EPSC644 Biomineralization

“Accommodation of the carbonate ion in hydroxyapatite”

Fleet, Liu and King (2004)

$$[{}^{A}CO_3 + {}^{A}\square = 2OH]$$

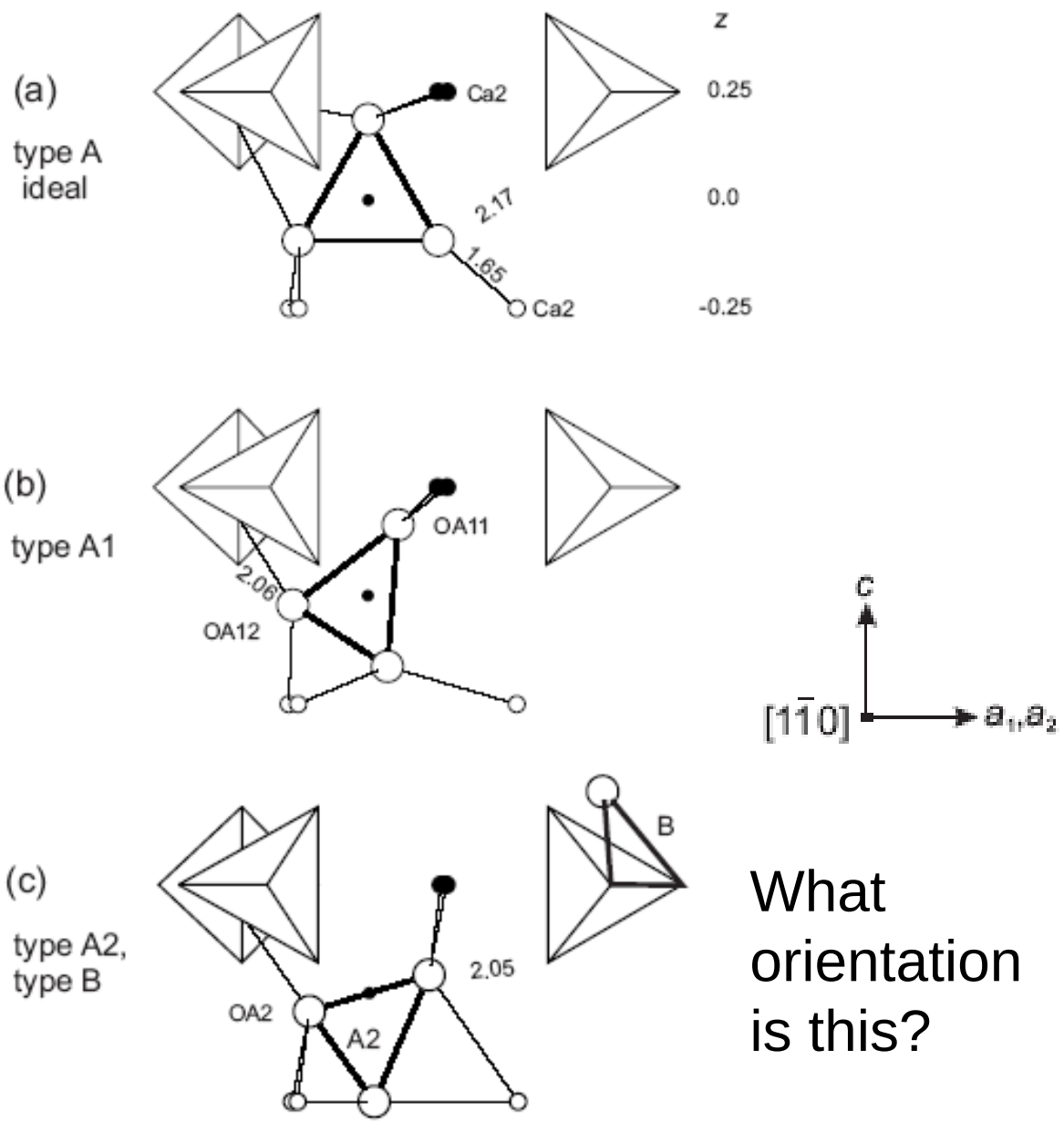
What does this equation describe?

Is anything missing from this equation?

Fig. 1

Fleet et al. (2004)

Caption mentions "…prohibitively short Ca-O and O-O distances (Å) are indicated; drawn with ATOMS (Dowty 1995)…"
What does this mean?



What orientation is this?

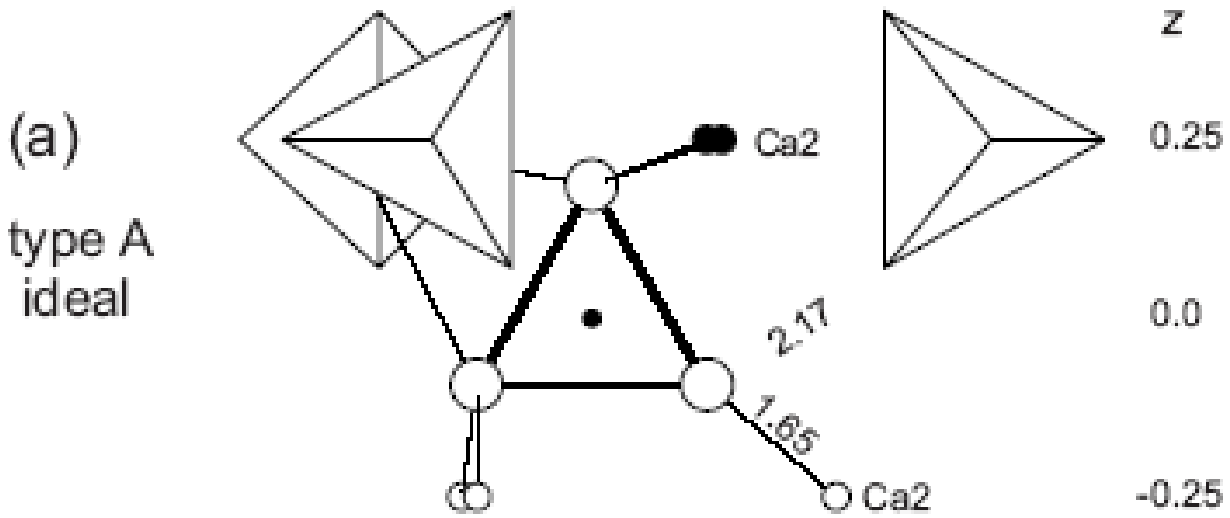
THE SPACE PROBLEM

Accommodation of carbonate by OHAp

The accommodation of the carbonate ion in the *c*-axis channel of hydroxylapatite is not a straightforward atom-for-atom substitution.

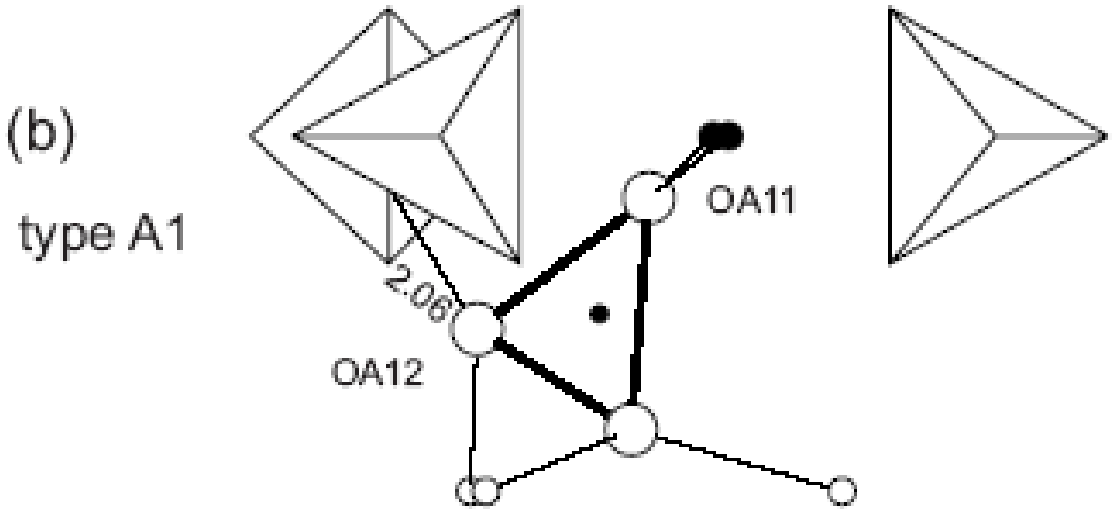
Compared with OH^-, carbonate is a bulky divalent anion (essentially a cluster of three non-bonded oxygen atoms replacing one), so that its accommodation in OHAp requires both displacement of atoms in the channel wall and redistributionof Ca-O bonds.

The type B carbonate ion is seemingly accommodated more readily, but still requires displacement of the second O3 atom away from the bonding sphere of the carbonate ion and extension of the overall structure in the *c*-axis direction.

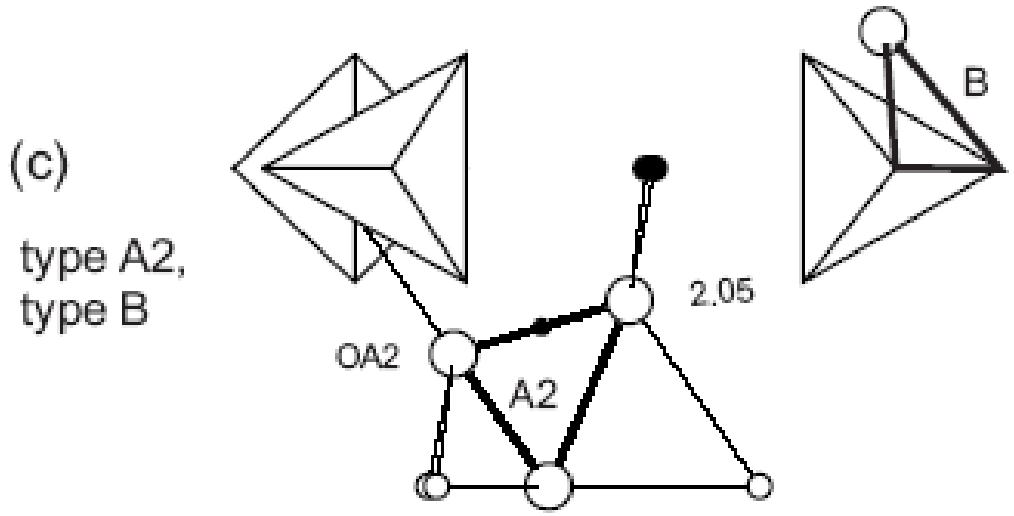


When a carbonate ion of ideal geometry is inserted into the channel of OHAp with the apical oxygen atom coincident with the position of OH, as in Figure 1a, it is evident that the other two (transverse) carbonate oxygen atoms interact unfavorably with the tricluster of Ca2 cations at z = –0.25. In the limiting orientation of Figure 1a, one of these oxygen atoms makes a short (1.65 Å) bond with a Ca2 atom and a short (2.17 Å) non-bonded O…O interaction with O3 of the nearby PO4 tetrahedron.

Clearly, the carbonate ion has to be twisted about the *c*-axis to optimize Ca-O and O-O distances, but this still leaves unacceptably short interactions in the absence of other displacements.



The type A1 carbonate ion is oriented with two of its oxygen atoms (OA11) close to the *c*-axis and its plane canted from the vertical by ~12°. It is located in the apatite channel by six bonds to Ca2 atoms, giving Ca2-O bond distances consistent with an ideal distribution of valence units for the carbonate ion oxygen atoms (i.e., 4/3 to C and 1/3 to 2 × Ca2).



This last possibility is described as a

"second (stuffed) channel position characterized by IR bands at 1563 and 1506 cm–1, which was present in subordinate amounts and appeared to charge-compensate the substitution of PO_4^{3-} by CO_3^{2-} (type A2 carbonate; Fig. 1c)."

$$[{}^{A}CO_3 + {}^{A}\square = 2OH]$$

What does this equation describe?

Is anything missing from this equation?

Maryam asked…

“Can we calculate how the morphology of hydroxylapatite would be modified by the presence of carbonate groups substituted in its structure?”

- Concept of equilibrium morphology: for every crystalline structure, there is a theoretical morphology corresponding to its lowest Gibbs free energy.

    - each single crystal is bound by surfaces offering the possible lowest density of unsatisfied bonds

    - this is how a crystalline solid would rearrange itself if it could freely break and reform bonds in a vacuum

- But during crystal growth from solution, the surface interacts with the solvent and its solutes.

    - what is the nature of those interactions?

TABLE 1. Synthesis experiments

Experiment	Starting composition*	*P* (GPa)	*T* (°C)	Time (hours)	Products†	Reference‡
PC16	9:1	4	1400	5.5	type A C-OHAp + Cc§	3
PC56	9:1	3	1400	5.5	type A CAp + Cc§	3
PC71	9:1	2	1400	6	type A CAp	1
PC74	9:1	2	1500	12	type A CAp	1
PC17	8:2	3	1400	5.5	type B C-OHAp	3
PC55	8:2	3	1400	5.5	type A-B CAp + Cc#	2
PC73	8:2	2	1450	6	type A-B CAp + Cc	3
PC18	7:3	3	1400	5.5	type A-B CAp + melt	3
PC53	7:3	3	1400	5.5		
			1000	13	type A-B CAp + Cc	3
PC57	7:3	3	1400	5.5	type A-B CAp + melt	3
PC59	7:3	3	1500	5.5	type A-B CAp + melt	3
PC26	6:4	2	1350	5.5	type A-B CAp + melt	3
PC58	7:2:1	2	1400	5.5	type B CFAp + melt	3

* Starting composition is proportion of 1/3($Ca_2P_2O_7$+CaO):$CaCO_3$; for PC58 proportion is for 1/3($Ca_2P_2O_7$+CaO):CaCO3:CaF_2.

† Melt is carbonate rich.

‡ 1 is Fleet and Liu (2003); 2 is Fleet and Liu (2004); 3 is present study.

§ Trace amounts of calcite (Cc).

PC55 products were used for annealing experiments at 1000 °C for 15 and 30 minutes, and 12 and 24 hours.

TABLE 5. Selected bond distances (Å)

		PC17 xt372	PC16 xt374	PC18 xt371	PC18 xt373
Ca1-O1	× 3	2.407(1)	2.409(1)	2.420(1)	2.419(1)
Ca1-O2a	× 3	2.458(1)	2.464(2)	2.479(1)	2.479(1)
Ca1-O3a	× 3	2.808(2)	2.814(2)	2.809(2)	2.808(2)
Mean		2.558	2.562	2.569	2.569
Ca2-O1b		2.708(2)	2.707(2)	2.716(2)	2.715(2)
Ca2-O2c		2.356(2)	2.350(2)	2.342(2)	2.341(2)
Ca2-O3d	× 2	2.510(2)	2.526(2)	2.557(2)	2.554(2)
Ca2-O3e	× 2	2.349(1)	2.344(2)	2.352(2)	2.355(1)
Mean		2.464	2.466	2.480	2.479
Ca2-O4		2.391(1)	2.411(1)	2.4089(6)	2.413*
P-O1		1.530(2)	1.537(2)	1.525(2)	1.526(2)
P-O2		1.533(2)	1.529(2)	1.513(2)	1.512(2)
P-O3	× 2	1.526(2)	1.527(2)	1.521(2)	1.521(2)
Mean		1.529	1.530	1.520	1.520

Notes: a = 1 – *x*, 1 – *y*, –*z*; b = 1 – y, *x* – *y*, *z*; c = 1 – *x* + *y*, 1 – *x*, *z*; d = 1 + *x*, *y*, *z*; e = 1 + *x* – *y*, *x*, –*z*.

* O4 (of type A2 carbonate and OH^- ions) not on *c* axis, resulting in three values for Ca2-O4 in the average structure, varying from 2.276 to 2.484 Δ.

TABLE 3. Experimental details for X-ray structural analysis

Experiment	PC17	PC16	PC18 nujol stored	PC18 dry stored
Crystal	xt372	xt374	xt371	xt373
Crystal size ($mm^3 \times 10^3$)	0.13	0.23	0.49	0.21
Crystal shape	prism	prism	cube	tablet
Formula weight	1003.8	1008.3	1017.5	1019.8
D_x (g/cm^3)	3.150	3.148	3.153	3.159
Reflections – unique	561	565	569	570
- number, with ($I<3\sigma_{(I)}$)	264	277	308	252
- R_{Int}*	0.034	0.035	0.029	0.027
Refined parameters	44	43	57	56
μ* (cm^{-1})	29.2	29.2	28.7	28.6
R†	0.025	0.025	0.025	0.025
R_w†	0.023	0.024	0.021	0.022
s†	1.25	1.35	1.19	1.35
Extinction (x 10^4)	1.04(7)	0.26(6)	0.51(6)	0.29(6)
Δρ‡ ($e/Å^3$) (+)	0.60	0.58	0.50	0.47
(-)	0.37	0.42	0.39	0.47

* R_{int} is residual index for intensities of equivalent reflections; μ is linear absorption coefficient.

† Least-squares refinement parameters: *R* is residual index; R_w is weighted residual index; s is goodness-of-fit.

‡ Δ is residual electron density.

TABLE 4. Atomic coordinates and isotropic displacement parameters (Å^2)

		$U_{eq} = (1/3)\ \Sigma_i\Sigma_j\ U^{ij}\ a^i a^j\ \mathbf{a}_i.\mathbf{a}_j$			
	Site occupancy	*x*	*y*	*z*	*U*,U_{eq}
		xt372 (PC17)			
Ca1	1.0	2/3	1/3	0.0017(1)	0.0148(5)
Ca2	1.0	0.99304(8)	0.24700(8)	1/4	0.0137(2)
P	0.976(3)	0.3688(1)	0.3988(1)	1/4	0.0101(3)
O1	1.0	0.4845(2)	0.3289(2)	1/4	0.0150(5)
O2	1.0	0.4649(2)	0.5866(2)	1/4	0.0200(6)
O3	0.988	0.2580(2)	0.3432(2)	0.0714(2)	0.0240(4)
O4	0.5	0	0	0.1950(7)	0.023(2)
H	0.72(5)	0	0	0.053*	0.023*
OB3	0.014(3)	0.36*	0.43*	0.47*	0.025*
		xt374 (PC16)			
Ca1	1.0	2/3	1/3	0.0018(1)	0.0156(5)
Ca2	1.0	0.99268(8)	0.24830(9)	1/4	0.0158(2)
P	1.0	0.3689(1)	0.3993(1)	1/4	0.0130(3)
O1	1.0	0.4845(2)	0.3287(2)	1/4	0.0151(5)
O2	1.0	0.4649(3)	0.5862(2)	1/4	0.0234(7)
O3	1.0	0.2587(2)	0.3435(2)	0.0710(2)	0.0285(5)
O4	0.5	0	0	0.1949(8)	0.035(3)
H	0.65(6)	0	0	0.53*	0.035*
C	0.01*	0	0	0	0.025*
OA12	0.012(3)	0.944*	0.126*	0.527*	0.025*

Limitations of X-ray diffraction:

Because of their extensive overlap and very weak electron density contributions, it was not possible to refine simultaneously both occupancy and displacement parameters for atoms of the carbonate ions.

(Elements with low atomic numbers, such as C, are difficult to locate precisely within the unit cell…)

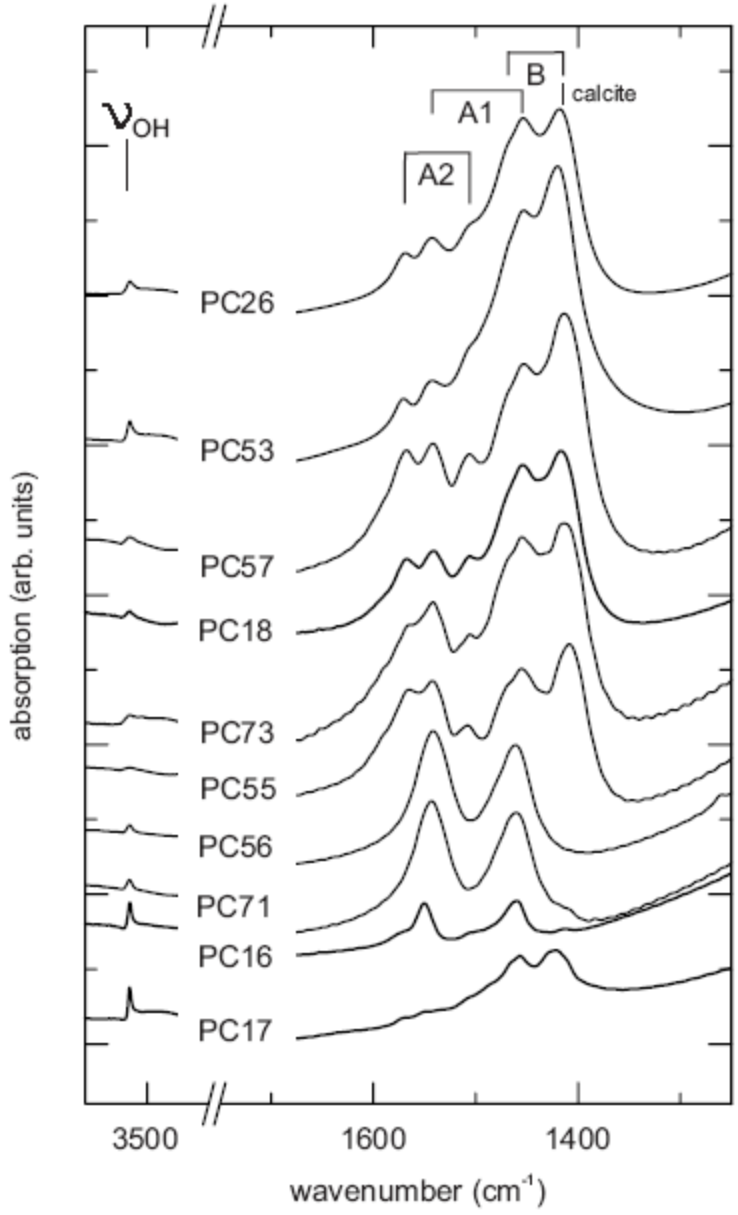


FIGURE 2. FTIR spectra of products of piston-cylinder experiments:

The C-O bond has characteristic vibration modes that can be identified by Fourier Transform Infra-Red spectroscopy.

The C-O bond does not have the same environment in the different types of substitutions. Could you show this using the GEOMETRY file?

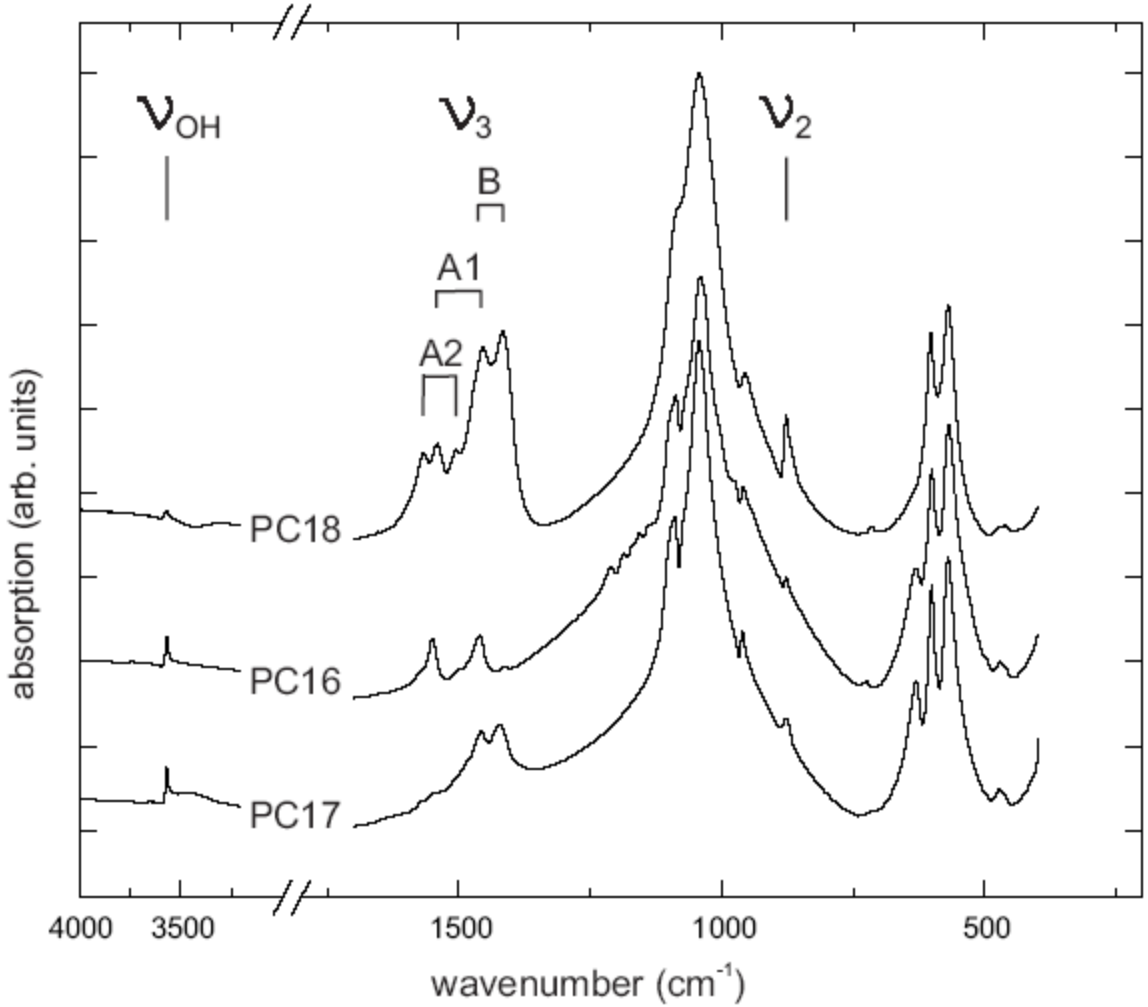


FIGURE 3. FTIR spectra for synthesis experiments yielding apatites investigated by X-ray structural analysis in this study, identifying bands due to OH stretching (ν_{OH}) and asymmetric stretching (ν_3) and out-of-plane bending (ν_2) of carbonate ion: PC17 is type B C-OHAp; PC16 is type A C-OHAp; and PC18 is type A-B CAp; note the relatively high content of OH in PC17 and PC16 (see Table 2 footnote).

In summary, the FTIR spectra (Figs. 2–5) may be used to infer information on OH^- and CO_3^{2-} in the experimental products, in the following manner:

(1) the area of the sharp band at ~3570 cm–1 is proportional to the content of OH– in the apatite channel,

with PC71 containing about 0.25 $(OH)_2$ per formula unit (pfu);

(2) calcite is characterized by a singlet carbonate asymmetric stretching band at ~1410 cm–1;

(3) type B carbonate is characterized by the doublet of the high-frequency shoulder to the ~1455 cm–1 band and the band at ~1410 cm–1;

(4) type A1 carbonate is characterized by the doublet of bands at ~1540 and ~1455 cm–1;

(5) type A2 carbonate is characterized by the doublet of bands at ~1565 and ~1505 cm–1.

However, the entry of moderate amounts of carbonate ion into the stuffed A2 channel location does appear to be a high-pressure feature.

Bands attributable to type A2 carbonate are only weakly present in IR spectra of low-pressure CAp, as a sharp peak or shoulder at ~1500 cm–1 and diffuse absorption at higher frequency (Nelson and Featherstone 1982; Vignoles et al. 1988; Barralet et al. 1998; Suetsugu et al. 1998).

Therefore, charge compensation for carbonate-for-phosphate substitution in low-pressure CAp is different from that in high-pressure CAp.

Description of substitution scheme in high-pressure carbonate-hydroxylapatite:

$$[^{A2}CO_3 + 2^{B}CO_3 = {}^{A2}\square + 2PO_4]$$

And a formula for high-pressure CAp:

$$Ca_{10}(PO_4)_{6-y}(CO_3)_y[(CO_3)_{x+(1/2)y}(OH)_{2-2x}] \quad (3)$$

Likely, the incorporation of carbonate ions in low-temperature, biogenic hydroxylapatite involves nonstoichiometry in the Ca positions, as well as partial substitution of Ca by Na, in bone and enamel.

Can you suggest a substitution scheme (written as an equation) involving the OH^- and CO_3^{2-} groups, as well as Ca^{2+} and Na^+ ?

Would your suggestion(s) result in non-stoichiometry in the Ca positions?

If this is the formula for a high-pressure carbonate-hydroxylapatite…

$$Ca_{10}(PO_4)_{6-y}(CO_3)_y[(CO_3)_{x+(1/2)y}(OH)_{2-2x}]$$

How would we write the formula for the low-pressure carbonate-hydroxylapatite?