ISFNT15
INTERNATIONAL SYMPOSIUM ON FUSION NUCLEAR TECHNOLOGY

10-15 SEPT 2023
AUDITORIO ALFREDO KRAUS
LAS PALMAS DE GRAN CANARIA, SPAIN

Selective adsorption properties of layered titanate for tritiated water

Yuki Edao[1], Yasunori Iwai[1], Hiroyoshi Mori[2], Nobuki Itoi[2], Toshiki Goto[2], Nobuhiro Kumada[3]

1. National Institutes for Quantum Science and Technology (QST)
2. Otsuka Chemical Co., Ltd.
3. Center for Crystal Science and Technology, University of Yamanashi

QST National Institutes for Quantum Science and Technology

Otsuka 大塚化学株式会社

山梨大学 UNIVERSITY OF YAMANASHI

Outline

1. Background

2. Experiments & Results
    1. HTO vapor exposure
        - ✓ Comparison among different samples
        - ✓ Effect of ion among layer structure

    2. HTO water exposure
        - ✓ Difference of HTO adsorption rate

    3. HTO desorption
        - ✓ Consideration of mechanism of adsorption

3. Conclusion

Background

Separation of hydrogen isotopes

- Difficult to separate tritiated water and light water because tritiated water (HTO) is similar in properties to light water (H2O)
- Necessary to separate and reuse tritium from the viewpoint of fuel for fusion reactors and effective use in various research and development.

Techniques of separation and concentration of tritiated water (HTO)

Separation techniques exist in the field of atomic power plant (CANDU reactor) and fusion energy

- ✓ Distillation
- ✓ Electrolysis
- ✓ Isotopic exchange

Current Issues

- To separate hydrogen isotopes from water, huge amounts of energy and cost are required for the separation of H2O and HTO, such as repeated distillation and electrolysis many times.

Background

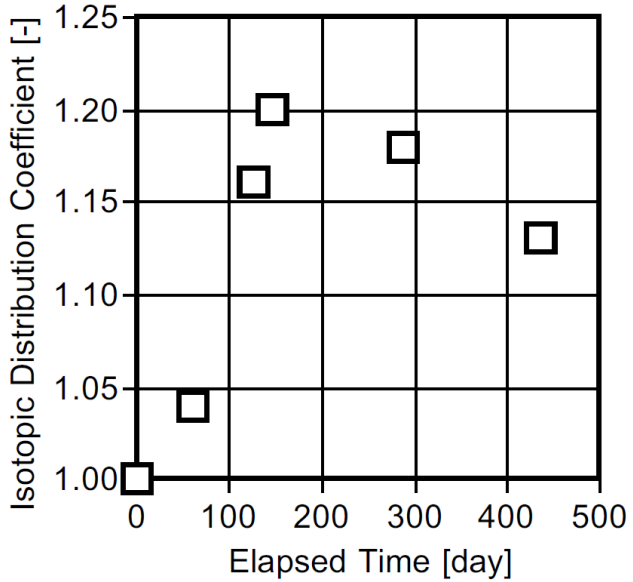
Promising method of separation and concentration of HTO

- Use of adsorbent for the process

Use of adsorbent as a packing material in the distillation process has been proposed to make the separation more efficient.

- Tritium separation efficiency has been reported to be improved in distillation systems using zeolite, a typical adsorbent
- Separation coefficient of zeolite is about 1.02 to 1.20.
  (1.0: No separation ability)

S. Fukada, FST 48 (2005)



Y. Iwai, FST 56 (2009)

The development of a new adsorbent is desired to improve the tritium separation efficiency.

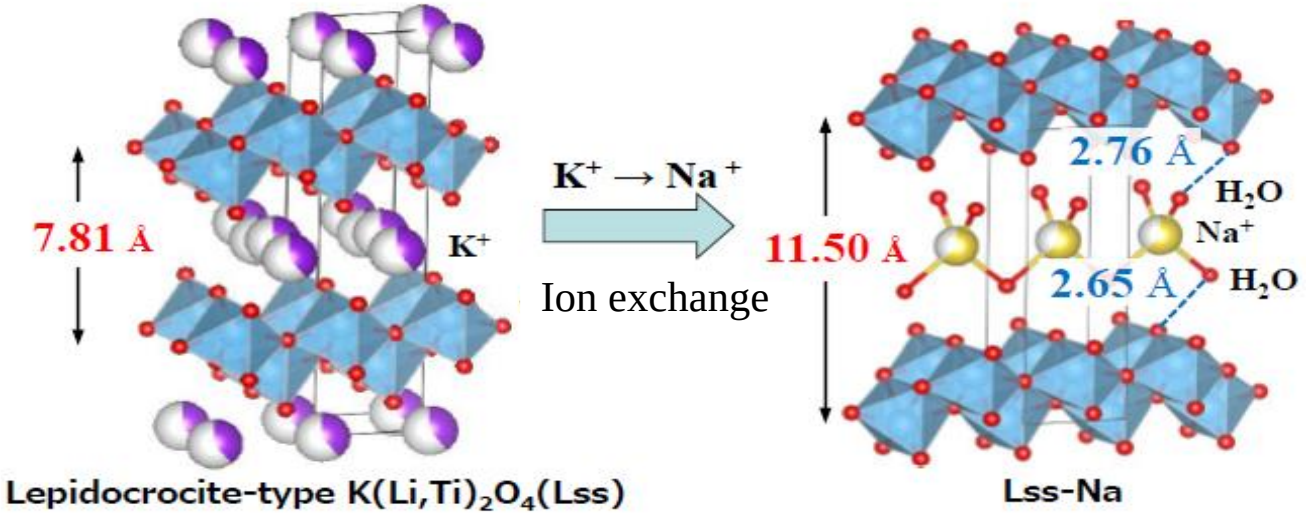
Material focused in this study

Focused Material:

✓ Layered titanate salt as a new adsorbent
✓ The characteristic can be changed depends on the interlayer metal ions
✓ The titanate sodium substituted has two-step water adsorption properties
(*K. Makise et. al, J. Asian Ceram. Soc., 11, 170 (2023)*)

Purpose:

Focusing on this unique property, the selective adsorption characteristics of tritiated water on the material were investigated experimentally.



"TERRACESS" produced by Otsuka Chemical Co., Ltd.
Unique property of two-step water adsorption

K. Makise et. al, *J. Asian Ceram. Soc.*, **11,** 170 (2023).

Outline

1. Background

2. Experimental & Results

1. HTO vapor exposure

- ✓ **Comparison among different samples**
- ✓ **Effect of ion among layer structure**

2. HTO water exposure

- ✓ Difference of HTO adsorption rate

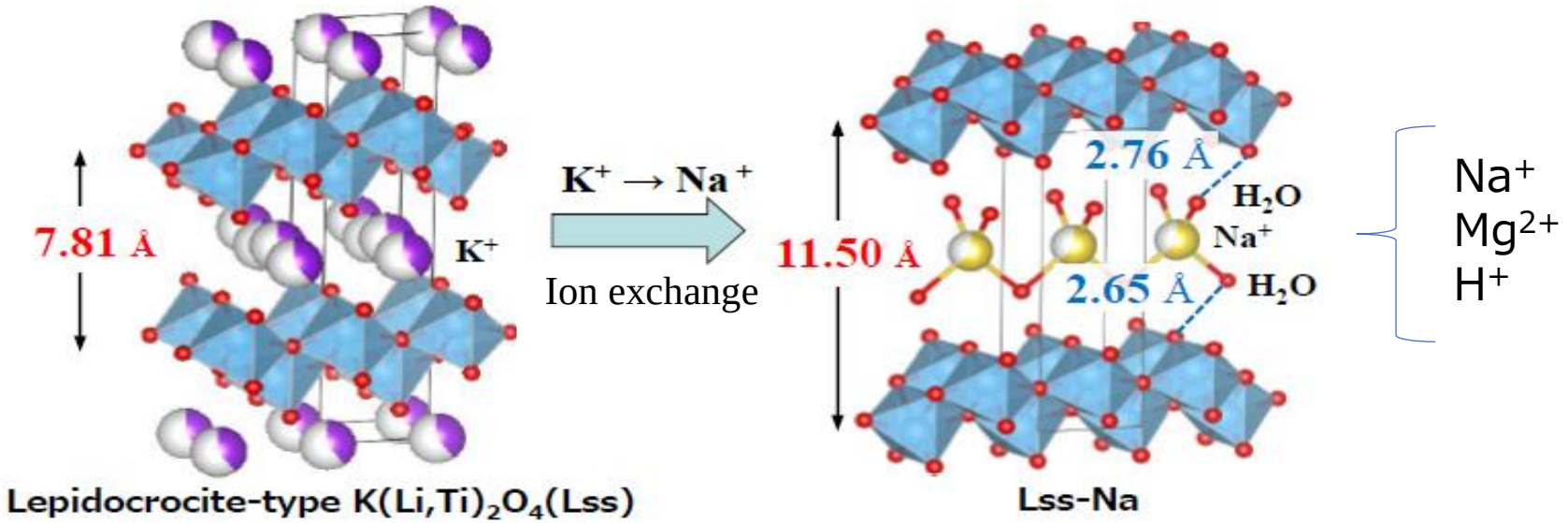
3. HTO desorption

- ✓ Consideration of mechanism of adsorption

3. Conclusion

Sample preparation

- Several types of powder samples with composition control based on a commercial potassium titanate salt (LSS-K) were prepared.
- The layered potassium titanate ($K_{0.75}Li_{0.25}Ti_{1.75}O_4$) Lss-K
- The Na substitute layered titanate ($Na_{0.75}$ ($Li_{0.25}Ti_{1.75}$)O_4) Lss-Na
- To investigate the effects of interlayer metal ions, Lss-Mg and Lss-H in which were introduced Mg ions and H ions, which were known to incorporate water molecules between layers, were fabricated by the same method.
- As a comparison, zeolite (MS3A: Molecular Sieves 3A) and empty (Blank) were prepared.



Experiment 1: HTO vapor exposure

Investigation of characteristic of HTO adsorption

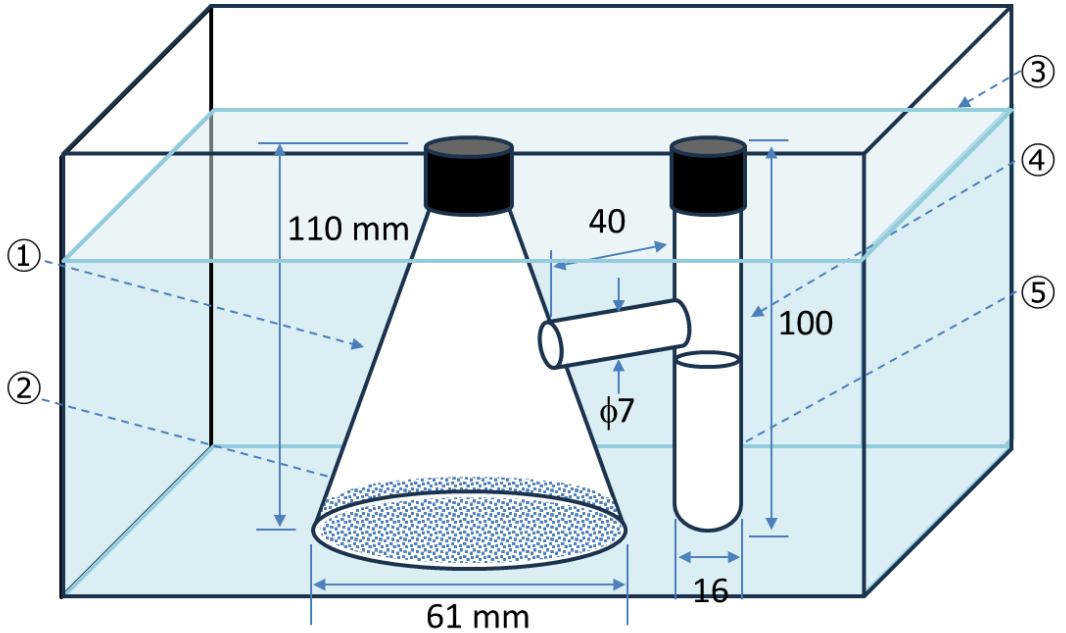
The static method is the best approach to measure the isotopic distribution considering the difference in adsorption rate though a long time is needed to reach isotopic equilibrium.

Experimental conditions

Sample: Lss-Na, Lss-Mg, Lss-H, Lss-K, MS3A (for reference)
Sample weight: 5 g , 15g
HTO water: 5g
HTO conc.: 0.38MBq/g
Temperature: 30°C (Water bath)

Procedure

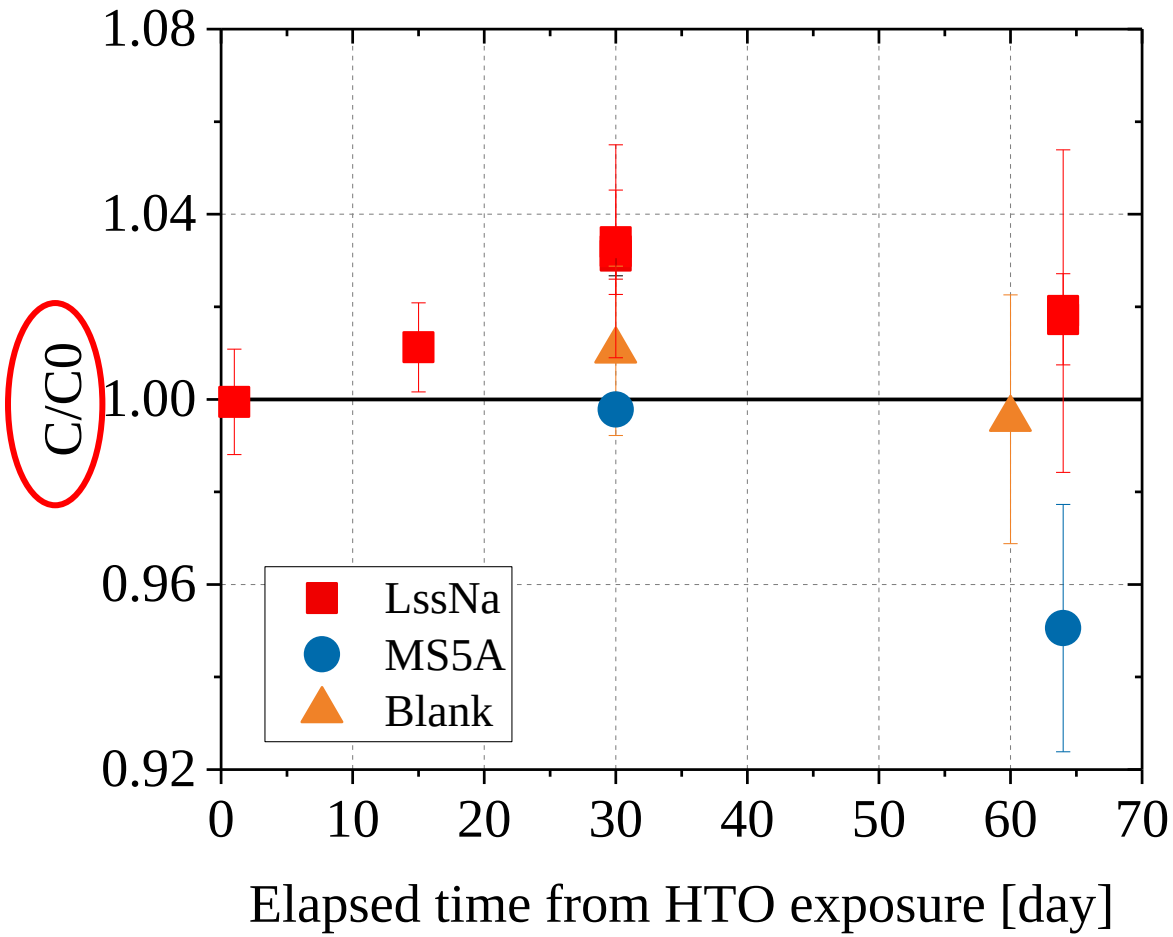
1. Dry sample at 200°C
2. Put the sample in the container with HTO water and leave it in water bath
3. Measure tritium conc. in the water by LSC
4. HTO in the sample was measured by the immersion method

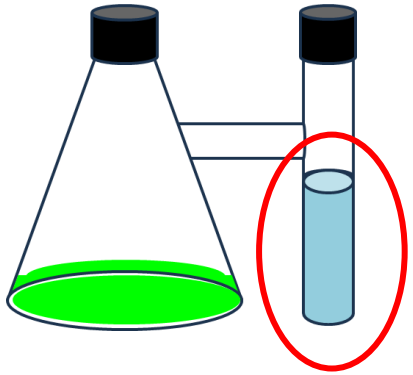


① Plug equipped Erlenmeyer flask (100mL)
② Adsorbent sample
③ Temperature controlled water tank
④ Plug equipped test tube (11mL)
⑤ Tritiated water (5mL)

Result 1-1: Changing in HTO concentration

Changing in concentration ratio of HTO (C/C0) with elapsed time

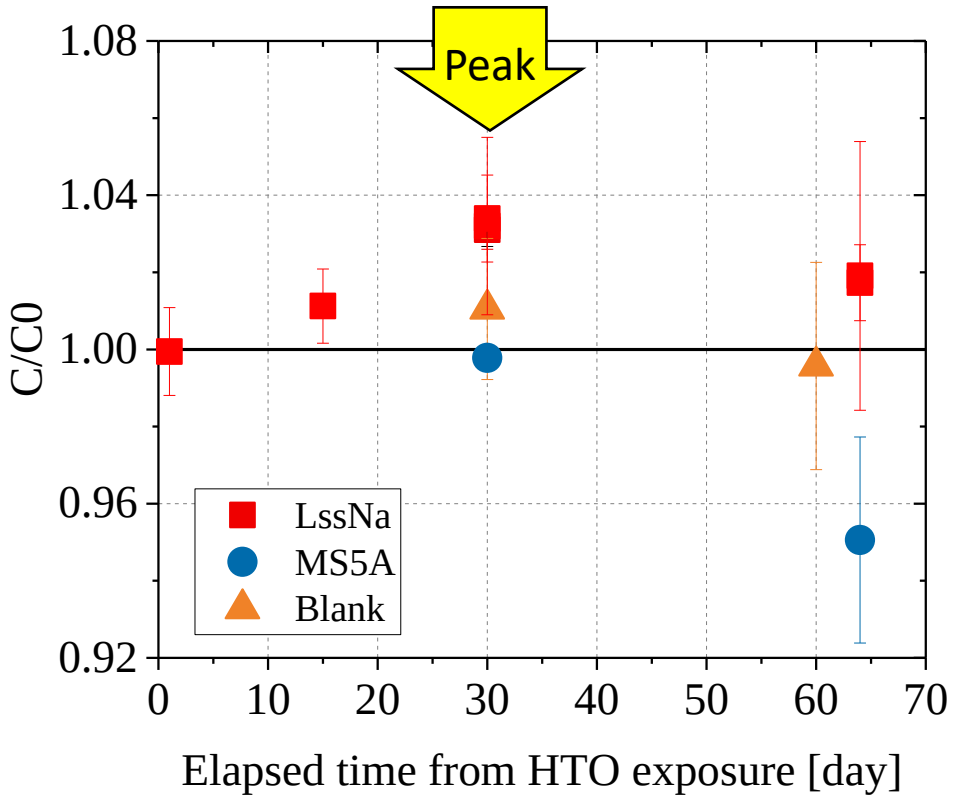


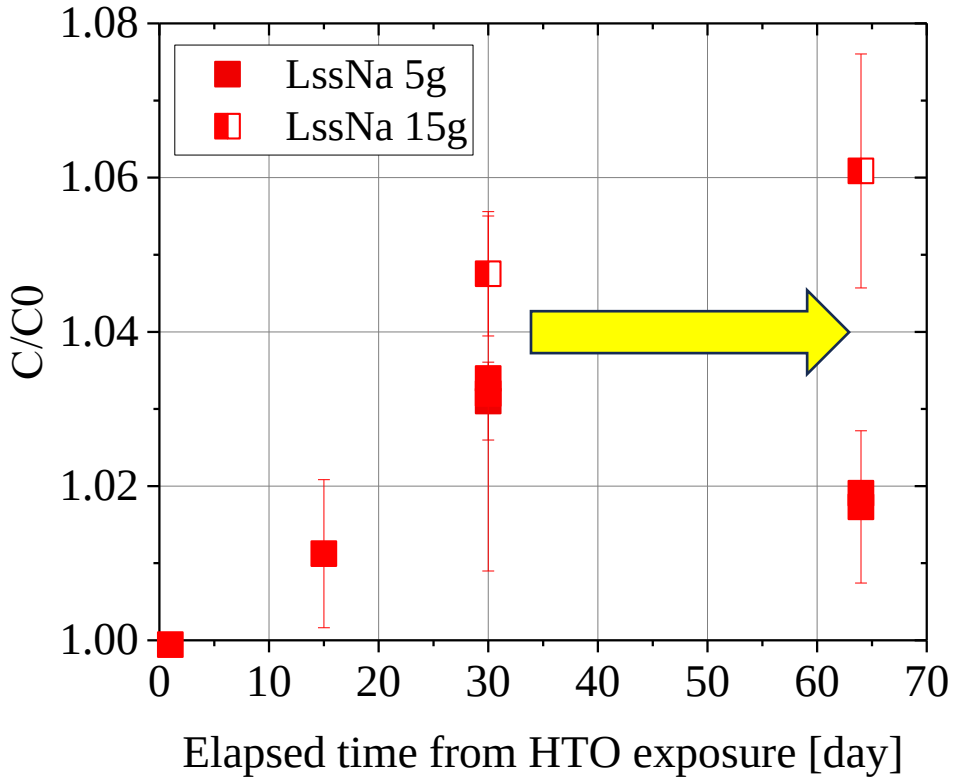


- ✓ Blank: No change (C/C0＝1)
- ✓ MS3A: Gradually decrease (C/C0 <1)
  - ➢ Consistent with conventional tendency to preferentially adsorb HTO
  - ➢ The validity of this experimental method was confirmed.
- ✓ LssNa: Concentrate HTO (C/C0 >1)
  - ➢ Opposite tendency to MS3A as a general absorbent. H2O was preferentially adsorbed
  - ➢ Selectively inhibit the adsorption of HTO onto the material

Result 1-2: Changing in HTO concentration

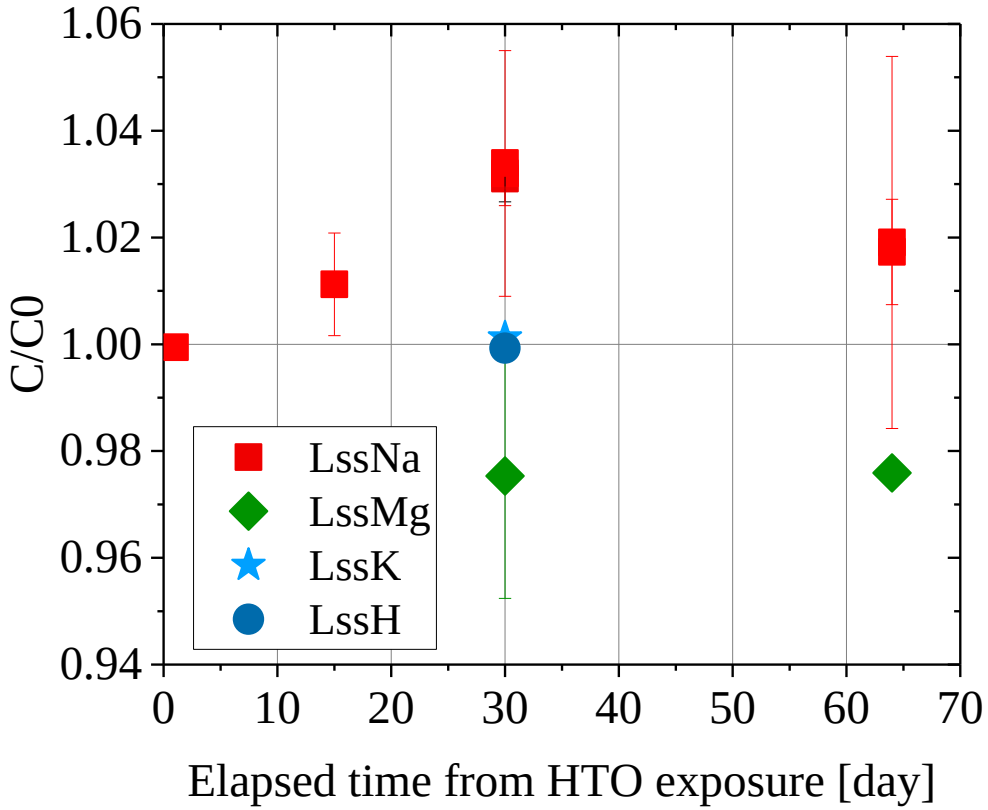
Changing in concentration ratio of HTO (C/C0) with elapsed time





- ✓ C/C0 has peak during the exposure period.
- ✓ The peak time became longer with increasing the amount of the sample Lss-Na.
  - ➢ These suggest the possibility that the adsorption mechanism is key to the difference in adsorption speed between HTO and H2O

Result 1-3: Effect of interlayer ion in structure



	Days	C/C0
LssNa	30	1.03 ±0.01
LssH	30	1.00 ±0.01
LssMg	30	0.98 ±0.02
LssK	31	1.00 ±0.00

Comparison among Lss-Na, Lss-H and Lss-Mg
(Lss-K: no-taking in water molecules between layers)

- ✓ LSS-H: No change C/C0=1
- ✓ LSS-Mg: C/C0<1
  - ➢ Interlayer ions affect adsorption properties of HTO
  - ➢ Only Lss-Na adsorbed H2O preferentially

Outline

1. Background

2. Experimental & Results

1. HTO vapor exposure

- ✓ Comparison among different samples
- ✓ Effect of ion among layer structure

2. HTO water exposure

- ✓ **Difference of HTO adsorption rate**

3. HTO desorption

- ✓ Consideration of mechanism of adsorption

3. Conclusion

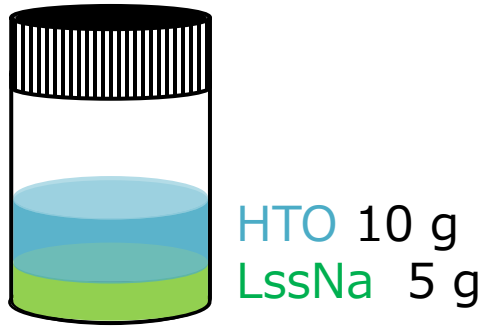
Experiment 2: HTO water immersion

Investigation of HTO adsorption rate

To confirm the HTO adsorption rate of LSS-Na in detail the sample was directly contacted with tritiated water

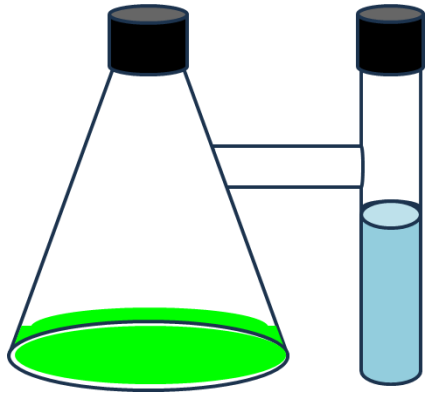
Fast

liquid contacting



Slow

Vapor contacting



Experimental conditions

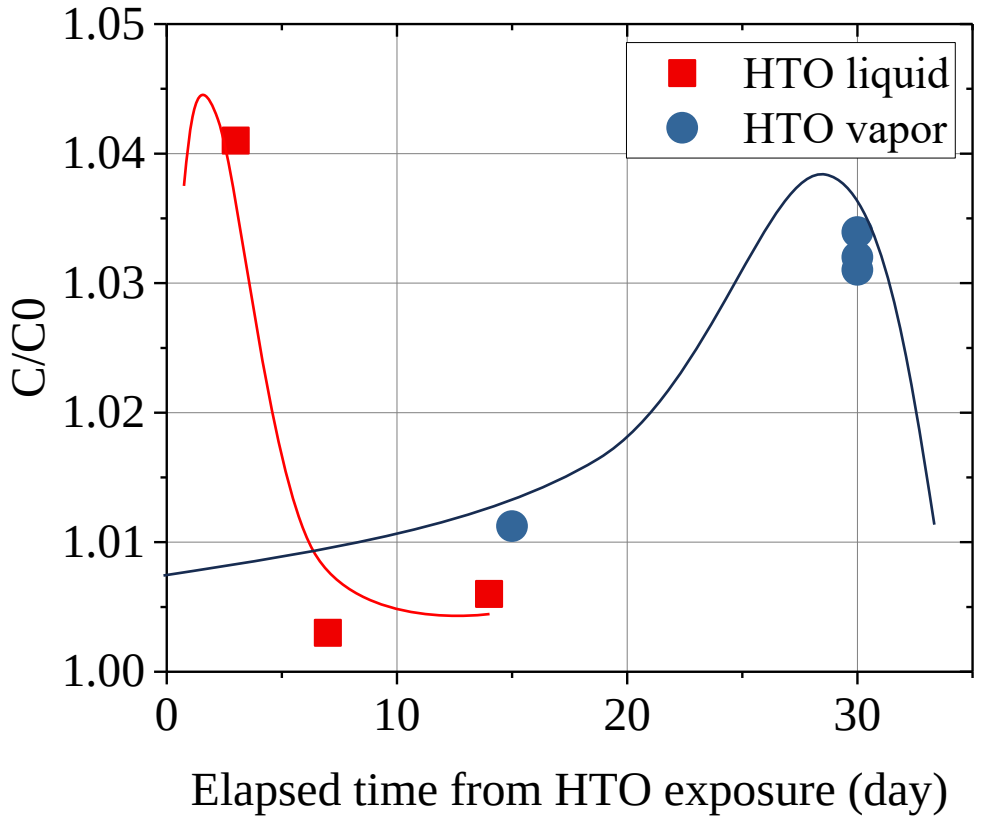
Sample: LssNa, 5 g
HTO water: 0.38MBq/g, 10 g
Temperature: RT
Duration: 3, 7, 14 days

Procedure

1. LssNa was immersed in HTO water
2. Leave it for over 3 days at RT
3. Sample the clean layer of HTO water after the predetermined days
4. HTO concentration was measured by LSC

Result 2: HTO adsorption rate

Difference of exposure between vapor (slow) and liquid (fast)



- ✓ The peak time was long in vapor exposure for slow HTO contacting.
- ✓ The peak time was short in liquid exposure for fast HTO contacting.
  - ➢ This result suggest that the adsorption mechanism is key to the difference in adsorption rate (speed) between HTO and H2O

Outline

1. Background

2. Experimental & Results

1. HTO vapor exposure
   - ✓ Comparison among different samples
   - ✓ Effect of ion among layer structure

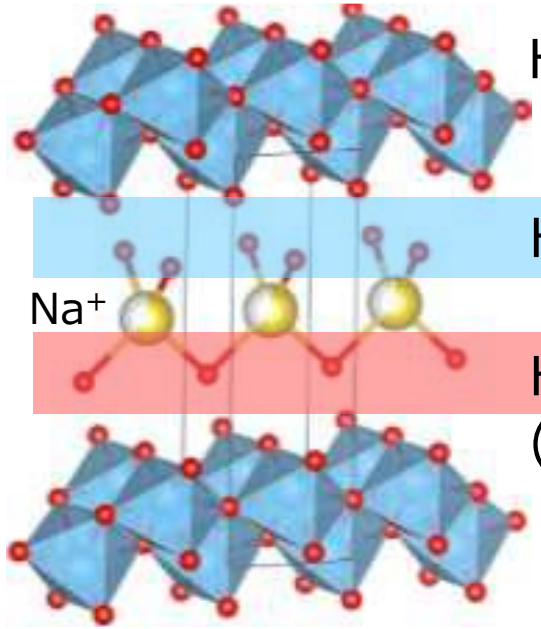
2. HTO water exposure
   - ✓ Difference of HTO adsorption rate

3. HTO desorption
   - ✓ **HTO distribution in the layer**
   - ✓ **Consideration of mechanism of adsorption**

3. Conclusion

Consideration of HTO adsorption mechanism

3 types of water absorbed on Lss-Na



H_2O-I: Surface water

H_2O-II: 2nd interlayer water

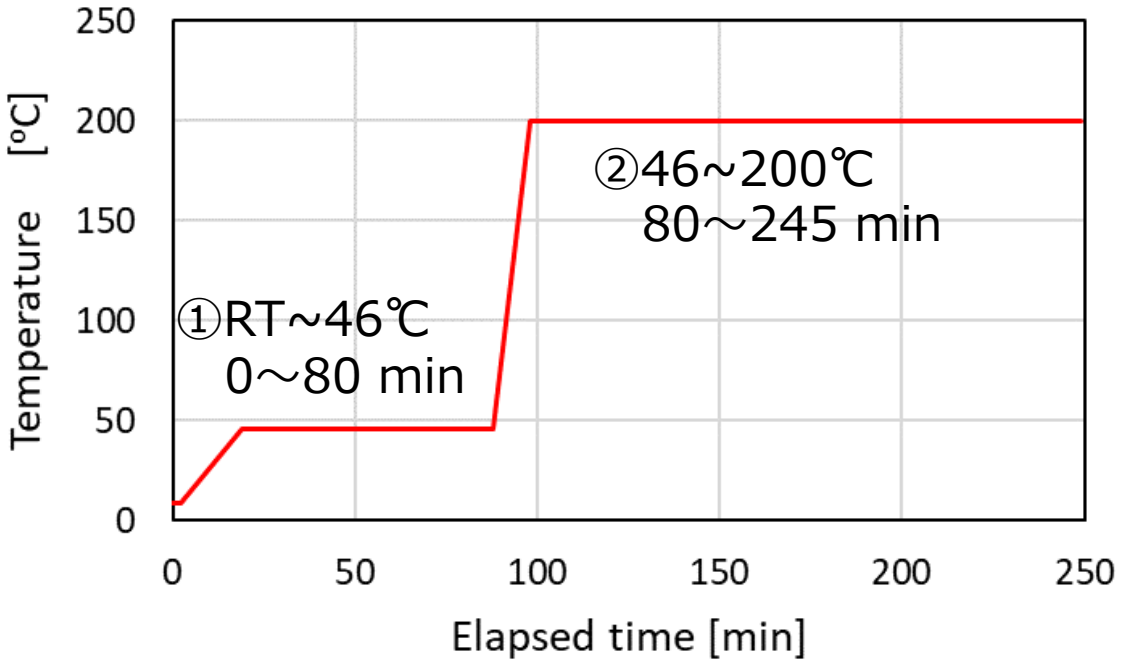
H_2O-III: 1st interlayer water
(preferentially adsorbed in the early stages)

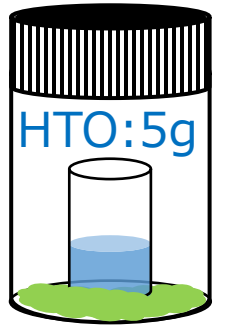
Which types of water HTO is exist in?

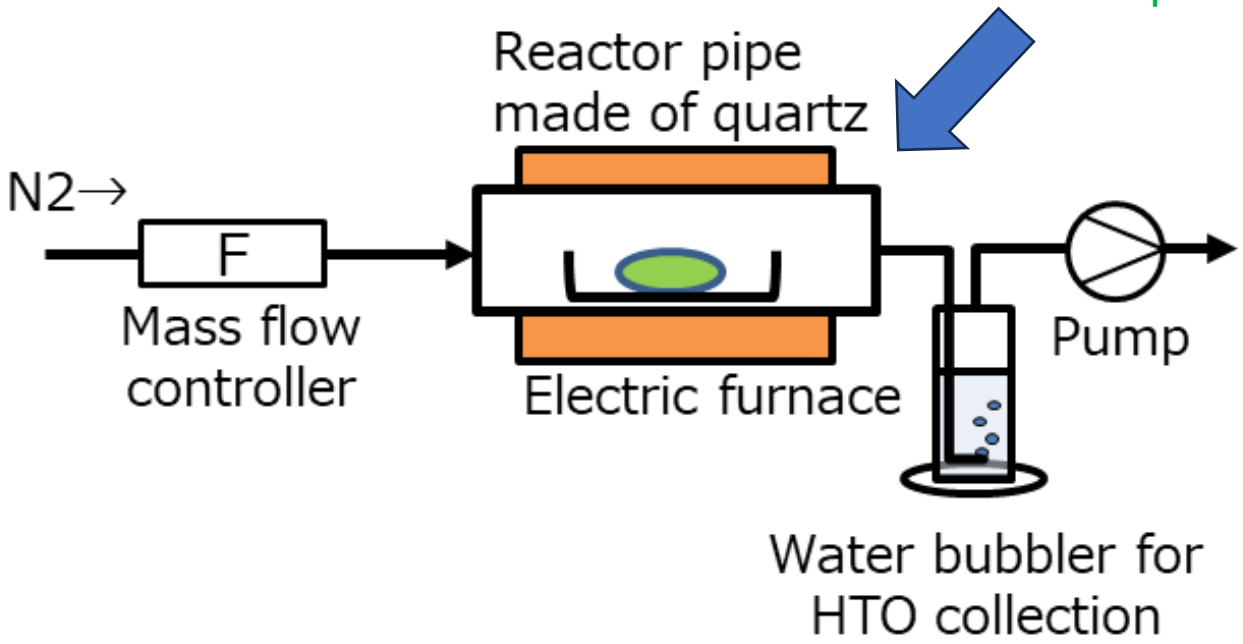
Experiment 3: HTO desorption

Investigation of HTO distribution in LssNa

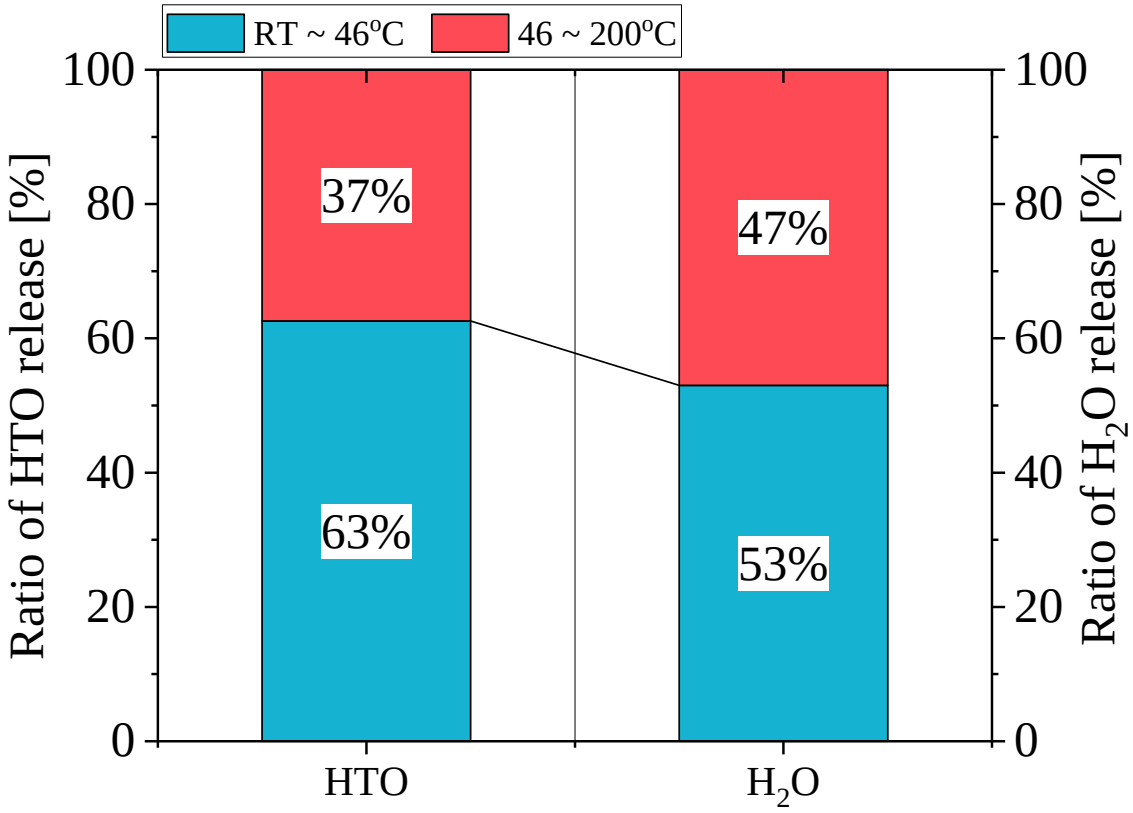
Experiment of water desorption from LssNa with HTO
Sample: LssNa, 5 g with HTO exposure
N2 purge gas flow rate: 0.5L/min
Water weight: 100ml
Temp and time:







Result 3: Characteristic of HTO adsorption



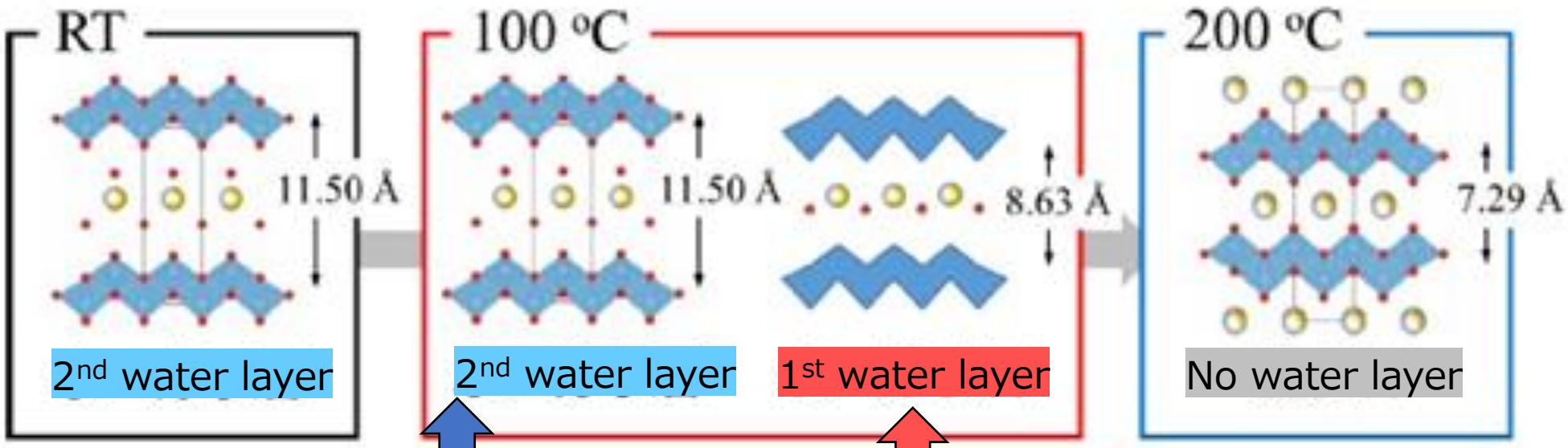
Temperature (°C)	HTO release amount (kBq)
46~200	105
RT~46	176

If tritium is uniformly distributed in LssNa, the ratio should be the same.

- Tritium was contained in H_2O desorbed at 46℃~200℃ (H_2O-III)
- Ratio of HTO in H_2O-III was lower than that in H_2O-II
  - ➢ Consistent with results of HTO exposure
    - ✓ No isotope effect: C/C0=1
    - ✓ Easy to adsorb HTO in adsorbent: C/C0<1, HTO water diluted
    - ✓ Easy to adsorb H_2O in adsorbent: C/C0>1, HTO water concentrated

Mechanism of HTO adsorption

Desorption rate is different between HTO and H2O in the process of adsorption on the first layer of LssNa



H_2O is taken in LssNa preferentially

H_2O and HTO is taken in LssNa equally

Outline

1. Background

2. Experimental & Results
   - HTO vapor exposure
     - ✓ Comparison among different samples
     - ✓ Effect of ion among layer structure
   - HTO water exposure
     - ✓ Difference of HTO adsorption rate
   - HTO desorption
     - ✓ Consideration of mechanism of adsorption

3. Conclusion

Conclusion

- ✓ Titanate layered inorganic compound has two-step moisture adsorption properties depending on the interlayer metal ions.
- ✓ LssNa adsorbed H2O preferentially. (the opposite of common knowledge which HTO preferentially adsorbs in adsorbent)
- ✓ As for layered titanates, only Na-substituted titanates preferentially adsorb light water better than tritiated water.
- ✓ H2O is easily taken up by the first layer.
- ✓ The mechanism of tritiated water separation and concentration is due to the difference in adsorption rates

Future prospect of the material

- ✓ Development of tritium contamination prevention technology
- ✓ Development for adsorbent supported tritiated water separation technology
  - ➢ Necessary to mold the layered titanate salt so that it can be actually used.