

COMPLEXES OF APATITIC LAYERED COMPOUND $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$
WITH DICARBOXYLATES

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ABSTRACT. Octacalcium phosphate(OCP), $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$, consists of alternative stackings of layers with an apatitic structure and a brushite-like composition. Here we consider whether or not OCP is able to complex with organic substances. The interplanar spacing (d_{100}) of OCP prepared in the presence of dicarboxylates ($\text{RC}_2\text{O}_4^{2-}$; R=organic group) expanded from the original value of 18.7 Å to 19.2-26.1 Å depending on the length of R. Examples of R were C_nH_{2n} (n=1-6), $\text{CH}(\text{CH}_3)\text{CH}_2$, $\text{C}(\text{CH}_3)=\text{CH}$, $\text{CH}=\text{CH}$, $\text{CH}_2\text{CH}=\text{CHCH}_2$ and C_6H_4 . Structural considerations and experimental data suggested that dicarboxylates were incorporated into the OCP structure through the replacement of HPO_4^{2-} by $\text{RC}_2\text{O}_4^{2-}$.

1. INTRODUCTION

Octacalcium phosphate ($\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$; OCP) is considered to be a precursor in the formation of hydroxyapatite(HAp) in bones and teeth. OCP as well as HAp has become of interest in connection with calcification in vivo and also biochemical applications such as the chromatographic separation of nucleic acids and proteins.

The structure of OCP (Fig. 1) is composed of alternative stackings of an "apatitic layer" (A-layer) similar to the apatite structure and a "hydrated layer" (B-layer) corresponding to the composition of brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) [1]. An unique feature of OCP is that $[\text{Ca}-\text{HPO}_4-\text{Ca}]$ groups in the B-layer are regarded as pillars supporting the space between A-layers, and that the pillars might be replaceable with other ionic species.

In this article, we consider whether or not OCP, having such a layer structure, is able to complex with organic substances.

2. STANDARD OCP [2]

Standard OCP was prepared by the hydrolysis of α -tricalcium phosphate ($\alpha\text{-Ca}_3(\text{PO}_4)_2$; α -TCP) as usual. Reaction products from the hydrolysis were brushite or monetite (CaHPO_4), OCP and HAp depending on the hydrolysis

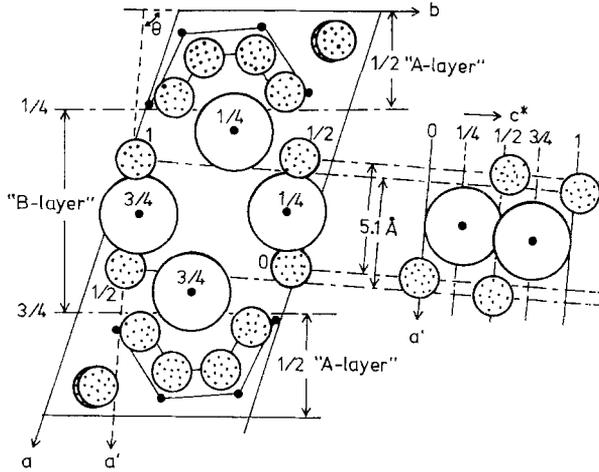


Figure 1. Simplified OCP structure illustrated according to [1] and a side-view of $[Ca-HPO_4-Ca]$ pillars, where \bullet :P, \odot :Ca, \ominus : HPO_4 . Oxygen atoms in the A-layer and H_2O molecules are omitted. c^* :Vertical to the a-b plane. θ : 94° .

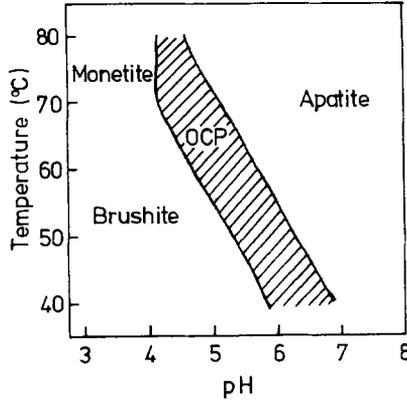
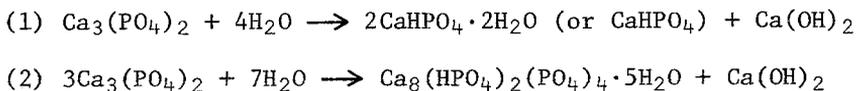
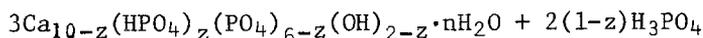
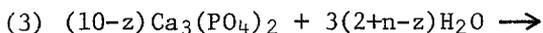


Figure 2. Apparent phase relationship according to the hydrolysis of α -TCP.

temperature and pH. Figure 2 shows the apparent phase relationship obtained. Hydrolysis reactions could be written as follows.





The solid product from reaction (3) is so-called nonstoichiometric HAp [3]. It was interesting that OCP, which was considered to be an apatite-brushite composite at a molecular level, formed at pH's intermediate between those for the formation of apatite and brushite. Table 1 shows examples of the preparation of standard OCP.

TABLE I. Preparations of standard OCP.

Preparative conditions ^a			OCP formed					
Reactant solution	pH	Temp. (°C)	Ca/P (mol ratio)	Interplanar spacing (Å)			Composition ^b	
				d ₁₀₀	d ₀₁₀	d ₀₀₂	z	m
H ₂ O	4.7	70	1.35	18.7	9.39	3.43	0	5.0
H ₂ O	4.7	65	1.35	18.7	9.40	3.41	0	5.0
0.5M Na-acetate	5.4	50	1.34	18.7	9.36	3.42	0	5.1

^a α -TCP was hydrolysed at solid/solution=1g/50ml with stirring. 0.5M=0.5mol/dm³. ^b See the footnote of Table II.

3. OCP FORMED IN THE PRESENCE OF DICARBOXYLATES [4,5]

By reference to the apparent phase relationship, α -TCP was hydrolysed in the presence of dicarboxylates. The OCP samples thus obtained are listed in Table II. It is evident that the dicarboxylates ($\text{RC}_2\text{O}_4^{2-}$; $\text{R}=\text{C}_n\text{H}_{2n}$ ($n=1-6$), and the others) caused both expansions of the interplanar spacing (d_{100}) and increases in the Ca/P ratio. In other words, the formation of dicarboxylate-complexed OCP (hereafter written as dicarboxylate-OCP) has been ascertained. In the case of oxalate ($n=0$), calcium oxalate formed without the formation of the OCP phase. Azelaate ($n=7$) and sebacate ($n=8$) were obscure. In addition, many other dicarboxylates listed in Table II produced also similar changes, whereas some monocarboxylates, tricarboxylates and disulfonates were shown to be ineffective.

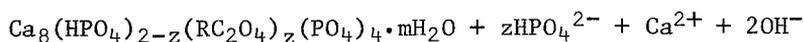
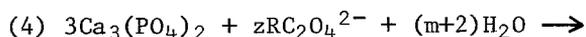
TABLE II. Preparations of dicarboxylate-complexed OCP.

Preparative conditions ^a		OCP formed					
Reactant solution ^b	R ^c	Ca/P (mol ratio)	Interplanar spacing (Å)			Composition ^d	
			d ₁₀₀	d ₀₁₀	d ₀₀₂	z	m
Malonate	CH ₂	1.43	19.6	—	3.43	0.42	~5
Succinate	(CH ₂) ₂	1.55	21.4	9.39	3.42	0.83	5.5
Glutarate	(CH ₂) ₃	1.42	22.3	9.42	3.43	0.35	~5
Adipate	(CH ₂) ₄	1.56	23.6	9.41	3.42	0.86	6.7
Pimelate	(CH ₂) ₅	1.38	24.4	9.36	3.42	0.22	~6
Suberate	(CH ₂) ₆	1.57	26.1	9.38	3.42	0.92	7.6
Methyl succinate	CH(CH ₃)CH ₂	1.43	20.4	9.36	3.42	0.40	6.0
Fumarate	CH=CH	1.48	21.6	9.42	3.42	0.60	6.3
Citraconate	C(CH ₃)=CH	1.56	22.8	—	3.43	0.86	5.0
β-Dihydro muconate	CH ₂ CH=CHCH ₂	1.52	23.7	9.34	3.42	0.73	7.0
Phthalate	C ₆ H ₄	1.44	23.7	—	3.43	0.44	7.5

^a See the footnote of Table I. ^b Solution concentration=0.25M (phthalate:0.1M). Reaction pH=6.0 (malonate:6.4). Reaction temperature=40°C. ^c RC₂O₄²⁻. ^d Ca₈(HPO₄)_{2-z}(RC₂O₄)_z(PO₄)₄·m H₂O.

4. ARRANGEMENT OF DICARBOXYLATES IN THE OCP STRUCTURE [5]

The changes in the d₁₀₀ and the Ca/P ratio keeping the OCP structure suggested that the replacement of HPO₄²⁻ by RC₂O₄²⁻ took place in the structure, not on the surface. The incorporation of RC₂O₄²⁻ would be generally given by the reaction,



Experimentally, the value of z seemed not to exceed one-half of the total number of HPO₄²⁻, i.e., z ≤ 1. Therefore, the following interpretation

was conceivable. Considering the OCP structure, it was speculated that there were two types of HPO_4^{2-} and that one was HPO_4^{2-} of $[\text{Ca}-\text{HPO}_4-\text{Ca}]$ in the B-layer and another was tightly bound to the A-layer by sharing its oxygen in the A-layer. Namely, the former HPO_4^{2-} must be more replaceable than the latter HPO_4^{2-} .

A possible model was proposed as shown in Fig. 3, assuming no changes in the b and c directions with the incorporation. The pillar

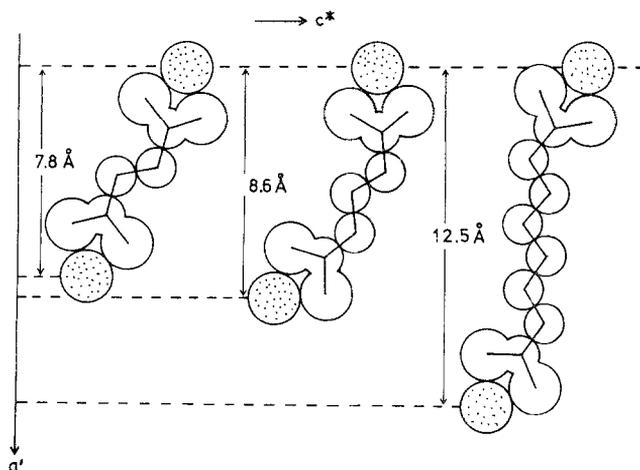


Figure 3. Examples of the arrangement of $[\text{Ca}-\text{C}_n\text{H}_{2n}\text{C}_2\text{O}_4-\text{Ca}]$ pillars ($n=2,3,6$) projected on the a' - c^* plane [5].

lengths (or d_{100}) obtained for $\text{C}_n\text{H}_{2n}\text{C}_2\text{O}_4^{2-}$ were in good agreement with the experimental data, except for $n=1$, as shown in Fig. 4. The pillar length increased almost linearly with the length (n) of the alkyl chain ($n=1-6$). The departure of the calculated data for $n=1$ from the line left an uncertainty about the model.

5. WEIGHT CHANGES ON HEATING

Weight changes on heating of standard OCP and dicarboxylate-OCP were followed by thermogravimetry (TG). Figure 5 shows TG curves using a heating rate of $10^\circ\text{C}/\text{min}$ in quiescent air. TG curves for dicarboxylate-OCP showed three characteristic decreases, i.e., I: $400-600^\circ\text{C}$, II: $700-850^\circ\text{C}$, and III: $850^\circ\text{C} \sim$. These decreases indicated the existence of organic substance in the samples, since no corresponding decreases were recognized on the curve for standard OCP. The existence of organic substance was confirmed also by thermal discoloration of samples, i.e., white up to ca. 400°C , light brown at $450-500^\circ\text{C}$, deep black at $600-850^\circ\text{C}$, and light gray or white above 850°C . Therefore, the first decrease I must be due to the decomposition of included organic substance, II due to mainly the burning of carbon, and III due to the gradual

liberation of CO_2 from "A-type" carbonate-HAp according to the reaction (5) as described below.

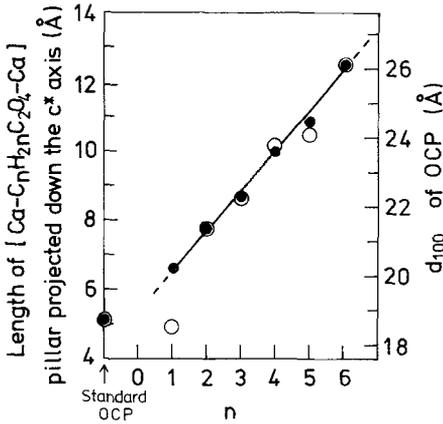


Figure 4. Pillar lengths and d_{100} of $\text{C}_n\text{H}_{2n}\text{C}_2\text{O}_4^{2-}$ -complexed OCP [5].

- : Experimentally obtained
- : Calculated values.

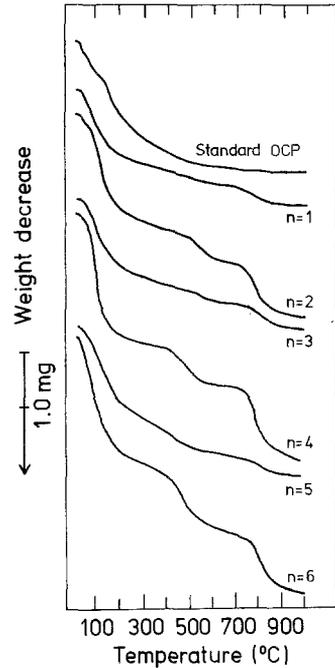
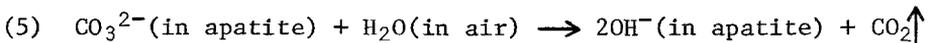


Figure 5. TG curves for $\text{C}_n\text{H}_{2n}\text{C}_2\text{O}_4^{2-}$ -complexed OCP.
OCP content (wt%): 45 (n=1), 100 (n=2), 60 (n=3),
100 (n=4), 80 (n=5), 70 (n=6).

6. INFRARED SPECTRA

Infrared spectra of succinate-OCP heated to various temperatures and reference samples are shown in Fig. 6. Characteristic bands of COO^- groups in unheated succinate-OCP were observed in the ranges of 1600-1550, 1470-1400, and $1330 \pm 5 \text{ cm}^{-1}$ which shifted slightly from the corresponding bands of calcium succinate. Each of these bands broadened with heating, and at ca. 500-650°C the decomposition of succinate was suggested to occur. At ca. 800°C characteristic bands of CO_3^{2-} in "A-type" carbonate-HAp ($\text{Ca}_{10}(\text{PO}_4)_6(\text{CO}_3, \text{OH})_2$) appeared at ca. 1546, 1465, and 879 cm^{-1} [6-8], and in addition the OH stretching mode in HAp appeared at 3575 cm^{-1} . On further heating, the CO_3^{2-} bands weakened and the OH band developed, probably, according to reaction (5).



Similar changes were also observed in the infrared spectra of the other dicarboxylate-OCP's.

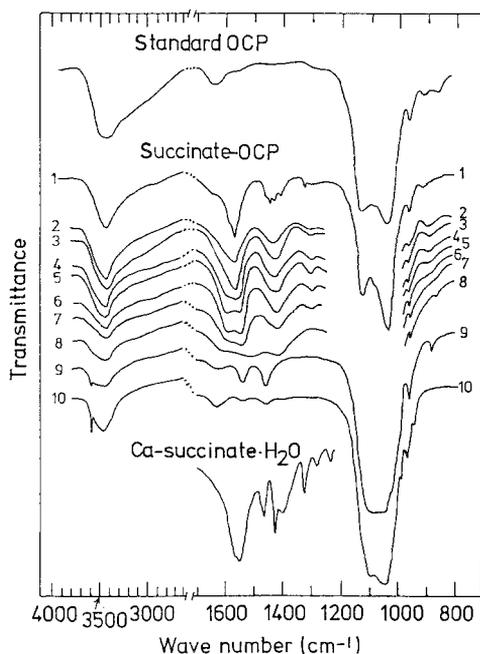
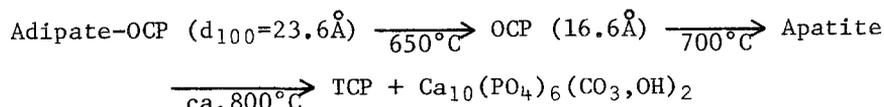
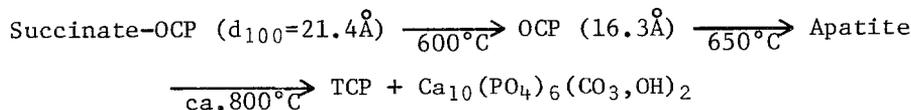
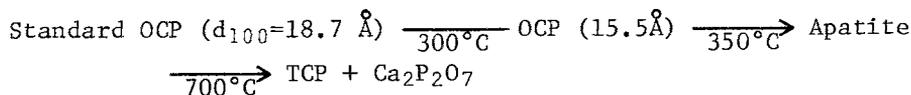


Figure 6. Infrared spectra of succinate-OCP heated to various temperatures, and reference samples [9].
Heat-treatment(°C); 1:40 and 100, 2:120, 3:150, 4:210, 5:350, 6:450, 7:515, 8:610 and 647, 9:830, 10:1000.

7. STRUCTURAL CHANGES ON HEATING

Thermal changes in the crystalline phase of standard OCP and dicarboxylate-OCP were followed by X-ray diffractometry. Summarizing X-ray diffraction, infrared and TG results, it was concluded that OCP with and without dicarboxylates underwent thermal changes such as contractions of d_{100} of OCP, transformation to apatite and decomposition of apatite on heating. Examples of the changes are shown below.



The contractions in the d_{100} on heating were possibly due to the liberation of H_2O from the B-layer. Temperatures for the transformation of OCP to apatite varied from 300 to 700°C depending on the kind of dicarboxylates incorporated, while the decomposition of apatite occurred commonly at ca. 800°C. The incorporation of dicarboxylates tended to increase the thermal stability of the OCP structure. The final product was TCP + $Ca_2P_2O_7$ for samples with $Ca/P < 1.50$, TCP for $Ca/P = 1.50$, and TCP + $Ca_{10}(PO_4)_6(CO_3,OH)_2$ for $Ca/P > 1.50$, respectively.

8. CONCLUSIONS

Many dicarboxylates were incorporated into the OCP structure. Such dicarboxylate-OCP's were prepared by the hydrolysis of α -TCP in the presence of dicarboxylate ions ($RC_2O_4^{2-}$; R=organic group). The incorporation caused expansions of the interplanar spacing (d_{100}) and increases in the Ca/P ratio of OCP. It was pointed out that OCP contained two types of HPO_4^{2-} , i.e., replaceable and nonreplaceable. The incorporation was considered to occur through the replacement of replaceable $HPO_4^{2-} \rightleftharpoons RC_2O_4^{2-}$. A possible model of $RC_2O_4^{2-}$ in the OCP structure was proposed. The complexes obtained underwent, on heating, thermal changes such as contractions of the d_{100} , transformation to apatite, and finally decomposition of apatite to TCP + $Ca_2P_2O_7$ or TCP or TCP + $Ca_{10}(PO_4)_6(CO_3,OH)_2$ depending on the Ca/P ratio of the complexes. The OCP structure tended to be stabilized by the incorporation of dicarboxylates.

References

1. W. E. Brown: 'Octacalcium phosphate and hydroxyapatite', Nature 196, 1048-1050 (1962).
2. H. Monma: 'Preparation of octacalcium phosphate by the hydrolysis of α -tricalcium phosphate', J. Mater. Sci. 15, 2428-2434 (1980).
3. H. Monma, S. Ueno, and T. Kanazawa: 'Properties of hydroxyapatite prepared by the hydrolysis of tricalcium phosphate', J. Chem. Tech. Biotechnol. 31, 15-24 (1981).
4. H. Monma and M. Goto: 'Succinate-complexed octacalcium phosphate', Bull. Chem. Soc. Jpn. 56, 3843-3844 (1983).
5. H. Monma: 'The incorporation of dicarboxylates into octacalcium bis(hydrogenphosphate) tetrakis(phosphate) pentahydrate', Bull. Chem. Soc. Jpn. 57, 599-600 (1984).
6. G. Bonel and G. Montel: 'A new synthetic carbonated apatite', C. R. Acad. Sci. 258, 923-926 (1964).
7. G. Montel: 'Physicochemical study of solids with an apatite structure', Ann. Chim. 4, 255-266 (1969).
8. N. S. Chickhrur, M. S. Tung, and W. E. Brown: 'A mechanism for incorporation of carbonate into apatite', Calcif. Tiss. Int. 32, 55-62 (1980).
9. H. Monma and M. Goto: 'Thermal alteration of succinate-complexed octacalcium phosphate', J. Mater. Sci. Lett. (in press).