BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (5), 1421—1422 (1976)

Effect of Hydroxylation on the Thermal Reactivities of Fluorapatite and Chlorapatite[1)]

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(Received October 23, 1975)

Synopsis. Thermal self-decomposition of hydroxyapatite was notably suppressed by partial fluorination or chlorination. The volatility of halogen from fluorapatite and chlorapatite was reduced by the incorporation of hydroxide ions in the apatites. The reactivities of fluor-hydroxyapatite and chlor-hydroxyapatite with silica increased with increasing hydroxide content, which resulted in an increase in the halogen volatility.

In a preceding report by the authors,[2)] it was stated that in the presence of silica and water vapor, fluorapatite (FAp) and chlorapatite (CAp) could be dehalogenated by the substitution of hydroxide ions for halogen ions and by the subsequent destructive reaction of partially hydroxylated FAp or CAp with silica. The aim of the present study is to examine the effects of decreasing the ratios of F/OH and Cl/OH on the thermal and chemical stabilities of FAp-hydroxyapatite (HAp) solid solutions [$Ca_{10}(PO_4)_6F_{2(1-x)}(OH)_{2x}$, F_xAp] and CAp–HAp solid solutions [$Ca_{10}(PO_4)_6Cl_{2(1-x)}(OH)_{2x}$, C_xAp]. The subscript x is the degree of substitution of OH^- for F^- or Cl^- and its value varies from 0 (for FAp or CAp) to 1 (for HAp).

Experimental

FAp (3.76% F), CAp (6.79% Cl) and HAp were prepared by the same methods as those described in a preceding paper.[2)] F_xAp was prepared by heating a mixture of $Ca_2P_2O_7$, CaF_2, and $CaCO_3$ having a molar ratio of 3 : $(1-x)$: 8 at 1200 °C for 3 h in an atmosphere of water vapor (90—240 mmHg), followed by washing with a 10% NH_4Cl aqueous solution to remove the excess CaO. The formation of FAp–HAp solid solutions is judged from the fact that the thermal self-decomposition degree of F_xAp was not in proportion to the OH content (refer to Fig. 1). C_xAp was prepared by heating pure CAp in an atmosphere of water vapor (17—360 mmHg) for various retention times.[2)] The precise values of x for these solid solutions were determined by chemical analysis. The silica used was siliceous sand (α-quartz) for optical glass making. All the samples prepared were ground to a 200 inch-mesh before use. Heating runs were performed in flowing nitrogen gas (150 ml/min) containing a trace water vapor (0.6 mmHg). A heating time of 3 h and a mixing molar ratio of silica/apatite of 3 were adopted as adequate reaction conditions.[2)] The conversion fraction of F_xAp into tricalcium phosphate was determined by quantitative X-ray analysis the procedure for which is given in detail elsewhere.[2)] Fluorine and chlorine were analyzed by thorium nitrate and potassium thiocyanate titrations, respectively.

Results and Discussion

Fluor-hydroxyapatite. Figure 1 shows the conversion fractions for F_xAp. Scarcely any self-decomposition of F_xAp at 1300 °C was observed in the range of x of 0—0.8. However, F_xAp for values of x above 0.9 decomposed considerably. In other words, the thermal stability of HAp ($x=1$) was remarkably decreased by partially substituting F^- for OH^-. The decomposition of F_xAp by silica increased monotonically with x. The fluorine volatilities of F_xAp without silica during heating at 1000—1300 °C for 3 h were 8% for FAp ($x=0$) and less than 4% over the range of x from 0.1—1.0. The volatility was accelerated by the addition of silica. Figure 2 shows the fluorine volatilities from silica-added F_xAp. The volatility curves have trends similar to the

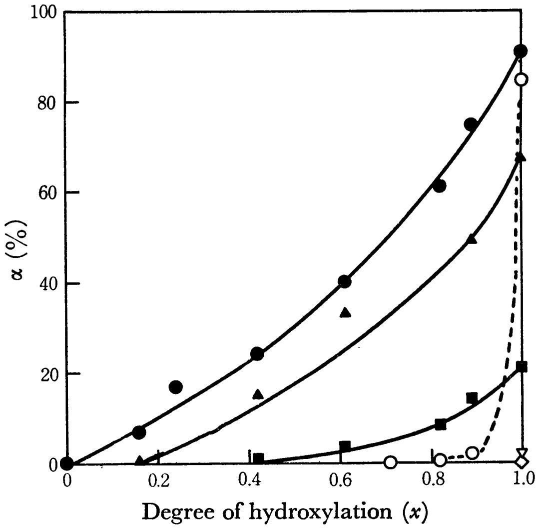

Fig. 1. Effects of hydroxylation and silica addition on conversion (α) of fluor-hydroxyapatite.
Sample: --- F_xAp, —F_xAp–silica mixture.
Temperature (°C): ○● 1300, ▽ 1250, ◇ 1200, ▲ 1100, ■ 1000.

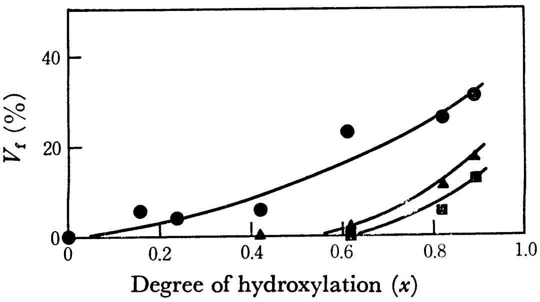

Fig. 2. Effects of hydroxylation and silica addition on fluorine volatility (V_f).
Sample: F_xAp–silica mixture. Temperature (°C): ● 1300, ▲ 1100, ■ 1000. V_f: [(Volatility for silica-added F_xAp)−(Volatility for F_xAp without silica)].

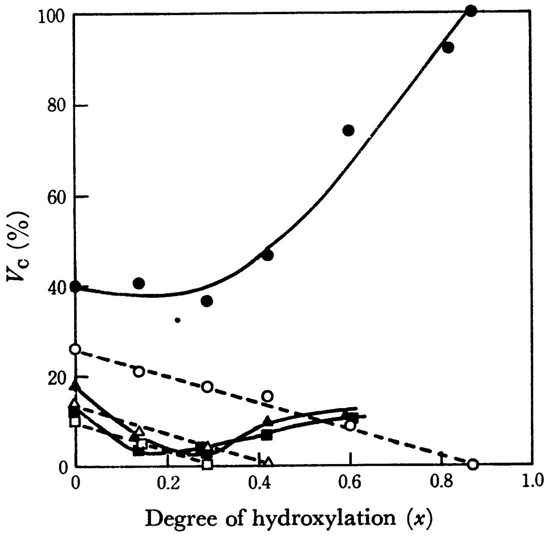

Fig. 3. Effects of hydroxylation and silica addition on chlorine volatility (V_C).
Sample: --- C_xAp, —C_xAp–silica mixture.
Temperature (°C): ○● 1300, △▲ 1100, □■ 1000.

decomposition curves in Fig. 1. This similarity supports the idea that the volatilization was mostly due to the destructive reaction of F_xAp with silica. However, the volatilities, which should be practially consistent with the decomposition fractions, were less than these fractions. This relationship suggests that a fluorine compound such as SiF_4 produced simultaneously during the destructive reaction may recombine with unreacted F_xAp.

Chlor-hydroxyapatite. The values of x for unreacted apatites after the heating of C_xAp with and without silica were determined by using a calibration curve of the lattice constant *vs.* x. The results are summarized as follows. The x values after heating became higher than those of the starting apatite under heating conditions permitting the stability of the apatite structure. This change of x was due possibly to the replacement of Cl^- with OH^- or O^{2-} of which a small amount was contained in the atmosphere as water vapor.[2] Under condition permitting the apatites structure to be unstable, the value of x of unreacted apatite agreed with those before heating. The chlorine volatilities from C_xAp and silica-added C_xAp are shown in Fig. 3. C_xAp without silica was structurally stable over the range of x from 0—0.9. This fact means that Cl ions incorporated into HAp also have a stabilizing effect on the apatite structure similar to that of F ions. The chlorine volatilities of C_xAp decreased linearly with x, while the volatilities of the C_xAp–silica mixture decreased in the range from 0—0.3 in which the apatite structure was stable and increased thereafter along with the decomposition of the apatite by silica. In conclusion, the volatility behavior of C_xAp in the presence of silica could be interpreted by both a suppression effect due to the incorporation of OH and an accelerating effect due to the decomposition reaction.

References

1) This paper was presented at the 32nd Annual Meeting of Spring of the Chemical Society of Japan, Tokyo, April, 1975.

2) H. Monma and T. Kanazawa, *Bull. Chem. Soc. Jpn.*, **48**, 1816 (1975).