The Mechanism of Thermal Reactions in Apatites–Silica–Water Vapor Systems[1]

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The reactions of fluor-, hydroxy-, and chlorapatites with silica in the presence of water vapor have been studied under various conditions—*i.e.*, various amounts of added silica, various temperatures (up to 1300 °C), and various heating times and water-vapor pressures (0.6—760 mmHg). As the pressure increased, the decomposition rate of hydroxyapatite with silica decreased considerably. Fluorapatite and chlorapatite were found to be decomposed with silica after being partially defluorinated or dechlorinated. In the case of fluorapatite, no effect of silica addition was recognized under a low water-vapor pressure (0.6 mmHg). This effect was observed under a high water-vapor pressure (760 mmHg), accompanied by rapid increases in the fluorine volatility and the destruction rate of the apatite in their time-dependence plots. In the reaction using chlorapatite, a similar effect was found under both low and high pressures. The results for the defluorination and dechlorination could mostly be interpreted by assuming the following changes: (1) halogen-oxyapatite formation, (2) the substitution of hydroxyl ions for halogen ions, and (3) the decomposition of apatite with silica.

Fluorine volatilization during the heat-treatment of rock phosphate in the presence of water vapor is accelerated by adding silica. In fact, thermal treatments above 1300 °C can be carried out by applying this reaction process to produce a defluorinated phosphate. Some thermodynamic considerations and a preliminary experiment on the fluorapatite (FAp)–silica–water vapor system were described in previous papers by the present authors.[2,3] On the basis of these studies, it was estimated that silica can react with partially or completely hydroxylated FAp, but not stoichiometric FAp. A similar estimation may also hold for chlorapatite (CAp).

The purpose of the present investigation is to obtain some information concerning the mechanisms of the destruction, defluorination, and dechlorination of apatites in the presence of both silica and water vapor.

Experimental

Materials. The FAp was prepared by heating a stoichiometric mixture of $Ca_3(PO_4)_2$ (thermally synthesized material) and CaF_2 (special-grade reagent) at 1150 °C for 2.5 hr in a N_2 gas flow. Another substance, CaF_2, was placed upstream near the mixture to minimize volatilization of fluorine from the reactant. This synthetic FAp contained 3.76% F. The hydroxyapatite (HAp) was synthesized by heating a mixture of $Ca_2P_2O_7$ and CaO (added as $CaCO_3$) in the molar ratio of 1 : 2.7 at 1200 °C for 3 hr in water vapor (p_{H_2O}=150—230 mmHg), and was then purified by washing it with an aqueous solution of NH_4Cl to remove the excess CaO. The CAp was prepared by heating a mixture of $Ca_2P_2O_7$, $CaCO_3$ and $CaCl_2$ in the molar ratio of 1 : 1 : 2.5 at 1200 °C for 3 hr, followed by air quenching and by washing with a NH_4Cl aqueous solution to remove the calcium salts other than apatite. The chlorine content in this synthetic CAp was 6.72%. Apatite-silica mixtures with molar ratios in silica/apatite of from 1/1 to 18/1 were prepared by manual mixing in an agate-mortar. As the SiO_2 sample, silica sand (α-quartz) for optical glass making was adopted after it had been purified with hydrochloric acid. All the samples thus prepared were ground to 200 mesh and then used.

Heat-treatment and Analyses. The reaction runs were carried out by heating the samples at various temperatures (up to 1300 °C) and times (up to 9 hr) in a Na-H_2O mixed gas flow of 150 ml/min (p_{H_2O}=0.6—760 mmHg). The partial water-vapor pressure in the flow of the N_2 gas used here was determined to be 0.6 mmHg from a comparison of the data shown in Fig. 2 with the thermal stability curve of HAp reported by Riboud.[4]

The decomposition rate of FAp or HAp was determined from a calibration curve of the apatite content *vs.* the relative X-ray diffraction intensity. This intensity means $I_{AP}/(I_{AP}+I_{\alpha-T}+I_{\beta-T})$, where the I's are the diffraction intensities obtained by using CuKα radiation at 31.8 °, 30.6 °, and 31.0 ° in 2 θ for apatite, α-, and β- tricalcium phosphates respectively.[5,6] The procedure described above was, however, inapplicable to the measurement of the CAp decomposition because of a considerable change in the diffraction pattern of CAp itself upon heating.[7] In this case, we investigated qualitatively whether or not the decomposition occurred.

The fluorine and chlorine contents were determined by thorium-nitrate and potassium-thiocyanate titrarions respectively. DTA was conducted in air from room temperature to 1350 °C at a rate of 10 °C/min. The sample weight was 400—600 mg, and the reference material used was α-Al_2O_3.

Results and Discussion

Thermodynamic Considerations. FAp and CAp are considered to be thermally stable up to their melting temperatures, whereas the thermal stability of HAp is strongly dependent on the pressure of the coexisting water vapor.[4,5] The reactivities of apatites with silica were determined by the calculation of the standard free-energy changes ($\Delta G°_r$) in these reactions, assuming $Ca_3(PO_4)_2$, Ca_2SiO_4, $CaSiO_3$, CaO, H_2O, HF, HCl, SiF_4, and $SiCl_4$ as reaction products. On the basis of these calculations, the following results were obtained: the $\Delta G°_r$ values for a reaction of HAp–SiO_2 system became negative above 600—700 °C, and even above 760 mmHg of coexisting water vapor it was considered possible for the decomposition of HAp to occur. On the other hand, the $\Delta G°_r$ values for the reactions of FAp–SiO_2 and CAp–SiO_2 systems were always positive in the range of 25—1300 °C. However, silica possibly reacts with FAp or CAp during heat-treatment in the presence of water vapor. The reason for this is that the standard free energies of formation of these apatites become close to the value of HAp with an increase in the substitution

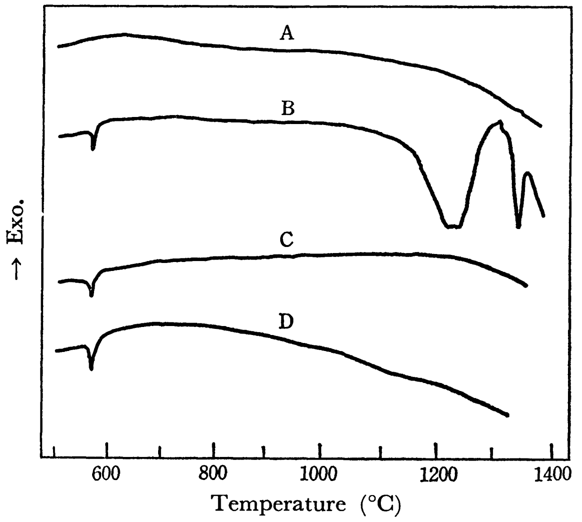

Fig. 1. DTA curves of HAp and apatites-silica mixtures.
Mixing molar ratio: apatite/silica = 1/3.
A: HAp, B: HAp-SiO_2, C: FAp-SiO_2, D: CAp-SiO_2.

degree of OH^- for F^- or Cl^-.[8)]

DTA. Each apatite and apatite-silica mixture was examined by DTA (Fig. 1). The broad endothermic peak at 1000—1300 °C was due to a decomposition reaction of HAp with silica, and the peak above 1300 °C suggested a thermal change due to the formation of different phosphates, such as $4CaO \cdot P_2O_5$, $Ca_7P_2Si_2O_{16}$, and $Ca_5P_2SiO_{12}$. HAp to which silica was added was completely decomposed to produce α-tricalcium phosphate after the heating test. On the other hand, the apatitic structures of all the samples except for the HAp-SiO_2 mixtures were maintained even after the heating.

Effect of the Addition of Silica to HAp. HAp and a HAp-SiO_2 mixture were heated at various temperatures for 3 hr in a flow of N_2 gas, and the decomposition rate (α) of HAp was measured (Fig. 2). The only product detected by X-ray powder diffraction was tricalcium phosphate. The decomposition apparently started from 1200—1250 °C for HAp and from 850—900 °C for the HAp-SiO_2 mixture. The former and the latter were due to the self-decomposition of HAp and the reaction of HAp with silica respectively.

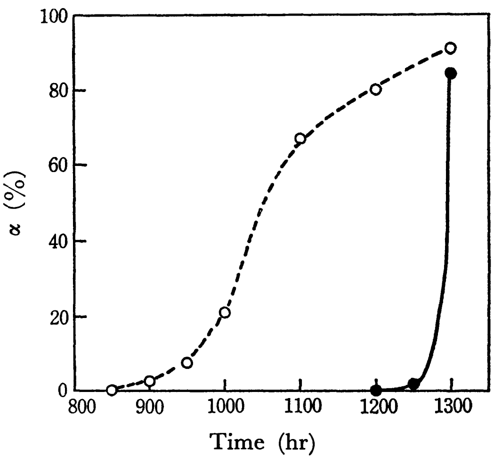

Fig. 2. Effect of added silica on decomposition (α) of HAp.
Heat-treatment: for 3 hr in N_2.
—●—: HAp, --○--: HAp-SiO_2 mixture (1 : 3).

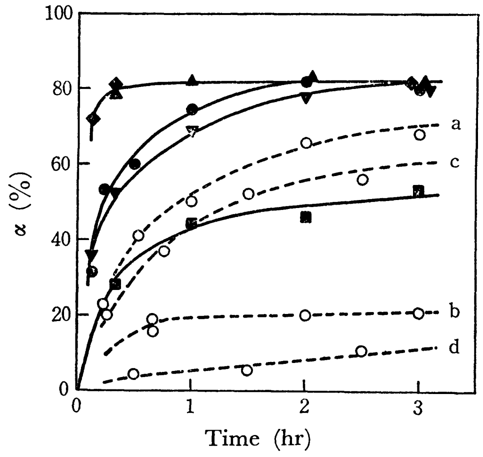

Fig. 3. Effects of heating condition and amount of added silica on decomposition (α) of HAp.
Sample: HAp-SiO_2 mixtures with various molar ratios; ▲: (1 : 13), ◆: (1 : 8), ●: (1 : 3), ○: (1 : 3), ▼: (1 : 2), ■: (1 : 1).
——: 1200 °C in N_2, ----a: 1100 °C in N_2, ----b: 1000 °C in N_2, ----c: 1200 °C in H_2O (760 mmHg), ----d: 1100 °C in H_2O (417 mmHg)

Figure 3 shows the effects of the amount of added silica and the heating condition on α. The values of α were largely influenced by the heating temperature and the water-vapor pressure (p_{H_2O}) in the atmosphere.

In order to find further quantitative relations between α and p_{H_2O}, α was plotted against p_{H_2O} and its logarithm (Fig. 4). From these plots, nearly linear relations were obtained as follows:

$$\alpha = K p_{H_2O} + C \qquad \text{(at 1200 °C)}$$

$$\alpha = K \log p_{H_2O} + C \qquad \text{(at 1000—1100 °C)}$$

where α is a value after an apparent steady state had been reached, both K and C are constants depending on the heating temperature.

Effect of the Addition of Silica to FAp. The FAp and FAp-SiO_2 mixtures were heated at 1000—1300 °C for 3 hr under various water-vapor pressures. Their heating weight losses were 0.1—0.7%. Table 1 represents the volatilities of fluorine upon the reactions. The difference in the volatilities between the samples with and without silica was negligible at 1000—1200 °C, while it was clear at 1300 °C under a high water-vapor pressure. On the other hand, the decomposition rates of FAp were less than 1% at 1100—1300 °C in a N_2 gas flow, regardless of the presence or absence of silica. Under a pressure of 760 mmHg of water vapor, however, the rate at 1300 °C was 45% for a 1 : 18 mixture of FAp and SiO_2, compared with the value of less than 1% for FAp without silica.

Figure 5 indicates the changes in the fluorine volatility and the decomposition rate with the heating time at 1300 °C under a pressure of 760 mmHg. No

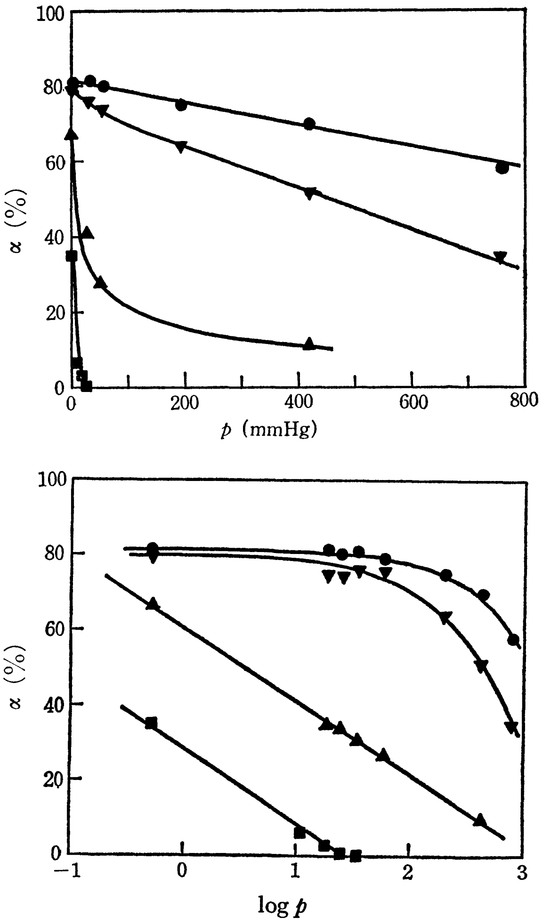

Fig. 4. Relation between docomposition (α) of HAp and water-vapor pressure (p_{H_2O}).
Sample: HAp-SiO_2 mixture (1 : 3).
●: 1200 °C-3 hr, ▼: 1170 °C-3 hr, ▲: 1100 °C-3 hr, ■: 1000 °C-9 hr.

TABLE 1. EFFECTS OF TEMPERATURE, WATER-VAPOR PRESSURE AND AMOUNT OF ADDED SILICA ON FLUORINE VOLATILITY

Sample[a]	Temperature (°C)	Fluorine volatility (%)[b] 0.6 mmHg[c]	18 mmHg	93 mmHg	234 mmHg	760 mmHg
FAp	1100	5.1	10.1	17.1	25.3	42.6
	1200	5.6	12.0	19.4	27.9	53.5
	1300	8.0	—	—	—	54.3
FAp-SiO_2 (1 : 3)	1100	5 0	9.4	17 6	23.9	38.7
	1200	7.2	11.3	20.8	28.0	56.3
	1300	7.2	—	—	—	67.6
FAp-SiO_2 (1 : 18)	1100	3.4	11.8	15.2	25.8	38.2
	1200	3.9	11.8	20.8	27.5	55.1
	1300	8.2	—	—	—	78.9

a) Value in parentheses shows mixing molar ratio of SiO_2 to FAp. b) Value after heating for 3 hr. c) Pressure of water vapor in the N_2 gas flow used here.

effect of silica addition on the volatility was observed up to 2 hr. The effect, however, was clearly observed after 2 hr; this time agreed approximately with the beginning of a rapid increase in the decomposition. The fluorine volatilization within 0—2 hr is based on the substitution of OH^- for F^-. Hence, the substitution degree required to decompose the apatite with silica was estimated to be about 40% under those heating conditions. In other words, no effect of silica addition is due to a low degree of substitution, which can rise upon further heating. For example, the defluorination is observed even at 1200 °C in a similar test using rock phosphate.[9]

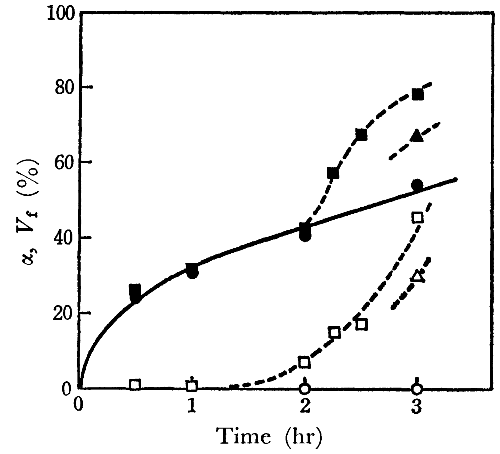

Fig. 5. Effects of added silica on decomposition (α) of FAp and fluorine volatility (V_f).
Heat-treatment: at 1300 °C in H_2O (760 mmHg).
●(FAp), ▲(FAp-SiO_2 (1 : 3)), ■(FAp-SiO_2 (1 : 18)) indicate volatility—time plots.
○(FAp), △(FAp-SiO_2 (1 : 3)), □(FAp-SiO_2 (1 : 18)) indicate decomposition rate—time plots.

Effect of the Addition of Silica to CAp. The effect of added silica on the chlorine volatility in the N_2 gas flow was also tested (Fig. 6). The chlorine volatilization was generally greater than the fluorine volatilization. The dechlorination due to silica addition was observed at all times; an especially rapid increase in the volatility appeared in the heating at 1300 °C. The starting point of this rapid increase was found to be about a 2-hr heating time and a 30% volatility; this agreed with the point at which tricalcium phosphate was first detected. On the other hand, the values of the volatility under a water-vapor pressure of 760 mmHg were unexpectedly decreased by adding silica at all times (Fig. 7). However, when the decom-

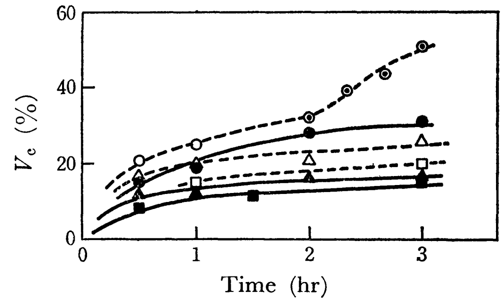

Fig. 6. Effect of added silica on chlorine volatility (V_c) in nitrogen gas.
—: CAp; ● 1300 °C, ▲ 1200 °C, ■ 1100 °C.
----: CAp-SiO_2 mixture (1 : 18); ○⊙ 1300 °C, △ 1200 °C, □ 1100 °C.
⊙: tricalcium phosphate was detected.

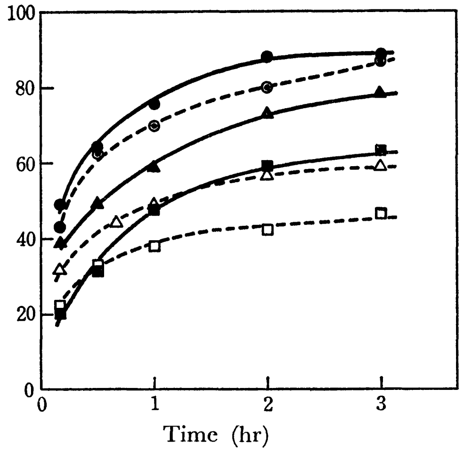

Fig. 7. Effect of added silica on chlorine volatility (V_c) in water vapor (760 mmHg).
——: CAp, ----: CAp-SiO_2 mixture (1 : 18). Symbols refer to Fig. 6.

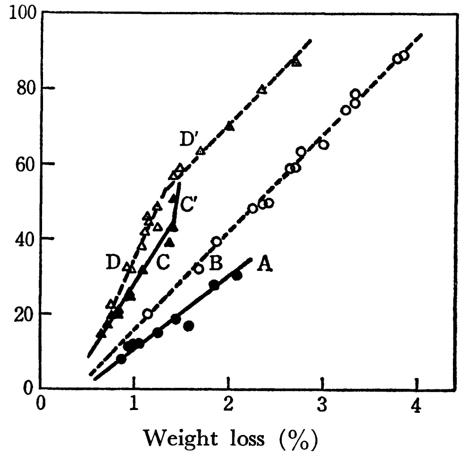

Fig. 8. Relationship between chlorine volatility (V_c) and weight loss after heating at various temperatures and times.
——: in N_2, ----: in H_2O (760 mmHg).
●○: CAp, ▲△: CAp-SiO_2 mixture (1 : 18).

position of a partially dechlorinated CAp began, its decreasing rate seemed to be reduced.

Figure 8 shows the relation between the chlorine volatilities and the heating losses. The fact that the extrapolated values are 0.3—0.4% in the loss may be ascribed to the evaporation of the water adsorbed on the samples. The changes in the slope from the (C) line to the (C′) line, and from the (D) to the (D′) line, in Fig. 8 were considered to be accompanied by the destruction of the apatite. The slopes of the (A), (B), (C), and (D) lines suggested the existence of some dechlorination processes, with a retention of the apatitic structure. Table 2 shows a comparison of the slopes calculated from the assumed reactions given in the footnote with the slopes determined from Fig. 8. The slopes of (A) and (C) agreed with that of chlor-oxyapatite formation.[10] The slopes of (B) and (D) agreed approximately with that of chlor-hydroxyapatite formation.

TABLE 2. SLOPES FOR CHLORINE VOLATILITY-HEATING LOSS PLOTS WITH LINEAR RELATION

Method of calculation	Slope (Volatility (%)/Loss (%)) CAp	CAp-SiO_2 (1 : 18)
From reactions assumed		
Chlor-oxyapatite formation[a]	19.0	38.6
Chlor-hydroxyapatite formation[b]	28.2	57.4
From straight lines in Fig. 8 (A)	19.5	—
(B)	26.0	—
(C)	—	38.0
(D)	—	57.5

a) $Ca_{10}(PO_4)_6Cl_2 \rightarrow Ca_{10}(PO_4)_6Cl_{2(1-x)}(OH)_{2x} \rightarrow Ca_{10}(PO_4)_6Cl_{2(1-x)}O_x\square_x$, where □ shows vacancy. b) $Ca_{10}(PO_4)_6Cl_2 \rightarrow Ca_{10}(PO_4)_6Cl_{2(1-x)}(OH)_{2x}$.

Summarizing the above results, the following interpretation may be given concerning the dechlorination processes: (1) Under low water-vapor pressures, chlor-oxyapatite is produced by the dehydration of the chlor-hydroxyapatite formed intermediately. (2) The substitution of OH^- for Cl^- proceeds under high water-vapor pressures. (3) In the presence of silica, a partially dechlorinated CAp is decomposed with silica.

References

1) This paper was read at the 31st Autumn Annual Meeting of the Chemical Society of Japan, Sendai, October, 1974.

2) T. Kanazawa, H. Monma, and T. Umegaki, *Sekko to Sekkai*, No. **112**, 31 (1971).

3) T. Kanazawa, H. Monma, and S. Ishii, *Kogyo Kagaku Zasshi*, **74**, 157 (1971).

4) P. V. Riboud, *Bull. Soc. Chim. Fr.*, **1968**, 1701.

5) H. Monma and T. Kanazawa, *Nippon Kagaku Kaishi*, **1972**, 339.

6) G. Otalora and H. H. Hess, *Amer. J. Sci.*, **267**, 822 (1969).

7) T. Kanazawa and H. Monma, *Kogyo Kagaku Zasshi*, **73**, 687 (1970).

8) E. J. Duff, *J. Chem. Soc.*, *A*, **1971**, 1895.

9) G. M. Il'in, *Tr. Nauchn. Inst. po Udobr. i Insektofung.*, No. **208**, 133 (1965); *Chem. Abstr.*, **63**, 9503 (1965).

10) J. S. Prener, W. W. Piper, and R. M. Chrenko, *J. Phys. Chem. Solid*, **30**, 1465 (1965).