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The Incorporation of Dicarboxylates into Octacalcium Bis(hydrogenphosphate) Tetrakis(phosphate) Pentahydrate

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Synopsis. Octacalcium bis(hydrogenphosphate) tetrakis(phosphate) pentahydrate (OCP) has been found to complex with saturated aliphatic dicarboxylate ions, $C_nH_{2n}C_2O_4^{2-}$; n=1—6. These organic substances were incorporated, instead of HPO_4^{2-}, into the "B-layer" of the OCP structure. The incorporation caused expansion in the basal spacing (d_{100}) of OCP from 18.7 Å to 19.6—26.1 Å. A possible structural model is proposed for the incorporation.

Octacalcium bis(hydrogenphosphate) tetrakis(phosphate) pentahydrate ($Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$; OCP), which has a structural similarity to hydroxyapatite, has become of biological and bio-material interest. The structure of OCP, as shown in Fig. 1, is composed of alternative stackings of "apatitic layers" (A-layers) similar to the apatite structure and "hydrated layers" (B-layers) corresponding to the composition of brushite ($CaHPO_4 \cdot 2H_2O$).[1-3] In the preceding paper,[4] it was pointed out as a feature of the OCP structure that the B-layers contained $-\!\![\mathrm{Ca{-}HPO_4{-}Ca}]\!\!-$ pillars. It was claimed that succinate ions ($C_2H_4C_2O_4^{2-}$) were able to replace the HPO_4^{2-} in the pillar, which resulted in an expansion of the basal spacing (d_{100}) of OCP. In the present work, a series of saturated aliphatic dicarboxylate ions were investigated to determined whether the ions were able to be incorporated into OCP or not.

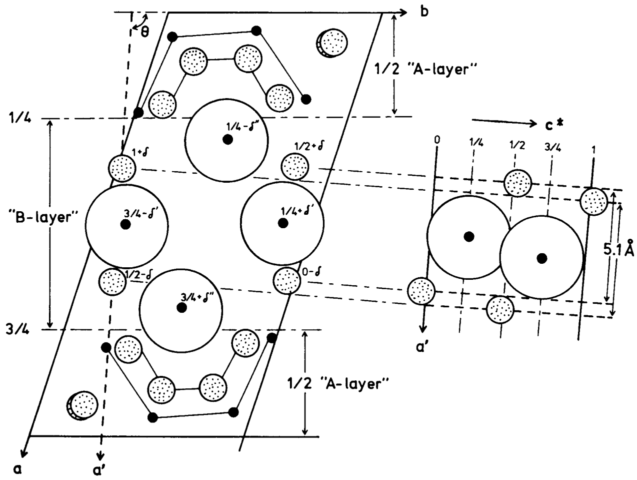

Fig. 1. Simplified OCP structure projected on the a–b plane and $-\!\![\mathrm{Ca{-}HPO_4{-}Ca}]\!\!-$ pillars projeted on the a′–c* plane, where ●: P, ⊙: HPO_4, ◍: Ca, c*: vertical to the a–b plane, δ: 0.0313, δ': 0.0168, δ'': 0.0045, θ: 94.1°, the corners of the larger and smaller half hexagons: P and Ca sites in hydroxyapatite, respectively. The illustration was based on the Ref. 1).

Experimental

Powdery α-tricalcium bis(phosphate) (α-$Ca_3(PO_4)_2$) synthesized by solid state reaction[4] was heated in aqueous solutions containing dicarboxylate ions ($C_nH_{2n}C_2O_4^{2-}$; n=0—6) at 40 °C for 3 h. All reactant solutions were prepared at a concentration of 0.25 mol dm^{-3} from chemical reagents of dicarboxylic acids and distilled water. Initial pH's were adjusted to 6.4 ± 0.1 for malonic acid (n=1) and 6.0 ± 0.1 for the other acids (n=0,2—6) with ammonia water. The resulting solid products were examined with respect to product phase and interplanar spacings of OCP by X-ray diffraction, and Ca/P ratio by chemical analyses. The chemical composition of OCP phase was estimated by distributing the residual amount on quantitative analyses of Ca and PO_4 among the other components (H, $C_nH_{2n}C_2O_4$, and H_2O), using the Ca/P ratio of products (OCP+ unreacted α-$Ca_3(PO_4)_2$), conversion of α-$Ca_3(PO_4)_2$ into OCP, and a general formula of dicarboxylate-complexed OCP determined in this work.[4]

Results and Discussion

In the case of the oxalate solution (n=0), α-$Ca_3(PO_4)_2$ was converted completely into calcium oxalate without formation of OCP. OCP was formed from the other reactant solutions (n=1—6). Table 1 lists interplanar spacings and chemical compositions of OCP, Ca/P ratios of products and some reference data. It was clear that the organic substances caused expansions of the basal spacing (d_{100}) of OCP and increases in the Ca/P ratio. Here, adopting the same structural consideration introduced in the preceding paper, dicarboxylate ions incorporated as $-\!\![\mathrm{Ca{-}C_nH_{2n}C_2O_4{-}Ca}]\!\!-$ instead of $-\!\![\mathrm{Ca{-}HPO_4{-}Ca}]\!\!-$ can be illustrated as shown in Fig. 2. The structures of the dicarboxylate ions were taken from those of corresponding acids,[5] and the arrangements and numerals were determined graphically using the radii of $r_{Ca^{2+}}$= 0.99 Å, r_C=0.77 Å, and $r_O \approx 1$ Å. The r_O of carboxyl oxygen was estimated from bond lengths of C–O and O–Ca in calcium carboxylate crystals, *e.g.*, calcium

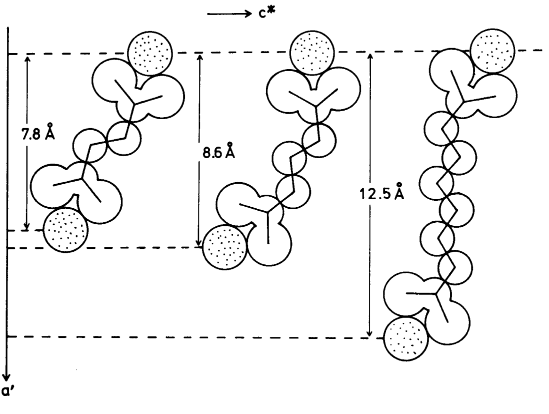

Fig. 2. Examples of the structural model for $-\!\![\mathrm{Ca{-}C_nH_{2n}C_2O_4{-}Ca}]\!\!-$pillars ($N$=2, 3, 6) projected on the a′–c* plane.

Table 1. Dicarboxylate-complexed OCP

Incorporated ion		OCP formed					Ca/P of product[d]	Conversion[e]/%
Name	n[b]	Interplanar spacing/Å			Formula[c]			
		d_{100}	d_{010}	d_{002}	z	m		
None[a]	—	18.7	9.36	3.42	0	5.1	1.34	100
Malonate	1	19.6	—	3.43	0.42	≈5	1.47	≈45
Succinate	2	21.4	9.39	3.42	0.83	5.5	1.55	100
Glutarate	3	22.3	9.37	3.43	0.35	≈5	1.45	≈60
Adipate	4	23.6	9.41	3.42	0.45	6.6	1.44	100
Pimelate	5	24.4	9.36	3.42	0.22	≈6	1.41	≈80
Suberate	6	26.1	9.38	3.42	0.92	7.6	1.55	≈70

a) Pure OCP.[4] b) $C_nH_{2n}C_2O_4^{2-}$. The case of $n=0$ (oxalate) formed calcium oxalate. c) $Ca_8(HPO_4)_{2-z}(PO_4)_4(C_nH_{2n}C_2O_4)_z \cdot mH_2O$. d) Mole ratio of OCP+unreacted α-$Ca_3(PO_4)_2$. e) Conversion of α-$Ca_3(PO_4)_2$ into OCP.

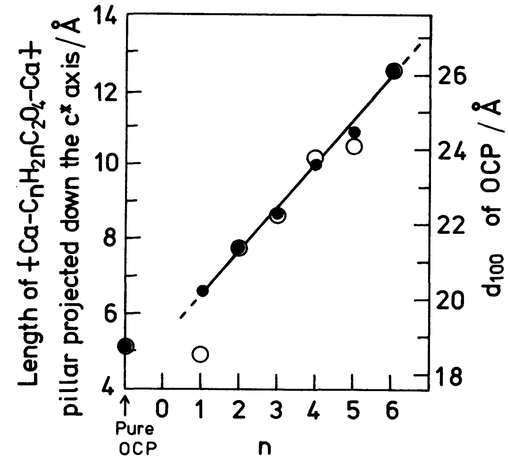

Fig. 3. Pillar lengths and basal spacings of dicarboxylate-complexed OCP.
●: Experimentally obtained, ○: graphically obtained.

formate and calcium oxalate.[5] In addition, we assumed there were no changes in the b and c* directions on the basis of the very small changes in d_{010} and d_{002}, *i.e.*, the b and c directions. Figure 3 shows plots of the lengths of $\text{-}[Ca\text{-}C_nH_2C_{2n}O_4\text{-}Ca]\text{-}$ pillars and d_{100} values *vs.* n, where $[d_{100}(\text{graphic})] \approx [d_{100}(\text{experimental}) - \text{pillar length down the } c^*]_{\text{pure OCP}} + [\text{pillar length down the } c^*]_{\text{dicarboxylate-complexed OCP}}$, because $\sin\theta \approx 1$ (refer to Fig. 1). The experimental data showed a good linearity, and supported the graphic data approximately. However, departures of graphic data for $n=1$ and $n=5$ from the line left an uncertainty about the structural model. The data given in Fig. 3 were considered to confirm the previous claim about succinate-complexed OCP.[4] A general formula would be apparently $Ca_8(HPO_4)_{2-z}(PO_4)_4(C_nH_{2n}C_2O_4)_z \cdot mH_2O$; $0 \leq z \leq 1$, $m \gtrsim 5$, $n=1$—6 in analogy with that of the succinate-complexed OCP.

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