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Carbonate apatite type A synthesized at high pressure: new space group ($P\bar{3}$) and orientation of channel carbonate ion

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Abstract

A new space group and structure are reported for type A carbonate apatite (CAp) of composition $Ca_{10}(PO_4)_6[(CO_3)_x(OH)_{2-2x}]$, $x \geqslant 0.5$, synthesized at 2 GPa, 1400–1500°C. Crystal data are trigonal, space group $P\bar{3}$, $Z = 1$; $x \approx 0.75$, $a = 9.5211(3)$, $c = 6.8725(2)$ Å, $V = 539.5$ Å^3, $R = 0.030$, and $D_x = 3.152$ g/cm^3; $x \approx 0.50$, $a = 9.4917(2)$, $c = 6.8758(3)$ Å, $V = 536.5$ Å^3, $R = 0.030$, and $D_x = 3.150$ g/cm^3. In the $P\bar{3}$ structure, the type A carbonate ion is ordered along the apatite channel at $z = 0.5$. Two of the oxygen atoms of the carbonate ion lie close to the *c*-axis, with the plane of the ion canted ~12°. FTIR spectra are similar to that of type A carbonate hydroxylapatite. The present structure may be an appropriate model for the orientation of the type A carbonate ion in bone and enamel.

Keywords: Carbonate apatite; CAp; Channel carbonate ion; Bone; Enamel; High-pressure phosphates

1. Introduction

The structure of apatite [$Ca_{10}(PO_4)_6(OH)_2$; OHAp; space group $P6_3/m$] is very accommodating to atomic substitution and nonstoichiometry in the Ca, P and channel anion (*X*) positions [1–11]. The apatite channel appears to be particularly adaptable for anion substituents, with hydroxyl-, fluor- (FAp), chlor- (ClAp) and carbonate apatites (CAp) being commonly encountered both as end-members and in mutual solid solution [4,5,10,12,13]. There is an increasing awareness of the contribution of carbonate and carbonated apatite (C-OHAp, C-FAp) to bone and dental enamel, as well as in the in vivo remodelling of bone material [14–17]; e.g., in a recent review, the content of CO_2 present as carbonate in the inorganic fraction of enamel, dentine and bone was reported to be 3.0, 4.8 and 4.8 wt%, respectively [14]. However, the structural roles of the carbonate ion in apatite remain unclear in spite of extensive study by X-ray diffraction, chemical analyses, infrared and Raman spectroscopy, and proton and ^{13}C NMR spectroscopy [18–23].

Nevertheless, most researchers agree that the carbonate ion can substitute both for OH in the apatite channel (type A CAp) and for the phosphate ion (type B CAp), and that the these different structural roles result in characteristic infrared signatures for the carbonate ion: type A carbonate has doublet bands at about 1545 and 1450 cm^{-1} (asymmetric stretching vibration, ν_3) and 880 cm^{-1} (out-of-plane bending vibration, ν_2), whereas type B has these bands at about 1455, 1410 and 875 cm^{-1}, respectively. Using polarized infrared spectra, Elliott [24] deduced that the type B carbonate ion in francolite (C-FAp) occupied a sloping tetrahedral face of the substituted phosphate ion, and the type A carbonate ion in enamel was oriented with its plane approximately parallel to the *c*-axis. Single-crystal X-ray diffraction structure analysis of CAp grown using a $CaCO_3$ flux resulted in a structure in space group $P\bar{6}$ with the type A channel carbonate ion parallel to the *c*-axis and oriented with the six-fold axis bisecting the equilateral triangle [22]; this orientation of the carbonate ion is presently referred to as the "open" configuration. Recent Rietveld refinement of X-ray powder diffraction data indicated that the type B carbonate ion in a synthetic Ca-deficient C-OHAp (space group $P6_3/m$) occupied the vertical face of the substituted phosphate ion [23]. In the present study, crystals of type A CAp

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are grown by direct reaction of calcium pyrophosphate, calcium oxide and calcium carbonate at high pressure and investigated by single-crystal X-ray diffraction, resulting in a new space group ($P\bar{3}$) for CAp and a new orientation for the carbonate ion in the apatite channel.

2. Experimental procedures

Single crystals of CAps were prepared by direct reaction of stoichiometric amounts of $Ca_2P_2O_7$ (Alfa Aesar; 98%), CaO (Alfa Aesar; 99.95%) and $CaCO_3$ (Alfa Aesar; 99.99%) in the ratio 3:3:1 at high pressure and temperature in an end-loaded piston-cylinder apparatus. All furnace parts were previously fired at 1000°C in air. Calcium pyrophosphate and CaO were dried at 1000°C, 12 h, and $CaCO_3$ at 200°C, 12 h. Pressure was calibrated from melting of dry NaCl at 1050°C [25] and transformation of quartz $\rightleftharpoons$ coesite at 500°C [26]. Temperature was measured by inserting a Pt–Pt90%Rh10% thermocouple into the high-pressure cell. The starting mixture was encapsulated in a sealed platinum tube with a diameter of 5 mm and a height of 12 mm, which was separated by MgO powder from a graphite tube. The run conditions for experiments PC71 and PC74 are given in Table 1. The experiments were quenched at pressure by switching off the furnace.

The products were characterized as single-phase carbonated apatite by optical petrography, powder X-ray diffraction, and Fourier transform infrared (FTIR) spectroscopy. The infrared spectra were obtained using KBr pellets; 10 mg of CAp product was diluted in an agate mortar with 1 g of KBr. Transparent pellets were made under vacuum at a pressure of 200 kg/cm^2. The spectra were measured with a Nicolet Nexus 670 FTIR spectrometer.

Table 1
Experimental details

	0.75CAp · 0.25OHAp	0.5CAp · 0.5OHAp
Experiment	PC71	PC74
Pressure (GPa)	2	2
Temperature (°C)	1400	1500
Time (h)	6	12
Crystal size (mm^3 × 10^3)	0.52	0.99
Crystal shape	Tablet	Tablet
a (Å)	9.5211(3)	9.4917(2)
c (Å)	6.8725(2)	6.8758(3)
Space group	$P\bar{3}$	$P\bar{3}$
Formula weight	1024.1	1017.6
D_x (g/cm^3)	3.152	3.150
Reflections—unique	1067	1055
Number, with ($I < 3\sigma_{(I)}$)	397	385
$R_{(I)}$	0.021	0.021
$R_{(I),w}$	0.041	0.036
Refined parameters	75	75
μ (cm^{-1})	28.8	29.0
R	0.030	0.030
R_w	0.029	0.029
s	1.47	1.45
g ($\times 10^4$)	0.39(5)	0.45(6)
$\Delta\rho$ (e Å^{-3}) (+)	0.76	1.11
(−)	0.54	0.60

Single-crystal fragments were prepared by trimming tablet-shaped grains of CAp with a scalpel blade and evaluated for X-ray structure analysis by optical petrography and X-ray precession photography. Single-crystal measurements were made at room temperature and pressure with a Nonius Kappa CCD diffractometer and graphite-monochromatized Mo$K\alpha$-radiation (50 kV, 32 mA, $\lambda = 0.71069$ Å). The COLLECT Nonius software was used for unit-cell refinement and data collection. The reflection data were processed with SORTAV-COLLECT, using an empirical procedure for absorption correction, and SHELXTL/PC [27]. Structure refinements were made with LINEX77 (State University of New York at Buffalo). Scattering factors for neutral atomic species and values of f' and f'' were taken, respectively, from Tables 2.2A and 2.3.1 of the *International Tables for* X-ray *Crystallography* [28]. Relevant experimental details are given in Table 1, final parameters in Table 2, and selected bond distances and angles in Table 3.

3. Results and discussion

The products of experiments PC71 and PC74 were characterized as single-phase apatite by X-ray powder diffraction and optical petrography. However, the synthesized apatites were not CAp as expected but carbonate-rich carbonated apatites belonging to the composition series $Ca_{10}(PO_4)_6[(CO_3)_x(OH)_{2-2x}]$, with $x \geqslant 0.5$. This was evident from the FTIR spectra (Fig. 1), unit-cell parameters and X-ray structure analysis discussed below. The spectrum of PC71 shows a prominent doublet in the asymmetric stretching region of the carbonate ion (ν_3) at 1542 and 1459 cm^{-1}, consistent with type A CAp. The slight shoulder on the low frequency side of the 1459 cm^{-1} band suggests a small contribution from type B carbonate ion, and the weak peak at 3567 cm^{-1} indicates OH in apatite channel sites. In PC74, the type A carbonate ion doublet is at 1545 and 1456 cm^{-1}, and somewhat reduced in intensity, and the type B doublet and OH stretching band (at 3564 cm^{-1}) correspondingly stronger. Sample PC17b is a carbonated OHAp synthesized using the same nominal starting composition as for PC71 and PC74, but with fewer precautions to avoid contamination by hydration. The X-ray structure (reported elsewhere) refined to essentially end-member OHAp, and the FTIR spectrum showed a sharp and relatively strong OH-stretching band at 3564 cm^{-1}, very weak absorption in the type A

Table 2
Positional and isotropic thermal parameters (Å^2) ($B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$)

	Equipoint; site occupancy	x	y	z	B^*, B_{eq}
PC71: 0.75CAp·0.25OHAp					
Ca(1A)	2*d*; 1.0	2/3	1/3	0.0114(1)	1.43(4)
Ca(1B)	2*d*; 1.0	1/3	2/3	0.4950(1)	1.23(4)
Ca(2)	6*g*; 1.0	0.98964(6)	0.25314(7)	0.24493(6)	1.80(1)
P	6*g*; 0.985(2)	0.37059(8)	0.40052(8)	0.25039(8)	1.21(2)
O(1)	6*g*; 1.0	0.4842(2)	0.3300(2)	0.2520(2)	1.53(3)
O(2)	6*g*; 1.0	0.4648(2)	0.5842(2)	0.2189(2)	2.56(4)
O(3A)	6*g*; 1.0	0.2463(2)	0.3226(2)	0.0877(2)	2.71(4)
O(3B)	6*g*; 1.0	0.7207(3)	0.6280(3)	0.5586(2)	3.43(5)
C	1*b*; 0.75	0	0	1/2	2.0(3)
OH(A)	2*c*; 0.125	0	0	0.200(3)	2.4(5)*
OH(B)	2*c*; 0.125	0	0	0.300(3)	2.4(5)*
OC(A)	6*g*; 0.25	0.991(2)	0.047(1)	0.6631(9)	4.2(2)*
OC(B)	6*g*; 0.125	0.105(3)	0.959(3)	0.522(2)	4.3(4)*
PC74: 0.5CAp·0.5OHAp					
Ca(1A)	2*d*; 1.0	2/3	1/3	0.0081(1)	1.33(3)
Ca(1B)	2*d*; 1.0	1/3	2/3	0.4973(1)	1.19(3)
Ca(2)	6*g*; 1.0	0.99089(6)	0.25131(6)	0.24697(8)	1.54(1)
P	6*g*; 0.983(2)	0.36973(8)	0.39994(7)	0.2501(1)	1.02(2)
O(1)	6*g*; 1.0	0.4843(2)	0.3296(2)	0.2516(3)	1.30(3)
O(2)	6*g*; 1.0	0.4645(2)	0.5845(2)	0.2305(3)	2.46(4)
O(3A)	6*g*; 1.0	0.2506(2)	0.3300(2)	0.0819(3)	2.75(4)
O(3B)	6*g*; 1.0	0.7291(2)	0.6387(2)	0.5636(3)	3.23(4)
C	1*b*; 0.50	0	0	1/2	1.8(4)
OH(A)	2*c*; 0.25	0	0	0.185(2)	2.1(2)*
OH(B)	2*c*; 0.25	0	0	0.315(2)	2.1(2)*
OC(A)	6*g*; 0.167	0.995(3)	0.046(2)	0.677(2)	5.0(4)*
OC(B)	6*g*; 0.083	0.091(4)	0.946(4)	0.519(4)	3.8(6)*

Note. *, Isotropic refinement.

carbonate ion asymmetric stretching region and distinct doublet bands at 1456 and 1428 cm^{-1} in the type B carbonate region (Fig. 1). We were unable to synthesize type A end-member CAp using the piston cylinder apparatus in spite of very careful precautions to avoid contamination by water. It was not possible to bake the loaded capsule at high temperature (say 600°C) before sealing due to decarbonation of $CaCO_3$ (calcite) in the starting mixture. The FTIR spectra and X-ray structure analyses suggested that the channel anion composition of PC71 was approximately $0.75CO_3$ and $0.25(OH)_2$ per formula unit (pfu), whereas that of PC74 was approximately $0.5CO_3$ and $0.5(OH)_2$ pfu. The contribution of the type B carbonate ion is presently ignored; the occupancy refinements for the P position (Table 2) are consistent with a maximum type B carbonate ion content of less than 0.1 pfu.

The response of the unit-cell parameters of apatite to accommodation of the carbonate ion is complex. Substitution of OH^- by type A carbonate results in progressive increase in a and decrease in c (hexagonal or equivalent hexagonal parameters; [29,30]), whereas substitution of phosphate by type B carbonate results in progressive decrease in a and increase in c [31,32]. Relative to the comprehensive results of Bonel [29] for type A (C,OH)Ap solid solutions, the present values of a and c (Table 1) correspond to 0.73 and 0.76 CAp, respectively, for PC71 and 0.56 and 0.62 CAp, respectively, for PC74, in good agreement with the compositions estimated from the FTIR spectra.

The single-crystal X-ray reflection data for the present high-pressure carbonated apatites (PC71 and PC74) were consistent with space group $P\bar{3}$, rather than $P6_3/m$, the space group for the average structures of synthetic and natural carbonated apatites [5], Pb for a powder of synthetic type A CAp [33], or $P\bar{6}$ for a single crystal of synthetic CAp of composition $Ca_{9.75}[(PO_4)_{5.5}(CO_3)_{0.5}]CO_3$ [22]. The intensity statistics were quite revealing in this respect: e.g., for PC71, $R_{(I)}$ and $R_{(I),w}$ were 0.18 and 0.92 for $P6_3/m$ and 0.021 and 0.041 for $P\bar{3}$ and, for PC74, they were 0.12 and 0.47 for $P6_3/m$ and 0.021 and 0.036 for $P\bar{3}$, respectively. The new space group ($P\bar{3}$) is associated with a new crystal structure for CAp. In all crystal structures of CAp reported so far, the carbonate oxygens [OC(A) and OC(B) in the present structures] have only partial occupancy, because the carbonate ion is disordered over six equivalent orientations. Also, in the $P6_3/m$ and $P\bar{6}$ structures the carbonate ion is disordered along the apatite channel at $z = 0.0, 0.5$. In contrast, the electron density distribution along the

Table 3
Selected bond distances (Å) and angles (deg)

		PC71 0.75CAp · 0.25OHAp	PC74 0.5CAp · 0.5OHAp
Ca(1A)–O(1)	× 3	2.388(1)	2.396(2)
Ca(1A)–O(2)	× 3	2.381(2)	2.413(2)
Ca(1A)–O(3A)	× 3	3.027(2)	2.950(2)
Mean		2.599(2)	2.586(2)
Ca(1B)–O(1)$^{\mathrm{I}}$	× 3	2.447(1)	2.433(2)
Ca(1B)–O(2)$^{\mathrm{II}}$	× 3	2.601(2)	2.548(2)
Ca(1B)–O(3B)	× 3	2.613(2)	2.685(2)
Mean		2.554(2)	2.555(2)
Ca(2)–O(1)		2.699(2)	2.703(2)
Ca(2)–O(2)$^{\mathrm{III}}$		2.335(2)	2.342(2)
Ca(2)–O(3A)		2.363(2)	2.357(2)
Ca(2)–O(3A)$^{\mathrm{III}}$		2.442(2)	2.466(2)
Ca(2)–O(3B)$^{\mathrm{I}}$		2.349(2)	2.348(2)
Ca(2)–O(3B)$^{\mathrm{IV}}$		2.755(2)	2.660(2)
Mean		2.491(2)	2.479(2)
Ca(2)–OC(A)		2.29(1)	2.27(2)
Ca(2)–OC(A)$^{\mathrm{V}}$		2.40(2)	2.32(3)
Ca(2)–OC(B)		2.32(2)	2.34(3)
Ca(2)–OC(B)$^{\mathrm{VI}}$		2.38(2)	2.29(3)
P–O(1)		1.532(2)	1.534(1)
P–O(2)$^{\mathrm{II}}$		1.530(2)	1.523(2)
P–O(3A)$^{\mathrm{II}}$		1.524(2)	1.518(2)
P–O(3B)		1.522(2)	1.521(2)
Mean		1.527(2)	1.524(2)
C–OC(A)$^{\mathrm{VII}}$		1.224(6)	1.30(1)
C–OC(B)$^{\mathrm{VIII}}$		1.25(2)	1.21(2)
OC(A)–OC(A)$^{\mathrm{VI}}$		2.295(9)	2.48(2)
OC(A)$^{\mathrm{VI}}$–OC(B)$^{\mathrm{IX}}$		1.93(2)	1.94(3)
OC(A)$^{\mathrm{VI}}$–OC(B)$^{\mathrm{X}}$		2.12(2)	2.12(3)
OC(A)$^{\mathrm{XI}}$–C–OC(A)$^{\mathrm{VIII}}$		139.3(6)	144.1(10)
OC(A)$^{\mathrm{XI}}$–C–OC(B)$^{\mathrm{XII}}$		118.2(8)	114.7(14)
OC(A)$^{\mathrm{XII}}$–C–OC(B)$^{\mathrm{VII}}$		102.5(9)	101.2(15)
O(1)–P–O(2)$^{\mathrm{II}}$		111.3(1)	111.20(9)
O(1)–P–O(3A)$^{\mathrm{II}}$		109.79(9)	110.46(9)
O(1)–P–O(3B)		112.38(9)	112.1(1)
O(2)$^{\mathrm{II}}$–P–O(3A)$^{\mathrm{II}}$		108.7(1)	108.6(1)
O(2)$^{\mathrm{II}}$–P–O(3B)		106.4(1)	106.9(1)
O(3A)$^{\mathrm{II}}$–P–O(3B)		108.1(1)	107.5(1)

Notes: (I) $1-x, 1-y, 1-z$; (II) $1-x, 1-y, -z$; (III) $2-x, 1-y, -z$; (IV) $1+x, y, z$; (V) $1-y, x-y-1, z$; (VI) $x-y, x-1, 1-z$; (VII) $x-1, y, z$; (VIII) $-y, x-y-1, z$; (IX) $2-x+y, 1-x, z$; (X) $2-x, -y, 1-z$; (XI) $x-y-1, x-1, 1-y$; (XII) $1-x, -y, 1-z$.

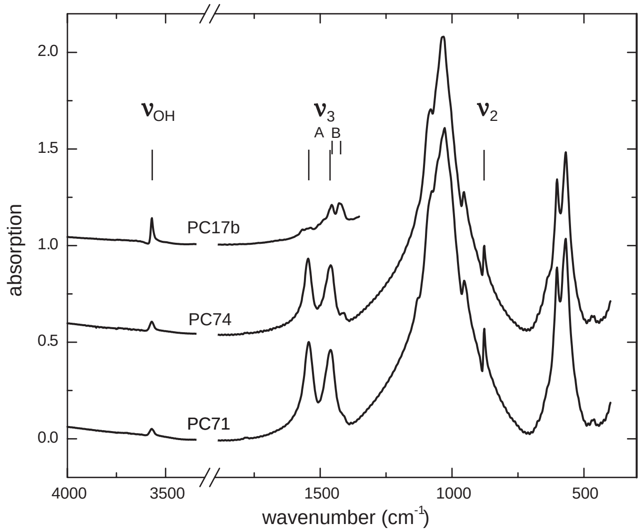

Fig. 1. FTIR spectra of synthetic OH-CAp (PC71, PC74) and OHAp with a small content of carbonate ion, identifying bands due to OH stretching (ν_{OH}), asymmetric stretching of carbonate ions (ν_3), and out-of-plane bending of carbonate ions (ν_2); A and B indicate absorption bands associated with type A (channel) and type B (phosphate) carbonate ions.

apatite channel of the $P\bar{3}$ structure indicates that the type A carbonate ion is ordered at $z = 0.5$ and the channel location at $z = 0.0$ is vacant. The local symmetry of the C atom is $\bar{1}$, and the local environment of a type A carbonate ion is depicted in Fig. 2. Evidently, the type A carbonate ion is oriented with its plane and two of its oxygen atoms close to the *c*-axis; an orientation which we presently refer to as the "closed" configuration. It is located in the channel by six bonds to Ca2 atoms (Fig. 2b), and the Ca–O bond distances are consistent with an ideal distribution of valence units for the carbonate ion oxygens (i.e., 4/3 to C and 1/3 to 2 × Ca). Note that, in the locally ordered structure, the channel location at $z = 0.0$ cannot be occupied by carbonate ions in closed configuration when there are carbonate ions of similar configuration at $z = 0.5$, in agreement with the present ordered $P\bar{3}$ structure.

The present structures were refined with an average atom [OC(A)] representing the two non-equivalent oxygen atoms close to the *c*-axis because their symmetry-related pairs coalesced rendering refinements with separate oxygen atoms unstable. OC(A) is also close to OH(B) in the average CAp structure. Therefore, it was not possible to refine simultaneously both occupancy and displacement parameters for atoms of the channel anions. The refined C–O bond distances, O–C–O bond angles and O–O distances for the type A carbonate ion of PC71 and PC74 (Table 3) are in reasonable agreement with the expected values (e.g., 1.281 Å, 120° and 2.219 Å, respectively, in calcite [34]), taking into account the partial occupancy of the atomic positions, near coincidence of the two axial oxygens, and the relatively large positional displacement/thermal parameters for all of the constituent atoms of the present CAp structures. We did not attempt refinement with a rigid carbonate ion of ideal geometry.

The phosphate groups are displaced slightly from ideal OHAp positions to expand the apatite channel at $z = 0.5$, to better accommodate the carbonate ion, and to contract it at $z = 0.0$. These adjustments are most

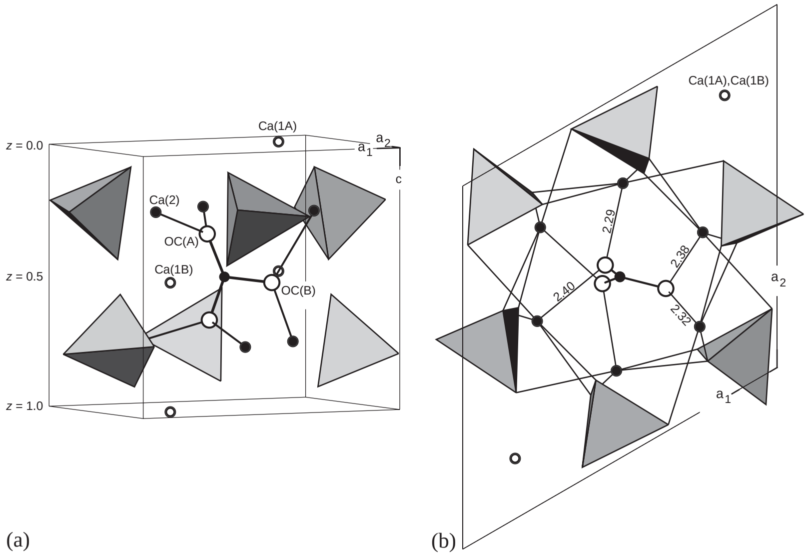

Fig. 2. Structure of high-pressure CAp in space group $P\bar{3}$, showing local ordering of type A carbonate ion at $z = 0.5$ in closed configuration with its plane canted about 12° with respect to the c-axis direction. Symmetry-related type A carbonate ions representing the average structure of the crystal and channel OH ions are not shown: bond distances to Ca(2) atoms are Å.

evident in the change in coordination of Ca(1) atoms. In the $P6_3/m$ structure of OHAp and FAp, Ca(1) has nine nearest-neighbor oxygens in the configuration of a tricapped trigonal prism, which also can be regarded as $6+3$ coordination [9]. In the $P\bar{3}$ structure, Ca(1A), at $z \approx 0.5$, is in a compact six-fold trigonal prismatic coordination, whereas Ca(1B), at $z \approx 0.5$, is in a stretched nine-fold coordination (Table 3).

There are two non-equivalent OH ions with oxygen atoms labelled OH(A) and OH(B) (Table 2). Interestingly, these OH ions are disordered over all possible channel positions, as in the $P6_3/m$ structure of OHAp. It is proposed similarly to other studies that crystals of C-OHAp have a disordered domain structure with locally ordered regions of CAp and OHAp. Moreover, in carbonate-rich C-OHAp, the content of type A carbonate ions is sufficiently high to dominate the overall structure and preserve the regular alternation of carbonate ion at $z \approx 0.5$ and vacancy at $z \approx 0.0$.

Finally, we suggest that the $P\bar{3}$ structure of OH-bearing CAp with the type A carbonate ion in closed configuration may be a more appropriate model for C-OHAp of bone and enamel than the $P\bar{6}$ structure of Suetsugu et al. [22] with the type A carbonate ion in open configuration. The method of synthesis of CAp was similar in both studies. However, the CAp crystal investigated by Suetsugu et al. [22] was synthesized at somewhat lower pressure (0.55 kbar, under Ar gas) with excess $CaCO_3$ reagent [21], which resulted in a high content of type B carbonate ion (0.5 pfu). Note that the refinement of the X-ray structure of this crystal was made with a constrained (ideal) carbonate ion geometry and resulted in very large displacement parameters for the two carbonate oxygen atoms that do not lie on the c-axis. The closed configuration for the type A carbonate ion appears to better fit the channel cavity (Fig. 2) at low contents of type B carbonate ion, whereas the open configuration requires considerable disruption of the basic apatite structure. On the other hand, the $P\bar{3}$ structure could represent a higher pressure modification of type A CAp. However, the good agreement for unit-cell parameters and FTIR spectra with the type A (C,OH)Ap solid solutions of Bonel [29], which were synthesized at low pressure in an atmosphere of CO_2 at 900°C, suggests that, in the present synthesis, the effect of the high pressure was mainly to confine a volatile component in a high-temperature reaction. In respect to unit-cell parameters and infrared spectrum, our CAp product appears to be equivalent to type A CAp synthesized in other studies and, like these earlier products, it is seemingly connected to the type A apatite component of bone and enamel by similarity in the asymmetric stretching vibration (ν_3) doublet bands in infrared spectra. This discussion will be continued elsewhere.

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