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MAGNESIUM-CONTAINING FLUORIDATED APATITES

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SUMMARY

Mg-containing fluoridated hydroxyapatites with various fluoride contents were synthesized (80°C and pH 7.4) to study the effect of magnesium on their crystallographic properties. With the increase of fluoride content, the crystallinity varied differently in each series: Mg-free fluoridated hydroxyapatites showed a minimum of crystallinity at low fluoride content; in those with lower Mg content this minimum was not observed; and in the series with higher Mg content, crystallinity rose to a maximum at about half of the maximum fluoride content, although on the whole crystallinity decreased with the increased Mg content. These crystallinity behaviors in each series were not analogous to the solubility behaviors.

INTRODUCTION

Recently, there is much evidence that magnesium may be closely associated with the metabolism and physiology of the human body [1]. However, its contribution to the properties of biological apatites is still not clear because magnesium is a minor constituent of human tooth and bone.

Our previous study [2] showed that a small amount of magnesium ions significantly affected the crystallinity and solubility of hydroxyapatite, and that magnesium acts as a caries-promoting substance.

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Fluoride, on the other hand, has been extensively studied with regard to its role in caries-prevention [3-6]. Therefore, it is important to examine the effect of magnesium ions on the caries-preventive action of fluoride.

In our present study, magnesium-containing fluoridated hydroxyapatites with various fluoride contents were synthesized, and the effect of magnesium on their crystallographic properties was examined.

SYNTHESIS

One series of fluoridated hydroxyapatites, FHAp, and two series of magnesium-containing fluoridated hydroxyapatites, Mg-FHAp$_{I}$ and Mg-FHAp$_{II}$, were synthesized at 80±1°C. Each sample was made by feeding 0.5 L of 100 mmol/L $Ca(CH_3COO)_2 \cdot H_2O$ solution containing 1 and 5 mmol/L concentrations of $Mg(CH_3COO)_2 \cdot 4H_2O$ and 0.5 L of 60 mmol/L $NH_4H_2PO_4$ solution containing 0-20 mmol/L concentration of HF into 1 L of mechanically stirred 1.3 mol/L CH_3COONH_4 solution. The two solutions were fed at 250 mL/h with a microtube pump. The pH was maintained at 7.4±0.1 automatically with concentrated NH_4OH solution. The suspension was stirred for 3 hr, then kept at 25°C for 24 hr. The slurry was filtered, washed with distilled water, then dried.

ANALYSIS

X-ray diffraction was employed to identify precipitates and estimate their lattice constants and crystallinity. Measurements were made on a Rigaku Denki X-ray Diffractometer with graphite-monochromatized CuKα radiation at 35 kV and 23 mA. The a- and c-axis dimensions were calculated from (300) and (002) reflections, using silicon as standard.

To estimate the crystallinity of samples, the inverse of the half-value breadth was calculated for the (300) and (002) reflections as representations of the a- and c-axes.

Transmission electron microscopy (TEM) with a Hitachi 12A microscope was employed to observe the size and shape of crystals.

Calcium and magnesium concentrations were determined by atomic absorption spectrophotometry. Total phosphate concentrations were determined by the UV-spectrophotometric method of Eastoe [7]. Fluoride concentrations were determined with an Orion 407 Specific Ion Meter and fluoride ion electrode.

In the solubility experiment, 50 mg of each sample was left to stand in 5 mL of 0.5 mol/L acetate buffer (pH 4.0) at 37°C for 1 month, then the calcium and phosphate concentrations in the solution were determined. The calcium concentration in solution was adopted as the apparent solubility of the apatites.

RESULTS AND DISCUSSION

The chemical compositions of the Mg-free and Mg-containing fluoridated hydroxyapatites are shown in Figure 1. No significant change was found in either calcium or phosphate contents of the fluoridated hydroxyapatites, FHAp, and Mg-containing fluoridated hydroxyapatites, Mg-FHAp$_{I}$ and Mg-FHAp$_{II}$, because of the low feed concentration of magnesium. Magnesium content, on the other hand, increased with an increase in fluoride content. This indicates that magnesium uptake may be promoted by fluoride.

The lattice dimensions of three series of the Mg-free and Mg-containing fluoridated hydroxyapatites are shown in Figure 2. The a-axis dimensions of FHAp, Mg-FHAp$_{I}$ and Mg-

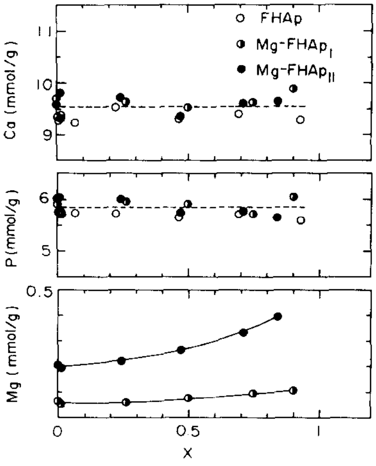

Fig.1. Chemical compositions of the Mg-free (FHAp) and Mg-containing fluoridated hydroxyapatites (Mg-FHAp$_I$ and Mg-FHAp$_{II}$).
X: Degree of fluoridation.

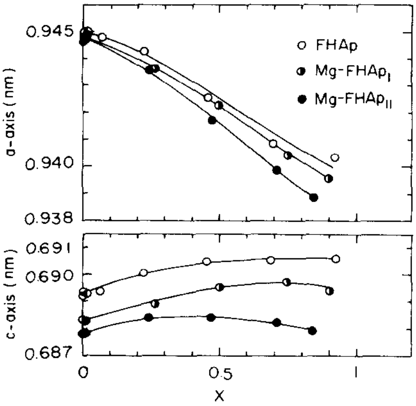

Fig.2. Dimensions of a and c-axes for Mg-free (FHAp) and Mg-containing fluoridated hydroxyapatites (Mg-FHAp$_I$ and Mg-FHAp$_{II}$).

FHAp$_{II}$ decreased with increased degree of fluoridation, X. This result suggests the substitution of F^- ions into the apatite crystals. The c-axis dimension decreased with the increase of magnesium content over the whole range of fluoride content. The decrease of c-axis dimension may be due to the substitution of Mg^{2+} ions into the apatite crystals. It has been reported that most of the magnesium in calcified tissue is probably located on the surface of the apatite crystals. But if this were true of our synthetic Mg-containing apatites, the magnesium might be expected not to affect the physicochemical properties of fluoridated apatites as significantly as it did. Also, it has been reported that magnesium may be substituted into the apatite crystals to a limited extent [2,8]. When considered with the results of chemical analysis, it is suggested that there may be an interaction between Mg^{2+} and F^- in the apatite crystals.

Figure 3 shows the crystallinity of the Mg-free and Mg-containing fluoridated hydroxyapatites as the inverse of the half-value breadth calculated from the (300) and (002) reflections, which are taken as representations of the crystallinity along the a- and c-axes. In fluoridated hydroxyapatites, FHAp, the crystallinity increased initially, then decreased, and finally increased (Fig.3A). In the series with lower Mg contents, Mg-$FHAp_I$, the minimum observed at low fluoride content of Mg-free fluoridated hydroxyapatites was obliterated (Fig.3B); and in the series with higher Mg

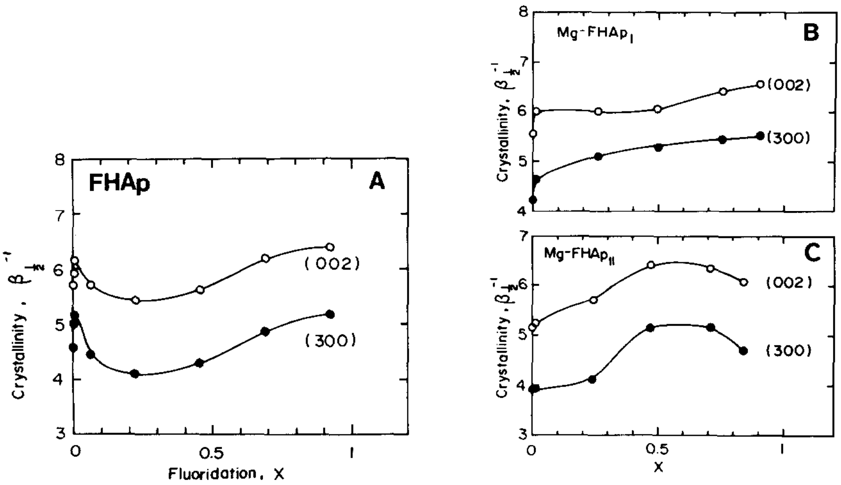

Fig.3. Crystallinity behavior of the Mg-free (A) and Mg-containing fluoridated hydroxyapatites, Mg-$FHAp_I$ (B) and Mg-$FHAp_{II}$ (C).

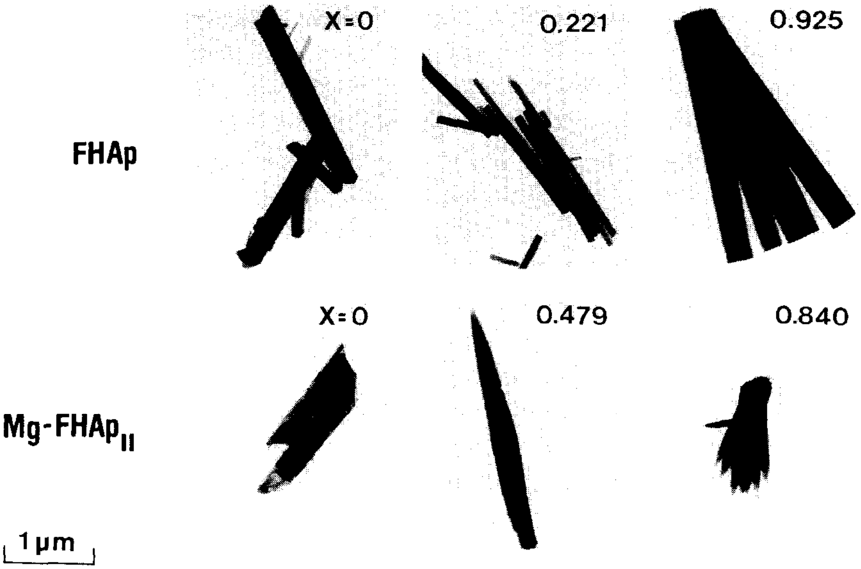

Fig.4. Typical transmission electron micrographs of the Mg-free (FHAp) and Mg-containing fluoridated hydroxyapatites (Mg-FHAp$_{II}$). X: Degree of fluoridation.

content, Mg-FHAp$_{II}$, crystallinity rose steadily to a maximum at about half of the maximum fluoride content (Fig.3C).

The transmission electron micrographs shown in Figure 4 seem to support in part these crystallinity behaviors. The Mg-free fluoridated hydroxyapatites, FHAp, are inhibited at lower fluoride content, X=0.221. On the other hand, Mg-containing fluoridated hydroxyapatites, Mg-FHAp$_{II}$, are promoted at about half of the maximum fluoride content, X=0.479. When compared with the results that crystallinity of the F-free Mg-containing hydroxyapatites (Mg-HAp) decreased monotonically with the increasing Mg content [2], these crystallinity behaviors of Mg-containing fluoridated apatites seem to be unexpected. In the presence of both magnesium and fluoride, there may exist an optimal structure for growth of the apatite crystal, and magnesium may act as a catalyst of growth. The crystal growth inhibition seen at lower fluoride content in FHAp (Fig.3A) may be due to a statistical imbalance between F^- ions and OH^- ions, which is relieved by the increase of fluoride content. Of course, perfect substitution of F^- ions makes fluorapatite (X=1) stable. When Mg^{2+} ions are added, probably, a small amount of Mg^{2+} ions has a restorative effect on the crystal growth of fluoridated apatites (Fig.3B and 3C). There may exist an optimal magnesium content at which apatite crystals become most compact and most likely to grow. The decrease of the crystallinity at high fluoride content of Mg-FHAp$_{II}$ may be related in part to the magnesium uptake promoted by fluoride.

Figure 5 shows the apparent solubility of FHAp, Mg-FHAp$_I$ and Mg-FHAp$_{II}$ as the dissolved calcium concentration in 0.5 mol/L acetate buffer solution (pH4.0, 37°C) in one month. The solubility of Mg-containing fluoridated apatites was higher than that of Mg-free fluoridated apatites at lower fluoride content, but at high fluoride content the difference between them was negligible.

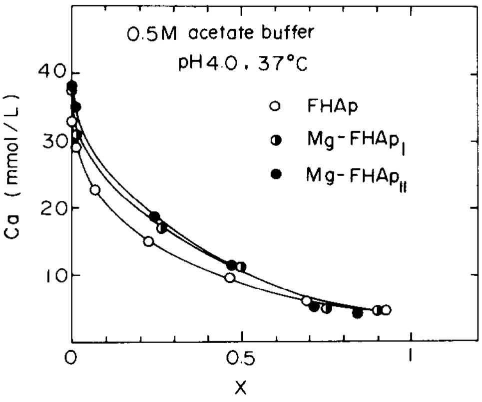

Fig.5. Apparent solubility of the Mg-free (FHAp) and Mg-containing fluoridated hydroxyapatites (Mg-FHAp$_I$ and Mg-FHAp$_{II}$) as the dissolved calcium concentration.

CONCLUSIONS

A small amount of magnesium affected significantly the crystallinity of synthetic fluoridated apatites. The patterns of crystallinity behavior with the increase of fluoride content were unique in each series with the different magnesium content, and not analogous to the solubility behaviors. These phenomena might have been caused by the Mg^{2+}-F^- interaction in the apatite crystals. On the other hand, even if crystal growth is controlled by the Mg^{2+}-F^- interaction, the strong bonding of fluoride ions with neighboring ions may be maintained against the acid attack, so that the solubility showed the monotonical decrease with increase of fluoride content.

REFERENCES

1 L. Stryer, 'Biochemistry', Freeman, San Francisco (1981).
2 M. Okazaki, J. Takahashi and H. Kimura, Caries Res., 20 (1986) 324.
3 H.G. McCann, J. Biol. Chem., 201 (1953) 247.
4 M.I.Kay, R.A. Young and A.S. Posner, Nature, 204 (1964) 1050.
5 E.C. Moreno, M. Kresak and R.T. Zahradnik, Caries Res., 11 (Suppl.1) (1977) 142.
6 M. Okazaki, J. Takahashi, H. Kimura and T. Aoba, J. Biomed. Mater. Res., 16 (1982) 851.
7 J.E. Eastoe, 'Calcified Tissue', Université de Liège, Liège (1965) p.265.
8 R.Z. LeGeros, 'Tooth Enamel IV', Elsevier, Amsterdam (1984) p.23.