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Some Physical Properties of Na- and CO_3-Containing Apatites Synthesized at High Temperatures

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The stability of Na- and CO_3-containing apatites was investigated at 870 °C in a nearly dry CO_2 atmosphere. In a P/Ca versus *Na/Ca plot the single-phase apatite field has a triangular form of which one extreme composition corresponds to $Ca_{10}(PO_4)_6(CO_3)$ and another to $Ca_{8.5}Na_{1.5}(PO_4)_{4.5}(CO_3)_{2.5}$. Chemical and physical analyses show that the stoichiometry of apatites with a composition varying between these two extremes can be accounted for by the substitution mechanism $Ca + PO_4 \longleftrightarrow Na + CO_3$. Although 40% of the carbonate ions of the sodium containing extreme component are on OH^- lattice sites, the IR spectrum is very similar to that of an apatite containing carbonate on phosphate sites only.*

Introduction

The best known prototype for minerals in calcified tissues is calcium hydroxyapatite with the formula

$$Ca_{10}(PO_4)_6(OH)_2 \tag{1}$$

Except in the case of very pure samples which have ordering of the orientation of their OH^- groups [1], this calcium phosphate is hexagonal and has the space group $P6_3m$, in which PO_4^{3-} and OH^- groups are located at the sites of one sublattice each whereas 6 and 4 of the 10 Ca^{2+} ions are divided over two other sublattices.

Most natural apatites contain sodium and carbonate, either with fluoride as in francolite or without fluoride as in dahlite [2], but it is still uncertain how the former ions substitute for the calcium, phosphate and hydroxyl ions in the apatite structure. Carbonate ions can substitute for hydroxyl ions in pure hydroxyapatite by subjecting it to an atmosphere of dry carbon dioxide at about 1000 °C [3]. The final result is a carbonatoapatite of the formula

$$Ca_{10}(PO_4)_6CO_3 \tag{2}$$

Typical IR absorption bands of this so-called A-type carbonate apatite occur at or near 883, 1465 and 1534 cm^{-1}. By using polarized IR it has been shown [4] that the plane of these CO_3^{2-} ions is nearly parallel to the crystallographic c axis. X-ray and neutron diffraction have shown that the angle is about 18° [5]. Except for a small part of the carbonate in the mineral of tooth enamel, A-type carbonate does not occur in natural apatites.

Synthesis of apatites by precipitation from neutral or slightly alkaline aqueous solutions, which contain $NaHCO_3$, results in the formation of Na- and CO_3-containing apatites [6]. In these compounds CO_3^{2-} substitutes for PO_4^{3-} and is called B-type. It gives a typical IR absorption at or near 872, 1412 and 1462 cm^{-1} [7]. This is the predominant type in natural apatites. From theoretical considerations about the birefringence of natural apatites it was deduced that the plane of the CO_3^{2-} ion in these apatites makes an

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angle of about 48° with the crystallographic *c* axis [8]. Bonel *et al.* [9] have shown that B-type carbonate apatites can be formed with, as well as without, any sodium content by precipitation from aqueous solutions.

Several mechanisms for the substitution of CO_3^{2-} for PO_4^{3-} are proposed [2, 7, 9]. According to McConnell [2] the stacking of oxygens is maintained in the lattice so that four CO_3^{2-} groups replace three neighbouring PO_4^{3-} groups. However, this necessitates some charge compensation in one or more of the other sublattices. On the other hand, the experiments of Bonel *et al.* [9] indicate that CO_3^{2-} substitutes for PO_4^{3-} on a 1:1 mole basis according to

$$Ca + PO_4 + OH \longleftrightarrow \Box_{Ca} + CO_3 + \Box_{OH}$$

or

$$3\ Ca + 3\ PO_4 + OH \longleftrightarrow 2\ Na + \Box_{Ca} + 3\ CO_3 + \Box_{OH}$$

depending on the presence of sodium during the precipitation of the apatite. $\Box_X$ represents a vacancy on a regular lattice site of the species X. However, it is not known whether the same mechanisms apply to apatites also containing A-type carbonate. For this reason the stability and stoichiometry of A-type carbonate apatites was investigated in the present study as a function of the sodium- and B-type carbonate content. In order to obtain homogeneous A-type carbonate apatite the samples were prepared by solid state reaction at a high temperature in a nearly dry carbon dioxide atmosphere.

Experimental

Mixtures of reagent grade $CaHPO_4$, $CaCO_3$ and Na_2CO_3 were made in the molar range $0.50 \leqslant P/Ca \leqslant 0.62$ and $0 \leqslant Na/Ca \leqslant 0.2$. Each mixture was homogenized by ball milling, pressed into tablets and heated at 870 °C on platinum foil in an electric furnace. During heating a continuous stream of carbon dioxide was carried over the sample. The gas was washed over 96% sulphuric acid at room temperature. Heating at 870 °C was continued during periods varying from 1 to 5 days. Then, the products were quenched, powdered and analyzed by X-ray diffractometry for their phase composition. This homogenization and sintering procedure was repeated until a constant phase composition was obtained which reflected thermodynamic equilibrium between the solid phase(s) and the gas phase at high temperature.

Single-phase apatitic products were selected to determine their lattice parameters. To this purpose X-ray diffraction was carried out in the Philips Guinier XDC-700 camera. The camera constant was determined with α-Al_2O_3 as an internal standard. CuKα radiation was used for an exposure time of about 8 h. The films were developed in the usual way. Densitograms were recorded on the Lin/Log Densitometer DD2 (Kipp) having logarithmic sensitivity. The cell parameters *a* and *c* were determined by measuring the position of as many apatite peaks as possible. A least-squares calculation on these positions produced the best fitting values for *a* and *c*. The accuracy is estimated to be better than 0.003 and 0.002 for *a* and *c* respectively.

The composition of the solids was checked regularly by a chemical analysis of the calcium, phosphorus, sodium and carbonate content. Calcium was determined by complexometric titration with EDTA after separation of the phosphate. Phosphorus was analyzed as phosphate using a slight modification of the spectrophotometric method of Brabson *et al.* [10]. Sodium was determined by atomic absorption spectrophotometry and carbonate by a gravimetric method based on the evolution of CO_2 from an acidic aqueous solution of the apatite. The uncertainties were estimated as 0.2, 0.2, 5 and 10% respectively of the amounts of Ca, P, Na and CO_3 determined.

Densities were measured with an automatic helium pycnometer (Micromeritics) with an accuracy of about 1%. IR absorption spectra were recorded in KBr pellets on a Perkin Elmer type 457.

Results and Evaluation

At high Na contents not more than three consecutive heating cycles were necessary to obtain a constant phase composition. However, without any Na and at low P/Ca ratios it took up to six months of heating before equilibrium was reached. The borders of the single-phase apatite field were determined by X-ray diffractometry by extrapolating the intensity of suitable X-ray diffraction peaks of the non-apatitic phase in homologous series of two-phase products to zero intensity. In a P/Ca *versus* Na/Ca plot the single-phase apatite field appeared to have, within the limits of experimental error, the form of a triangle of which the extreme compositions with their respective standard deviations are given in Table I.

The results of the chemical analysis as compared to the original weights of the basic materials used, showed that there were no changes in the molar ratios P/Ca and Na/Ca during heating, so that apparently no loss of calcium, sodium or phosphate occurred during the heating cycles. Only CO_2 and H_2O were apt to exchange between solid phases and gas phase. However, the lattice parameters and the density of single-phase apatites along the joint A–B or parallel to it were not reproducible. This could be ascribed

TABLE I. Extreme Compositions (Points A, B and C) of the Single-Phase Apatite Field in the System $CaO–P_2O_5–Na_2O–CO_2(–H_2O)$ at 870 °C in Terms of the Molar P/Ca Ratio of the Solid.

Point	P/Ca	Na/Ca
A	0.600 ± 0.003	0
B	0.574 ± 0.003	0
C	0.530 ± 0.003	0.18 ± 0.01

to an uptake by the samples of water from the CO_2-gas stream and/or from the surroundings through the furnace tubing during sintering. Inspection of the latter showed that it was somewhat permeable to water vapour. The slow uptake of water also explains why it took so long for samples near point B to reach an equilibrium composition.

Along the joint A–C the uptake of water appears to be not so critical. Table II gives the chemical composition, the lattice parameters and the density of single-phase apatites along this joint. The IR spectra of the samples show absorptions around 1452, 1415 and 873 cm^{-1} typical for B-type carbonate [7, 11]. At low Na/Ca ratios absorptions around 1549, 1472 and 880 cm^{-1} which are attributed to A-type carbonate [3] are also observed. However, when the composition of the samples approaches that given by point C (Table I), the absorptions around 1549 and 880 cm^{-1} can no longer be detected.

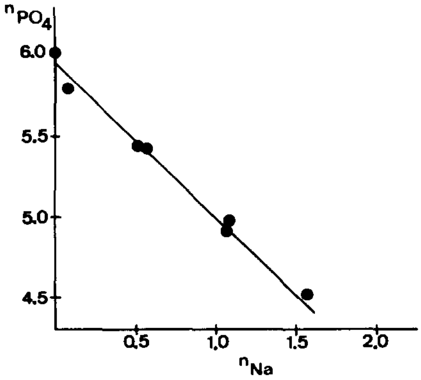

Fig. 1. Number of phosphate ions *versus* the number of sodium ions in the unit cell of Na- and CO_3 containing apatites.

From the data in Table II the content of the unit cell was calculated for each sample. The results are summarized in Table III. The number of OH groups was estimated on the basis of the electroneutrality condition. Table III shows that these samples have also acquired some water during the sintering process as shown by their hydroxyl content. A weighed least-

TABLE II. Lattice Parameters *a* and *c* (Å), Chemical Composition (wt. %) and Density d (g cm^{-3}) of Single-Phase Na- and CO_3-containing Apatites along the Joint A–C.

Sample	*a*	*c*	Ca	P	Na	CO_3	d
18	9.539	6.865	38.98	18.14	0.00	4.7	3.16
28	9.426	6.910	38.14	16.84	1.30	8.5	3.12
43	9.418	6.901	39.27	17.97	0.16	3.8	3.13
45	9.423	6.909	38.19	16.92	1.20	7.6	3.12
47	9.389	6.926	36.76	15.86	2.56	11.7	3.06
48	9.380	6.928	36.93	15.70	2.54	11.6	3.05
49	9.367	6.934	35.66	14.67	3.79	15.4	3.01

TABLE III. Number (n) of Ions in the Unit Cell of Na- and CO_3-containing Apatites along the Joing A–C. $n_{CO_3\text{-}B}$ and $n_{CO_3\text{-}A}$ denote the Number of CO_3^{2-} Ions on Phosphate- and Hydroxyl-Lattice Sites, respectively (see text).

Sample	n_{Ca}	n_{Na}	n_{PO_4}	n_{OH}	n_{CO_3}	$n_{CO_3\text{-}B}$	$n_{CO_3\text{-}A}$
18	10.01	0.00	6.03	0.32	0.81	0.00	0.81
28	9.51	0.57	5.43	0.45	1.42	0.47	0.85
43	9.79	0.070	5.80	1.01	0.63	0.20	0.43
45	9.51	0.52	5.45	0.65	1.27	0.55	0.72
47	8.94	1.09	4.99	0.18	1.91	1.01	0.90
48	8.93	1.07	4.92	0.44	1.88	1.08	0.80
49	8.50	1.57	4.52	0.10	2.45	1.48	0.97

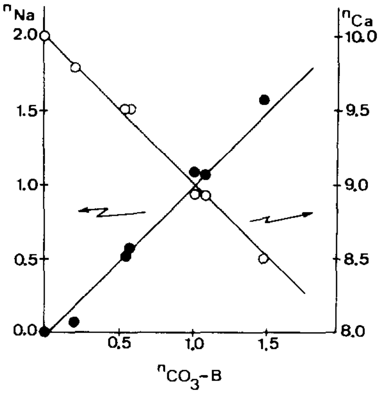

Fig. 2. Number of calcium (○) and sodium (●) ions in the unit cell of Na- and CO_3-containing apatites as a function of the number of carbonate ions on phosphate lattice sites.

squares analysis shows that n_{Ca} and n_{PO_4} change linearly with the number of sodium ions in the unit cell as illustrated in Fig. 1 by a plot of n_{PO_4} *versus* n_{Na}. The parameters describing the relations n_{Ca}–n_{PO_4}, n_{Ca}–n_{Na} and n_{PO_4}–n_{Na} are summarized in Table IV.

According to McConnell [2] the stacking of oxygen is maintained when CO_3^{2-} substitutes for PO_4^{3-}. The solid-state chemical rules for site balance and electric charge balance then predict that the most probable substitution mechanism becomes

$$Ca + 3PO_4 \longleftrightarrow Na + 4\ CO_3 \qquad (3)$$

However, the data in Table IV show that the changes in n_{Ca}, n_{PO_4} and n_{Na} differ significantly from those predicted by eqn. (3). For this reason the substitution of PO_4^{3-} by CO_3^{2-} on a 3:4 mole basis according to eqn. (3) can be excluded. On the other hand, according to Bonel *et al.* [9] the CO_3^{2-}/PO_4^{3-} substitution occurs on a 1:1 mole basis. On this basis the number of CO_3^{2-} ions on PO_4^{3-} and OH^- lattice sites, respectively, denoted by $n_{CO_3\text{-}B}$ and $n_{CO_3\text{-}A}$, were calculated from n_{CO_3} and n_{PO_4} resulting in the values given in Table III. Figure 2 shows that n_{Na} and n_{Ca} change linearly with $n_{CO_3\text{-}B}$. The parameters describing these straight lines were calculated by a weighed least-squares analysis and are included in Table IV.

Discussion

When CO_3^{2-} substitutes for PO_4^{3-} on a 1:1 mole basis the substitution mechanism according to the solid-state chemical rules for site balance and electric charge balance could be

$$Ca + PO_4 \longleftrightarrow Na + CO_3 \qquad (4)$$

TABLE IV. Parameters with Their Respective Standard Deviation of the Linear Relations Describing the Changes in the Unit Cell Content of Na- and CO_3-containing Apatites.

Relation	Intercept	Slope
n_{Ca} *vs.* n_{PO_4}	3.88 ± 0.20	1.02 ± 0.04
n_{PO_4} *vs.* n_{Na}	5.95 ± 0.04	−0.95 ± 0.11
n_{Ca} *vs.* n_{Na}	9.95 ± 0.04	−0.90 ± 0.08
n_{Ca} *vs.* $n_{CO_3\text{-}B}$	10.01 ± 0.02	−0.99 ± 0.04
n_{Na} *vs.* $n_{CO_3\text{-}B}$	−0.03 ± 0.03	1.01 ± 0.13

or

$$3\ Ca + 3\ PO_4 + OH \longleftrightarrow 2\ Na + \square_{Ca} + 3\ CO_3 + \square_{OH} \qquad (5)$$

The latter is proposed by Bonel *et al.* [9] on the basis of products prepared by precipitation from aqueous solutions. Both mechanisms are in line with the general observation that in ionic compounds the sublattice of the most polarizable anion is filled up completely so that vacancies occur preferentially in the other sublattices.

A comparison of the changes in n_{Ca}, n_{PO_4}, n_{Na} and $n_{CO_3\text{-}B}$ with increasing sodium and carbonate content as predicted by the mechanisms (4) and (5) with those given in Table IV, shows that the substitution mechanism (4) applies to the Na- and CO_3-containing apatites in this study. This is corroborated by the following observation. The IR spectra and the data in Table III show that in the hydroxyl sublattice OH^- ions are substituted for by CO_3^{2-} ions. According to Bonel [3] the mechanism of this substitution is given by

$$2\ OH \longleftrightarrow CO_3 + \square_{OH} \qquad (6)$$

However, the substitution mechanism (5) would increase the number of vacancies in the hydroxyl sublattice with increasing sodium content. This implies that the total number of OH^- ions exchangeable with CO_3^{2-} according to eqn. (6) and given by

$$N_{OH} = n_{OH} + 2\ n_{CO_3\text{-}A} \qquad (7)$$

would decrease with increasing n_{Na} and $n_{CO_3\text{-}B}$. A calculation of N_{OH} from the data in Table III shows that this quantity is independent of n_{Na} and/or $n_{CO_3\text{-}B}$. The mean value of (2.02 ± 0.04) corresponds within experimental error to that expected for apatites containing only A-type carbonate. This indicates that no vacancies are created in the hydroxyl sublattice when phosphate ions are substituted for by carbonate ions.

As mentioned before mechanism (5) was derived for products prepared by precipitation from aqueous solutions. However, it must be pointed out that such precipitations [6, 9] do not reflect quasi-equilibrium conditions and due to their high speed may give rise to ion entrapment and intra- or inter-crystalline inhomogeneities. Recently, Nelson [12] investigated the reason for the poor crystallinity of such Na- and CO_3-containing apatites prepared by precipitation using high resolution transmission electron microscopy. He came to the conclusion that the reason was not a decrease in the particle size but the fact that each particle consisted of several domains. The domain size appeared to decrease with carbonate content and could become as small as 90 Å. It cannot be excluded that such domains represent apatites of different compositions.

In this respect it can be noted that an analysis [7] of the data of LeGeros [13] indicates that the substitution mechanism

$$2\ \mathrm{Ca} + \mathrm{PO_4} + \mathrm{OH} \longleftrightarrow 2\ \mathrm{Na} + \mathrm{CO_3} + \Box_{\mathrm{OH}} \qquad (8)$$

applies to Na- and CO_3-containing apatite precipitates prepared by this author. Mechanism (8) differs markedly from that represented by eqn. (5) applying to the same type of precipitates obtained by Bonel *et al.* [9]. Apparently the composition of the precipitate depends critically on the precipitation conditions as is also clearly seen from the experiments of Labarthe *et al.* [14] on B-type carbonate apatites. Consequently, it is very difficult to decide whether the composition of the precipitate is determined by one or several substitution mechanisms acting simultaneously (see also reference [9]) or by a more complex substitution mechanism like (5) or (8). On the contrary, the products obtained in the present study are in accordance with thermodynamic equilibrium with the (in this case gaseous) environment and are homogeneous throughout each particle due to the solid-state diffusion occurring at those high temperatures. For these reasons it is not possible to conclude that the presence of A-type carbonate in Na- and CO_3-containing apatites inhibits a PO_4^{3-}–CO_3^{2-} substitution according to mechanism (5) and promotes the mechanism (4).

Taking into account the composition of the single-phase apatite at point C (Table I), the substitution mechanism (4) ultimately leads to the stoichiometry

$$\mathrm{Ca_{8.5}Na_{1.5}[(PO_4)_{4.5}(CO_3)_{1.5}]\,CO_3} \qquad (9)$$

Although formula (9) indicates that 40% of the carbonate groups are located in the OH^- sites, the IR absorptions around 1549 and 880 cm^{-1} characteristic for A-type carbonate are not observed. The IR spectrum of the apatite of formula (9) is hardly distinguishable from that of an apatite containing only B-type carbonate. On the contrary, for AB-type carbonate containing fluoridated apatites the typical IR absorptions for A- and B-type carbonate are both observed but changes in the peak positions occur [7]. According to Bonel [3] the IR absorptions of A-type carbonate are strongly influenced by the orientation of the CO_3^{2-} ion with respect to the crystallographic *c* axis. On this basis it can be assumed that the orientation of this ion along the *c* axis in pure A-type carbonate apatite differs from that in the Na- and CO_3-containing apatites investigated in this study. This hypothesis is now under investigation.

Recently, Driessens *et al.* [15, 16] have proposed that the compound of formula (9) forms part of the mineral in bone, dentine and tooth enamel. As such the synthesis of this compound permits the investigation of its physicochemical properties separately from those of the other components occurring in the mineral of these calcified tissues. The solubility behaviour is believed to be of particular interest, as it is of importance for the physiology and pathology of these calcified tissues.

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