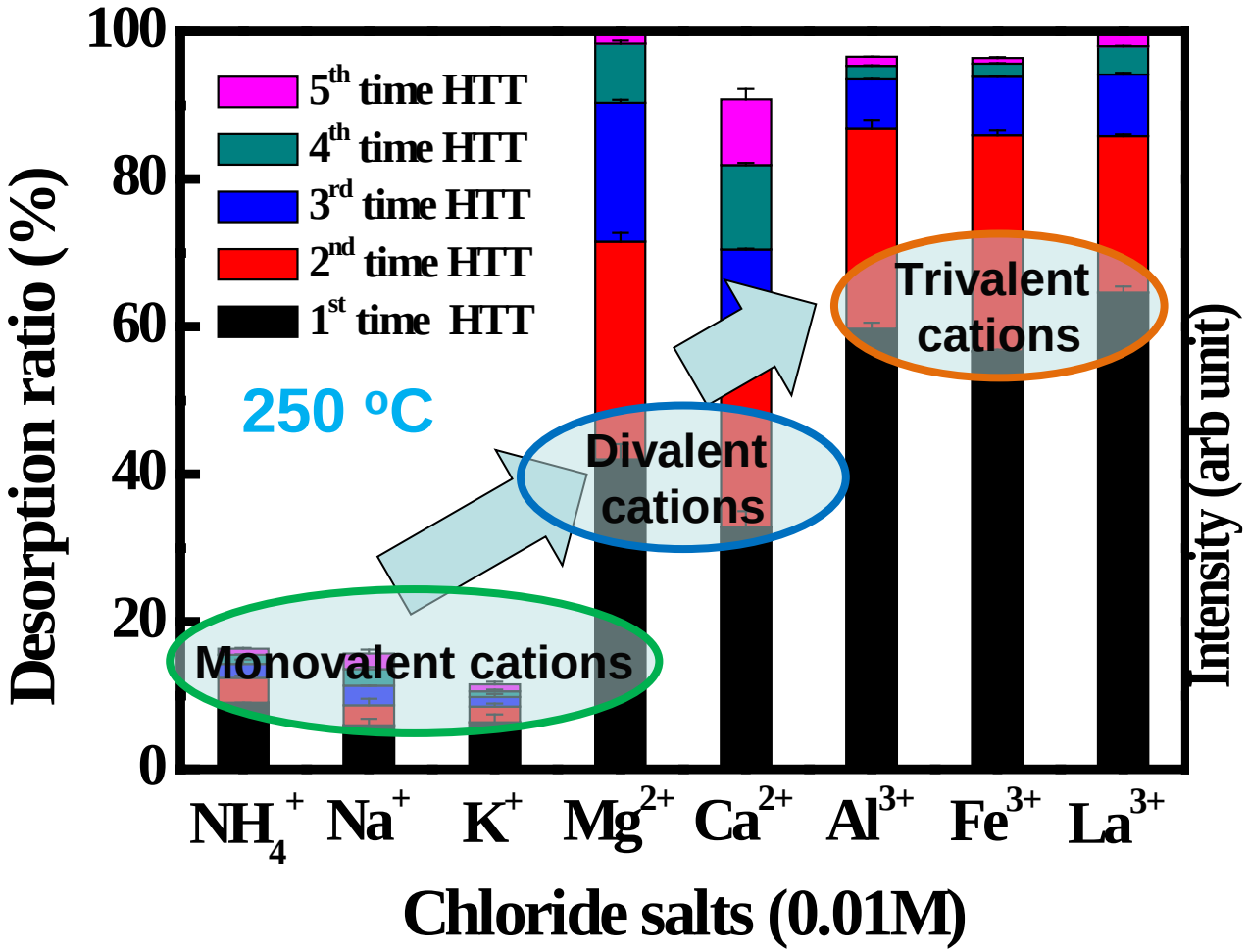
Cs Desorption by HTT with Mg^{2+}

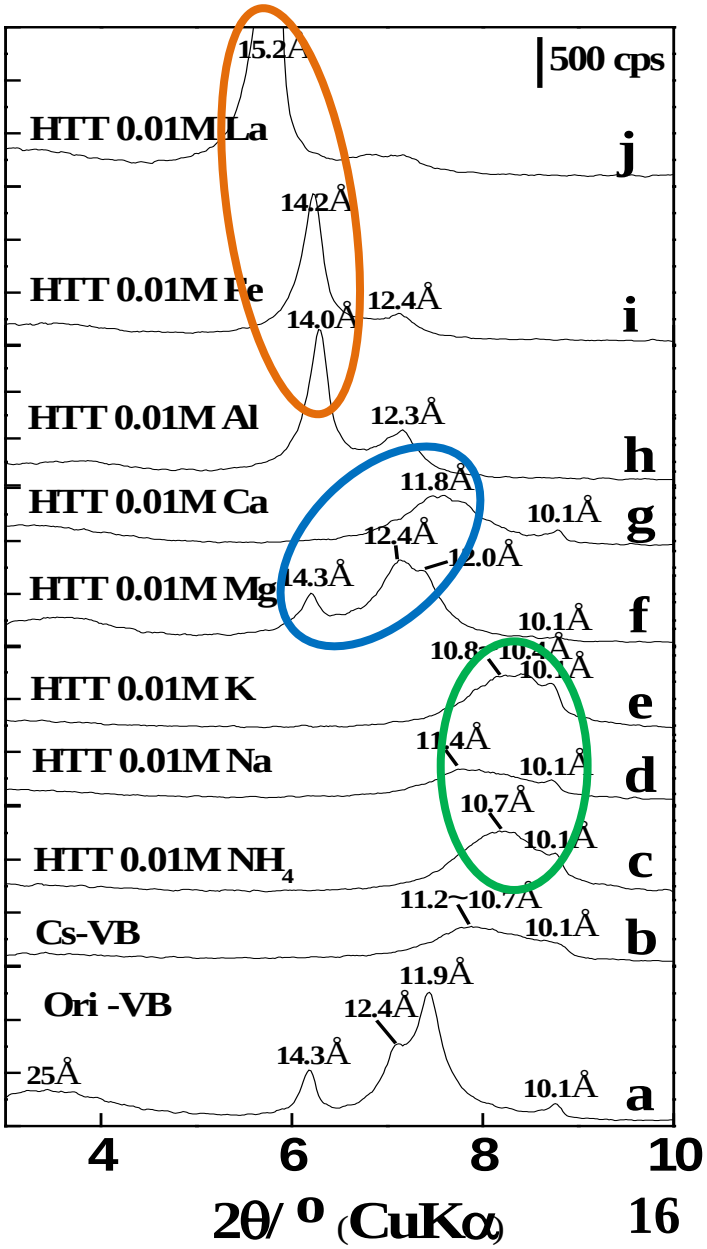




- ✓ After HTT at 150 °C, **partial Cs** in center area is not removed.
- ✓ After HTT at 250 °C, **all Cs** in both edge and center is removed.
- ✓ Mg^{2+} diffuses into collapsed interlayers from **near-edge to interior central region** with increase of treating temperature.

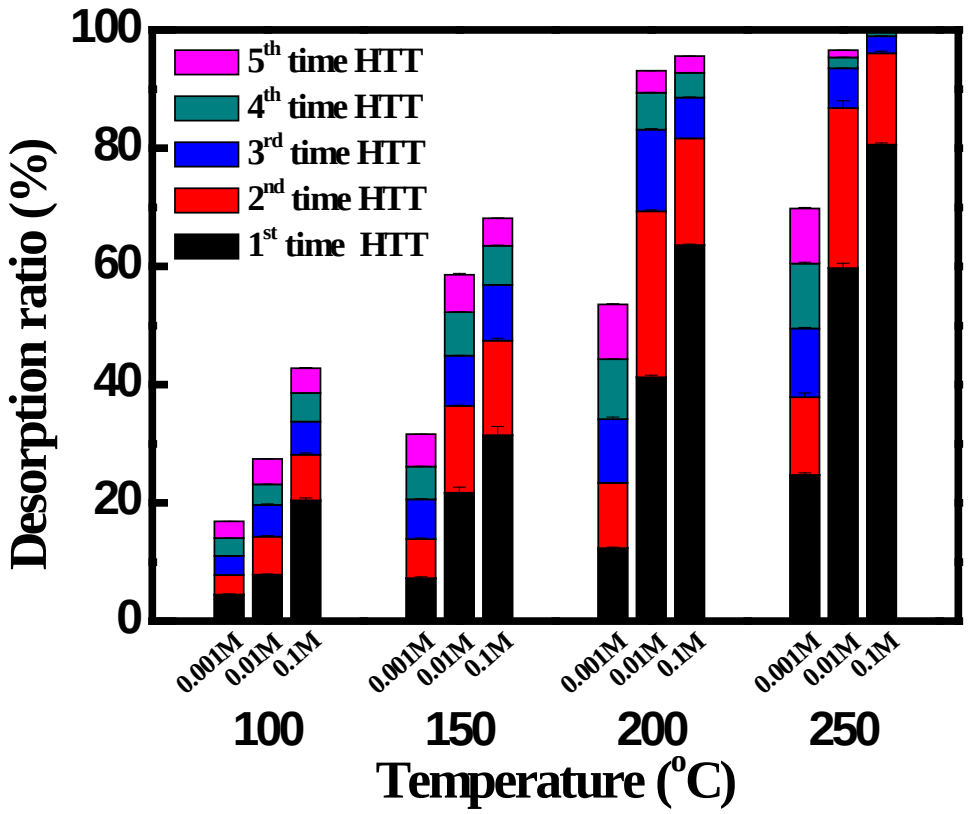
Enhanced Cs Desorption by HTT with M^{3+} Cations



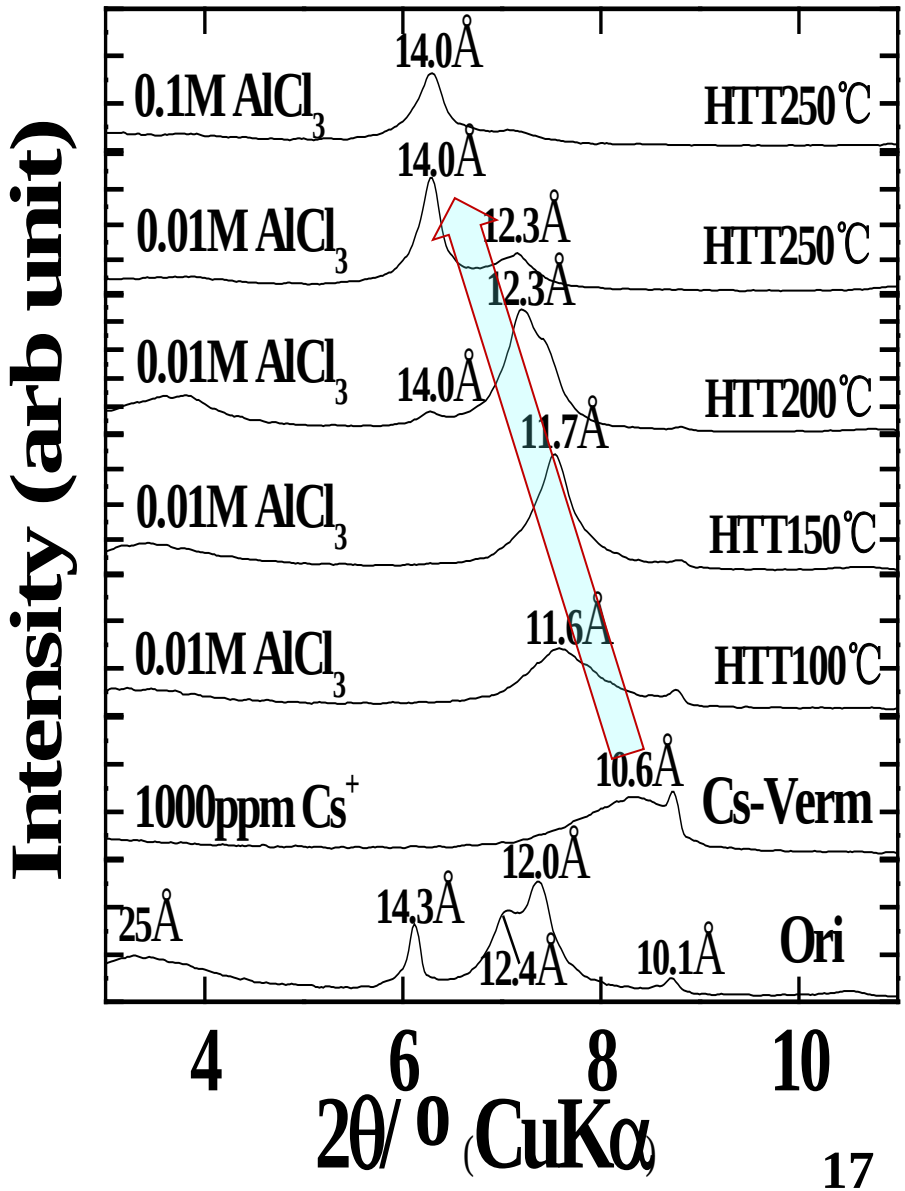


- ✓ M^{3+} **(Al^{3+}/Fe^{3+}/La^{3+})** have the stronger ability to desorb Cs than that of M^{2+}/M^{+}.
- ✓ XRD confirms the **substitution** process.

Cs Desorption by HTT with Al^{3+}

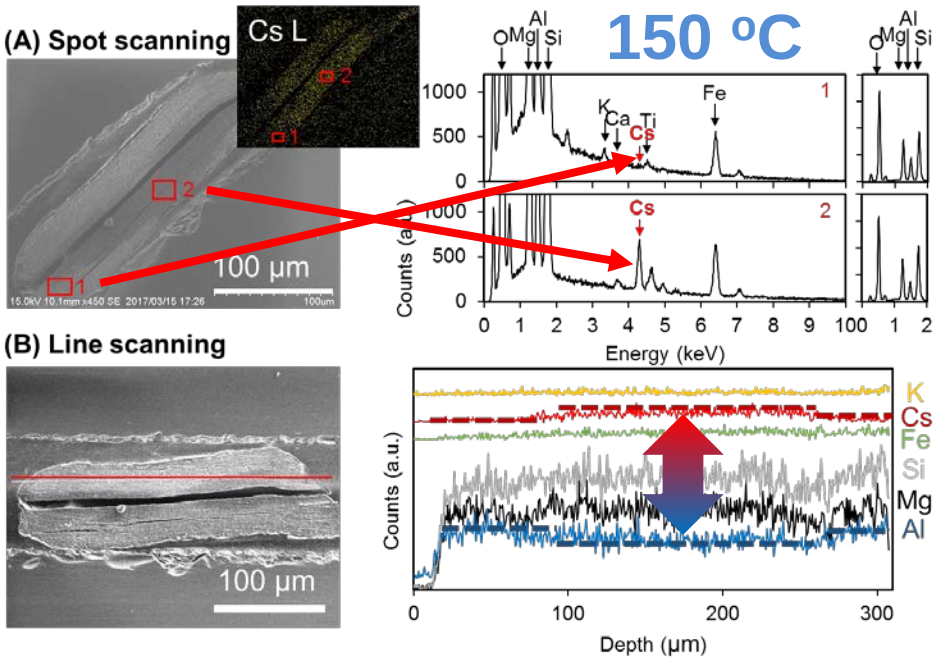


- ✓ Same as Mg^{2+}, desorption ratios improves with the increase of **Al^{3+} concentration and temperature**.
- ✓ XRD confirms the **expansion of interlayers** after Al^{3+} extraction.

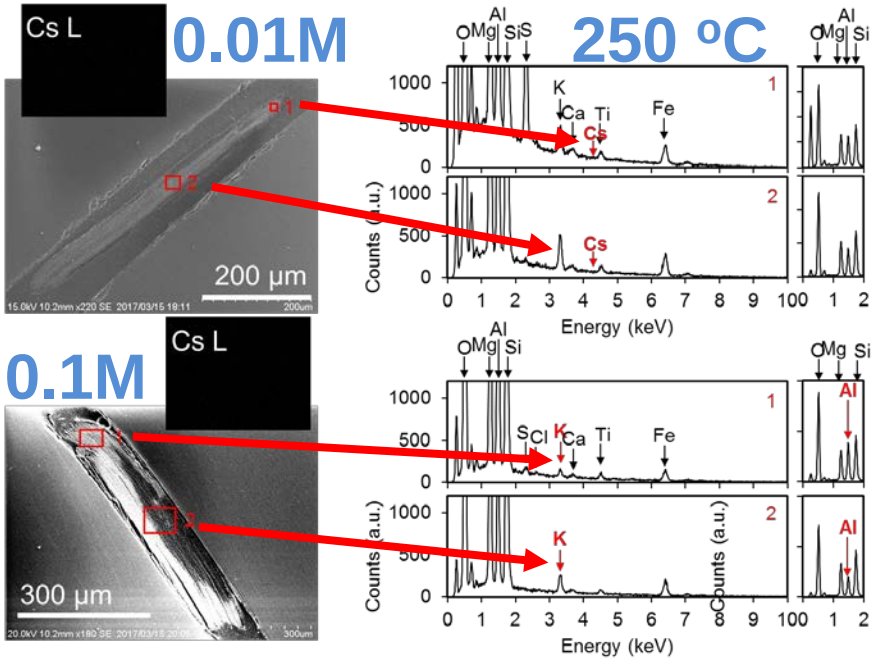


Cs Desorption by HTT with Al^{3+}

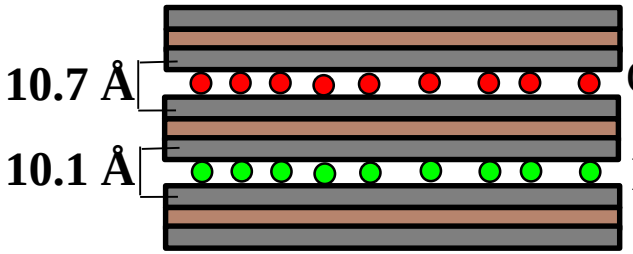
Cs^+ substitution by Al^{3+}



K^+ substitution by Al^{3+}

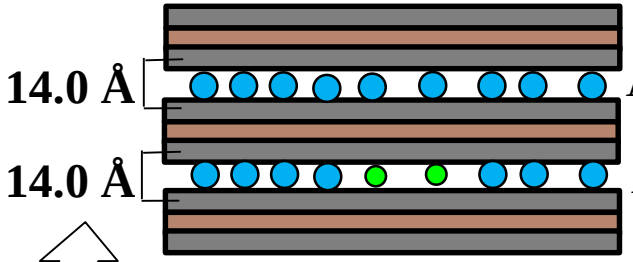


Cs^+ Saturated VB



Al+ HTT

Cs^+ Desorbed VB

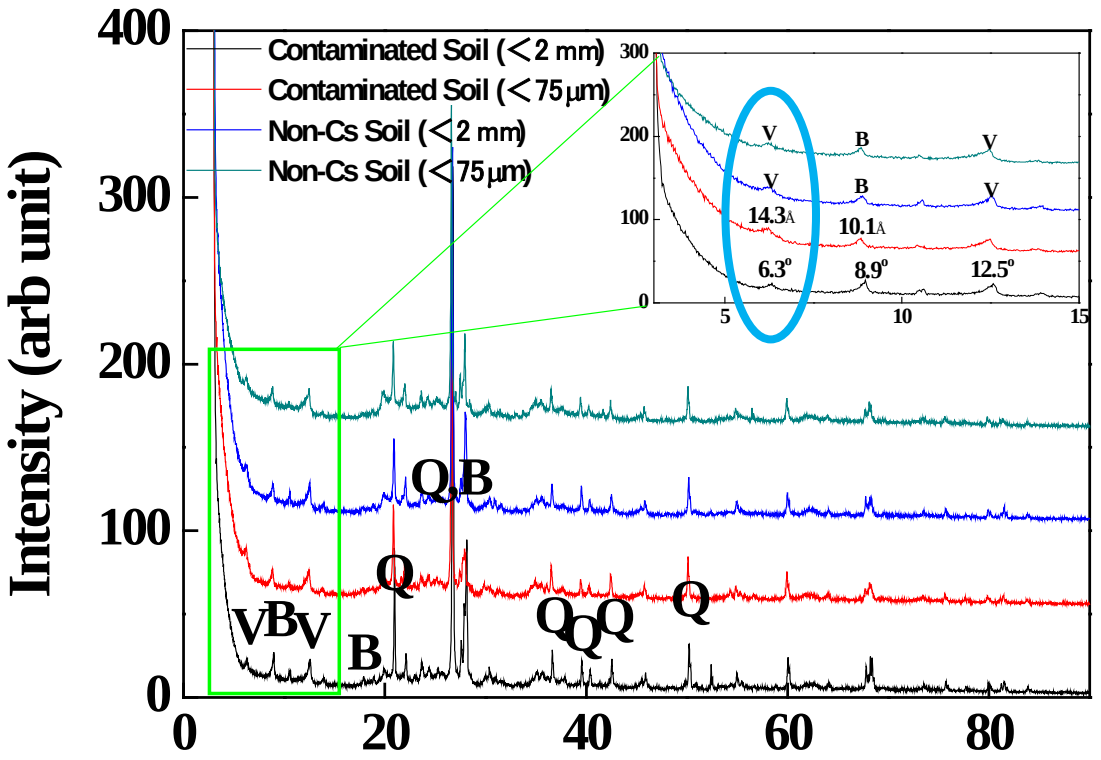


Ion Exchange

Cs Desorption for Actual Contaminated Soil

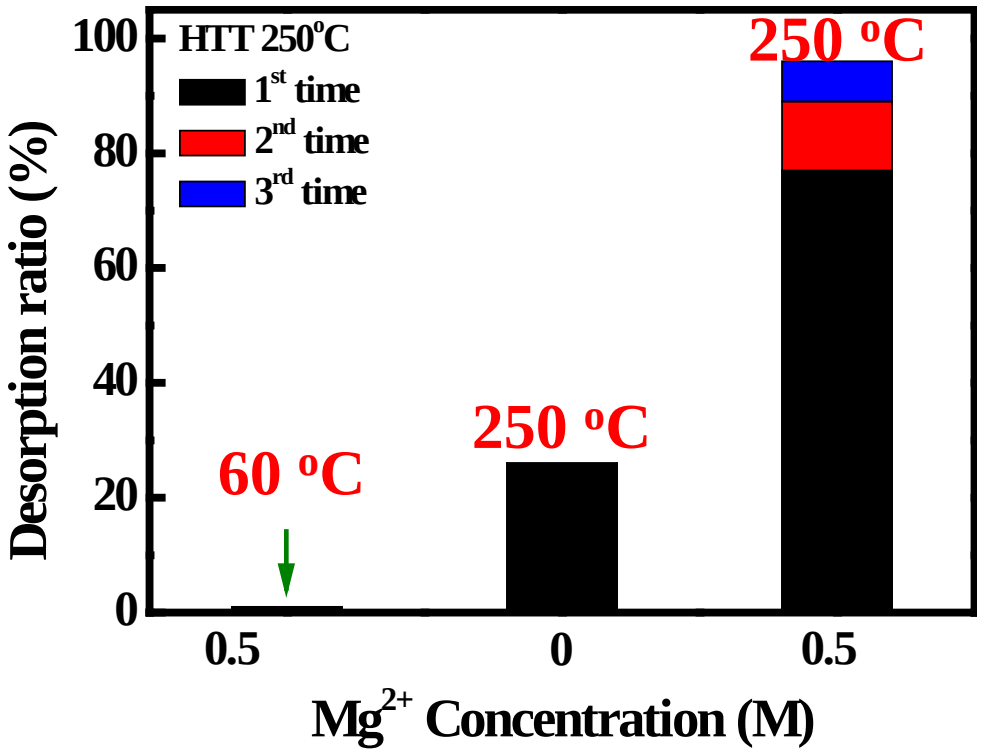
Radioactivity: 15,500 Bq/kg

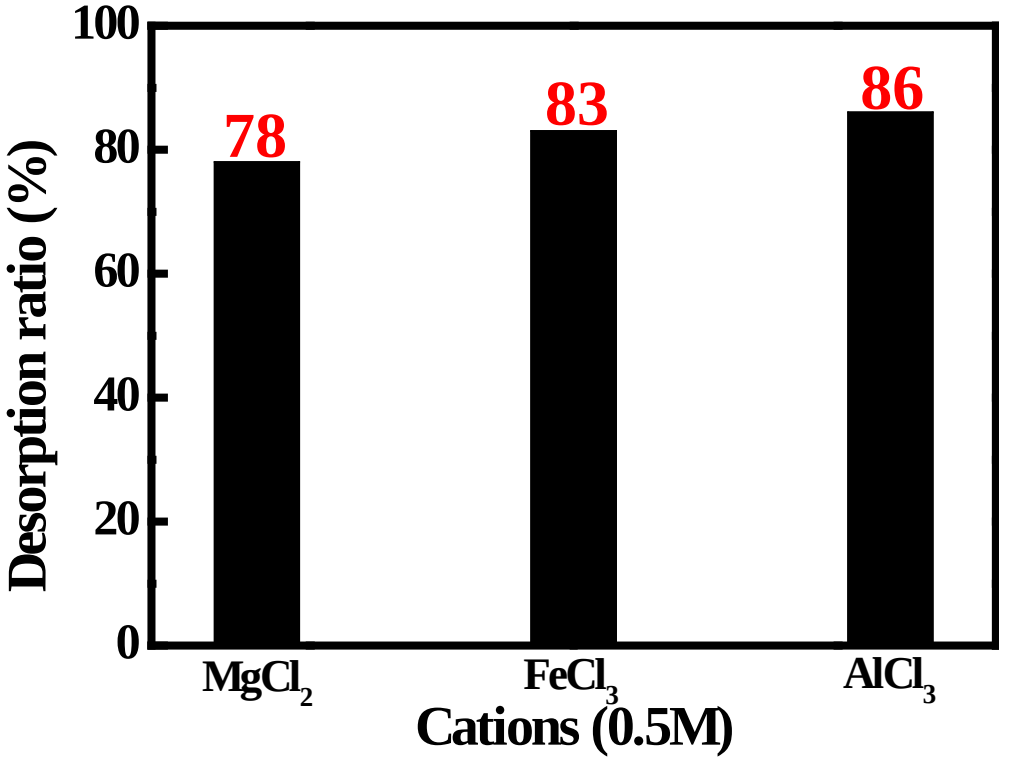
HTT: 0.5g/50ml, 30 min



- ✓ Actual contaminated soil is sampled **near a gutter inlet in Tokaimura**, Ibaraki Prefecture.
- ✓ XRD confirms the **existence of weathered micaceous clay** in soil.

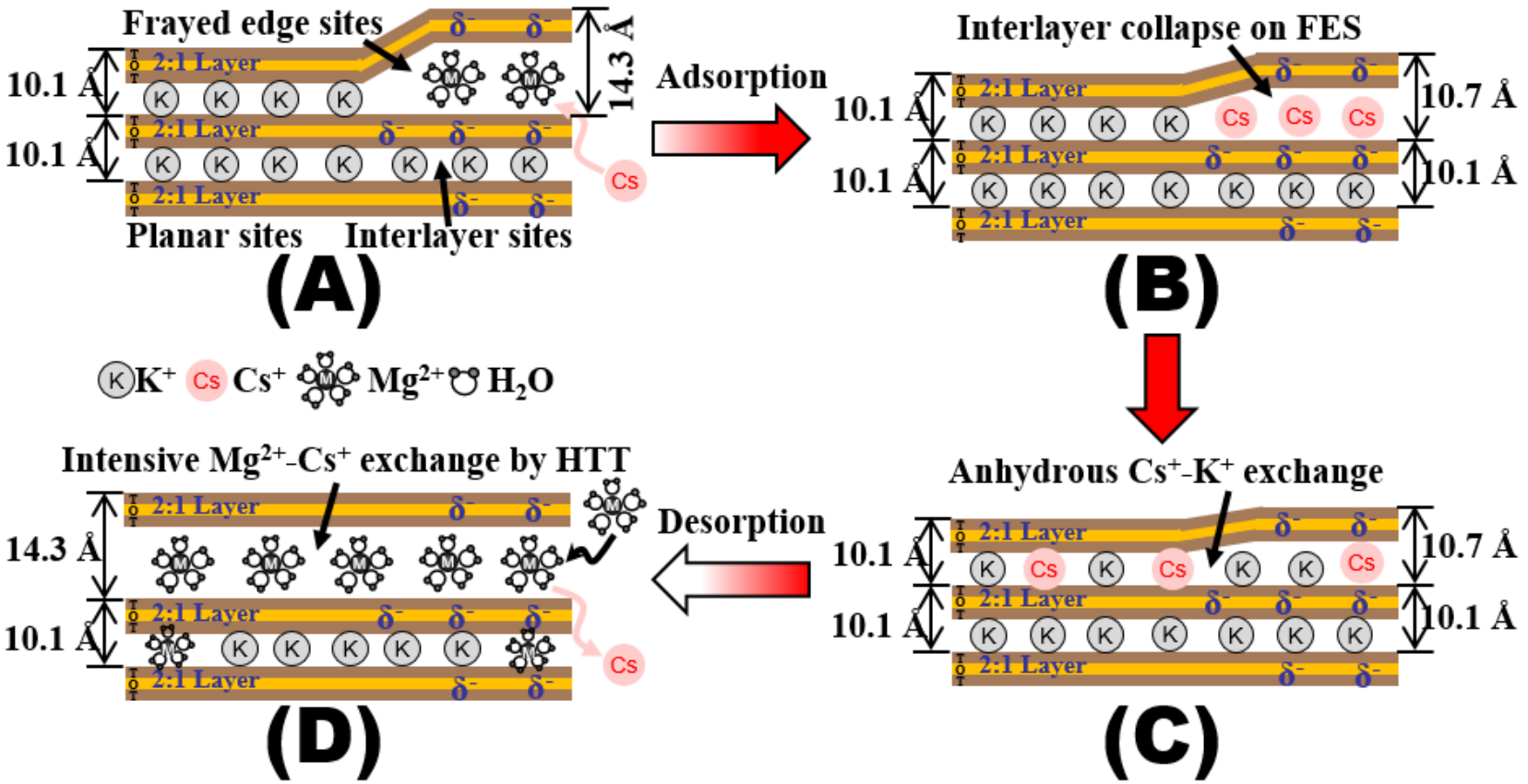
Cs Desorption from Radioactive Fukushima Soil





- ✓ HTT with 0.5 M Mg^{2+} at 60 °C is **not useful** for Cs desorption.
- ✓ **Decomposition** of Cs-sorbed organic material releases 25% of Cs.
- ✓ Cs desorption is **significant enhanced** by HTT with Mg^{2+} at 250 °C.
- ✓ **M^{3+} (Fe^{3+}/Al^{3+})** cations indeed desorb more Cs than **M^{2+} (Mg^{2+})**.

Mechanism Discussion



① Before Cs^+ adsorption, **Mg^{2+} and K^+** originally occupy the interlayers

② During Cs^+ adsorption, Cs^+ gradually replace **Mg^{2+}** in **frayed edge sites.**

③ Edge of interlayer region collapsed and **Cs diffused into deeper region**

④ By HTT, **M^{2+}/M^{3+} expanded** collapsed layer again and readily replace Cs^+

Summary and Conclusion

1. Cs^+ is successfully fixed in **collapsed interlayers** by saturation sorption to simulate its tight fixation on FES of clay mineral into soil.

2. **Higher temp** can significant enhance $M^{2+/3+}$ to desorb Cs^+ from collapsed interlayer regions of clay minerals.

3. **Mechanism** underlying the desorption process of Cs by divalent cations and the **applicability** of the hydrothermal treatment to remove trace amounts of Cs from actual radioactive soil are clarified.


THANK YOU FOR YOUR ATTENTION!