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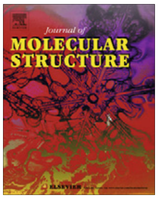

Ion substitutions and non-stoichiometry of carbonated apatite-(CaOH) synthesised by precipitation and hydrothermal methods

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ABSTRACT

Apatite-(CaOH), either carbonate-free or with different concentrations of carbonate ions of the predominantly (not less than 60%) B type, was synthesised by precipitation from solutions, by hydrothermal methods from solid compounds and by hydrothermal treatment of calcite. In B type apatite, the concentration of CO_3^{2-} ions could be up to 20.5 wt.%. The reverse precipitation method and hydrothermal treatment of calcite obtained monophase samples with a maximal concentration of CO_3^{2-} ions of 10.3–10.5 wt.%. In apatites of a mixed type, the total concentration of CO_3^{2-} ions did not exceed 8 wt.%.

The synthesised apatites could be divided into three groups according to the degree and origin of non-stoichiometry:

1. Apatite of nearly stoichiometric composition. Apatite of this type was synthesised by all methods.
2. Calcium-deficient apatite. The Ca deficit was mainly due to CO_3^{2-} incorporation. Monophase samples with maximal concentrations of CO_3^{2-} ions were synthesised by the reverse precipitation method and by hydrothermal treatment of calcite.
3. Calcium-deficient apatite. The Ca deficit was mainly due to a deficit of OH^- ions and resulted in the incorporation of water into channels of the crystal structure. This group was synthesised by reverse precipitation and hydrothermal methods. This apatite was a crystal chemical analogue of the apatite formed in the hard tissues of the human body such as teeth, bone and different stones.

Apatites formed by the precipitation methods revealed higher variations in composition (including variations in the concentration of CO_3^{2-} ions), compared to hydrothermally-synthesised samples. The observed effect of aqueous solution composition on the ion substitution and apatite composition was stronger than previously reported.

1. Introduction

Carbon in the form of the carbonate ion CO_3^{2-} was detected for the first time in 1850 as apatite-(CaF) (fluorapatite) in Wheal Franco, Devonshire (Great Britain), and was named francolite. In 1886, a mineral named staffelite from the phosphorites of Staffele (Germany) was described. Subsequently, this mineral was found to be identical to francolite.

The presence of the carbonate ion is common in apatite, which is formed in living organisms. Carbonated apatite-(CaOH) (hydroxyapatite) is the main component of dental and bone tissues in humans and in many living organisms of different taxonomy. This apatite transforms into carbonated apatite-(CaF) in the course of fossilisation. Bedded and nodular phosphorites composed of biogenic carbonated apatite-(CaF) (francolite) represent the main source of phosphate raw material.

Incorporation of the carbonate ion into the apatite crystal structure (Fig. 1) is of special interest, because the CO_3^{2-} ion increases the solubility of phosphate [1] and also has an impact on different pathologies of human tissues, such as dental caries [2,3]. It is well-known that the carbonate ion can replace OH^- and F^- anions in channels of the apatite crystal structure (substitution of the A type) as well as PO_4^{3-} anions (substitution of the B type). These two types of CO_3^{2-} substitution can be easily distinguished by means of infrared spectroscopy. They also have different effects on the lattice constants. Substitution of the A type results in an increase of the lattice constant ***a*** and a decrease of the lattice constant ***c*** [4,5], whereas substitution of the B type is accompanied by a decrease of the lattice constant ***a*** and an increase of the lattice constant ***c*** [6,7]. The charge imbalance can be compensated in different ways.

In biogenic apatite, the CO_3^{2-} ion preferentially replaces PO_4^{3-} groups that should result in a smaller lattice constant ***a*** and larger

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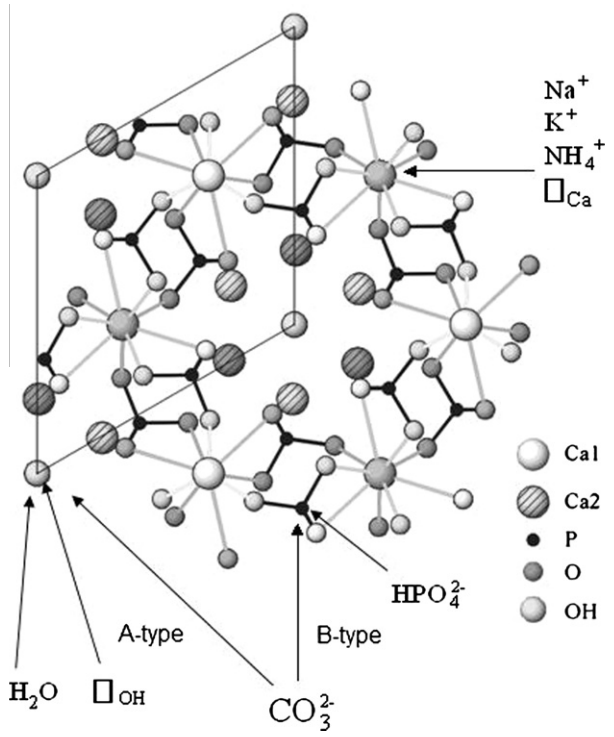

Fig. 1. Atomic structure of apatite-(CaOH). Projection onto (0 0 0 1) plane. Ion substitutions in synthesised apatites are shown.

c with respect to the stoichiometric hydroxyapatite-(CaOH) $Ca_5(PO_4)_3(OH)$ (hereafter, *Apst*). In many cases, however, biogenic apatites have larger ***a*** and smaller ***c*** in relation to *Apst*. The increase in ***a*** is due to the incorporation of molecular water [8] and, to a significantly lesser extent, HPO_4^{2-} ions [9], whereas the decrease in ***c*** is due to the presence of vacancies at calcium sites, especially, at the Ca2 site [10].

A significant level of attention is paid worldwide to the development of apatite-(CaOH) synthesis methods, and to the effect of carbonate ions on the properties of apatite, mostly due to the creation of medically biocompatible materials for teeth and bone repair [11–16]. Nevertheless, there is a lack of systematic information on the ion substitutions in carbonated apatite and on the relationships between apatite composition and synthesis conditions.

This paper summarises our data on the isomorphic substitutions in carbonated apatite-CaOH synthesised by precipitation and hydrothermal methods. Its aim was to reveal the influence of synthesis conditions on the main mechanisms of charge imbalance compensation arising from CO_3^{2-} ion incorporation. Special attention is paid to the origin of non-stoichiometry of carbonate apatites and to samples whose composition is close to biogenic apatites.

2. Experimental section

2.1. Synthesis

The carbonated apatite-(CaOH) was synthesised by precipitation from aqueous solutions [5,17–21], by high-temperature hydrothermal synthesis from solid compounds [22] and by the calcite reaction with a phosphate solution [23,24]. The Ca/P ratio in the solutions varied from 0.2 up to 2.25 (in stoichiometric apatite, Ca/P = 1.667). Addition of CO_3^{2-} ions into the system without admixture of additional cations was only possible for methods involving hydrothermal synthesis. If precipitation methods were applied, monovalent cations R (Na^+, K^+ and NH_4^+) were added. The initial R/Ca ratios varied: Na/Ca from 2 up to 90; K/Ca from 2.9 up to 7.4; NH_4/Ca from 1 to 7.

2.1.1. Precipitation methods

An aqueous solution of calcium acetate or nitrate (I) was mixed with a mixture of hydrophosphate and hydrocarbonate of Na, K or NH_4 (II).

Direct method (solution I was added into solution II): The 0.02 M $Ca(CH_3COO)_2$ solution was dropped into a stirred 0.1 M aqueous solution of $NaHCO_3 + Na_2HPO_4$. The C/P ratio was kept equal to 0, 8, 16, 24, 32, or 40, $T = 25$ or 100 °C. The precipitate was filtered, washed by distilled water and dried in an oven at $T = 110$ °C for 1 day.

Reverse method (solution II was added into solution I): An aqueous solution containing hydrophosphate and hydrocarbonate of Na^+, K^+ or NH_4^+ with the C/P ratio equal to 0, 0.053, 0.11, 0.176, 0.25, 0.5, 1.0, or 2.5 was dropped into a stirred 1 M aqueous solution of $Ca(NO_3)_2{\cdot}4H_2O$ (200 mL). The synthesis was carried out at $T = 85$–90 °C. The required pH value = 9–11 was achieved by adding NaOH, KOH or NH_4OH, respectively. After the completion of precipitation, the solution was kept at $T = 90$–100 °C for 2 h. Then precipitate was then filtered, washed by distilled water and dried in an oven at $T = 110$ °C for 1 day.

2.1.2. Hydrothermal methods

High-temperature hydrothermal synthesis from solid compounds was performed in a reactor with a cold seal under water pressure. The reagents $Ca(H_2PO_4)_2$, $Ca(OH)_2$, $CaCO_3$ and $NaHCO_3$ were mixed in amounts corresponding to carbonate apatite of different compositions. The C/P ratio varied in the range from 0.17 up to 1.0. The materials were placed into a platinum capsule and kept at $T = 300$–500 °C, $P = 0.5$–1 kbar for 3–4 days. The reactor was then quenched in air, and the sample was dried.

Hydrothermal treatment of calcite was performed by using solutions containing Na^+, K^+ or NH_4^+ phosphate in self-sealing autoclaves. Fine milled calcite powder was treated by those solutions in a platinum crucible at $T = 250$–300 °C, $P = 0.5$–1 kbar. The reactor was then quenched in water, and the sample was washed and dried.

2.2. Analytical procedures

Synthesised apatite was studied by various methods including X-ray powder diffraction, infrared spectroscopy and chemical analysis.

Powder diffraction investigations (phase identification, lattice constant measurement) were carried out with the diffractometer DRON (Cu Kα or Co Kα radiation, graphite monochromator). Lattice constants (Fig. 2, Tables 1 and 2) were calculated by the least squares method using 10–14 reflections. Germanium powder was used as an internal standard.

Infrared (IR) spectroscopy was used for localisation of CO_3^{2-} ions, detection of OH^- and HPO_4^{2-} ions and detection of molecular water. The spectra were collected with a modified two-wave spectrometer (UR-20) in the range of 400–4000 cm^{-1} with a frequency resolution of 1 cm^{-1} (Figs. 3 and 4). The samples were prepared as a paste in refined paraffin oil (ranges 1900–2100 and 3200–3700 cm^{-1}) or the powder was suspended on a KBr plate (range 400–1600 cm^{-1}). The layer thickness was checked by comparing transmission at the maximum of the P–O band (1200 cm^{-1}) (20–25%) and far from it (80%). The P–O bond vibrations were detected using absorption bands at 1105, 1070, 1040, 975, 640, 610, 570 and 480 cm^{-1}. The presence of OH^- ions, molecular water and HPO_4^{2-} ions was detected using absorption bands at 640 cm^{-1} (P–OH) and 3580 cm^{-1}, a group of bands in the range of 3300–3500 cm^{-1} and a band at ~2000 cm^{-1}, respectively. The carbonate ion was localised using C–O absorption bands. The bands at 1460 and 1420 cm^{-1} indicated substitution of the B type, whereas the