

Ion Exchange on α -Titanium Phosphate and Formation of New Crystalline Phases by Hydrolysis of the Ion-Exchanged Phases

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The ion-exchange reactions of well crystallized α -titanium phosphate in 1.0 M sodium phosphate solutions were studied at various temperatures. Two new phases formed at 5°C by ion exchange, viz. $\text{TiHNa}(\text{PO}_4)_2 \cdot 5 \text{H}_2\text{O}$ and $\text{Ti}(\text{NaPO}_4)_2 \cdot 4 \text{H}_2\text{O}$, were characterized. These phases and the previously known $\text{TiHNa}(\text{PO}_4)_2 \cdot 4 \text{H}_2\text{O}$ and $\text{Ti}(\text{NaPO}_4)_2 \cdot 3 \text{H}_2\text{O}$ were not stable in sodium phosphate solutions. In these solutions they were converted to new crystalline titanium phosphate phases containing hydroxide or oxide ions in addition to sodium ions. Three new phases were obtained at three different pH values. Possible formulas are $\text{Na}_2\text{Ti}(\text{OH})_2(\text{HPO}_4)_2 \cdot \sim 10 \text{H}_2\text{O}$, $\text{Na}_3\text{Ti}(\text{OH})_2(\text{HPO}_4)(\text{PO}_4) \cdot \sim 10 \text{H}_2\text{O}$ and $\text{Na}_4\text{TiO}(\text{PO}_4)_2 \cdot \sim 7 \text{H}_2\text{O}$. These phases have a layered structure; however, the packing of titanium atoms within the layers is less dense than within a layer in α -titanium phosphate. The mechanism of ion exchange in α -titanium and α -zirconium phosphate is discussed. It is shown that the dimensions of the cavities in the structure determine the ion-exchange properties.

α - $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (α -TiP) has the same structure as α - $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (α -ZrP),¹ i.e. monoclinic with space group $P2_1/n$.² According to Troup and Clearfield² this is a layered structure without any hydrogen bonds between the layers. Thus, the forces holding the layers together are very weak. The hydrogen in the phosphate groups can be exchanged with monovalent cations, often followed by an uptake of water molecules. The incorporated cations and the water molecules are located in cavities between the layers, and the interlayer distance normally increases during the ion exchange.

Different ion-exchange characteristics can be observed in α -TiP and α -ZrP. The pH at which they exchange alkali metal ions is shown in Fig. 1. The obtained ion-exchanged phases differ for α -TiP and α -ZrP. For α -ZrP, the phases first formed when ion exchanged with alkali metal ions are: α -ZrHLi(PO_4)₂ · 4 H₂O,⁵ α -ZrHNa(PO_4)₂ · 5 H₂O,⁶ α -ZrHK(PO_4)₂ · H₂O,⁷ α -ZrH_{1.5}Rb_{0.5}(PO_4)₂ · 0.5 H₂O and α -ZrH_{1.5}Cs_{0.5}(PO_4)₂ · 0.5 H₂O.^{8,9} For α -TiP the phases formed are: α -Ti(LiPO₄)₂ · H₂O,¹⁰ α -TiHNa(PO_4)₂ · 4 H₂O (at 15°C), α -TiHNa(PO_4)₂ · H₂O (at 45°C)^{11,12} and α -Ti(KPO₄)₂ · 3 H₂O.¹³ Alberti *et al.*¹² have reported the

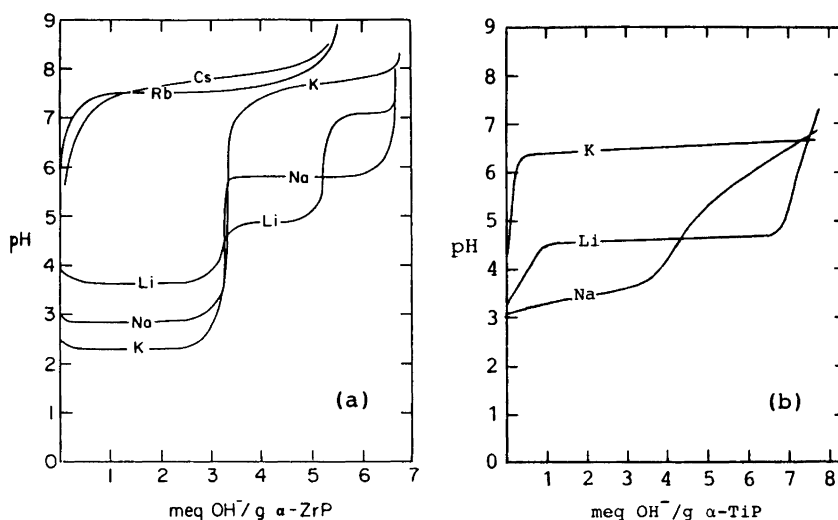


Fig. 1. Variation of pH with amount of alkali metal hydroxide added for M^+/H^+ exchange on (a) α -ZrP and (b) α -TiP (Reproduced with permission from Refs. 3 and 4).

formation of α -TiHK(PO₄)₂·H₂O, but this phase has not been verified by others.^{4,13} Rubidium- and cesium-exchanged phases cannot be obtained from α -TiP.¹² Clearfield *et al.*⁶ have attributed the difference between α -TiP and α -ZrP to the difference in size of the openings between the cavities. The openings in α -ZrP are larger than in α -TiP and therefore, according to Clearfield *et al.*⁶ α -ZrP ion exchanges large cations more easily.

The sodium and the potassium ion-exchanged phases of α -TiP are much more easily hydrolyzed than those of α -ZrP. At neutral pH the ion exchange of α -TiP results in extensive hydrolysis of the phosphate groups.^{4,12,13}

The ion exchange on α -TiP described in the literature has only been performed in chloride solutions at various temperatures. In this paper the result of ion exchange in 1.0 M (Na,H)₃PO₄ solution is reported. The phosphate solution was used in order to reduce the hydrolysis. The mechanism for the ion-exchange process is also discussed.

Experimental

Preparation of α -TiP. Well crystallized α -TiP was prepared by heating a solution of Ti(IV) in 15 M H₃PO₄ at 125 °C in an oven. The Ti(IV) solution was prepared by dissolving 0.5 g of titanium powder in 60 g of 15 M H₃PO₄ at 100–120 °C. The blue solution of Ti(III) obtained was cooled to about 25 °C and was then oxidized with H₂O₂ until only a very faint blue colour remained. When this solution was heated, crystalline α -TiP was slowly precipitated, forming hexagonal platelets with a diameter of up to 20 μ m. This method yielded a product that had more reproducible properties and was more crystalline than the product precipitated from Ti(III) solutions described previously.⁴

Ion exchange of α -TiP. 0.2–0.3 g of α -TiP was added to 50 ml of 1.0 M (Na,H)₃(PO₄) at a pH of 3.0 and at three different temperatures. The pH was then slowly increased by adding 5 M NaOH while stirring. Samples were taken at various pH and times and were analyzed by X-ray diffraction.

Preparation of α -ZrHK(PO₄)₂·H₂O for density measurement. α -Zirconium phosphate was prepared by heating amorphous zirconium phosphate under reflux in 15 M H₃PO₄ for 48 h. The α -ZrP was added to a solution of 1 M KH₂PO₄, and the pH was increased to 8.0 by addition of KOH. One then obtains α -Zr(KPO₄)₂·3 H₂O. To obtain α -ZrHK(PO₄)₂·H₂O the pH was decreased to 5.0 by addition of phosphoric acid.⁷ The formation of α -ZrHK(PO₄)₂·H₂O directly from α -ZrP is a very slow process at pH 5.0.^{14,15} It is also doubtful whether the conversion to α -ZrHK(PO₄)₂·H₂O is complete. However, the formation of α -Zr(KPO₄)₂·3 H₂O at pH 8.0, and the formation of α -ZrHK(PO₄)₂·H₂O from it by decreasing the pH to 5.0 are fast processes.

X-Ray diffraction patterns. In order to characterize new phases and to identify phases already known, the X-ray powder diffraction patterns were recorded for both wet and dry samples. Ni-filtered CuK α radiation was used.

Determination of the chemical composition. The PO₄/Ti ratio was determined by the method described previously.¹⁶ The sodium content was determined by atomic-adsorption spectrometry, and the water content by measuring the weight loss at various temperatures. The polyhydrated phases were dried above a saturated solution of ZnSO₄·7 H₂O (relative humidity 90 %).

Results

Sodium-exchanged phases of α -TiP. The ion-exchanged phases of α -TiP formed in 1.0 M (Na,H)₃PO₄ at three different temperatures are summarized in Fig. 2 and characterized in Tables 1 and 2. The ion exchange of α -TiP at 25 °C and 60 °C gave the same phases as in 0.1 M Na(Cl,OH).^{4,11} However, at 5 °C a new half-exchanged phase, TiHNa(PO₄)₂·5 H₂O (interlayer distance 10.9 Å), was formed when the pH was increased to 4.0. This phase was converted to a fully-exchanged phase, Ti(NaPO₄)₂·4 H₂O (10.5 Å), when the pH was further increased to 6.0. To prevent precipitation of hydrated Na₂HPO₄, the temperature of the solution was increased to 20 °C simultaneously.

The half-exchanged phase was converted to TiHNa(PO₄)₂·4 H₂O (10.4 Å) when stored at 25 °C and at a relative humidity (r.h.) of 90 %. The fully-exchanged phase was more resistant to dehydration, but when dried in air at 35 °C it was converted to Ti(NaPO₄)₂·3 H₂O (9.7 Å).

The number of water molecules in TiHNa(PO₄)₂·5 H₂O has not been experimentally confirmed. However, since the dehydration of the half- and the fully-exchanged phases to TiHNa(PO₄)₂·4 H₂O and Ti(NaPO₄)₂·3 H₂O, respectively, was followed by a nearly equally large decrease in interlayer distance, it is probable that the number of water molecules lost was the same. It can also be observed that the pentahydrate ZrHNa(PO₄)₂·5 H₂O (11.8 Å) is formed

Table 1. Water content in some ion-exchanged phases of α -TiP.

| | Weight loss at 800 °C | | $W_{\text{aq}}/W_{800^\circ\text{C}}^{\text{a}}$ |
|---|-----------------------|-------------|--|
| | Experimental | Theoretical | |
| Ti(NaPO ₄) ₂ ·4 H ₂ O | 20.7 | 20.2 | |
| Ti(HPO ₄) ₂ ·2 H ₂ O | 19.8 | 19.6 | |
| Ti(HPO ₄) ₂ ·4 H ₂ O | | | 0.7754 |

^aWeight of a sample in water at 25 °C divided by its weight in air after drying at 800 °C.

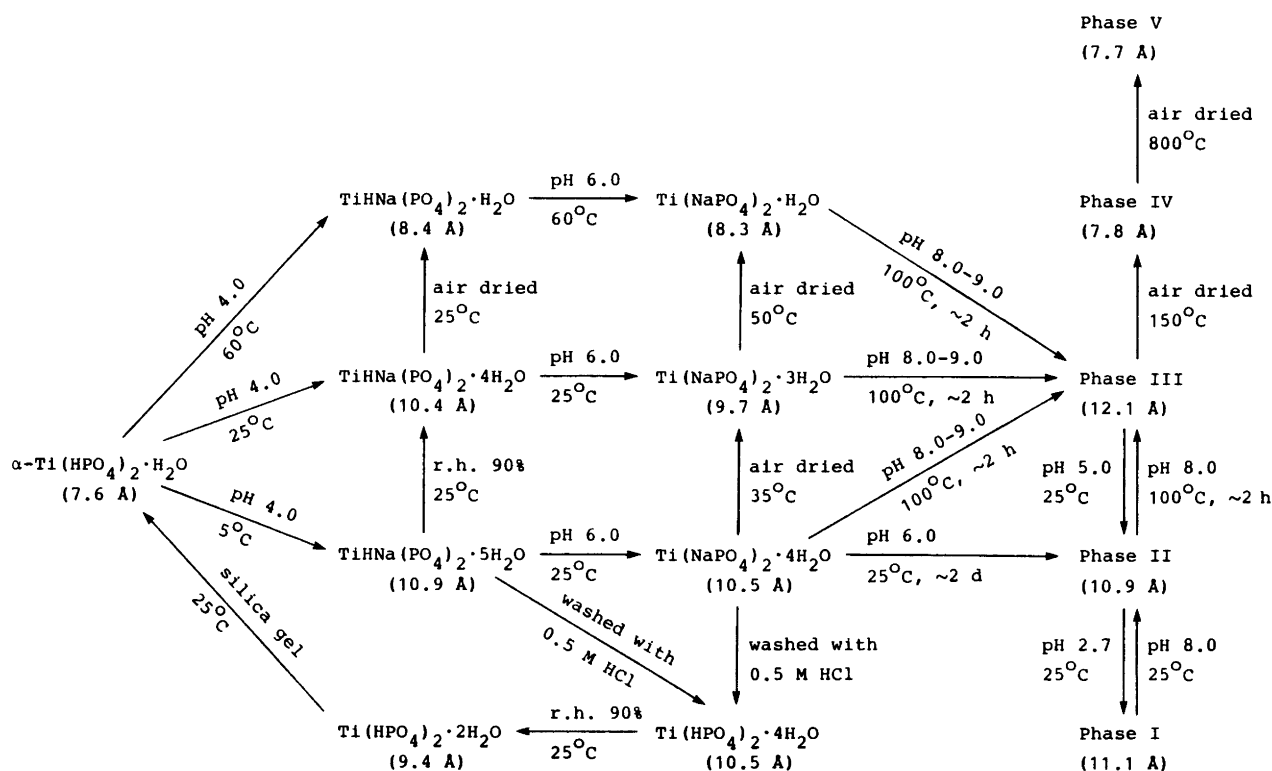


Fig. 2. Phases formed from α -TiP in 1.0 M $(\text{Na,H})_3\text{PO}_4$.

when α -ZrP is ion exchanged with sodium ions.⁶ It seems unlikely that the half-exchanged titanium phosphate phase, having a shorter interlayer distance than

$\text{ZrHNa}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$, should have more than five water molecules.

It was observed that the new phases, $\text{TiHNa}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$

Table 2. X-Ray diffraction patterns of the new ion-exchanged phases of α -TiP.

| $\text{TiHNa}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ | | $\text{Ti}(\text{NaPO}_4)_2 \cdot 4\text{H}_2\text{O}$ | | $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ | | $\text{Ti}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ | |
|---|---------|--|---------|---|---------|---|---------|
| $d/\text{Å}$ | l/l_0 | $d/\text{Å}$ | l/l_0 | $d/\text{Å}$ | l/l_0 | $d/\text{Å}$ | l/l_0 |
| 10.9 | 100 | 10.5 | 100 | 9.40 | 100 | 10.5 | 100 |
| 5.47 | 10 | 4.33 | 10 | 4.70 | 10 | 5.25 | 10 |
| 4.24 | 25 | 4.02 | 20 | 4.27 | 10 | 4.78 | 5 |
| 4.03 | 30 | 3.82 | 30 | 4.19 | 10 | 4.37 | 5 |
| 3.93 | 40 | 3.30 | 40 | 3.98 | 25 | 4.15 | 15 |
| 3.80 | 70 | 3.18 | 30 | 3.90 | 10 | 3.97 | 25 |
| 2.47 | 50 | 3.12 | 10 | 3.74 | 5 | 3.91 | 15 |
| 3.31 | 10 | 3.02 | 5 | 3.66 | 10 | 3.75 | 5 |
| 3.16 | 50 | 2.90 | 5 | 3.41 | 30 | 3.57 | 35 |
| | | 2.80 | 5 | 3.28 | 5 | 3.46 | 5 |
| | | 2.57 | 30 | 3.15 | 5 | 3.42 | 10 |
| | | 2.47 | 10 | 3.09 | 5 | 3.27 | 30 |
| | | 2.11 | 5 | 2.92 | 15 | 3.21 | 20 |
| | | | | 2.77 | 5 | 2.93 | 15 |
| | | | | 2.70 | 5 | 2.83 | 5 |
| | | | | 2.57 | 5 | 2.62 | 10 |
| | | | | 2.52 | 5 | 2.56 | 10 |
| | | | | 2.43 | 5 | 2.49 | 10 |
| | | | | 2.35 | 10 | | |
| | | | | 2.23 | 2 | | |
| | | | | 1.99 | 5 | | |
| | | | | 1.94 | 5 | | |

and $\text{Ti}(\text{NaPO}_4)_2 \cdot 4\text{H}_2\text{O}$, were obtained as the sole products in the ion exchange only if freshly made α -TiP precipitated from a solution of Ti(IV) in 15 M H_3PO_4 was used. If the α -TiP had been stored for a few days, or if it had been precipitated from a solution of Ti(III) in 15 M H_3PO_4 , $\text{TiHNa}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ti}(\text{NaPO}_4)_2 \cdot 3\text{H}_2\text{O}$ were formed as well. The longer the α -TiP had been stored, the greater the amount of the latter phases formed.

Reverse Na^+/H^+ ion exchange. The exchange of hydrogen ions with sodium ions in α -TiP can be reversed. If the back exchange of $\text{Ti}(\text{NaPO}_4)_2 \cdot 4\text{H}_2\text{O}$ is performed in 1.0 M $(\text{Na},\text{H})_3\text{PO}_4$ by acidification with phosphoric acid, α -Ti $(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ is recovered. However, as has been reported before for α -ZrP and α -TiP,^{12,17,18} the original phase is not always regained. If $\text{TiHNa}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ or $\text{Ti}(\text{NaPO}_4)_2 \cdot 4\text{H}_2\text{O}$ is prepared in 1.0 M $(\text{Na},\text{H})_3\text{PO}_4$, filtered off and washed first with cold water and then with cold 0.5 M HCl (ca. 5°C), a polyhydrated form of α -TiP is obtained, viz. $\text{Ti}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ (10.5 Å). When it is dried at 25°C and 90% r.h. a dihydrate is formed, viz.

$\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ (9.4 Å). This dihydrate is converted to the original $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ when dried over silica gel.

Since $\text{Ti}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ loses water molecules when dried at 25°C and 90% r.h., the water content was determined by an indirect method. A sample of $\text{Ti}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ was weighed in water and then in air after drying at 800°C (Table 1). At 800°C TiP_2O_7 is formed. By calculating the weight of the original sample in air for different numbers of water molecules in the formula unit, the density of the phase can be calculated for the different numbers of water molecules.¹⁹ The density of titanium atoms within the layers, n , can thereby be calculated. The calculated values of n for three, four and five water molecules are 8.59, 7.48 and $6.63 \cdot 10^{-10}$ mol Ti per cm^2 , respectively. The calculated value for four water molecules is very near the value determined for α -TiP.^{1,4} It is therefore probable that this phase has the formula $\text{Ti}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$.

Reversed Na^+/H^+ exchange of $\text{TiHNa}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ or $\text{Ti}(\text{NaPO}_4)_2 \cdot 3\text{H}_2\text{O}$ yielded the dihydrate $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$. Therefore, if $\text{Ti}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$ is to be obtained as the sole product of the reversed Na^+/H^+ exchange, it is necessary

Table 3. X-Ray diffraction patterns of the phases I–V.

| Phase I | | Phase II | | Phase III | | Phase IV | | Phase V | |
|--------------|---------|--------------|---------|--------------|---------|--------------|---------|-------------------|---------|
| $d/\text{Å}$ | l/l_0 | $d/\text{Å}$ | l/l_0 | $d/\text{Å}$ | l/l_0 | $d/\text{Å}$ | l/l_0 | $d/\text{Å}$ | l/l_0 |
| 11.1 | 100 | 10.9 | 100 | 12.1 | 100 | 7.83 | 80 | 7.69 | 50 |
| 8.68 | 25 | 9.31 | 30 | 7.17 | 5 | 7.32 | 25 | 7.45 | 40 |
| 7.31 | 15 | 6.68 | 10 | 5.04 | 10 | 4.85 | 100 | 5.37 | 15 |
| 6.62 | 10 | 5.44 | 40 | 4.65 | 15 | 4.22 | 10 | 4.90 | 35 |
| 5.60 | 55 | 5.22 | 50 | 3.87 | 5 | 3.66 | 55 | 4.82 | 25 |
| 5.19 | 30 | 4.69 | 35 | 3.62 | 5 | 3.54 | 30 | 4.22 | 5 |
| 4.53 | 20 | 4.35 | 5 | 3.53 | 5 | 3.31 | 30 | 3.86 | 10 |
| 3.85 | 5 | 3.83 | 25 | 3.16 | 10 | 3.23 | 55 | 3.68 | 25 |
| 3.75 | 20 | 3.63 | 10 | 3.11 | 20 | 3.19 | 45 | 3.59 | 30 |
| 3.67 | 15 | 3.58 | 10 | 3.05 | 15 | 2.68 | 95 | 3.51 | 10 |
| 3.59 | 5 | 3.53 | 25 | 2.69 | 15 | 2.64 | 90 | 3.44 | 45 |
| 3.38 | 20 | 3.36 | 10 | 2.66 | 10 | 2.61 | 85 | 3.38 | 25 |
| 3.21 | 20 | 3.31 | 5 | 2.53 | 15 | 2.14 | 10 | 3.26 | 10 |
| 3.15 | 40 | 3.28 | 5 | 2.18 | 5 | 2.06 | 10 | 3.18 ^a | 35 |
| 3.03 | 10 | 3.16 | 25 | 2.01 | 5 | 1.97 | 20 | 3.05 | 10 |
| 3.00 | 15 | 3.02 | 60 | 1.97 | 5 | 1.83 | 20 | 2.98 | 5 |
| 2.89 | 75 | 2.90 | 20 | 1.94 | 5 | 1.77 | 25 | 2.91 ^a | 10 |
| 2.85 | 15 | 2.88 | | | | | | 2.70 | 100 |
| 2.81 | 80 | 2.86 | 75 | | | | | 2.65 | 45 |
| 2.60 | 20 | 2.84 | | | | | | 2.57 | 80 |
| 2.47 | 40 | 2.77 | 20 | | | | | 2.50 | 5 |
| 2.45 | 10 | 2.74 | 10 | | | | | 2.33 | 5 |
| 2.39 | 5 | 2.72 | 10 | | | | | 2.11 | 10 |
| 2.36 | 5 | 2.69 | 10 | | | | | 2.05 | 10 |
| 2.29 | 10 | 2.62 | 20 | | | | | 1.98 | 5 |
| 2.25 | 10 | 2.59 | 15 | | | | | 1.94 | 25 |
| 2.23 | 2 | 2.55 | 10 | | | | | 1.88 | 10 |
| 2.21 | 5 | 2.52 | 5 | | | | | 1.80 | 15 |
| 2.19 | 5 | 2.43 | 15 | | | | | 1.76 | 10 |
| 2.15 | 2 | 2.37 | 5 | | | | | | |
| 2.14 | 5 | 2.35 | 15 | | | | | | |
| 2.12 | 10 | 2.30 | 10 | | | | | | |
| 2.08 | 5 | | | | | | | | |

^aDoublets.

that only $\text{TiHNa}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ and $\text{Ti}(\text{NaPO}_4)_2 \cdot 4\text{H}_2\text{O}$ be formed during the forward Na^+/H^+ exchange.

Stability of the sodium-exchanged products of α -TiP. The polyhydrated sodium-exchanged phases of α -TiP are not stable in an 1.0 M $(\text{Na},\text{H})_3\text{PO}_4$ solution. At 25°C and a pH of 4 or higher they became amorphous. The higher the pH, the faster the transformation to an amorphous phase. However, at pH between 4.0 and 6.0 new crystalline phases were formed after some time. At pH 4.0 a mixture of two phases was formed. These phases will be called phase I and phase II. At pH 6.0 only phase II was formed. The pH of the solutions decreased somewhat during the transformation.

The time needed for the crystalline phases to form was dependent on the age of the α -TiP sample and on the pH. The fastest transformation was obtained at pH 6.0 with freshly prepared α -TiP precipitated from a solution of Ti(IV). The amorphous product was then formed after about one day, and phase II after another day. The crystallinity of phase II was increased if it was kept in the solution for one week. At pH 4.0 and with less crystalline α -TiP the transformation took several months.

The phase II product formed at pH 6.0 had about the same particle size as the original sample of α -TiP. However, the crystalline product formed at pH 4.0 consisted of small particles mixed with very thin 0.2 mm long needles.

Neither the polyhydrated sodium-exchanged phases of α -TiP nor the phases I and II were stable in the $(\text{Na},\text{H})_3\text{PO}_4$ solution at 100°C. They were all converted to an amorphous product.

At pH 8.0 and 25°C the transformation to an amorphous phase was not followed by a crystallisation. However, if the pH of the solution with $\text{Ti}(\text{NaPO}_4)_2 \cdot 3\text{H}_2\text{O}$ or $\text{Ti}(\text{NaPO}_4)_2 \cdot 4\text{H}_2\text{O}$ was increased to 8–9 and the solution was boiled immediately, another new crystalline phase, phase III, was formed after about two hours. This phase was also obtained if $\text{Ti}(\text{NaPO}_4)_2 \cdot \text{H}_2\text{O}$ or sodium-exchanged phases of γ - $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ were boiled in 1.0 M $(\text{Na},\text{H})_3\text{PO}_4$ at pH 8–9.

The X-ray diffraction patterns for the phases I, II and III are summarized in Table 3.

Ion exchange of phase III. If the pH of an 1.0 M $(\text{Na},\text{H})_3\text{PO}_4$ solution with phase III was decreased to 5.0 by addition of phosphoric acid at 25°C, phase II was obtained. A further decrease of the pH to 2.7 gave phase I. At pH 2.5 this phase slowly dissolved, and at pH 2.0 it dissolved very quickly giving a clear solution. Phase II was recovered from phase I if the pH was increased to 8.0. To recover phase III, the solution with phase II had to be boiled at pH 8–9. Both phase II and phase III were stable in sodium hydroxide solutions with pH 10 at 25°C. At pH 12 they became amorphous.

Dehydration of the sodium-containing phases. The weight loss at 800°C of the phases I, II and III, dried at 25°C and

Table 4. Chemical composition and density of the phases I–III.

| Compound | Phase I | Phase II | Phase III |
|---|---------|----------|-----------|
| Ti/mmol g ⁻¹ | 2.15 | 1.95 | 2.20 |
| PO ₄ /Ti mole ratio | 2.0 | 2.0 | 2.0 |
| Na/PO ₄ mole ratio | 1.1±0.1 | 1.4±0.1 | 2.1±0.1 |
| Weight loss at 800°C/% | 42 | 41 | 27 |
| Interlayer distance/Å | 11.1 | 10.9 | 12.1 |
| Density/g cm ⁻³ | 1.79 | 1.86 | 2.00 |
| n/mol Ti cm ⁻² ×10 ¹⁰ | 4.3 | 4.0 | 5.3 |

90% r.h., are given in Table 4. The high water content of phase I and phase II makes them unstable in dry air. At relative humidities lower than 90% at 25°C the water content decreased and they became amorphous. Phase III lost about 10% in weight in dry air (ca. 20–40% r.h.) without any changes in the X-ray diffraction pattern. The TGA curve for phase III dried in dry air is shown in Fig. 3. As can be seen from the curve, the remaining water disappears in one single step at 40–100°C. The X-ray diffraction patterns for phase III dried at 150°C and 800°C, called phase IV and phase V, respectively, are given in Table 3. The pattern for phase V contains more peaks than that for phase IV, but otherwise the two patterns are very similar. It is therefore possible that phase V is just a more crystalline form of phase IV.

The phases I and II became amorphous when dried, but if they were heated to 800°C a mixture of phase V and $\text{NaTi}_2(\text{PO}_4)_3$ was formed. A mixture of these two phases was also formed when $\text{Ti}(\text{NaPO}_4)_2 \cdot 4\text{H}_2\text{O}$ was heated to 800°C, whereas $\text{TiHNa}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ gave only $\text{NaTi}_2(\text{PO}_4)_3$ as a crystalline product at 800°C.

Composition of the phases I–V. Some data for the phases I, II and III are given in Table 4. The PO₄/Ti ratio is 2.0 for all three phases. The phases II and III contain more than one sodium ion per phosphate group. Thus, they must contain some other anion than the phosphate ion. The only possible anions are oxide and hydroxide ions.

The IR spectra of the phases III, IV and V are shown in Fig. 4. In the spectra for the phases IV and V the character-

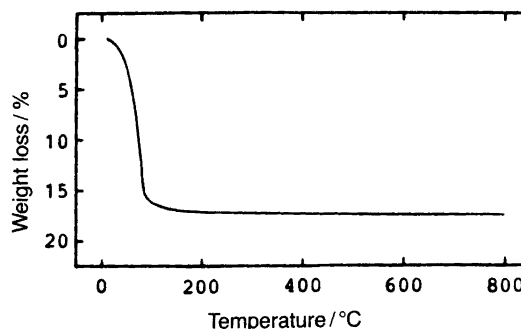


Fig. 3. Thermogravimetric analysis of phase III, dried in air. Heating rate 4°C min⁻¹.

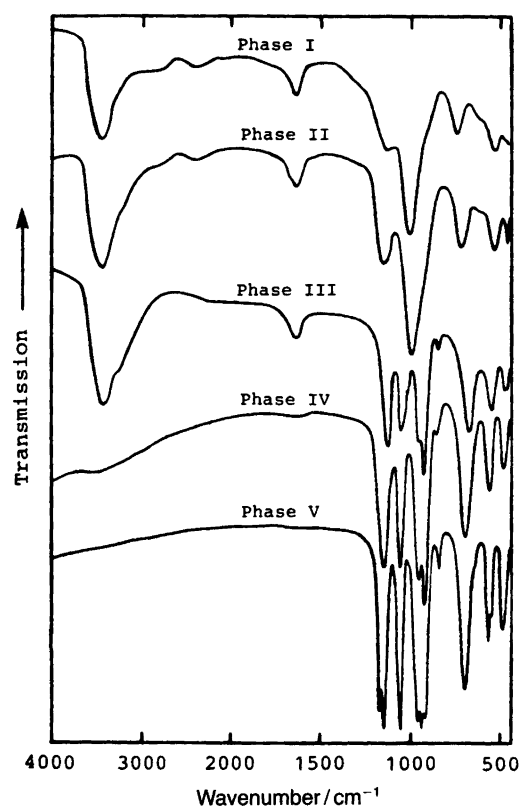


Fig. 4. Infrared spectra (KBr discs) of the phases I-V.

istic peaks for hydroxide and water are missing, but otherwise the spectra for the three phases are very similar. Hence, phase IV and phase V do not contain hydroxide ions.

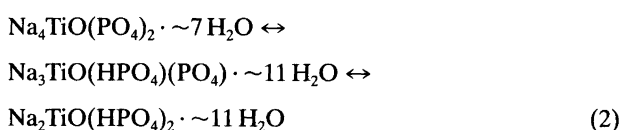
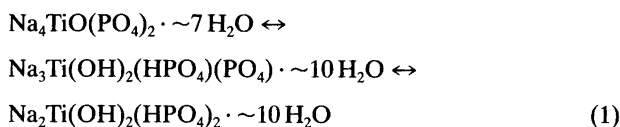
Chernorukov *et al.*²⁰ have prepared a titanium hydroxide phosphate, $\text{Ti}(\text{OH})\text{PO}_4$. The compound was stable up to 400 °C. Above this temperature it was dehydrated and $\text{Ti}_2\text{O}(\text{PO}_4)_2$ was formed. The IR spectrum of $\text{Ti}(\text{OH})\text{PO}_4$ had three bands at 3330, 1538 and 735 cm^{-1} which could be assigned to the TiOH group. The bands at 3330 and 1538 cm^{-1} disappeared when the compound was heated to above 400 °C, and were therefore assigned to $\nu(\text{TiOH})$ and $\delta(\text{TiOH})$. The band at 735 cm^{-1} was considered to arise from stretching vibrations of Ti-O bonds. Besides the absence of the bands at 3330 and 1538 cm^{-1} in the IR spectrum of the dehydrated compound, there were also some other changes in the spectrum.

Phase III is completely dehydrated at 150 °C, which is a very low temperature if it should contain hydroxide ions. The IR spectrum does not have a peak near 1538 cm^{-1} , except the peak due to water at 1640 cm^{-1} . In the interval 500–1500 cm^{-1} it is almost identical with the spectra for the phases IV and V. Therefore, it is not probable that phase III contains hydroxide ions. That leaves oxide as the only possible anion. The formula for phase III should then be $\text{Na}_4\text{TiO}(\text{PO}_4)_2 \cdot \sim 7\text{H}_2\text{O}$, and for both phase IV and phase V, $\text{Na}_4\text{TiO}(\text{PO}_4)_2$. It should be noted that the IR spectra for

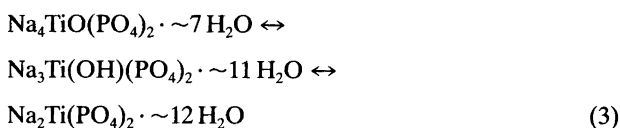
all three phases have a strong band near 700 cm^{-1} , probably due to stretching vibrations of Ti-O bonds.

Phase I and phase II have very similar IR spectra (Fig. 4), but these are quite different from that of phase III. Phases I and II contain a lot of crystal water and become amorphous when dried. It is therefore difficult to determine whether they contain hydroxide or oxide ions.

Starting from phase III, i.e. $\text{Na}_4\text{TiO}(\text{PO}_4)_2 \cdot \sim 7\text{H}_2\text{O}$, the ion-exchange reactions, with possible formulas for phase II and phase I, could be written as follows:



or



Structure of the phases I-V. A suspension of α -TiP in water which was allowed to dry on a flat surface showed a strong X-ray diffraction intensity of the (002) planes. This means that the crystals were orientated with the layers parallel with the underlying surface. The same orientation was observed for all ion-exchanged phases of α -TiP when dried in the same way. The phases I, II and III were also orientated so that the intensity of the first reflection in the X-ray diffraction pattern increased.

When a sample with phase III orientated in this way was dried at 150 °C or 800 °C, the intensity of the first reflection in the X-ray diffraction patterns for the then formed phase IV and phase V was also increased. Further, the dehydration of phase III resulted in a decrease of the d value for the first reflection by about 4.5 Å. These properties are typical for layered structures. Therefore, it is probable that the phases III, IV and V have layered structures. The swift transformation of phase III to phase II and phase I in acidic solutions indicates that these phases also have layered structures, with the first reflection in the X-ray diffraction pattern representing the distance between the layers.

Discussion

The mechanism of ion exchange in α -ZrP. Clearfield *et al.*⁶ have calculated the diameter of the openings between the cavities in α -ZrP to be 2.61 Å. When calculating the size of the openings they started from the covalent radius of oxygen (0.74 Å) as given by Wells.²¹ From this value and the

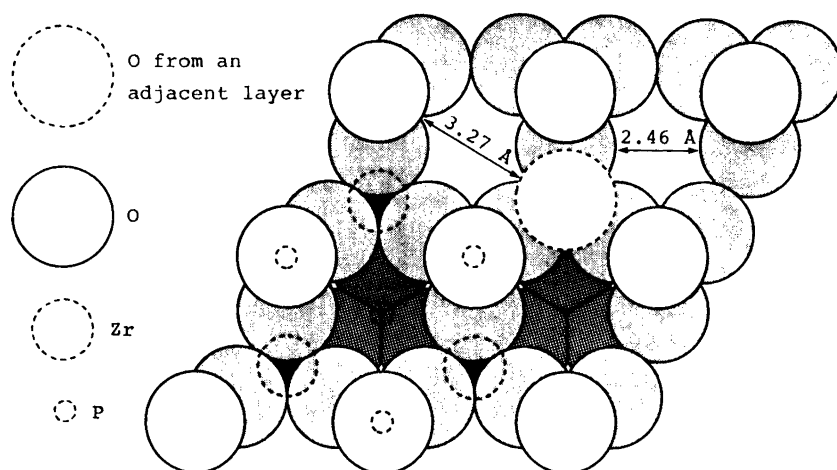


Fig. 5. An idealized layer in α -ZrP seen from above. The action radius of oxygen is assumed to be 1.40 Å.

bond distances in α -ZrP, they obtained the covalent radius of zirconium and phosphorus. In order to calculate the size of the openings they assumed that all atoms were spherical with action radii equal to the covalent radii. However, the action radius of oxygen toward an unbounded species should be the van der Waals radius, more or less equal to the ionic radius of oxygen, that is 1.40 Å. This implies that the largest openings in the α -ZrP structure are only about half the size of that calculated by Clearfield *et al.* Therefore, of all the alkali metal ions α -ZrP should be able to ion exchange only Li^+ (diam. 1.36 Å), provided that the openings cannot be expanded. There are only weak forces between the layers in α -ZrP, and the openings can therefore be widened without the breaking of any bonds. In fact, the interlayer distance almost always changes during the ion exchange. Thus, there must be another explanation for the difference in ion exchange of the different alkali metal ions.

The importance of the cavity size for selective bonding of alkali metal ions is well known from the chemistry of crown ethers.²²⁻²⁴ The bottom of a cavity in α -ZrP is shown in Fig. 5. A cation located there would be coordinated with nine oxygen atoms from phosphate groups and one oxygen atom from the water molecule located in the middle of the cavity. Thus, the cation would have a very high coordination number. The distance between two oxygen atoms opposite to each other in the ring of six oxygen atoms is 5.26 Å (Fig. 5). If the action radius of oxygen is assumed to

be 1.40 Å, the diameter of the depression will be 2.46 Å. Hence, the depression is too large for sodium ions (diam. 1.96 Å) and too small for potassium ions (diam. 2.66 Å), unless the zirconium phosphate layer can be contracted or expanded.

The densities of zirconium atoms in the layers in four different phases are given in Table 5. The values for the anhydrates α -ZrHNa(PO₄)₂ and α -ZrHK(PO₄)₂ are perhaps not representative since the layers in these phases are shifted with respect to α -ZrP,^{25,26} and the water molecule is removed. The cavities in these phases therefore have another structure. The structure of the cavities in α -ZrHK(PO₄)₂ · H₂O is not known. However, it is probably not very different from that in α -ZrP. The water molecule is still present and the interlayer distance is only 0.4 Å larger than in α -ZrP. In any case, the layers in α -ZrP expand considerably when ZrHK(PO₄)₂ · H₂O is formed (Table 5). If the layers in ZrHK(PO₄)₂ · H₂O expand evenly, the diameter of the depression at the bottom of a cavity is increased to 2.67 Å. This depression is perfectly suited for a potassium ion. To fit a sodium ion equally well, the depression has to shrink considerably. Instead a polyhydrated phase, ZrHNa(PO₄)₂ · 5H₂O, is formed with the sodium ions probably located between the layers and coordinated with oxygen atoms mostly from water molecules.

Rubidium ions (diam. 2.96 Å) and cesium ions (diam. 3.34 Å) are too large to fit in the depression at the bottom

Table 5. The density of titanium and zirconium atoms in the layers in α -TiP, α -ZrP and in some ion-exchanged phases of α -ZrP, calculated from unit cell dimensions or density measurements.

| | (a · b) / Å ² | Density / g cm ⁻³ | Interlayer distance / Å | n / mol Me cm ⁻² · 10 ¹⁰ |
|---|--------------------------|------------------------------|-------------------------|--|
| α -Ti(HPO ₄) ₂ · H ₂ O ^a | 43.17 | | | 7.69 |
| α -Zr(HPO ₄) ₂ · H ₂ O ^b | 47.99 | | | 6.92 |
| α -ZrHNa(PO ₄) ₂ ^c | 47.54 | | | 6.99 |
| α -ZrHK(PO ₄) ₂ ^d | 49.29 | | | 6.74 |
| α -ZrHK(PO ₄) ₂ · H ₂ O ^e | | 2.74 | 7.95 | 6.42 |

^aFrom Ref. 1. ^bFrom Ref. 2. ^cFrom Ref. 25. ^dFrom Ref. 26. ^eThis investigation.

of a cavity. There is only one place large enough for them, which is the middle of a cavity where the water molecule is located (Fig. 5).^{3,8} When the Rb^+ and Cs^+ ions are exchanged up to 30% they are accommodated in the α -ZrP structure with the formation of solid solutions.⁹ The formulas for 25 per cent ion-exchanged phases are $\text{ZrH}_{1.5}\text{Rb}_{0.5}(\text{PO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ (7.6 Å) and $\text{ZrH}_{1.5}\text{Cs}_{0.5}(\text{PO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ (7.7 Å). In other words, the alkali metal ions have indeed replaced water molecules in the structure.

In the presence of sodium ions, the sequence of decreasing alkali metal ion preference for α -ZrP is $\text{K}^+ > \text{Cs}^+ > \text{Na}^+ > \text{Li}^+$, and the selectivity towards K^+ and Cs^+ is very high.^{27,28} How can the high selectivity toward Cs^+ compared with Na^+ be explained? It seems strange, since α -ZrP ion exchanges Na^+ at a much lower pH than it exchanges Cs^+ . Both in the presence and in the absence of sodium ions, the uptake of Cs^+ is followed by a decrease in water content. One water molecule is released for every cesium ion taken up. There is not sufficient space for both a cesium ion and a water molecule in a cavity. Thus, the diffusion of cesium ions in α -ZrP is rendered difficult because every cavity is occupied by a water molecule. However, in the presence of sodium ions, $\text{ZrHNa}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ (11.8 Å) is probably formed first.²⁸ The large interlayer distance in this phase makes the diffusion of cesium ions easy. Once the cesium ions have entered the structure, the sodium ions and the water molecules are released, restoring the original cavities that seem so favourable to cesium ions.

Differences between α -TiP and α -ZrP. Within the layers, α -TiP has a more dense packing than α -ZrP. The depression at the bottom of the cavity is therefore smaller in α -TiP. The unit cell dimensions for α -TiP are $a = 8.631$, $b = 5.002$ and $c = 16.176$ Å.¹ The values of a and b establish the diameter of the depression as 2.19 Å. Thus, the depression is too small for a potassium ion. Therefore, it is not surprising that α -TiP does not exchange potassium ions in acidic solutions, and that α -TiHK $(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ cannot be obtained by ion exchange.

Even if the depression is somewhat too big for a sodium ion, it is more suitable for a sodium ion than the corresponding depression in α -ZrP. Consequently, the monohydrate $\text{TiHNa}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ can be obtained, although only at high temperatures.

Lithium ions (diam. 1.36 Å) are too small to fit in the depressions in the layers of α -ZrP and α -TiP. Thus, polyhydrated phases are expected to form during the ion exchange of lithium ions. This is indeed what is found for the ion exchange on α -ZrP. $\text{ZrHLi}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ is formed.⁵ However, the ion exchange on α -TiP results in the formation of $\text{Ti}(\text{LiPO}_4)_2 \cdot \text{H}_2\text{O}$.^{4,10} No half-exchanged phase has been prepared. Moreover, only one plateau is observed in the titration curve (Fig. 1) and the interlayer distance is unchanged during the ion exchange. Therefore, the lithium ions are probably not located in the depressions.

Ammonium ion exchange on α -ZrP is similar to lithium ion exchange on α -TiP. Only one plateau is present in the

titration curve and no half-exchanged phase is formed.²⁹ For $\text{Zr}(\text{NH}_4\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, it has been confirmed that the ammonium ions do not occupy the depressions.³⁰ In this case, it is probably the ability of ammonium ions to form hydrogen bonds which makes them prefer other sites than the depressions.

The potassium-exchanged and the polyhydrated sodium-exchanged phases of α -TiP are not stable. They hydrolyze in chloride solutions. In sodium phosphate solutions the sodium-exchanged phases become rearranged and new crystalline phases are formed. This instability of α -TiP compared to α -ZrP is probably caused by the smaller size of titanium ions than zirconium ions.

Formation and structure of the new phases I–V. It is unlikely that the titanium atoms have a higher coordination number than six in the phases I–V. The oxide ion in the phases III–V must either be bonded to one titanium atom or bridge two titanium atoms. Consequently, on the average, fewer than three of the oxygen atoms in a phosphate group can be bonded to titanium atoms.

The formation of phase II and phase III from a sodium-exchanged phase of α -TiP was always preceded by a conversion of the α -titanium phosphate phase to an amorphous phase. A mixture of the original phase and phase II or phase III was never observed. Further, the time needed for the conversion was the same whether the solution was stirred or not. Therefore, the formation of phase II and phase III may proceed by a rearrangement within the layers in the α -titanium phosphate phase. During the rearrangement, bonds between phosphate groups and titanium atoms are broken, and the layers expand.

The ion-exchange reactions to form phase II and phase I from phase III, and the back exchange to form phase II from phase I, are fast at 25°C. However, to obtain phase III from phase II the solution has to be boiled. Further, the density of titanium atoms within a layer, as well as the IR spectra, are very similar for phase I and phase II, but quite different for phase III. Of the suggested reactions 1–3, reaction 1 seems to be best in accordance with these properties. In reaction 2 the transformation from phase II to phase III ought to be easy, and in reaction 3 the formulas for phase I and phase II are too different from each other. Furthermore, the phosphate groups ought to be protonated in phase I at pH 2.7.

Conclusions

The difference in the ion exchange properties of α -layered ion exchangers is due to the different dimensions of the cavities in the structure. The size of the cation sites in the cavities is more important than the diameter of the openings to the cavities. There are two different kinds of sites in the cavities: the depression at the bottom of the cavities, and the middle of the cavities where the water molecules are located in α -TiP and α -ZrP. The ion exchangers prefer cations that fit perfectly in either of the two possible sites.

If the cations are too small or too large for the depression at the bottom of a cavity, the layers can contract or expand somewhat to better fit the cation in question. If the depression is still too large, the exchanged cations are hydrated.

Sodium-exchanged phases of α -TiP with large interlayer distances are not stable. In sodium phosphate solutions they are converted to new crystalline phases. These phases also have layered structures, but with a much less dense packing of titanium atoms in the layers.

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