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$Ca_3(PO_4)_2$ - $CaNaPO_4$ System

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As a fundamental research of a calcined defluorinated phosphate containing a small amount of sodium, the system $Ca_3(PO_4)_2$(tricalcium phosphate, T) - $CaNaPO_4$(Rhenanite, R) was studied by high temperature X-ray diffraction, differential thermal analysis, *etc.*, and the phase diagram determined. During heating, T inverted from β to α at 1180°C, and then possibly from α to α' at 1280°C. R inverted from β to α at 690°C. In the composition range containing R from about 10 to 98% by weight, (βT+βR), the stable phase at room temperature, inverted to (βT+αR) at 650°C. The (βT+αR) changed at 980°C to form a compound "A" $Ca_5Na_2(PO_4)_4$ for the sample containing 50.5% R, and ("A"+βT) for samples containing a smaller amount of R. The ("A" +βT) then changed to "A" solid solution at elevated temperatures. The crystals of "A" consisted of a superlattice of αR. "A" and the solid solution changed to αR solid solution at higher temperature. By quenching the samples containing 35 to 50.5% R from 1400°C, a single phase "A" or "A" solid solution was obtained at room temperature. The "A" solid solution was the major phase of the calcined defluorinated phosphate. During heating of samples containing more than 50.5% R, (βT+αR) changed to αR solid solution at or below 980°C; during cooling of the solid solution ("A" + βR) formed at 650°C.

Recently in Japan, and in the United States of America, a large amount of defluorinated phosphate for fertilizer, as well as for animal food, has been produced by the calcination of phosphate ore blended with small amounts of phosphoric acid and sodium carbonate at 1350°C to 1400°C.

Ando[1,2] identified the principal mineral of the phosphate to be a solid solution of a new compound "A" $Ca_5Na_2(PO_4)_4$, and suggested that the crystals of "A" might consist of a superlattice of hexagonal α-$CaNaPO_4$.

The compound "A" is highly soulble in both 2% citric acid, and ammonium citrate. The products of the calcined defluorinated phosphate, however, contained not only "A", but also considerable amounts of β-$Ca_3(PO_4)_2$, which was less soluble.[3]

In the present study, the system $Ca_3(PO_4)_2$-$CaNaPO_4$ was investigated to determine the phase diagram, and to find the optimum condition to increase the "A" content of the calcined defluorinated phosphate.

Experimental

The samples of tricalcium phosphate and Rhenanite were prepared with refined calcium oxide, phosphoric acid, and sodium carbonate by blending and calcination at 1100°C. The samples, and their mixtures in various ratios, were submitted for differential thermal and high temperature X-ray diffraction analyses up to 1450°C. Some fusion tests were carried out in an effort to make a complete phase diagram; however, these tests, were not successful because of the high melting points of the samples (above 1700°C), and the volatilization of sodium at the high temperature.

In another series of tests, the mixtures were heated to 1400°C, cooled at different rates to room temperature, and tested by quantitative X-ray analysis to determine the amounts of the compounds in the products. The lattice constants of "A" and its solid solutions were also determined by X-ray diffraction.

Results and Discussion

Phase Changes. Differential thermal analysis curves taken during heating at a rate of 5°C/min are shown in Fig. 1. The temperatures at which thermal reactions started are plotted in Fig. 2. High temperature X-ray diffraction tests were made during heating and cooling for many compositions including all of those shown in Figs. 1 and 2. Some of the diffraction patterns are shown in Figs. 3 to 6.

Differential thermal analysis was also carried out during cooling. Four examples of the curves taken during cooling at a rate of 5°C/min are shown in Fig. 7, in which phases identified by X-ray tests are indicated. The phase diagram obtained from the above tests is shown in Fig. 8.

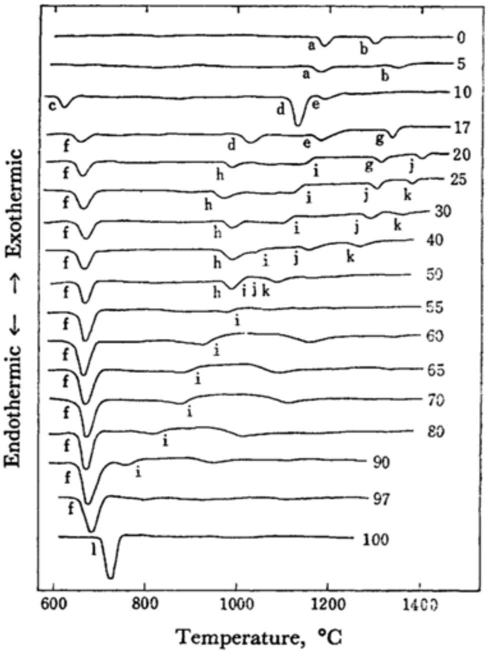

Fig. 1. DTA curves during heating (5°C/min). (Numbers in the figure indicate R content.)

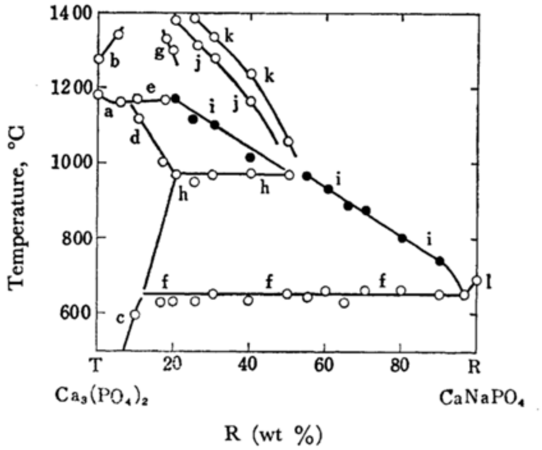

Fig. 2. Temperatures at which thermal reactions started during heating (5°C/min.).
○ endothermic reactions
● slow exothermic reactions

During heating, pure tricalcium phosphate (T) inverted from βT to αT at 1180°C, and then showed another thermal change around 1280°C. Nurse[4] recently reported the stable presence of α'T at above 1430°C. The present tests, however, did not show any appreciable change around 1430°C. In other tests with tricalcium phosphate produced from phosphate ore containing about 3% R_2O_3, a change occurred around 1430°C. For pure tricalcium phosphate, the inversion between αT and α'T might occur around 1280°C. Pure

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[1] J. Ando, K. Sumi and Y. Shikatani, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **63**, 1971 (1960).

[2] J. Ando, *Reports of Faculty of Engineering, Chuo University*, D-20, No. 74 (1961).

[3] J. Ando, Studies on Chemical Fertilizers, Nissin Shuppan K. K., Tokyo (1965), p. 215.

[4] R. W. Nurse, J. H. Welch and W. Gutt, *Nature*, **182**, 1230 (1958).

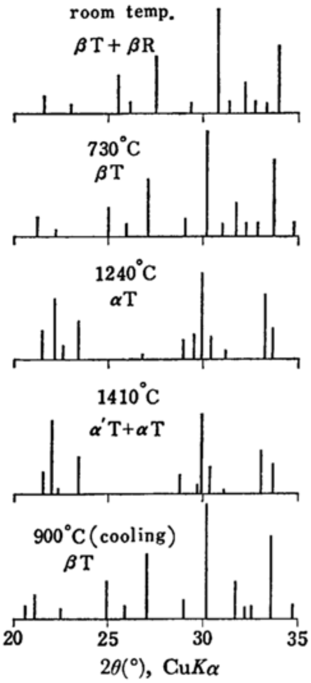

Fig. 3. High temperature X-ray diffraction patterns of the sample containing 10% R.

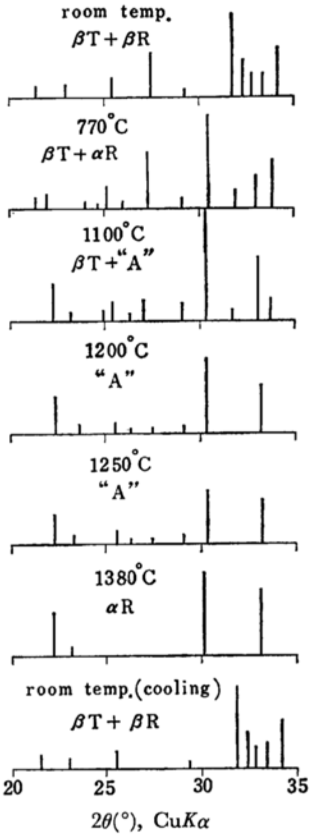

Fig. 4. High temperature X-ray diffraction patterns of the sample containing 30%.

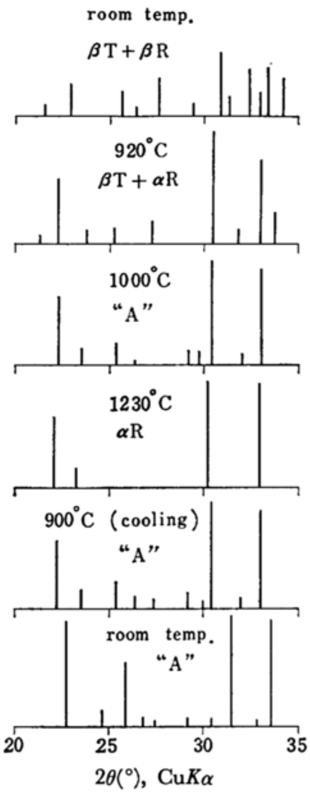

Fig. 5. High temperature X-ray diffraction patterns of the sample containing 50% R.

Rhenanite (R) inverted at 690°C from βR to αR during heating.

Complicated changes occurred for samples blended with T and R. When the R content was less than about 10% by weight, R dissolved during heating into βT to form βT solid solution which then inverted to αT a little below 1180°C. For samples containing 10 to 97% R, βR changed to αR at 650°C to give mixtures of βT and αR.

In the samples containing 20 to 50.5% R, mixtures of "A" and βT formed at 980°C. Larger amounts of "A" with smaller amounts of βT formed as the R content approched 50.5%, where single phase "A" with a stoichiometric composition of $Ca_5Na_2(PO_4)_4$ formed. At elevated temperatures, the βT dissolved into "A" to form "A" solid solution. At yet higher temperature, "A" and the solid solution inverted to αR solid solution.

When the αR solid solution was cooled, "A" solid solution formed again, βT separated during further cooling, and then "A" diminished at 980°C to form αR and βT. The decomposition of "A" occurred more slowly for solid solutions containing a larger amount of R. "A" with the stoichiometric composition, $Ca_5Na_2(PO_4)_4$, decomposed very slowly as will be described later in detail.

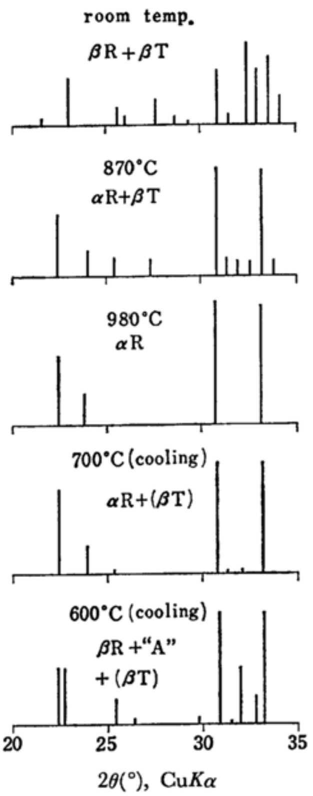

Fig. 6. High temperature X-ray diffraction patterns of the sample containing 70% R. (βT in the parentheses means very minor.)

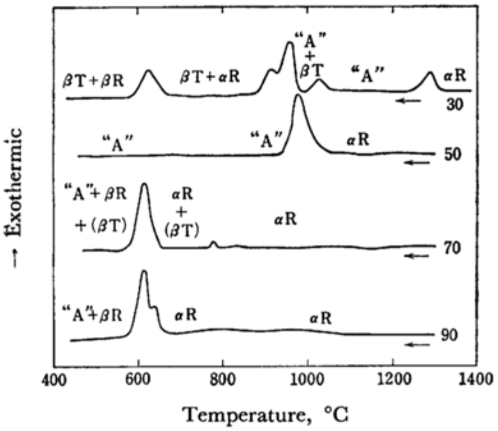

Fig. 7. DTA curves during cooling (5°C/min). (Numbers in the figure indicate R content. βT in the parentheses means very minor.)

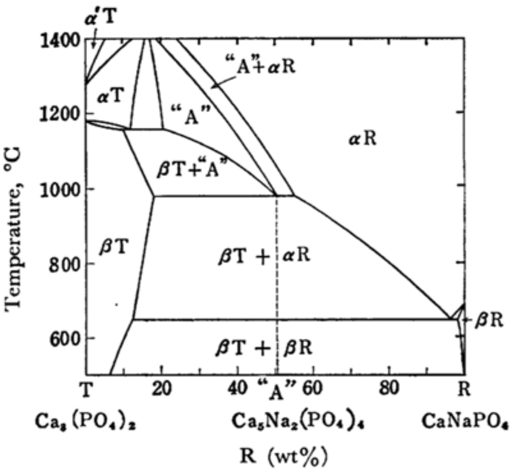

Fig. 8. Phase diagram of the system $Ca_3(PO_4)_2$-$CaNaPO_4$. (In the range containing 50.5 to 97% R, αR solid solution is easily supercooled to 650°C without forming βT, thereby "A" and βR form.)

In samples containing R from 50.5 to 97%, βT disappeared during heating between 650°C and 980°C to form αR solid solution. The formation of "A" was not detected by high temperature X-ray diffraction during heating.

The phase diagram shows that when the αR solid solution containing 55 to 97% R was cooled, βT should first form from the solid solution. The rate of formation of βT, however, was so small that appreciable amounts of βT did not form at the cooling rate of 5°C/min. The αR solid solution was thus supercooled down to 650°C, where βR and "A" formed simultaneously and rapidly as shown in Fig. 7.

Mineral Content of the Cooled Products. The mineral content of the samples cooled from 1400°C to room temperature at a rate of 10°C/min is given in Fig. 9.

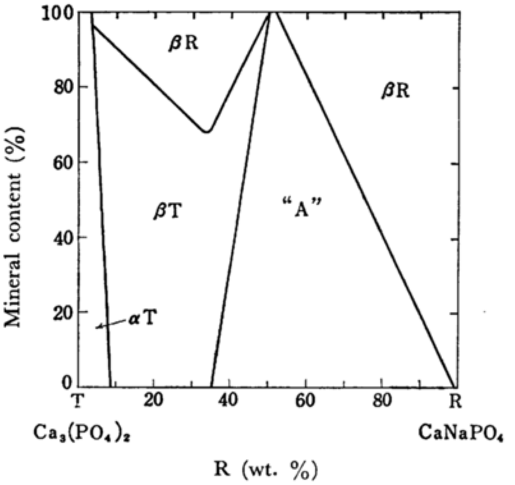

Fig. 9. Mineral content of the products cooled at a rate of 10°C/min.

For a pure sample of T, an α modification was obtained at room temperature because the inversion from α to β was very slow. When a small amount of R was present, the inversion was promoted and mixtures of βT and βR were obtained.

"A" was present in samples containing more than 35% R. The amount of "A" increased to 100% as the R content increased to 50.5%, indicating that the decomposition rate of "A" during cooling was decreased as the R content approached the stoichiometric amount. Samples containing more than 50.5% R consisted of "A" and βR.

Although "A" with the stoichiometric composition was fairly stable, decomposition occurred slowly below 980°C. When "A" was maintained at 850°C, decomposition occurred to the extent of 20% in 20 hr, and to the extent of 80% in 120 hr. The "A" solid solutions containing 35 to 40% R decomposed nearly completely at this temperature in 20 min, but the decomposition was very slow at 500°C.

In an other series of tests, the samples were quenched by air from 1400°C to 500°C in about 30 sec, and to room temperature in an additional 1 min. The mineral content of the quenched products is shown in Fig. 10.

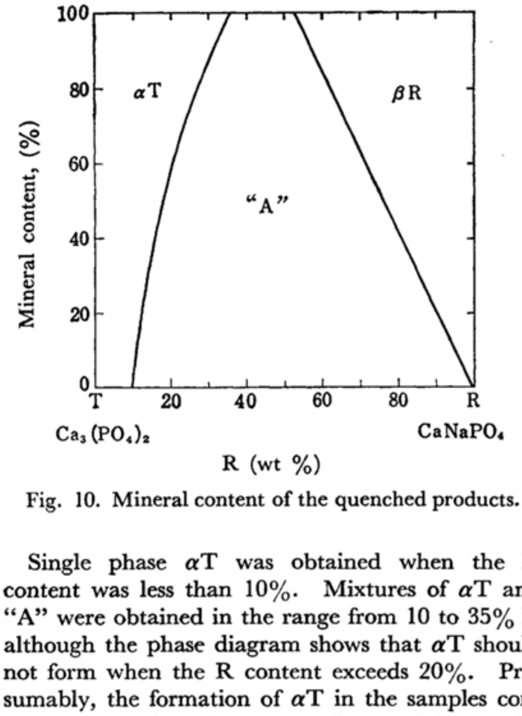

Fig. 10. Mineral content of the quenched products.

Single phase αT was obtained when the R content was less than 10%. Mixtures of αT and "A" were obtained in the range from 10 to 35% R although the phase diagram shows that αT should not form when the R content exceeds 20%. Presumably, the formation of αT in the samples containing 20 to 35% R was peculiar, and due to the rapid cooling from the high temperature at which the αR solid solution was present. Other tests showed that when samples containing 20 to 35% R were cooled rapidly after being kept for a while between 1200 and 1250°C, where "A" was stable, essentially no αT was present in the products while the main mineral "A" was accompanied by small amounts of βT which seemed to have formed from the "A" solid solution during cooling.

Single phase "A" was obtained in the 35 to 50.5% R range. Mixtures of "A" and βR were obtained when the R content exceeded 50.5% in the same manner as shown in Fig. 9.

These results show that to maximize the amount of "A" in the calcined defluorinated phosphate, the raw materials should be blended to maintain an R content of between 35 and 50.5%, and the calcined phosphate should be quenched to below 500°C from the temperature range in which single phase "A" is stable, or from a higher temperature.

Composition and Structure of "A". The X-ray diffraction data of "A" which has the stoichiometric composition, $Ca_5Na_2(PO_4)_4$, are shown in Table 1, and compared with those of pure α-$CaNaPO_4$.⁵⁾ The principal diffractions of "A" agree with those of αR, indicating that the structure of "A" is related to that of αR. "A" shows other minor diffractions which are not shown by αR.

The compound "A" contains a smaller number of cations in comparison with αR, $Ca_4Na_4(PO_4)_4$. Apparently "A" has lattice vacancies due to the lack of cations, and the vacant lattice points are arranged to form a superlattice of αR which is fourfold in *a* direction and threefold in *c* direction (Table 1).

At high temperature, the lattice vacancies are disordered by an endothermic reaction resulting in the formation of a lattice which is similar to that of αR except for the presence of the lattice vacancies which are distributed at random, and therefore do not give the typical diffraction lines of "A". When the αR solid solution was cooled, the lattice vacancies were again arranged to form "A" by an exothermic reaction.

It is also quite likely that Nagelschmidtite, $Ca_7Si_2P_2O_{16}$, which is isomorphic with "A", consists of a superlattice of α-Ca_2SiO_4 which is isomorphic with αR.¹,²⁾

Although the formation of "A" was not detected by X-ray during heating of samples containing more than 50.5% R, as was already mentioned, differential thermal analysis showed that considerable exothermic reactions occurred slowly after βT disappeared to form αR solid solution. For example, exothermic reactions occurred slowly between 930 and 1180°C for a sample with 60% R, and between 750 and 950°C for another sample with 90% R (Fig. 1).

The exothermic reactions may indicate the formation of "A" which has considerable disorder and do not give clearly the typical X-ray diffraction lines of "A". In those samples, the number of lattice vacancies is less than that required to form "A" because of the presence of an excessive R component. The formation of well-arranged "A" thus may not be easy.

During cooling, the imperfect "A", which is similar to the αR solid solution, was easily supercooled down to 650°C. The separation of βR

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5) R. Bredig, *J. Phys. Chem.*, **46**, 754 (1942).

TABLE 1. X-RAY POWDER DIFFRACTION DATA OF "A" AND α-$CaNaPO_4$

"A" (Hexagonal $a_0=21.33$ $c_0=21.69$)				α-$CaNaPO_4$ (Hexagonal $a_0=5.23$ $c_0=7.04$)		
I	*d*(exp.)	*d*(calc.)	(*hkl*)	(*hkl*)	*d*(exp.)	*I*
10	8.52	8.50	201			
10	7.05	7.03	202			
10	5.71	5.70	203			
10	4.79	4.79	222			
70	3.892	3.892	403	101	3.82	60
10	3.618	3.614	006	002	3.51	40
40	3.445	3.447	421			
20	3.323	3.325	422			
10	3.152	3.145	423			
10	2.993	2.992	226			
20	2.938	2.935	424			
100	2.845	2.846	406	102	2.78	100
10	2.720	2.711	008			
80	2.666	2.666	440	110	2.62	100
10	2.414	2.414	623			
10	2.330	2.338	408			
10	2.309	2.310	800			
20	2.199	2.199	803	201	2.17	40
10	2.032	2.031	643			
10	1.974	1.975	644			
40	1.946	1.946	806	202	1.91	80
10	1.806	1.807	0012	004	1.77	40

from the solid solution at this temperature resulted in an increase in the number of lattice vacancies in the remaining component which resulted in the formation of "A". Presumably, if the αR solid solution was cooled so slowly that a sufficient amount of βT could first separate from the solid solution, the formation of "A" at 650°C would be depressed.

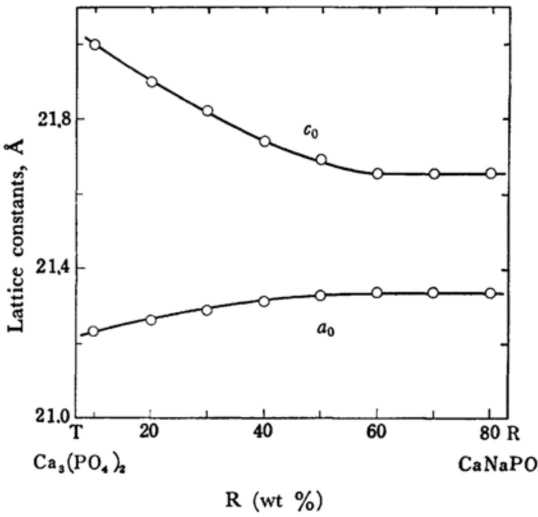

Fig. 11. Relation between R content and lattice constants of "A" and the solid solution present in the quenched products.

The relation between the R content and the lattice constants of "A" and "A" solid solution present in the products quenched from 1400°C is shown in Fig. 11.

The lattice constant a_0 increased slightly, and c_0 decreased remarkably as the R content increased from 10 to 50.5%. Essentially no change was observed when the R content exceeded 50.5%, indicating that the composition of "A" formed in the samples was close to the stoichiometric composition, $Ca_5Na_2(PO_4)_4$, due to the separation of the excessive R component at 650°C.

The "A" solid solution formed in samples containing less than 50.5% R includes more lattice vacancies than required to form "A", because tricalcium phosphate $Ca_6(PO_4)_4$ contains less cations than does $Ca_5Na_2(PO_4)_4$. The rate of the decomposition of the solid solution during the cooling thus increased with decrease in R content, due to the increase in the number of vacancies.