Supporting Information for

Na Ion-Exchanged Zirconium Phosphate Crystal with High Calcium Ion Selectivity

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Materials and Methods

Growth of (Na,H)-ZrP crystals

(Na,H)-ZrP is synthesized by using α-ZrP (manufactured by Toa Gosei) and commercially available reagents: $NaH_2PO_4\cdot 2H_2O$ (reagent grade, Wako Pure Chemical Industries), NaF (special grade, Wako Pure Chemical Industries), and H_3PO_4 (reagent grade, Wako Pure Chemical Industries). Typically, the components were weighed in a atomic/molar ratio of Zr : PO_4 : F = 1 : 4.5 : 0.3 to achieve a total mass of approximately 3.5 g. Subsequently, the mixture was ground in an agate mortar for 15 minutes and then transferred to a Teflon container with a volume of about 100 mL. A solution of H_3PO_4 (30 mL) was added to the Teflon container, and the pH was adjusted to approximately 1-4. The hydrothermal synthesis was conducted under the conditions of holding temperatures at 150, 190, 220, and 250 °C, and holding times of 24 hours. After heating, the mixture was cooled to room temperature, separated by suction filtration, and dried at 50 °C.

Transformation of (Na,H)-ZrP into γ-ZrP is achieved through the immersion in 6 M HCl aqueous solution at room temperature for 24 hours.

Characterization. X-ray diffraction (XRD) patterns were collected using a MiniflexII diffractometer (Rigaku, Japan) and SmartLab (Rigaku, Japan) with monochromated Cu K_{α} radiation (λ = 0.15418 nm). Field-emission scanning electron microscopy (FE-SEM) images and energy dispersive X-ray (EDX) spectrometry data were obtained using a JSM-7600F instrument (JEOL, Japan). Thermogravimetry–differential thermal analysis (TG-DTA, Thermo Plus EVOII TG8120, Rigaku, Japan) was used to analyze the water content in the samples at a heating rate of 10 °C min^{-1} in an air flow. Bright-field TEM images and SAED patterns were obtained using an 80-kV electron microscope (JEM-2100F, JEOL) equipped with a double-aberration corrector (CESCOR/CETCOR, CEOS).

Adsorption Experiments.

Reagent were purchased from FUJIFILM Wako Pure Chemical Industries unless otherwise stated. The ion exchange reactions are performed through the immersion of the prepared ZrP samples in 0.25-8 mM alkaline earth metal chloride MCl_2 solution (M = Mg, Ca, Sr, Ba) at 25, 40, and 70 °C for 10-5000 min, and the final pH of the solution was 3-6. For example, ZrP samples (70 mg) was immersed in 70 mL of an aqueous alkaline earth metal chloride solution.

For the Kielland plot analysis, 70 mg specimens were equilibrated for 2 h in 70 mL of a binary chloride solution (MCl_2-NaCl/HCl, M = Mg, Ca, Sr, Ba) at various ratios of the two salts to determine the thermodynamic parameters at a total molarity of 8 mM at 70 °C for 2 h. The adsorption experiments were conducted at least twice under the same adsorption conditions.

The distribution coefficient K_d was used to evaluate the selectivity of (Na,H)-ZrP toward various cations (Eq. 1):

$$K_d = \frac{(C_0 - C_e)}{C_e}\frac{V}{m}, \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations (mmol·L^{-1}) of Ca^{2+}, V is the volume (cm^3) of the testing solution, and m is the amount of ion-exchanger (g).

The ion exchange reaction of Na^+/H^+ in (Na,H)-ZrP and γ-ZrP with Ca^{2+} can be represented by Eqs. 2 and 3 (the bar refers to the solid phase):

$$2\overline{Na^+} + Ca^{2+} \leftrightarrow \overline{Ca^{2+}} + 2Na^+. \quad (2)$$

$$2\overline{H^+} + Ca^{2+} \leftrightarrow \overline{Ca^{2+}} + 2H^+. \quad (3)$$

The thermodynamic equilibrium constant K of the ion exchange reaction (presented in Eq. 2 or 3) can be defined by Eq. 4 in the case of Na^+ exchange reaction:

$$K_{Na\to Ca} = \frac{m_{Na}{}^2 \cdot \bar{X}_{Ca} \cdot \gamma_{Na}{}^2 \cdot \bar{f}_{Ca}}{m_{Ca} \cdot \bar{X}_{Na}{}^2 \cdot \gamma_{Ca} \cdot \bar{f}_{Na}{}^2} = K_{Na}^{Ca}\ \frac{\bar{f}_{Ca}}{\bar{f}_{Na}{}^2} \quad (4)$$

where K_{Na}^{Ca} is defined as the corrected selectivity coefficient, m_{Na} and m_{Ca} are the molalities of the cations in solution, $\bar{X}_{Na}$ and $\bar{X}_{Ca}$ are the equivalent fractions of Na^+ and Ca^{2+} in the solid phase, γ_{Na} and γ_{Ca} are the ionic activity coefficients of Na^+ and Ca^{2+} in the aqueous phase, and $\bar{f}_{Na}$ and $\bar{f}_{Ca}$ are the ionic activity coefficients of Na^+ and Ca^{2+} in the solid phase. The value of the ionic activity coefficient ratio γ_{Na}/γ_{Ca} in solution is assumed to be unity owing to the dilute conditions. The thermodynamic equilibrium constant can be evaluated by Eq. 5 using a simplified form of the Gaines-Thomas equation,[S1] with the assumption that the change in the water activity in the solid and aqueous phase is negligible.

$$ln\ K = \int_0^1 lnK_{Na}^{Ca} d\bar{X}_{Ca}. \quad (5)$$

The Kielland plot[S2] corresponds to the graph of ln K_{Na}^{Ca}versus $\bar{X}_{Ca}$, is represented by Eq. 6:

$$ln\ K_{Na}^{Ca} = 4.606\ C\ \bar{X}_{Ca} + (\ln K_{Na}^{Ca})_{\overline{X \to 0}}, \tag{6}$$

where C is the Kielland coefficient and $(\ln K_{Na}^{Ca})_{\overline{X \to 0}}$ is the value of ln K_{Na}^{Ca} when $\bar{X}_{Ca}$ is nearly zero. The standard free energy change for the Ca^{2+} exchange reaction is evaluated by Eq. 7 using the $(\ln K_{Na}^{Ca})_{\overline{X \to 0}}$ value:

$$\Delta G^0 = -RT \ln K, \tag{7}$$

where R and T are the molar gas constant and temperature, respectively.

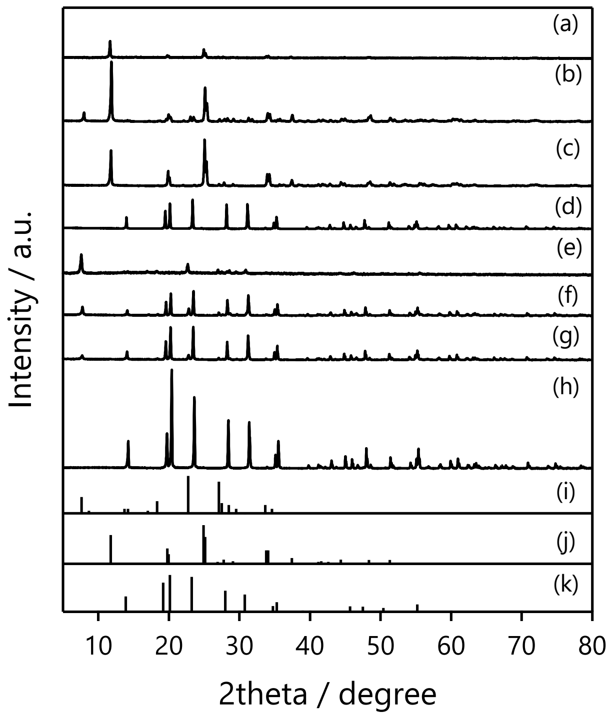

Figure S1. XRD patterns of hydrothermally grown (Na,H)-ZrP at (a) 150, (b) 190, (c) 220, and (d) 250 ºC for pH = 1, and at (e) 150, (f) 190, (g) 220, and (h) 250 ºC for pH = 3 together with those of references (i) γ-ZrP (PDF 00-048-0727), (j) α-ZrP (PDF 00-033-1482) and (k) $Zr_2H(PO_4)_3$ (PDF 00-038-0004). Condition: holding time, 24 h; atomic/molar ratio, Zr : PO_4 : F = 1 : 4.5 : 0.3.

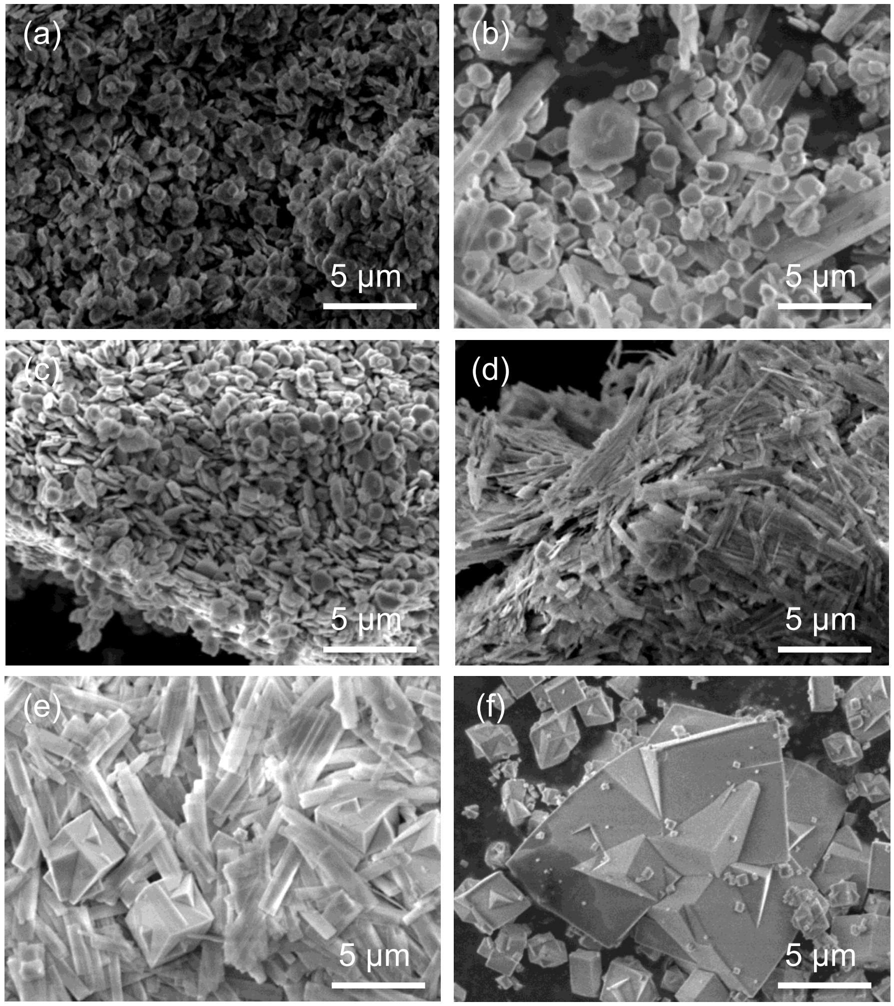

Figure S2. SEM images of hydrothermally grown (Na,H)-ZrP at (a) 150, (b) 190, and (c) 250 ºC for pH = 1, and at (d) 150, (e) 190, and (f) 250 ºC for pH = 3. Condition: holding time, 24 h; atomic/molar ratio, Zr : PO_4 : F = 1 : 4.5 : 0.3.

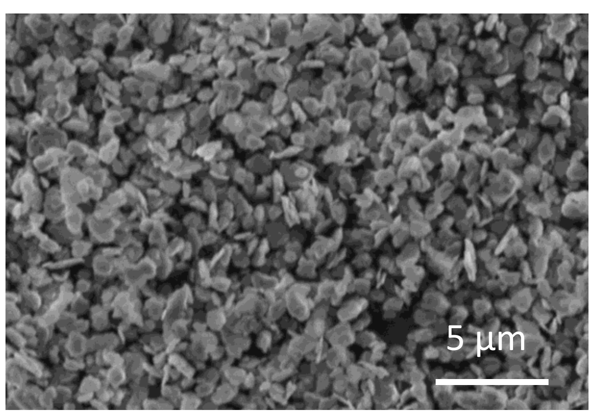

Figure S3. SEM image of α-ZrP used as a seed crystal.

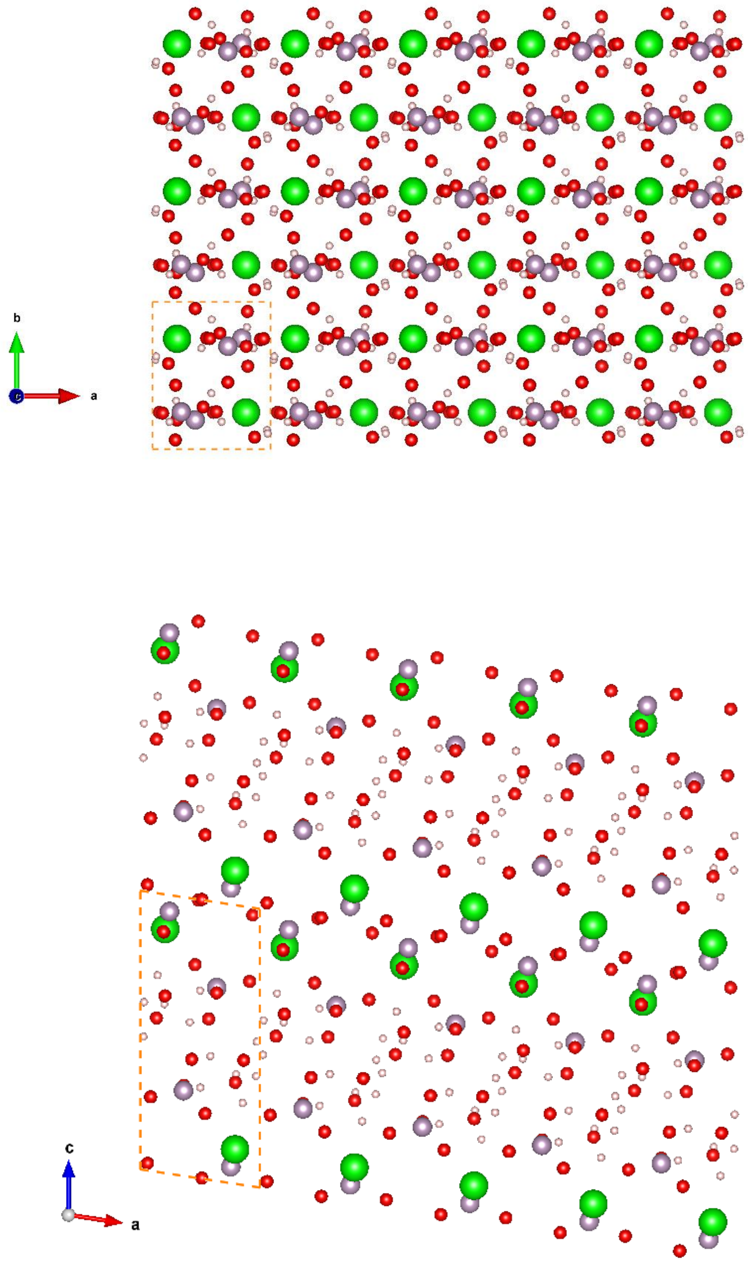

Figure S4. Crystal structures of γ-ZrP (ICSD (Inorganic Crystal Structure Database) collection code 79262). Color: green, Zr; gray, P; red, O; and white, H. Crystals structures are depicted using the VESTA program (K. Momma and F. Izumi, *J. Appl. Crystallogr.* **2011**, 44, 1272-1276).

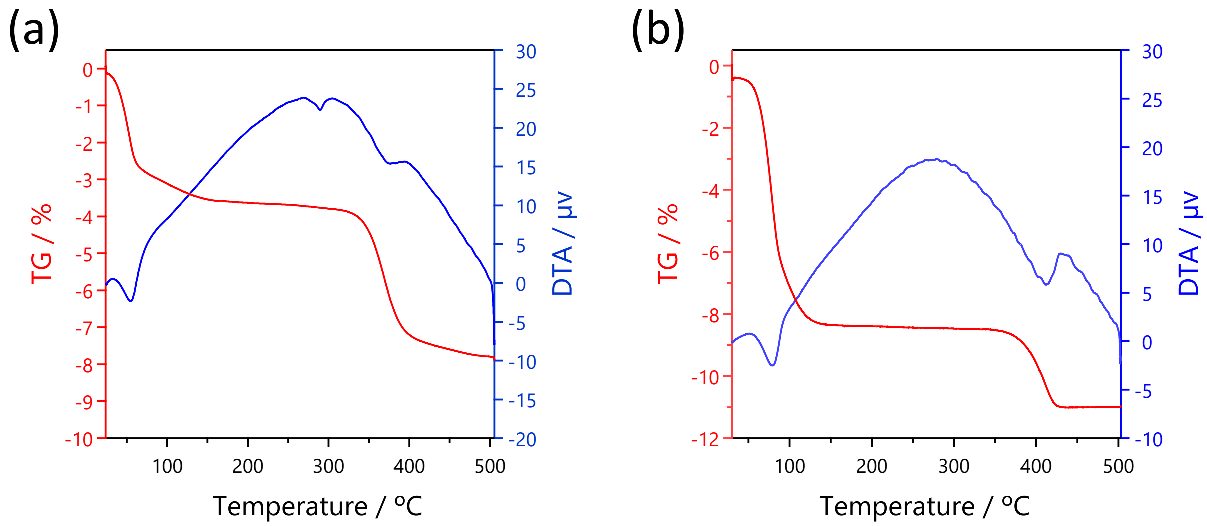

Figure S5. TG-DTA profiles of (a) (Na,H)-ZrP grown at 150 °C at pH = 3 and (b) corresponding γ-ZrP.

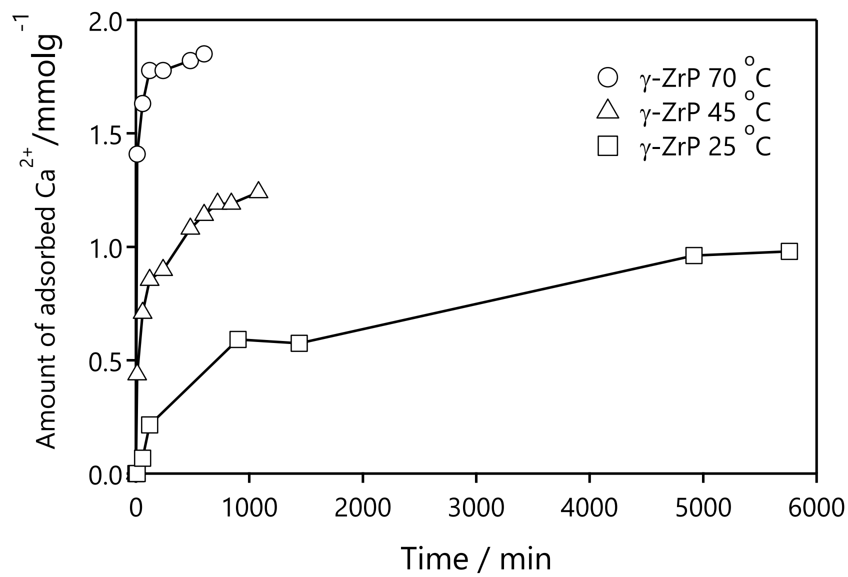

Figure S6. Kinetic curves for Ca^{2+} adsorption on γ-ZrP at □, 25 °C; △, 45 °C; ○; 25 °C. Condition: Initial concentration, 4 mM; solid to liquid ratio, 1 g L^{-1}.

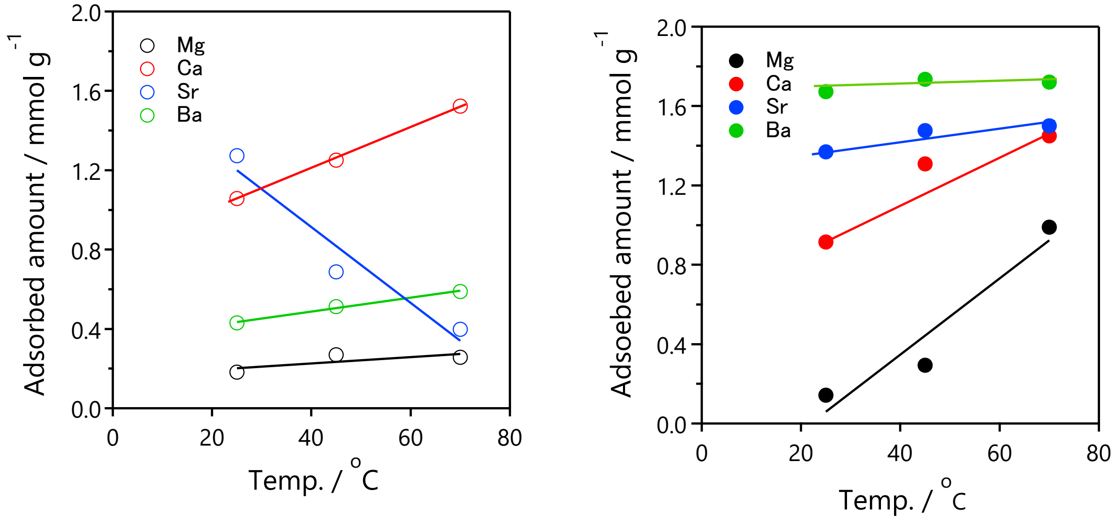

Figure S7. Temperature dependence of respective alkaline earth ion adsorption on (a) (Na,H)-ZrP and (b) γ-ZrP. Condition: Initial conc., 4 mM; solid to liquid ratio, 1 g L^{-1}; time, 72 h for 25 ºC, 8 h for 45 ºC, and 2 h for 70 ºC.

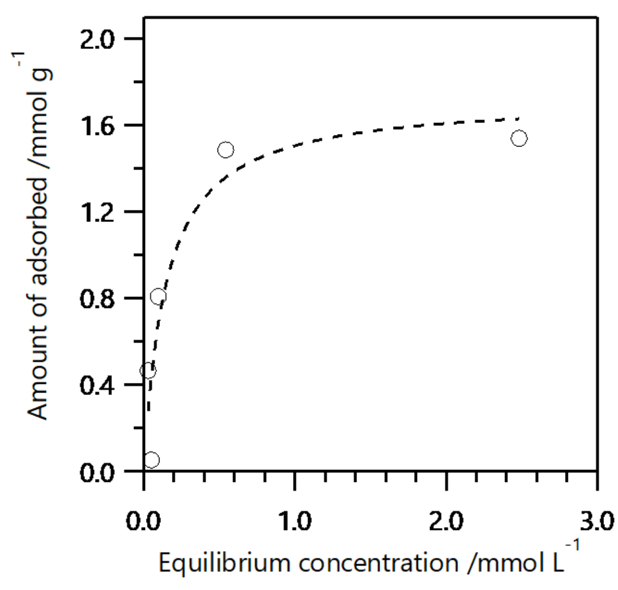

Figure S8. Ca^{2+} adsorption isotherm on the (Na,H)-ZrP at 70 ºC with Langmuir model fitting result (dashed black line). Condition: Initial conc., 0-4 mM; solid to liquid ratio, 1 g L^{-1}.

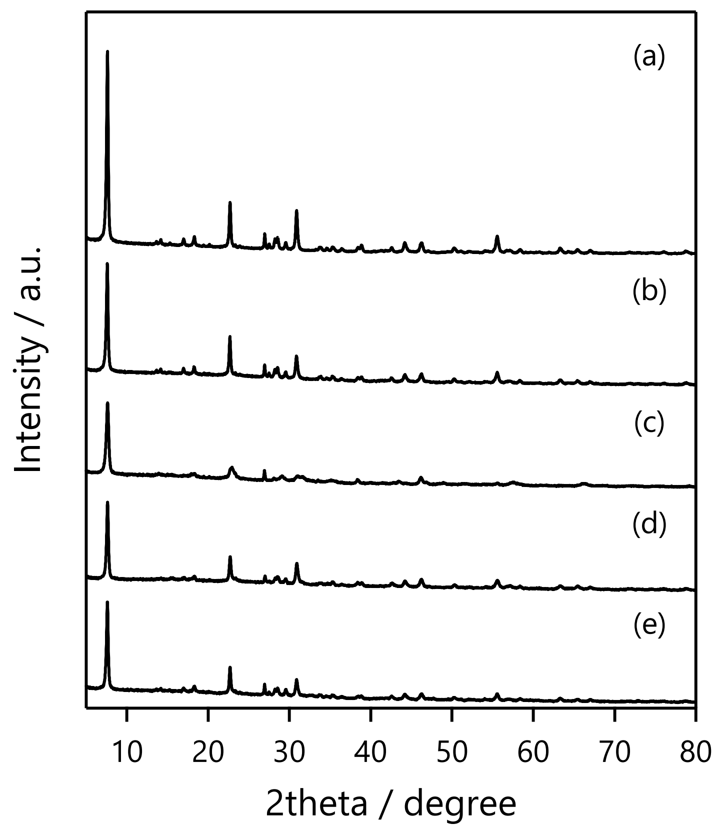

Figure S9. XRD patterns of (a) parent (Na,H)-ZrP and that after the (b) Mg^{2+}, (c) Ca^{2+}, (d) Sr^{2+}, and (e) Ba^{2+} exchange reactions.

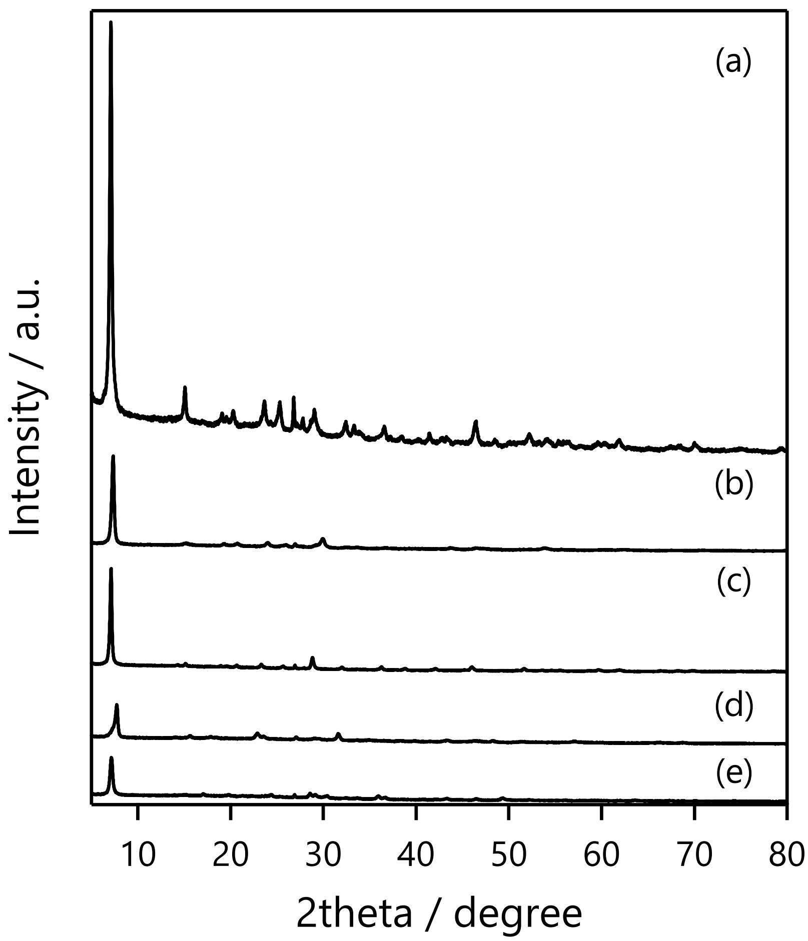

Figure S10. XRD patterns of (a) parent γ-ZrP and that after the (b) Mg^{2+}, (c) Ca^{2+} (d) Sr^{2+}, and (e) Ba^{2+} exchange reactions.

REFERENCES

S1) Gaines, G. L. Jr.; Thomas, H. C. Adsorption Studies on Clay Minerals. II. A Formulation of the Thermodynamics of Exchange Adsorption. *J. Chem. Phys.* **1953**, 21, 714–718.

S2) Kielland, J. Thermodynamics of Base-Exchange Equilibria of Some Different Kinds of Clays. *J. Soc. Chem. Ind. (London)* **1935**, 54, 232–234.