

Supporting Information: Prediction of Sodium Substituted Site of Octacalcium Phosphate: the Relationship of Ionic Pair Ratio in Reacting Solutions

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Experimental setting of the SH-malate containing system for OCP-SH-malate substitution

Thiomalate (SH-malate) was purchased from Tokyo Kasei Industrial Co., Japan. In the case of an acidic solution with increasing pH (OCP-SH-malate(Na)), 5.5 g of CaCO_3 was immersed into 20 mL of 1 mol/L- H_3PO_4 and 500 mmol/L SH-malate with/without 2 mol/L NaCl solution. Following the elimination of initially formed CO_2 , the samples were packed and incubated at 60°C for 1 day.

In the case of weak basic solution with decreasing pH (OCP-SH-malate-Na), we prepared two mother solutions; 2 mol/L Na_2HPO_4 and 1 mol/L SH-malate which pH was adjusted at 8.0 by NH_3aq . Then, they were mixed 1: 1 in volume. 2.39 g of DCPD was immersed into 20 mL of cocktail solution containing 2 mol/L Na, 1 mol/L PO_4 and 500 mmol/L at pH-8.36. The sample was packed and incubated at 60 °C for 1 day.

All samples were washed by distilled water for several times, then, dried in dry oven at 40 °C for overnight.

Table S1. Initial and final pH values of the SH-malate containing systems.

Sample	initial	Final
OCP-SH-malate	<1.00	5.02
OCP-SH-malate(Na)	<1.00	5.18
OCP-SH-malate-Na	8.36	6.86

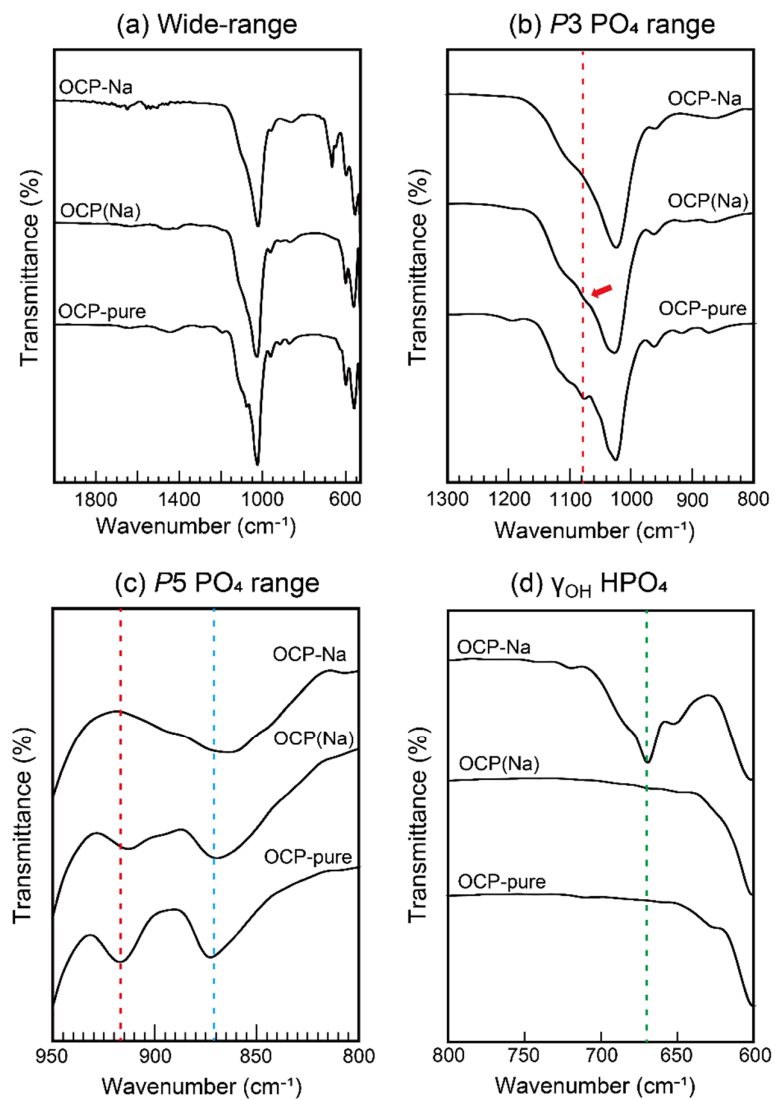


Figure S1. ATR-FT-IR spectra of the treated samples. (a) Wide range. (b) $P3\text{ PO}_4$ vibration; the red broken line corresponds to the $P3\text{ PO}_4$ vibration. (c) $P5\text{ PO}_4$ vibration; the blue broken line corresponds to the $P5\text{ PO}_4$ vibration. The green broken line corresponds to the $\gamma_{\text{OH}}\text{ HPO}_4(P6\text{ PO}_4)$ vibration.

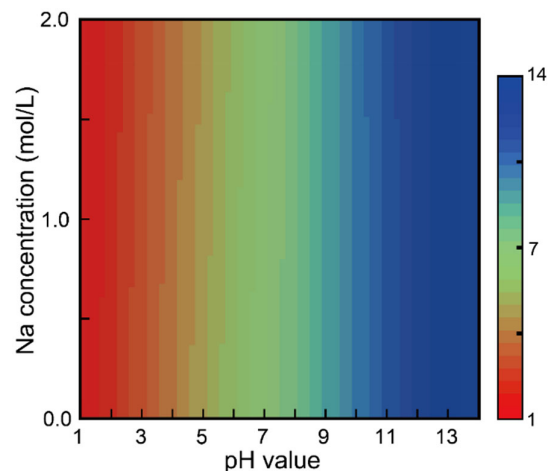


Figure S2. Calculated pH value of reacting solution as a function of Na concentration in the system of 1.0 mol/L PO_4 at $60\text{ }^\circ\text{C}$ and 1 atm .

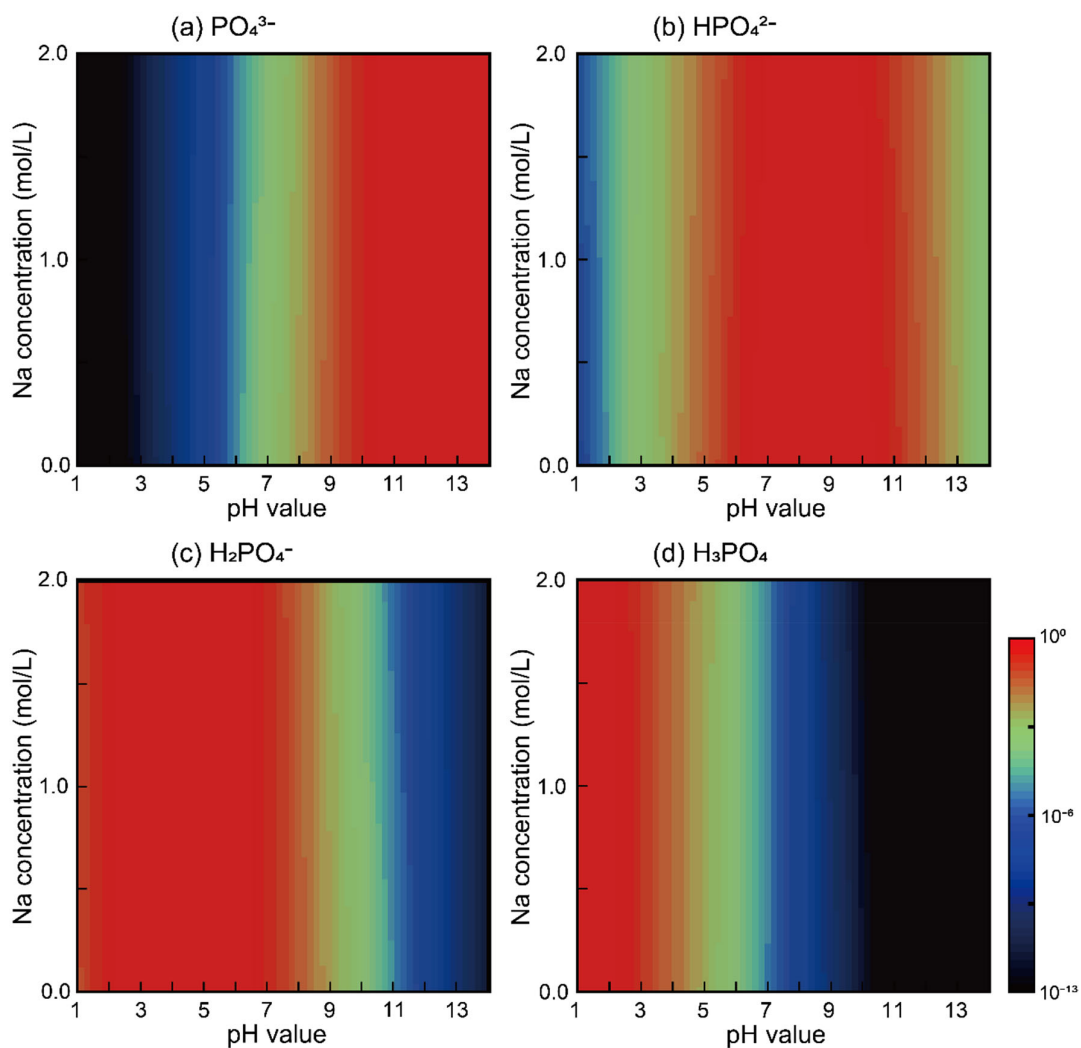


Figure S3. Calculated concentration of ionic pairs as a function of NaCl concentration in the systems of 1 mol/L PO_4 and 2.0 mol/L Na containing solution at 60 °C. (a) PO_4^{3-} . (b) HPO_4^{2-} . (c) H_2PO_4^- . (d) H_3PO_4 .

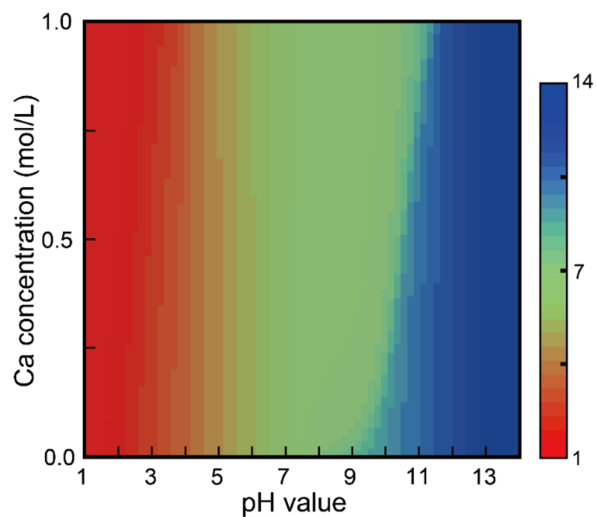


Figure S4. Calculated pH value of reacting solution as a function of Ca concentration in the system of 1.0 mol/L PO_4 and 2.0 mol/L Na at 60 °C and 1 atm.

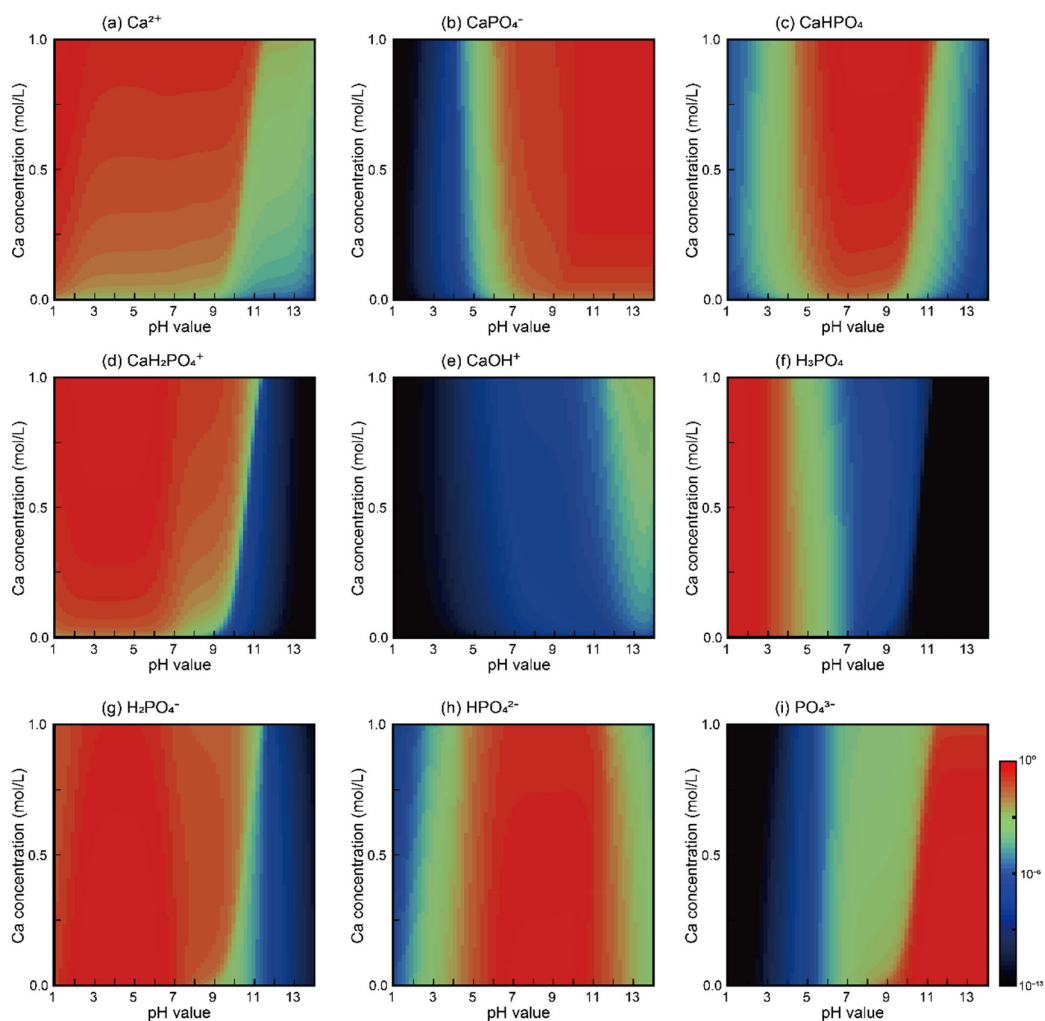


Figure S5. Calculated concentration of ionic pairs as a function of CaCl₂ concentration in the systems of 1 mol/L PO₄ and 2.0 mol/L Na containing solution at 60 °C. (a) Ca²⁺. (b) CaPO₄⁻. (c) CaHPO₄. (d) CaH₂PO₄⁺. (e) CaOH⁺. (f) PO₄³⁻. (g) HPO₄²⁻. (h) H₂PO₄⁻. (i) H₃PO₄.