Effect of K$^+$ on the Stoichiometry of Carbonated Hydroxyapatite Obtained by the Hydrolysis of Monetite

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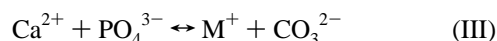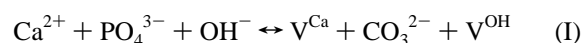
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This study investigates the stoichiometry and the thermal stability of K$^+$- and CO$_3^{2-}$-containing apatites (KCAp's) obtained by the hydrolysis of monetite. The analysis results of the samples after drying reveal that the KCAp's start to lose carbonate at temperatures ≤ 400 °C. The predominant substitution mechanisms for the K$^+$- and CO$_3^{2-}$ incorporation in calcium hydroxyapatite are [Ca^{2+} + PO$_4^{3-}$ + OH$^-$ ↔ V^{Ca} + CO$_3^{2-}$ + V^{OH}] and [Ca^{2+} + PO$_4^{3-}$ ↔ K$^+$ + CO$_3^{2-}$], where V^X stands for a vacancy in the X-sublattice. Moreover, a small part of the CO$_3^{2-}$ ions are presumably incorporated according to [Ca^{2+} + 2PO$_4^{3-}$ ↔ V^{Ca} + 2CO$_3^{2-}$]. A comparison of the contributions of these fundamental mechanisms with the results for precipitated Na$^+$- and CO$_3^{2-}$-containing apatites shows that no intrinsic coupling whatsoever exists between these mechanisms.

Introduction

It is well-known that calcium hydroxyapatite, Ca$_{10}$(PO$_4$)$_6$-(OH)$_2$ (HAp), can accommodate a large number of different ions in its lattice. Of these, CO$_3^{2-}$ is generally considered the most important, as it is the most abundant minor component found in apatite minerals such as francolite and dahllite as well as in the calcified tissues of higher vertebrates. The incorporation of CO$_3^{2-}$ has considerable influence on the physical and chemical as well as physicochemical properties of the solid and hence on the mineralization, demineralization, and remineralization processes of these minerals.[1,2] The importance of such an effect becomes clear when one considers the fact that the inorganic part of calcified tissues such as bone and teeth is presumed to be entirely composed of an apatite mineral.[2] Despite numerous investigations, however, the mechanism(s) by which carbonate is incorporated in the apatite lattice is (are) not yet known or resolved in detail.[2]

It is generally accepted that CO$_3^{2-}$ can replace OH$^-$ as well as PO$_4^{3-}$ ions in the apatite lattice, resulting respectively in so-called A-type and B-type carbonated apatites.[2] Whereas the mechanism of the A-type carbonate incorporation has been well established,[2] the B-type incorporation apparently can involve different mechanisms.[2-4] In the presence of sodium ions, the carbonate incorporation into precipitated apatites on B-type sites is considerably enhanced.[5,6] This could be related to the results of recent studies[4,7] where it was found that the incorporation of B-type CO$_3^{2-}$ into precipitated Na$^+$- and CO$_3^{2-}$- containing apatite (NCAp) obtained by the hydrolysis of monetite (CaHPO$_4$) in Na$_2$CO$_3$ solutions is the result of two simultaneously occurring mechanisms represented by

$$Ca^{2+} + PO_4^{3-} + OH^- \leftrightarrow V^{Ca} + CO_3^{2-} + V^{OH} \qquad (I)$$

$$Ca^{2+} + PO_4^{3-} \leftrightarrow M^+ + CO_3^{2-} \qquad (III)$$

where M represents the alkali metal, i.e. Na$^+$, and V^X stands for a vacancy on a regular apatite lattice site occupied by X. In accordance with our previous studies, these mechanisms are respectively referred to as mechanisms I and III.[3,4,7] Although indications were found that there is no complete coupling between these mechanisms for NCAp, a partial coupling could not be excluded.[7] In order to further explore such coupling, the relative driving forces for the fundamental substitution mechanisms should be varied.

In the presence of K$^+$ instead of Na$^+$, K$^+$- and CO$_3^{2-}$-containing apatites (KCAp's) are precipitated which contain less carbonate and considerably less alkali metal in comparison with NCAp.[2,8,9] Although it has been shown[10] that mechanism III also can occur for M$^+$ = K$^+$, it is not known whether the carbonate incorporation into precipitated KCAp's also involves mechanisms I and III. If these mechanisms also would account for the stoichiometry of precipitated KCAp's, then their relative contributions to the stoichiometry and hence the respective driving forces must be quite different as compared to those for NCAp. For this reason, the chemical and physical characteristics of KCAp's prepared by the hydrolysis of monetite in K$_2$CO$_3$ solutions were determined and an attempt was made to deduce the fundamental substitution mechanisms which determine their stoichiometry.

Experimental Section

Preparation of KCAp. The KCAp's were prepared in a PTFE reaction vessel using the method previously described for the synthesis of NCAp.[4,11] According to this method, 0.75 g of monetite (Baker AR grade; chemical analysis yields 29.58 ± 0.06 wt % Ca and 22.30 ± 0.04 wt % P with a molar Ca/P ratio of 1.025 ± 0.005) was hydrolyzed at 95 °C in a 1-L K$_2$CO$_3$ solution (Merck; Suprapur) with

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Table 1. Chemical Composition (Weight Percent) and Total Mass Balance $\Sigma\%$ of the Precipitates Obtained by the Hydrolysis of Monetite in Solutions Containing c_{kc} M K_2CO_3 and Dried at 25 °C

sample	c_{kc}	%Ca	%P	%CO$_3$	%K	%OH	$\Sigma\%$
K4	0.0100	37.42	15.62	7.5	0.362	1.95 ± 0.12	95.10 ± 0.16
K5	0.0114	37.27	15.44	8.1	0.390	1.79 ± 0.12	94.87 ± 0.16
K6	0.0114	37.28	15.46	8.1	0.380	1.77 ± 0.12	94.89 ± 0.16
K7	0.0250	37.30	15.00	9.5	0.66	1.85 ± 0.13	95.30 ± 0.17
K8	0.0284	36.90	14.79	9.9	0.70	1.64 ± 0.14	94.50 ± 0.17
K9	0.0568	36.66	14.35	11.3	1.01	1.49 ± 0.15	94.49 ± 0.17
K10	0.0568	36.68	14.40	11.3	1.02	1.43 ± 0.15	94.61 ± 0.17
K11	0.0852	36.30	14.10	11.8	1.25	1.46 ± 0.15	94.00 ± 0.18
K12	0.1136	36.14	13.88	12.4	1.37	1.35 ± 0.16	93.86 ± 0.18
K13	0.1420	35.97	13.86	12.6	1.52	1.21 ± 0.16	93.80 ± 0.18
K14	0.1420	36.03	13.86	12.6	1.53	1.26 ± 0.16	93.93 ± 0.18

a concentration c_{kc} ranging from 0.010 to 0.150 M. The suspension was continuously and thoroughly stirred for 24 h, and precautions were taken to prevent a CO_2 contamination from the atmosphere. In a previous study,[3] it was found that under these conditions a complete hydrolysis of monetite occurs at pH $\cong$ 10 with the formation of a single-phase CAp. The precipitates were then filtered off, thoroughly washed with hot distilled water ($\pm$95 °C), and finally dried under vacuum at 25 °C until a constant weight was obtained, which usually took about 2 weeks.

Chemical Analysis. The calcium content of the precipitates was determined by a complexometric titration with ethylenediaminetetraacetic acid,[12] and the phosphorus content was determined spectrophotometrically as the orthophosphate by using a slight modification of the method of Brabson *et al.*[13] The potassium and sodium contents of the samples were determined by atomic absorption spectrophotometry. The method of Godinot *et al.*[14] was adapted for the determination of the carbonate content. This method consists of a gas chromatographic determination of the carbon dioxide evolved from an acidified aqueous solution of the apatite. The relative uncertainties in the amounts of Ca, P, CO$_3$, and K analyzed were determined as 0.2, 0.2, 2, and 2%, respectively.

Physical Analysis. X-ray powder diffraction patterns of the samples were recorded by step-scanning using a microprocessor-controlled diffractometer system (Philips PW 1830). Ni-filtered copper Kα radiation was used with an automatic divergence slit PW1836 and a graphite monochromator. The dimensions a and c of the hexagonal unit cell of the apatites were calculated from the position of the most intense and sharp reflections (usually $n > 19$) using a least-squares refinement program. The experimental errors in a and c were estimated as 0.0006 and 0.0002 nm, respectively. IR spectra of the samples dispersed in CsBr tablets were recorded using a Mattson Galaxy 6030 FTIR spectrophotometer.

Results

Chemical Composition. The chemical composition of the precipitates after drying at 25 °C is summarized in Table 1. The sodium content of the samples ranges from 0.004 to 0.008 wt % independently of c_{kc} and can be neglected. The HPO$_4^{2-}$ content was checked for some representative samples (i.e. K5, K8, K10, K11, and K14) according to the method described by Meyer and Fowler.[15] The results show that the KCAp's do not contain HPO$_4^{2-}$ within experimental error, indicating that at most 0.2% of the total amount of phosphorus determined would be present as HPO$_4^{2-}$ and hence can be neglected. On this basis, the hydroxide content of the samples (%OH) can be calculated

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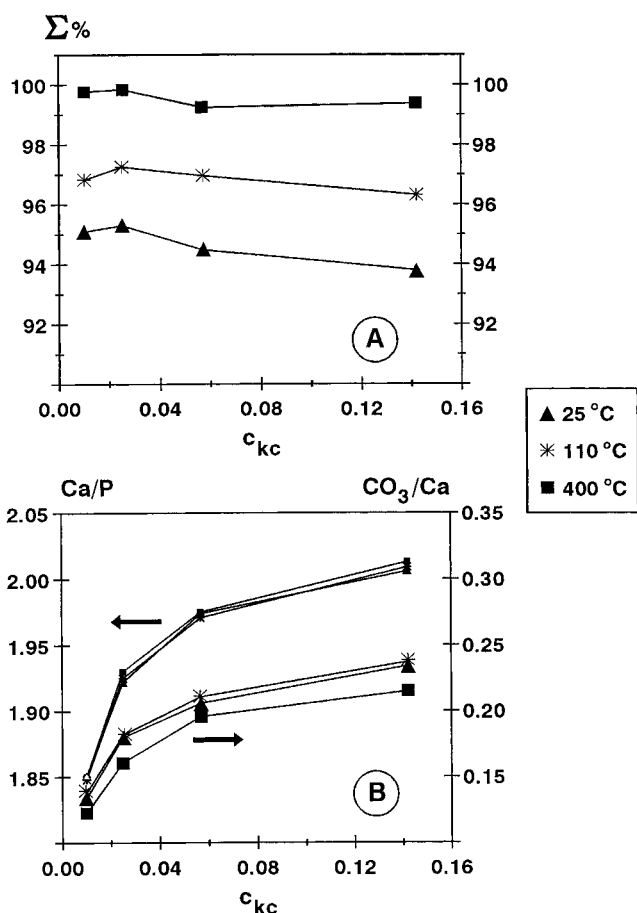(15) Meyer, J. L.; Fowler, B. O. *Inorg. Chem.* **1982**, *21*, 3029.

Figure 1. (A) Total mass balance $\Sigma\%$ and (B) molar Ca/P and CO$_3$/Ca ratios as a function of c_{kc} (M) for some representative KCAp's dried at 25, 110, and 400 °C.

using the electroneutrality condition and the total mass balance $\Sigma\%$ is then obtained from the equation

$$\Sigma\% = \%Ca + \frac{(\%P)M_{PO_4}}{M_P} + \%CO_3 + \%K + \%OH \quad (1)$$

with M_X the atomic or ionic mass of X. The errors in %OH and $\Sigma\%$ were estimated by means of the error propagation theory. According to Table 1, the Ca, P, and OH contents of the precipitates decrease whereas the K and CO$_3$ contents increase as the K_2CO_3 concentration in the solution increases.

The values of $\Sigma\%$ in Table 1 indicate that the KCAp's still contain 5−6 wt % water after drying under vacuum at 25 °C. In view of our previous experience with precipitated NCAp,[7] an attempt was made to remove this water. Some representative precipitates (i.e. K4, K7, K9, and K13) were dried at 110 °C and subsequently at 400 °C until a constant weight was obtained, which required about 3 weeks at each temperature. When the total mass balance is calculated from the chemical composition determined at each drying temperature T, it is seen from Figure 1A that more H$_2$O is lost from the samples as T is increased. $\Sigma\%$ approaches 100 wt % after drying at 400 °C. However, the stoichiometry of the samples is significantly affected by the heating process. An analysis of variance (ANOVA)[16] on the basis of a two-factor design (i.e. the temperature T and the concentration c_{kc}) shows that the molar CO$_3$/Ca ratio as well as the molar CO$_3$/P ratio of the solids significantly depends on both c_{kc} and T ($p \ll 0.001$) and that c_{kc} and T do not interact ($p > 0.7$). A Neuman−Keuls multiple-range test at the 95% confidence level further reveals that CO$_3$/Ca and CO$_3$/P are
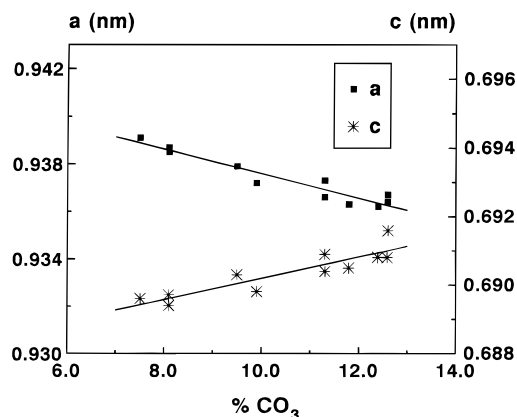
Figure 2. Lattice parameters *a* and *c* (nm) of the KCAp's as a function of the carbonate content (wt %) after drying at 25 °C.

significantly lower at 400 °C as compared to the respective ratios at 25 and 110 °C, which do not differ. This can be illustrated with Figure 1B where the molar CO_3/Ca and Ca/P ratios of the precipitates are plotted versus c_{kc} as a function of the drying temperature. The ANOVA further shows that the molar Ca/P ratio of the solids is independent of T, but is significantly affected by c_{kc} as could be expected (see also Figure 1B). These results indicate that the KCAp's lose CO_3^{2-} upon heating at 400 °C and corroborate the absence of HPO_4^{2-}, which upon pyrolysis should result in the formation of $P_2O_7^{4-}$ with a concomitant apparent decrease of the Ca/P ratio.[15,17]

Physical Analysis. The peaks in the X-ray diffraction patterns of the samples dried at 25 °C are relatively sharp and well resolved, characteristic for a relatively high crystallinity of the precipitated KCAp's. Extraneous peaks attributable to phases other than apatite could not be detected in the diffractograms. All reflections can be attributed to the hexagonal crystal form of hydroxyapatite.[18] A weighted regression analysis indicates that at the 95% significance level the hexagonal lattice dimensions of the KCAp's vary linearly with the carbonate content according to

$$a = (0.9428 \pm 0.0013) - (5.2 \pm 1.2) \times 10^{-4}(\%CO_3) \quad (2)$$

and

$$c = (0.6871 \pm 0.0012) + (3.1 \pm 1.2) \times 10^{-4}(\%CO_3) \quad (3)$$

which is illustrated in Figure 2, where the full lines correspond to eqs 2 and 3. Equations 2 and 3 indicate that the *a* and *c* dimensions for $\%CO_3 = 0$ equal the values for pure HAp within experimental error.[19] Moreover, the *a* dimension systematically decreases and the *c* dimension increases with an increasing carbonate content. The variation of the lattice dimensions with the carbonate content according to eqs 2 and 3 corresponds well with that found for precipitated NCAp's in a previous study.[4] As argued before,[4] such variation of *a* and *c* with the carbonate content is typical for CO_3^{2-} substituting for PO_4^{3-} in the apatite lattice (so-called B-type CO_3^{2-}).

Heating the solids at 110 and 400 °C induces no additional reflections or apparent peak broadening in the X-ray diffractograms of the solids. However, a two-way ANOVA shows that the *a* and *c* lattice dimensions are both significantly ($p \ll 0.001$) affected by the drying temperature *T*. According to the
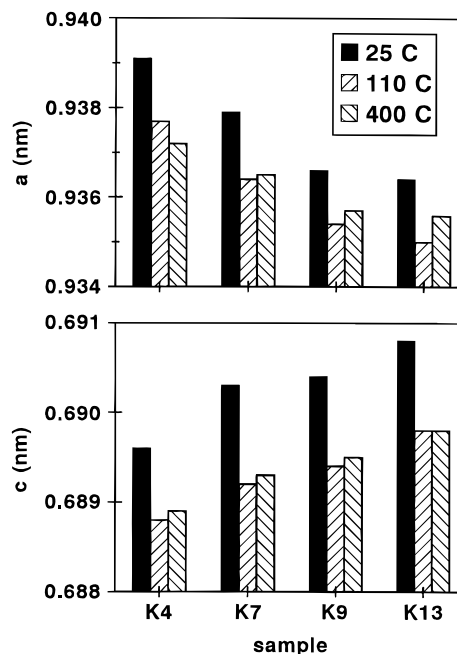
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Figure 3. Lattice parameters *a* and *c* (nm) as a function of the drying temperature for some representative KCAp's.
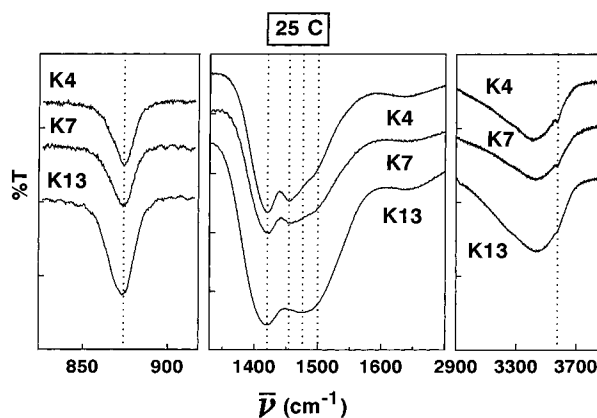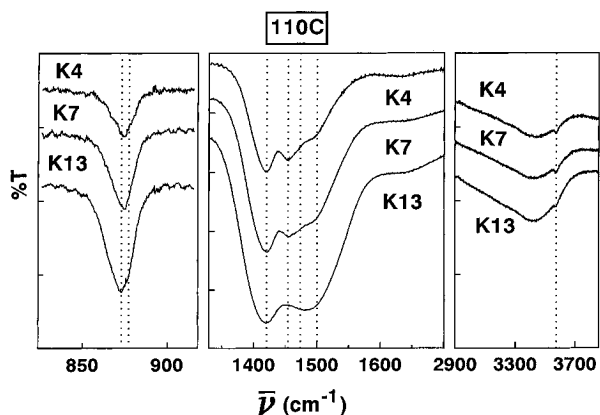

Figure 4. IR spectra of some representative KCAp's dried at 25 °C (% transmittance versus wavenumber).

Newman–Keuls multiple-range test at the 95% confidence level, the *a* and *c* dimensions after drying at 25 °C are significantly greater than those found after drying at 110 and 400 °C, which do not differ (see also Figure 3). Consequently, heating at higher temperatures apparently results in a distinct contraction of the unit cell of the KCAp's.

The IR spectra of the samples are typical for carbonated hydroxyapatites.[2,4] Apart from the characteristic PO_4^{3-} absorptions in the ranges 960–1100 and 570–610 cm⁻¹, the spectra of the samples dried at 25 °C (see Figure 4) display broad absorptions around 3400 and 1630 cm⁻¹ which can be assigned to H_2O. Absorptions of HPO_4^{2-} ions[17] could not be detected, corroborating the results of the chemical analysis that the phosphorus is presumably completely present as PO_4^{3-} in the apatite lattice. Whereas the stretching vibration of the OH^- ion in the apatite lattice can be clearly observed at ~3572 cm⁻¹, the libration mode at ~630 cm⁻¹ can not be detected. Typical absorption bands for CO_3^{2-} are observed at ~873 and ~1420 cm⁻¹ and between 1450 and 1500 cm⁻¹, as is illustrated by Figure 4. The absorptions at 873 and 1420 cm⁻¹ are caused by the vibrations of CO_3^{2-} on PO_4^{3-} lattice sites (B-type CO_3^{2-}).[2,4,10] Whereas the KCAp's with a high carbonate content display only one band around 1475 cm⁻¹, this band apparently is composed of two absorptions situated near 1455 and 1500

Figure 5. IR spectra of some representative KCAp's dried at 110 °C (% transmittance versus wavenumber).
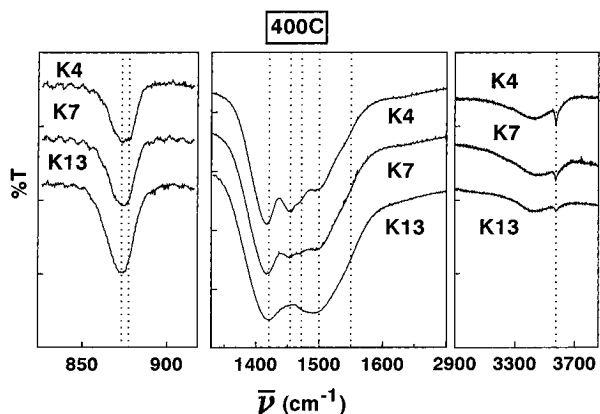

Figure 6. IR spectra of some representative KCAp's dried at 400 °C (% transmittance versus wavenumber).

cm^{-1} for the samples with a low carbonate content (compare the spectra of samples K4 and K13 in Figure 4). This evolution is merely due to a distinct broadening of the absorption peaks and a concomitant increase of the relative intensity of the band around 1500 cm^{-1} with respect to the band near 1455 cm^{-1} with increasing carbonate content. In a previous study,[10] the latter absorption was found to be due to a B-type CO_3^{2-} vibration. Absorptions at 880 and 1550 cm^{-1}, which are the most characteristic for CO_3^{2-} ions substituting for OH^- ions in the lattice (so-called A-type CO_3^{2-}),[2,10] could not be detected in the IR spectra of the precipitated KCAp's after drying at 25 °C (see also Figure 4).

Upon heating, the broad water absorption bands gradually decrease as can be seen from Figures 5 and 6. This results in an enhanced detectability of the 3572 cm^{-1} stretching absorption of the OH^- ions. From Figure 6 it can be clearly seen that the intensity of this absorption decreases with increasing carbonate content, corroborating the chemical analyses (see Table 1) as well as the trend observed in Figure 4 and indicating that the OH^- ions might be involved in the substitution mechanism(s) responsible for the carbonate incorporation. Whereas the phosphate bands are not markedly affected by the heating process and additional absorptions, e.g. from $P_2O_7^{4-}$, could not be detected, the CO_3^{2-} bands are changed to some extent by this process. A comparison of Figures 4–6 shows that, upon heating of the samples above 110 °C, the 873 cm^{-1} band acquires a shoulder around 878 cm^{-1} which apparently is more distinct at the lower carbonate contents. In the 1300–1700 cm^{-1} region, the position of the most intense absorption band is shifted from ∼1421 cm^{-1} to a lower wavenumber after heating above 110 °C. This shift apparently increases with decreasing CO_3 content of the samples and amounts to ∼4 cm^{-1} for sample

K4. For the samples with a low carbonate content, the relative intensity of the 1456 cm^{-1} band remains constant with respect to the 1420 cm^{-1} absorption, but that of the 1500 cm^{-1} absorption increases upon heating above 110 °C. Moreover, an additional absorption becomes visible around 1470 cm^{-1}, especially for the samples with a low carbonate content (see Figure 6). In the spectra of the latter, a weak shoulder also appears around 1545 cm^{-1}. These changes could not be observed in the spectra of the samples with a high carbonate content. The increase of the relative intensity and the broadening toward higher wavenumbers of the band centered around 1500 cm^{-1}, however, could indicate that similar changes also occur upon heating these samples. The additional CO_3^{2-} absorptions which appear after heating the samples above 110 °C can be attributed to vibrations of A-type CO_3^{2-}.[2,10]

Discussion

On the basis of the chemical and physical analyses, the precipitated KCAp's prepared in this study can be considered as B-type carbonate-containing hydroxyapatites which contain an appreciable amount of water that cannot be removed by drying under vacuum at 25 °C. Moreover, the results of the chemical and physical analyses clearly demonstrate that these precipitated KCAp's display some drastic constitutional changes upon heating. After the samples are dried at 400 °C, a significant amount of CO_3^{2-} is lost from the crystal lattice (Figure 1B). Moreover, this loss is apparently accompanied by the appearance of an IR absorption band around 880 and 1550 cm^{-1} (Figure 6). The appearance of these A-type CO_3^{2-} bands can be accounted for by the mechanism of carbonate loss as originally proposed by Holcomb and Young[20] for the thermal decomposition of tooth enamel, which is substantiated by other investigators for tooth enamel[21] as well as for synthetic NH_4^+- and CO_3^{2-}-containing apatites.[22,23] According to this mechanism, part of the B-type CO_3^{2-} migrates upon heating the apatite to an A-type site before leaving the crystal lattice, with CO_2 as an intermediate. This intermediate with a typical absorption at 2340 cm^{-1} could not be detected in the IR spectra of the present samples. However, the heating period was considerably longer in the present study as compared to that used in other investigations.[20–23] The fact that the presence of CO_2 in the lattice of the KCAp's could not be detected most probably indicates that the B-type to A-type CO_3^{2-} migration and the CO_3^{2-} loss were probably completed after the prolonged drying at 400 °C, thus leaving no CO_2.

It is remarkable that, whereas the CO_3^{2-} loss occurs between 110 and 400 °C, the minor contraction of the apatite lattice occurs between room temperature and 110 °C. As there is no evidence for a loss of CO_3^{2-} upon heating between room temperature and 110 °C, this indicates that the lattice contraction most probably is correlated with the loss of (structural) water between these temperatures as indicated by the increasing $\Sigma\%$ (Figure 1A) and by the decreasing water absorption bands in the IR spectra (Figures 4 and 5). The constitutional changes that occur in the KCAp's between 110 and 400 °C as seen in the IR spectra obviously are not accompanied by a change of the mean lattice dimensions.

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Table 2. Unit Cell Composition of KCAp's Obtained by Hydrolysis of CaHPO$_4$ in Solutions Containing c_{kc} M K$_2$CO$_3$ and Dried at 25 °C As Calculated from the Data in Table 1 by Means of Eqs 6 and 12

sample	c_{kc}	n_{Ca}	n_P	n_{CO_3}	n_K	n_{OH}	$n_{V^{Ca}}$	$n_{V^{OH}}$	O_{Ca}
K4	0.01	8.91 ± 0.04	4.81 ± 0.02	1.19 ± 0.02	0.088 ± 0.002	1.09 ± 0.07	1.01 ± 0.04	0.91 ± 0.07	10.10 ± 0.03
K5	0.0114	8.81 ± 0.04	4.72 ± 0.02	1.28 ± 0.02	0.095 ± 0.002	1.00 ± 0.07	1.09 ± 0.04	1.01 ± 0.07	10.09 ± 0.03
K6	0.0114	8.81 ± 0.04	4.73 ± 0.02	1.27 ± 0.02	0.092 ± 0.002	0.98 ± 0.07	1.10 ± 0.04	1.02 ± 0.07	10.08 ± 0.03
K7	0.0250	8.69 ± 0.05	4.52 ± 0.02	1.48 ± 0.02	0.158 ± 0.003	1.02 ± 0.08	1.15 ± 0.05	0.98 ± 0.08	10.17 ± 0.03
K8	0.0284	8.60 ± 0.05	4.46 ± 0.02	1.54 ± 0.02	0.167 ± 0.004	0.90 ± 0.08	1.24 ± 0.05	1.10 ± 0.08	10.14 ± 0.03
K9	0.0568	8.42 ± 0.05	4.26 ± 0.03	1.74 ± 0.03	0.238 ± 0.005	0.81 ± 0.09	1.35 ± 0.05	1.19 ± 0.09	10.15 ± 0.03
K10	0.0568	8.40 ± 0.05	4.27 ± 0.03	1.73 ± 0.03	0.239 ± 0.005	0.77 ± 0.09	1.36 ± 0.05	1.23 ± 0.09	10.13 ± 0.03
K11	0.0852	8.35 ± 0.05	4.19 ± 0.03	1.81 ± 0.03	0.295 ± 0.006	0.79 ± 0.09	1.36 ± 0.06	1.21 ± 0.09	10.15 ± 0.03
K12	0.1136	8.26 ± 0.06	4.10 ± 0.03	1.90 ± 0.03	0.321 ± 0.007	0.73 ± 0.09	1.42 ± 0.06	1.27 ± 0.09	10.15 ± 0.03
K13	0.1420	8.19 ± 0.06	4.08 ± 0.03	1.92 ± 0.03	0.355 ± 0.008	0.65 ± 0.09	1.46 ± 0.06	1.35 ± 0.09	10.11 ± 0.03
K14	0.1420	8.20 ± 0.06	4.08 ± 0.03	1.92 ± 0.03	0.357 ± 0.008	0.68 ± 0.09	1.44 ± 0.06	1.32 ± 0.09	10.12 ± 0.03

The effects of the heating process on the constitution of the KCAp's clearly indicate that these carbonated apatites are less stable than analogously prepared NCAp's.[7] Whereas the KCAp's lose a considerable amount of CO$_3^{2-}$ upon heating at 400 °C, the NCAp's only display some barely detectable constitutional changes.

The precipitated samples dried at 25 °C still contain a considerable amount of water. Analogous to that of NCAp's prepared in a similar manner, this water is most probably partly structural and partly nonstructural.[7] Consequently, it is not possible to obtain a reliable estimate of the unit cell contents on the basis of the analyses of the samples obtained after drying at 25 °C.[4] Moreover, the chemical analysis suggests (see Figure 1B) that a heating temperature of at least 400 °C is required to remove all the water from the KCAp's. However, because there is thermal decomposition at the higher temperatures and since the exact mechanism of the decarbonation is not known, the exact composition of the unit cell of the precipitated KCAp's can not be calculated on the basis of the chemical and physical analyses of samples heated at 400 °C.

On the other hand, in a previous study[7] it was found that the phosphate sublattice for precipitated NCAp's is always fully occupied, i.e.

$$n_P + n_{B\text{-}CO_3} = 6 \qquad (4)$$

with n_X the number of X atoms or ions per unit cell. Provided that the carbonated apatite does not contain A-type CO$_3^{2-}$, eq 4 equals eq 5 where n_{CO_3} corresponds to the total number of

$$n_P + n_{CO_3} = 6 \qquad (5)$$

CO$_3^{2-}$ ions per unit cell. As the precipitated KCAp's dried at 25 °C in the present study can be considered as pure B-type carbonated hydroxyapatites within the limits of the physical analyses, eq 5 forms a basis for estimating the number of each ion X per unit cell from the analytical composition given in Table 1 according to

$$n_X = \frac{\%X}{M_X} \frac{6}{\dfrac{\%P}{M_P} + \dfrac{\%CO_3}{M_{CO_3}}} \qquad (6)$$

where %X represents the content of X (wt %) and M_X its atomic or ionic mass. The results of these calculations are summarized in Table 2. $n_{V^{Ca}}$ and $n_{V^{OH}}$, respectively, give the number of vacancies on Ca^{2+} and OH$^-$ lattice sites as derived from the difference between the calculated site occupancies (n_X) and the HAp stoichiometry. The errors were estimated by means of error propagation theory.

From Table 2, it is seen that n_{Ca} decreases with increasing n_{CO_3}. A weighted regression analysis shows that the relation

between these quantities at the 95% confidence level is given by eq 7. From the intercept of eq 7 it can be seen that, within

$$n_{Ca} = (10.02 \pm 0.11) - (0.935 \pm 0.068)n_{CO_3} \qquad (7)$$

experimental error, a carbonate-free apatite ($n_{CO_3} = 0$) contains 10 Ca^{2+} ions per unit cell. The slope of eq 7 then suggests that the substitution of a PO$_4^{3-}$ ion by a CO$_3^{2-}$ ion is accompanied by the loss of approximately one Ca^{2+} ion. This indicates that, from the four fundamental mechanisms for B-type CO$_3^{2-}$ incorporation,[3] substitution mechanisms I and III should mainly be considered for the carbonate incorporation in precipitated KCAp's. According to Table 2, n_{CO_3} and n_K are positively correlated, but $n_{CO_3} \gg n_K$ and $n_{V^{Ca}} \approx n_{V^{OH}}$. These observations then clearly indicate that mechanisms I and III both contribute to the carbonate incorporation, resulting in a stoichiometry of the KCAp's as given by (8), where x and y

$$\text{Ca}_{10-x-y}\text{K}_y(\text{PO}_4)_{6-x-y}(\text{CO}_3)_{x+y}(\text{OH})_{2-x} \qquad (8)$$

represent their respective contributions per unit cell to the stoichiometry. This was also found for precipitated NCAp's.[4,7]

In view of the fact that $n_{V^{Ca}} \approx n_{V^{OH}}$, an individual alkali metal incorporation[3] according to mechanism IV is rather unlikely to

$$\text{Ca}^{2+} + \text{OH}^- \leftrightarrow \text{M}^+ + \text{V}^{OH} \qquad (IV)$$
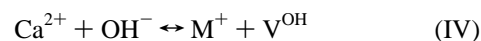
occur for K$^+$. Moreover, on the basis of eq 8 one should expect that

$$O_{Ca} = n_{Ca} + n_{CO_3} = 10 \qquad (9)$$

However, as is seen from Table 2, O_{Ca} is slightly, but significantly, greater than 10 for the individual KCAp's. This can hardly be explained when substitution mechanism IV would occur, as this results in a negative deviation of O_{Ca} from 10. Consequently, whereas for precipitated NCAp's an individual alkali metal incorporation according to mechanism IV occurs,[7] this is not the case for the precipitated KCAp's. This is hardly surprising, since even for Na$^+$, with a higher affinity for incorporation into apatite, mechanism IV contributes only to a very small extent to the stoichiometry of the precipitated NCAp.[7] The fact that K$^+$ is not incorporated individually in HAp is substantiated by the results of Christoffersen *et al.*,[24] who prepared HAp in K$^+$-containing aqueous solutions containing no CO$_3^{2-}$ and found that K$^+$ was not incorporated into the apatite lattice.

The finding that $O_{Ca} \geq 10$ could be explained by the occurrence of a small carbonate incorporation according to

(24) Christoffersen, J.; Christoffersen, M. R. *J. Cryst. Growth* **1978**, *43*, 501.

Table 3. Contributions of Mechanisms I (x), III (y), and II (w) to the Stoichiometry of the Unit Cell of KCAp's Calculated by Means of Eqs 16−18 on the Basis of Table 2

sample	x	y	w
K4	0.91 ± 0.07	0.088 ± 0.002	0.10 ± 0.03
K5	1.01 ± 0.07	0.095 ± 0.002	0.08 ± 0.03
K6	1.02 ± 0.07	0.092 ± 0.002	0.08 ± 0.03
K7	0.98 ± 0.08	0.158 ± 0.003	0.17 ± 0.03
K8	1.10 ± 0.08	0.167 ± 0.004	0.14 ± 0.03
K9	1.19 ± 0.09	0.238 ± 0.005	0.16 ± 0.03
K10	1.23 ± 0.09	0.239 ± 0.005	0.13 ± 0.03
K11	1.21 ± 0.09	0.295 ± 0.006	0.15 ± 0.03
K12	1.27 ± 0.09	0.321 ± 0.007	0.15 ± 0.03
K13	1.35 ± 0.09	0.355 ± 0.008	0.11 ± 0.03
K14	1.32 ± 0.09	0.357 ± 0.008	0.12 ± 0.03

the fundamental substitution mechanism II or V.[3] In view of

$$Ca^{2+} + 2PO_4^{3} \leftrightarrow V^{Ca} + 2CO_3^{2-} \qquad (II)$$

$$PO_4^{3-} \leftrightarrow CO_3^{2-} + OH^- \qquad (V)$$
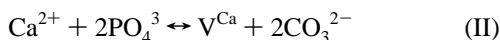
the results of Beshah *et al*,[25] mechanism V is not very likely to occur. Moreover, OH^- ions situated on PO_4^{3-} lattice sites as a result of mechanism V have a completely different lattice environment as compared to OH^- ions in their normal sites on the hexagonal apatite axis. Consequently, one can expect that they absorb at different wavenumbers in the IR spectra. If next to mechanisms I and III, mechanism V would account for the stoichiometry of the KCAp's, it can be calculated that, depending on the carbonate content, 10−20% of all OH^- lattice ions would be situated on PO_4^{3-} lattice sites according to mechanism V. However no additional absorptions around the OH^- bands near 633 and 3572 cm^{-1} could be observed.

On this basis, mechanism II most probably accounts for the deviation of O_{Ca} from 10. Consequently, the stoichiometry of the KCAp's of this study would be given by (10) reflecting the occurrence of the mechanisms I, III, and II. The respective contributions of these mechanisms, i.e. x, y, and w, to the stoichiometry of the unit cell can then be calculated according to eqs 11−13. The results are given in Table 3. The errors
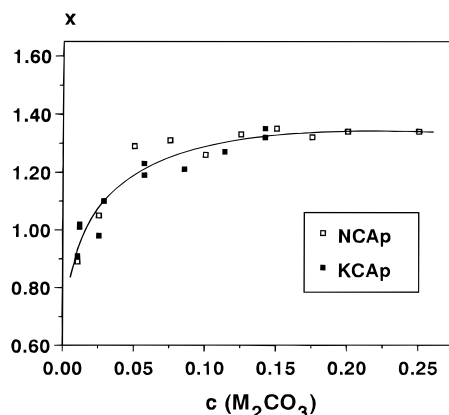
$$Ca_{10-x-y-w}K_y(PO_4)_{6-x-y-2w}(CO_3)_{x+y+2w}(OH)_{2-x} \qquad (10)$$
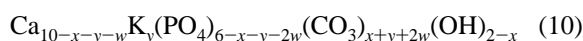
$$x = n_{VOH} \qquad (11)$$

$$y = n_K \qquad (12)$$

$$w = n_{VCa} - n_{VOH} \qquad (13)$$

were estimated by means of the error propagation theory.

Table 3 shows that contribution w of mechanism II hardly changes with the carbonate concentration in the aqueous solution, whereas contributions x and y of mechanisms I and III increase with increasing c_{kc}. The latter is more clearly illustrated by Figures 7 and 8, which represent the respective contributions x and y of the fundamental substitution mechanisms I and III as a function of the concentration of M_2CO_3 in the aqueous solution. For comparison, the corresponding data for the precipitated NCAp's obtained in a previous study[7] are also given. From Table 3 and Figure 7, it can be seen that mechanism I is the predominant mechanism for pure B-type CO_3^{2-} incorporation. Moreover, the dependencies of x on the M_2CO_3 concentration in the aqueous solution seem to be the same for NCAp's and KCAp's, and x reaches the same

(25) Beshah, K.; Rey, C.; Glimcher, M. J.; Shimizu, M.; Griffin, R. G. *J. Solid State Chem.* **1990**, *84*, 71.

Figure 7. Contribution per unit cell of mechanism I (x) to the stoichiometry of the NCAp's[7] and of the KCAp's of this study as a function of the carbonate concentration in the hydrolysis solution $c(M_2CO_3)$ (M).
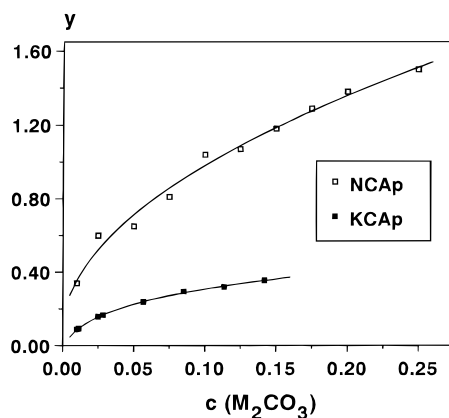
Figure 8. Contribution per unit cell of mechanism III (y) to the stoichiometry of the NCAp's[7] and of the KCAp's of this study as a function of the carbonate concentration in the hydrolysis solution $c(M_2CO_3)$ (M).

borderline value of $\sim$1.35. On the other hand, contribution y of mechanism III for the coupled M^+ and CO_3^{2-} incorporation (Figure 8) is much smaller for the KCAp's than for the NCAp's. This reflects the difference in affinity between Na^+ and K^+ for incorporation into HAp.[10] Apparently, the enhanced incorporation of carbonate into the apatite lattice in the presence of Na^+ as reported by several investigators[5,6] is mainly due to the considerably more pronounced occurrence of mechanism III. Another striking difference between NCAp and KCAp is that a minor part of the Na^+ incorporation in the former is accounted for by mechanism IV, whereas a minor part of the CO_3^{2-} in KCAp's is incorporated according to mechanism II.

In view of the different mechanisms (I, II, and III) by which B-type CO_3^{2-} can be incorporated into the apatite lattice and their relative contributions to the unit cell stoichiometry, the rather complex IR spectra of the resulting carbonated apatites (see Figure 4 and ref 4) are hardly surprising. The different absorptions between 1300 and 1600 cm^{-1} in the spectra of the KCAp's prepared in this study and dried at 25 °C most probably arise from the vibrations of B-type CO_3^{2-} in different lattice environments resulting from the different substitution mechanisms. In this respect, it can be noted that some authors attribute the absorption at $\sim$1500 cm^{-1} to A-type CO_3^{2-} distorted by B-type CO_3^{2-},[26] while undistorted A-type CO_3^{2-} would absorb near 1550 cm^{-1}.[2] This assumption could explain the increase

(26) Rey, C.; Renugopalakrishnan, V.; Shimizu, M.; Collins, B.; Glimcher, M. J. *Calcif. Tissue Int.* **1991**, *49*, 259.

of the band near 1500 cm^{-1} after heating at 400 °C, when some of the B-type CO$_3^{2-}$ is turned over into A-type CO$_3^{2-}$, whereas the majority of the CO$_3^{2-}$ ions remain on B-type sites. However, the fact that the samples with a high carbonate content after drying at 25 °C display a relative intense absorption around 1500 cm^{-1} but do not show the most characteristic absorption of A-type CO$_3^{2-}$ near 880 cm^{-1} renders the attribution of this band to this type of CO$_3^{2-}$ less likely. The absorption near 1500 cm^{-1} most probably arises from a B-type CO$_3^{2-}$ with a lattice environment different from the one giving rise to an absorption at lower wavenumber.[7,10] The increased visibility of these absorptions with increasing drying temperature might then be due to a stabilization of the CO$_3^{2-}$ ions in the lattice upon heating,[7] which increases the resolution of the entire band. On the same basis, the shift of the absorption near 1422 cm^{-1} can be attributed either to a stabilization of the B-type CO$_3^{2-}$ ions or to the disappearance of a component of this band, corresponding to the B-type CO$_3^{2-}$ which migrates to A-type lattice sites.

Conclusion

KCAp's obtained by hydrolysis of monetite are much less stable upon heating than analogously prepared NCAp's. Apparently, the Na$^+$ incorporation in HAp causes a stabilization of the solid solution as compared to the K$^+$ incorporation. This is corroborated by the fact that, at the same concentration of M$_2$CO$_3$ in the aqueous solution, the K$^+$ incorporation is much smaller than the Na$^+$ incorporation. Moreover, K$^+$ is incorporated exclusively coupled with CO$_3^{2-}$ (mechanism III), whereas Na$^+$ can be incorporated individually as well (mechanism IV).

Mechanism II obviously has a low relative stability since it does not contribute to the stoichiometry of the NCAp's. However it seems that, as a consequence of the lower stability of the K$^+$ incorporation, mechanism II becomes competitive and hence contributes to the B-type CO$_3^{2-}$ incorporation in KCAp's. The strained configuration resulting from the carbonate incorporation according to eq 13 could possibly be responsible for the reduced thermal stability of KCAp when compared to NCAp.

On the other hand, the contribution of the predominant mechanism for B-type CO$_3^{2-}$ incorporation (mechanism I) and the borderline of the solid solubility of the corresponding component seem to be hardly influenced by the alkali metal. Probably, the stability of this mechanism is so high that its contribution is much less influenced by the stability of the other mechanisms. These results then indicate unambiguously that there is no intrinsic coupling whatsoever between fundamental mechanisms I and III. This means that the contributions of these mechanisms are only determined by the respective driving forces of the individual components and not by a fixed combination of some fundamental mechanisms.[1] This corroborates in a more definite way our assumption[4] that coupled substitution mechanisms as reported in literature should probably be ascribed to casual results.

Appendix. List of Symbols

HAp	Ca$_{10}$(PO$_4$)$_6$(OH)$_2$; calcium hydroxyapatite
CAp	CO$_3^{2-}$-containing calcium hydroxyapatite
NCAp	Na$^+$- and CO$_3^{2-}$-containing calcium hydroxyapatite
KCAp	K$^+$- and CO$_3^{2-}$-containing calcium hydroxyapatite
c_{kc}	K$_2$CO$_3$ concentration in the solution during the hydrolysis of monetite
$\Sigma\%$	total mass balance of the samples calculated on the basis of the chemical analysis results
M_X	atomic or ionic mass of X
n_X	number of X atoms or ions per apatite unit cell
O_{Ca}	sum of the number of Ca^{2+} and CO$_3^{2-}$ ions per apatite unit cell
V^X	vacancy on a regular apatite lattice site occupied by X
x, y, w	contributions per apatite unit cell of the substitution mechanisms I, III, and II, respectively.

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