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Effects of carbonate on hydroxyapatite formed from $CaHPO_4$ and $Ca_4(PO_4)_2O$

Jacqueline Lee Sturgeon · Paul Wencil Brown

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Abstract Carbonated hydroxyapatites were formed via reactions in $NaHCO_3$/NaH_2PO_4 solutions from a mixture of particulate tetracalcium phosphate (TetCP) and anhydrous dicalcium phosphate (DCPA). Reactions were followed by determinations of pH and ion concentrations. The solids formed were analyzed by XRD and FTIR. Rates of heat evolution were established by isothermal calorimetry. Reactions in the absence of NaH_2PO_4 did not reach completion within 24 h. Constitution of reactants to achieve a DCPA-to-$NaHCO_3$ ratio of 1, in conjunction with the presence of NaH_2PO_4 as a buffer, was found to be optimal for formation of apatite with no remaining reactant. The amount of carbonate incorporated in this apatite was 4–5 wt%. Calorimetry indicated the reaction mechanism to depend on the bicarbonate concentration in solution. The presence of NaH_2PO_4 was found to increase the reaction rate but decrease the extent of carbonate uptake.

1 Introduction

Hydroxyapatite is the mineral component of bones and teeth. Many substitutions can occur within this structure; those most significant physiologically include carbonate, fluoride, magnesium, and sodium [1]. The amount of carbonate present in biological apatite varies; enamel typically contains 3.5 wt% while bone typically incorporates approximately 7.4 wt% [1]. The presence of carbonate in HAp increases its solubility [2]. Because this is of consequence for bone remodeling and caries formation, many studies related to carbonate substitution have been performed. Carbonate can substitute in two locations in the HAp structure, namely in the phosphate and hydroxyl group sites. These substitutions are known as type B and type A, respectively. Apatite containing type A substitutions usually forms at high temperatures, while type B apatite forms at low temperatures. However, type A substitution has been observed with low carbonate content in aqueous solutions [3]. Both types of substitutions occur simultaneously in biological apatites [4], although the type B substitution accounts for approximately 90% of the carbonate [5].

Most studies of type B carbonate incorporation into apatites have been carried out by relying on precipitation of particulate apatite from soluble calcium and phosphate sources. Gibson and Bonfield [6] employed a Ca/P ratio of 1.76 during the initial synthesis step of an AB-type carbonated apatite from solutions of calcium hydroxide and phosphoric acid. However, it is of interest to establish substitutional chemistries of apatites that can be formed as continuous solids rather than as precipitates. Consequently, the current study focused on apatites formed by cement-type reactions. The precursor phases were tetracalcium phosphate ($Ca_4(PO_4)_2O$, TetCP) and dicalcium phosphate anhydrous ($CaHPO_4$, DCPA) and their reactions at physiologic temperature to form stoichiometric and calcium-deficient HAp have been well studied [7–10]. While the effects of carbonate additions on apatites formed in this manner have also been examined [10–12] the simultaneous effects of carbonate substitution and buffering to avoid tissue damaging pH values have not received appropriate evaluation. Thus, the objective of this study was to establish the effects on carbonate substitution on the kinetics of

J. L. Sturgeon · P. W. Brown (✉)
Department of Materials Science and Engineering,
The Pennsylvania State University, 136 Materials Research
Laboratory Building, University Park, PA 16802, USA
e-mail: etx@psu.edu

HAp formation and on the variations in solution chemistry. Experiments were designed to elucidate the kinetics and solution chemistry pertinent to the formation of calcium-deficient carbonated apatite via a cement-type reaction of particulate calcium-phosphate precursor phases. Depending on the molar ratios of these reactants, a range of HAp compositions can theoretically be formed. In particular if the $CaHPO_4$-to-$Ca_4(PO_4)_2O$ ratio is 1-to-1, stoichiometric HAp forms. In the absence of carbonate, if the ratio is 2-to-1, the calcium deficient composition $Ca_9HPO_4(PO_4)_5OH$ forms. In general, $Ca_{(10-x)}(HPO_4)_x(PO_4)_{(6-x)}(OH)_{(2-x)}$ forms and x ranges from 0 to 1 where the $CaHPO_4$-to-$Ca_4(PO_4)_2O$ mol ratio is $(1 + x)$-to-1.

In the presence of sodium bicarbonate, a broad range of HAp compositions can be formed. This is because Na can partially substitute for Ca, and carbonate can substitute either for phosphate or for hydroxyl. The chemistry is further complicated by the opportunity for the formation of $CaCO_3$ if its solubility product is significantly exceeded.

In the present study, the effects of sodium bicarbonate on the reaction of $CaHPO_4$ and $Ca_4(PO_4)_2O$ were examined when the Ca/P ratio was maintained at 1.8. This ratio was selected because 1.8 is near the ratio typical of mature bone apatite which is 1.7 [1]. This ratio can be realized by reacting $CaHPO_4$ and $Ca_4(PO_4)_2O$ at a molar ratio of 1:2. However, reacting these constituents at this ratio would not be expected to produce calcium deficient compositions unless other substituents are available. In particular, carbonate for phosphate substitution is required.

The full range of compositions that can form in the presence of sodium bicarbonate can be expressed as follows:

$$\begin{aligned}&CaHPO_4 + 2Ca_4(PO_4)_2O + xNaHCO_3(aq)\\&\rightarrow \text{carbonated HAp} \left(+ Na_2HPO_4(aq)\right.\\&\left.+ NaOH(aq) + CaCO_3\right)\end{aligned} \tag{1}$$

According to LeGeros, approximately 3 mol of carbonate can be added to the structure before calcite is precipitated [1]. The products formed are anticipated to exhibit a dependence on the proportion of $NaHCO_3$ present. When $x = 1$, the limiting compositions that can theoretically form are $Ca_9Na(PO_4)_5(CO_3)(OH)_2$ and $Ca_9CO_3(PO_4)_5OH + NaOH(aq)$. Although the formation of compositions at the Na-rich end are unlikely, this compositional range can be expressed as $Ca_9Na_{(1-x)}(PO_4)_5(CO_3)_x(OH)_{(2-x)} + xNaOH(aq)$.

At values of $x < 1$, insufficient carbonate is available to permit only the formation of HAp. At values of $x > 1$, excessive carbonate is present. In these instances, a variety of compositions are possible. On the low end, vacancies in the phosphate sites would be necessary. As this is an unlikely site for a vacancy [13], the low concentration should have the most difficulty forming a carbonated apatite and completely reacting. When $x > 1$, more possibilities for carbonate incorporation exist, and allow for a variety of substitutions.

In the event that a sodium hydroxide solution evolves, the associated pH would likely be aggressive if such a reaction occurred in vivo. Consequently, the effect of a buffer to limit the resultant pH was evaluated. Sodium phosphate monobasic was therefore proportioned to buffer the sodium hydroxide produced. The reaction anticipated is:

$$\begin{aligned}&2Ca_4(PO_4)_2O + CaHPO_4 + NaHCO_3(aq)\\&+ NaH_2PO_4(aq) \rightarrow Ca_9(PO_4)_5CO_3OH\\&+ Na_2HPO_4(aq) + H_2O\end{aligned} \tag{2}$$

The effects of the presence of this buffer were evaluated by determination of pH, calorimetry and X-ray diffraction analyses. The presence of NaH_2PO_4 also provides supplemental phosphate, which would be advantageous when $x < 1$, as discussed above.

2 Materials and methods

TetCP was synthesized by milling $CaCO_3$ and monocalcium phosphate monohydrate ($Ca(H_2PO_4)_2 \cdot H_2O$, MCPM) for 16 h and firing the product at 1400°C for 1 h followed by rapid quenching. TetCP phase purity was confirmed by X-ray diffraction analysis. TetCP was ground in a mortar and pestle and sieved through a 38 μm mesh screen, ball milled and attrition milled to a particle size of approximately 1–2 μm. Finally, the TetCP was mixed with MCPM in a molar ratio 13:2 and milled for 24 h. All milling was performed in anhydrous heptane. The powder was stored in a sealed desiccator. Solutions of $NaHCO_3$ in distilled water, with $NaH_2PO_4 \cdot H_2O$ as appropriate, were made just prior to their use in experiments. Solution concentrations were calculated with respect to $CaHPO_4$ such that the amount of $NaHCO_3$ was added in a molar ratio of 0.5, 1.0, or 1.5 times $CaHPO_4$ (i.e. $x = 0.5$, 1.0, or 1.5 in Eq. 1).

Variations in solution chemistry during hydrolysis in water and in sodium bicarbonate solutions, with and without buffer, were followed in two ways. First, the pH was measured using an Orion pH electrode attached to an Orion 920 digital pH meter. The slurries were placed in Nalgene beakers in a glass jacketed reaction vessel attached to a water bath maintained at 37°C. The solutions were stirred and nitrogen gas was bubbled through the slurries for the duration of the experiments. For the second set of experiments, slurries were stored in plastic vials without agitation for up to 7 days at 37°C. Aliquots were removed from these vials and passed through 0.2 μm filters and the liquids analyzed. Ca and Na concentrations were measured using atomic absorption spectroscopy, and PO_4 and C (for CO_3) concentrations were measured using ion chromatography. After 24 h, the solids were filtered from the liquid, and rinsed with distilled water followed by acetone. Both sets of solution chemistry experiments were carried out at a liquid-to-solids ratio of 50-to-1.

Isothermal calorimetry was performed to determine the kinetics of reaction in the absence and presence of buffers. The powder precursors and liquid solutions were placed in the calorimeter and allowed to equilibrate for 30 min before the liquid was injected onto the powder. A liquid to solid ratio of 3-to-1 was used in these samples. A datum point was collected every 3 s over 24 h. The temperature was maintained at 37°C by an attached water bath.

X-ray diffraction analyses were performed using a Scintag 2 diffractometer (Scintag, Inc., Sunnyvale, CA). The samples were scanned from 20 to 40° 2θ using a step scan in 0.02 increments and 4° per minute. Phase formation was assessed by comparing the patterns to ICDD cards 25-1137, 9-80, and 9-432, or TetCP, DCPA, and HAp, respectively.

Infrared spectroscopy was performed using a Nicolet Nexus 670 FT-IR spectrometer using the MCT detector mode. Potassium bromide pellets with 1 wt% sample powder were pressed under vacuum. Changes with heating were assessed by thermogravimetric analysis (SDT 2960, TA Instruments, New Castle, DE) using a heating rate of 10°C/min to 1000°C under a nitrogen atmosphere.

3 Results and discussion

Figure 1 shows the pH variations over the first 24 h of reaction. Reactions in water and in the $NaHCO_3$ solutions elevate the pH to a value near 12 regardless of $NaHCO_3$ proportion. There is no practical distinction between the variations in pH when reaction occurred in water, at a $NaHCO_3$-to-$CaHPO_4$ molar ratio of 0.5, and at a $NaHCO_3$-to-$CaHPO_4$ molar ratio of 1.0. The behavior at the $NaHCO_3$-to-$CaHPO_4$ molar ratio of 1.5 suggests that this solution develops some buffer capacity in that a rapid elevation in pH initiating after about 8 h does not occur. This behavior is consistent with the formation of $Na_xH_{(3-x)}PO_4$ solution. Eventually, however, elevation to pH $\sim$12, indicative of the formation of a NaOH solution, does occur. These data indicate limited incorporation of Na into the HAp and also indicate that in vivo formation of these compositions could be problematic with regard to producing locally aggressive conditions.

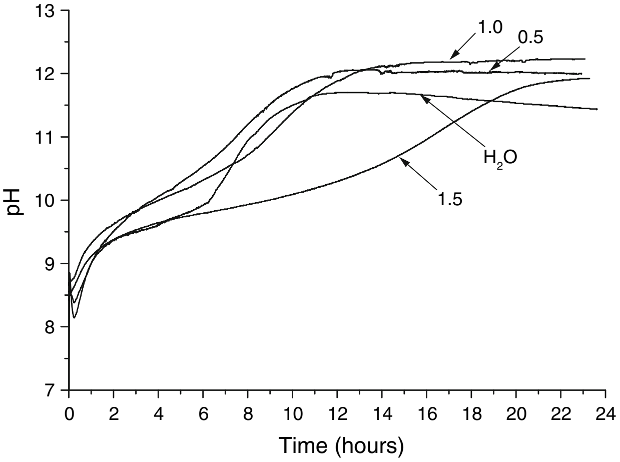

Fig. 1 Variation in pH over 24 h when a TetCP/DCP mixture with Ca/P ratio of 1.8 is reacted in $NaHCO_3$ solutions with $NaHCO_3$-to-$CaHPO_4$ ratios of 0.5, 1.0, and 1.5 and in water

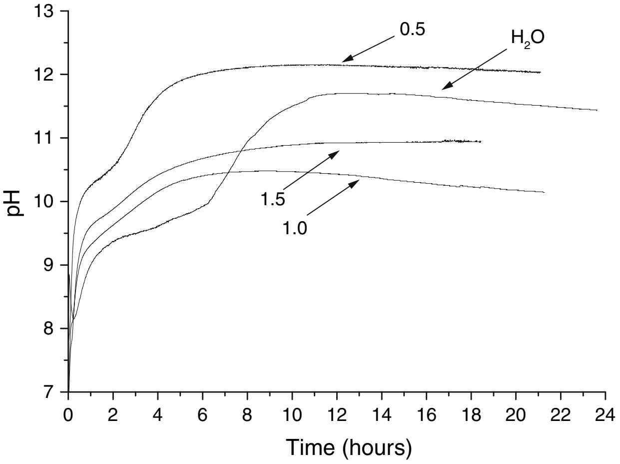

Fig. 2 Variation in pH over 24 h when a TetCP/DCP mixture with Ca/P ratio of 1.8 is reacted in water or $NaHCO_3$ solutions containing equimolar amounts of NaH_2PO_4 added

To offset the increase in pH due to NaOH formation, hydrolysis reactions were carried out in the presence of NaH_2PO_4 "buffer." Sufficient NaH_2PO_4 was present to react with the NaOH to produce Na_2HPO_4. Figure 2 shows the variations in pH during the first 24 h of reaction. With the exception of molar ratio $NaHCO_3$-to-$CaHPO_4$ of 0.5-to-1, the use of this buffer limited the pH values of the bicarbonate solutions. While behavior similar to that in unbuffered solutions was observed, the changes in pH occurred more rapidly and pH maxima were lower. A pH maximum for $NaHCO_3$-to-$CaHPO_4$ of 1-to-1 was reached in 4 h compared to 12 h in unbuffered solution. A pH maximum in the solution where the $NaHCO_3$-to-$CaHPO_4$ ratio is 1.5-to-1 occurred in 8 h versus approximately 24 h in unbuffered solution. The behavior when the molar ratio of $NaHCO_3$-to-$CaHPO_4$ is 0.5-to-1, is anomalous. Although reaction was accelerated when compared to that in unbuffered solution, there was no reduction in pH. If a

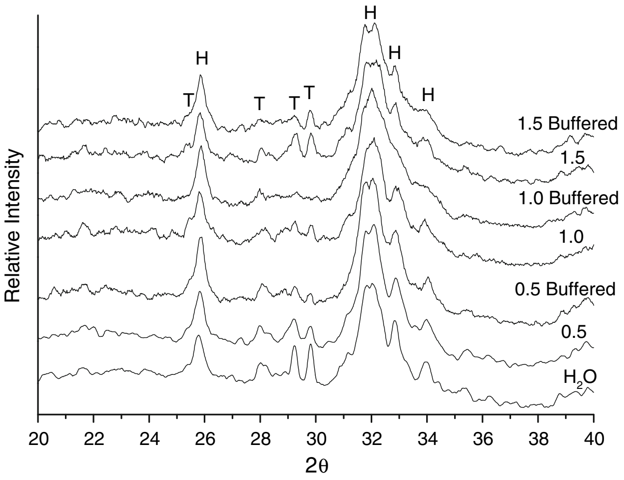

Fig. 3 XRD patterns of solids obtained after 24 h of reaction in water and various $NaHCO_3$ or $NaHCO_3/NaH_2PO_4$ solutions. T and H represent TetCP and HAp peaks, respectively

portion of the supplementary phosphate added as a buffer is consumed in the formation of HAp, then the pH will be elevated because of NaOH formation according to the following equation:

$$2Ca_4(PO_4)_2O + CaHPO_4 + 0.5NaHCO_3 + 0.5NaH_2PO_4 \rightarrow Ca_9(CO_3)_{0.5}(PO_4)_{5.5}(OH)_{0.5} + NaOH + 0.5H_2O.$$

As shown in Fig. 3, X-ray diffraction analyses of the powders indicated the formation of HAp in all instances. However, residual TetCP was observed in almost all samples that had hydrolyzed for 24 h. Hydrolysis in water resulted in the greatest proportion of residual TetCP. This accords with prior results in that the reactions will occur in two stages. In the first the $CaHPO_4$ will be consumed to produce HAp. Subsequently, TetCP will slowly hydrolyze over a period of weeks to produce HAp and $Ca(OH)_2$ [14]. Residual TetCP was present after hydrolysis for 24 h in solutions where the $NaHCO_3$-to-$CaHPO_4$ mole ratio was 0.5 or 1.5 regardless of whether the solutions were buffered or non-buffered.

Although residual TetCP remained after 24 h of hydrolysis in the unbuffered system when the mole ratio was 1.0, buffering allowed the hydrolysis reaction to approach completion. With buffer present, the lowered pH permitted the consumption of TetCP and formation of carbonated apatite to approach completion as shown in Eq. 2. These data, in combination with pH data in Fig. 2, indicate an optimum proportion of constituents can produce carbonated HAp in the absence of excessively elevated pH values. Alternatively, in buffered solution having a mole ratio of 0.5, NaOH forms because the buffer is consumed.

Based on these results, solution chemistry analyses were limited to systems where the mole ratio of $NaHCO_3$-to-$CaHPO_4$ was 1.0. Both buffered and non-buffered solutions were studied and variations in solution chemistry over 7 days were compared to those in water. X-ray diffraction analyses were carried out in association with solution chemistry analyses. These showed the intensities of TetCP peaks continuously decreased. When hydrolysis was carried out in water, residual TetCP was still present at the end of the experiments. When hydrolysis was carried out in non-buffered solutions, the TetCP was consumed between 3 and 7 days. TetCP was consumed within 24 h of hydrolysis in buffered solution. The variations in ion concentrations during this period of reaction are plotted in Fig. 4.

Figure 4a shows a small Na background in the sample hydrolyzed in water. In addition, atmospheric exposure to air resulted in minor carbonate uptake. The calcium concentration remained nominally constant for 24 h but then increased. This increase is likely associated with the continued hydrolysis of TetCP after the exhaustion of $CaHPO_4$. The concentration of phosphate ion decreased to below the limit of detection after 16 h; this also indicates that HAp formation by reaction between TetCP and DCPA approaches completion over this time period. As described above, unreacted TetCP persisted throughout the duration of this experiment.

Variations in ion concentration during hydrolysis in unbuffered carbonate solution are shown in Fig. 4b. Except for a minor decrease in [P_i], the variations in ion concentrations appear to be complete at 24 h. In spite of this, a small proportion of residual TetCP persists for 3 days. The presence of $NaHCO_3$ has a significant effect on [Ca] and [P_i]. [Ca] remains low throughout and is lower than when hydrolysis is carried out in water. The common ion effect of hydroxyl involving NaOH depressed the calcium ion concentration in solution. [P_i] shows a concentration spike of about 24 h in duration; the duration of the [P_i] spike and maximum concentration reached is higher in the unbuffered carbonate solution than in water. [CO_3] remains constant for about 16 h; between 16 and 24 h it deceases to a value that remains constant thereafter. Not all the available carbonate was consumed thereby indicating that the (PO_4)-to-(CO_3) ratio in the solid is greater than 5-to-1 as it would be if $Ca_9Na_{(1-x)}(PO_4)_5(CO_3)(OH)_{(2-x)}$ had formed. [Na] decreased as well indicating uptake during HAp formation. [CO_3], [Na] and [P_i] decrease in concert. These data indicate an uptake of Na and carbonate that would be in accord with paired substitution. These data also indicate the formation of HAp of composition $Ca_{(10-a-b)}[\ ]_a Na_b (PO_4)_{6-y}(CO_3)_y(OH)_{(2-x)}$, where [ ] is a vacancy and $2(10 - a - b) + b = 3(6 - y) + 2y + (2 - x)$ to maintain electroneutrality. The elevated pH condition under

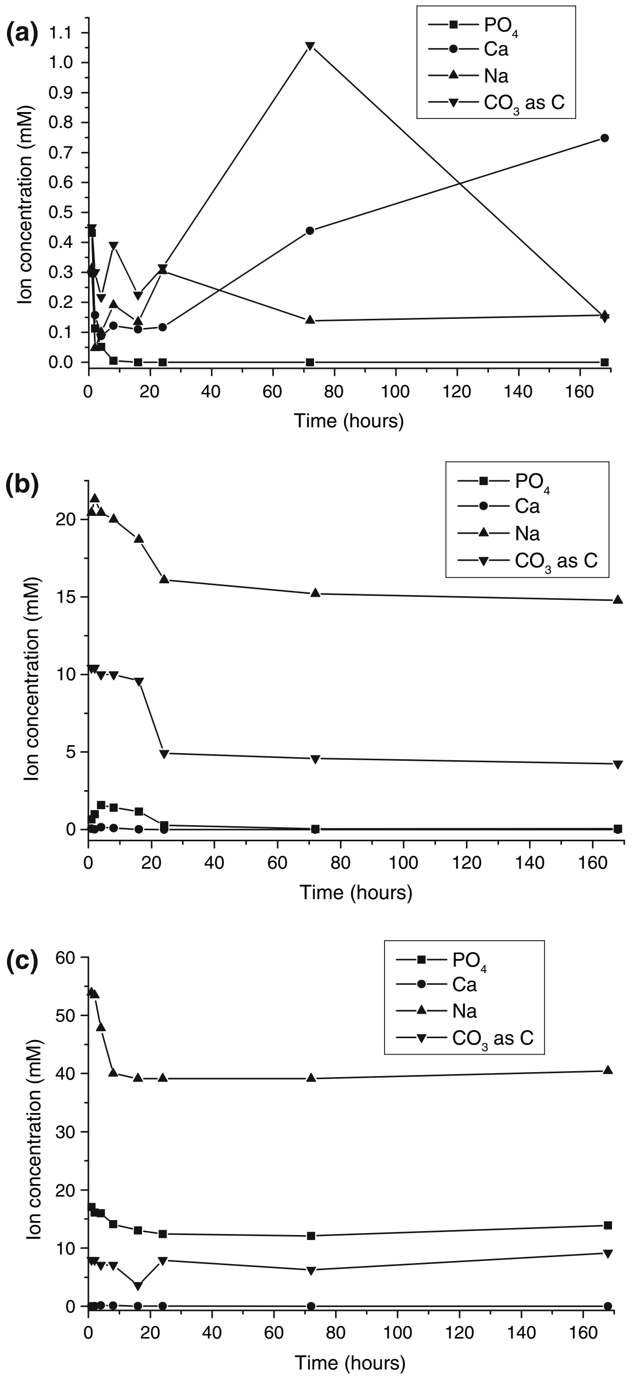

Fig. 4 Variations in Ca^{2+}, phosphate ion [P_i], CO_3^{2-}, and Na^+ over 168 h (7 days) for solutions reacted in solutions of **a** water **b** $NaHCO_3$ with $NaHCO_3$-to-$CaHPO_4$ ratio of 1, and **c** NaH_2PO_4 added in an equimolar amount to conditions of (**b**)

which the HAp is forming is inconsistent with the presence of HPO_4 groups.

The variations in solution chemistry during hydrolysis of DCPA/TetCP in the solution buffered by NaH_2PO_4 are shown in Fig. 4c. As during hydrolysis in the non-buffered solution, [Ca] remained low throughout. Although the pH is lower in the buffered solution, the effect of elevated [P_i] contributed to the solution by the buffer would reduce [Ca] via the common ion effect involving HAp. In addition, TetCP will hydrolyze more rapidly in a buffered solution. Excepting a minor reduction in [CO_3] at about 16 h, its concentration remained constant throughout the reaction. This indicates the absence of significant carbonate uptake under this circumstance. Lack of carbonate incorporation would be expected because of high [P_i] concentration conferred by the buffer in that carbonate-substituted HAp is less stable than non-substituted HAp. There is also a reduction in [Na] during the first 12 h of hydrolysis. This is accompanied by reduction in [P_i] that is somewhat longer in duration. Taken together, these data indicate the formation of Na-substituted, low-carbonate HAp.

Mass balance equations based on the solution chemistry data were also used to calculate the compositions of the hydroxyapatites formed in those systems where the solid precursors had been consumed. The results for 7 days are shown in Table 1. These calculations indicate the solution without buffer incorporated the most carbonate during reaction for 7 days. A Ca/P ratio of 1.8 is expected for incorporation of 1 mol carbonate. However the phosphate-to-carbonate ratio is 6, indicating incomplete carbonate incorporation according to the idealized product in Eq. 2. While the Ca/CO_3 ratio of 11 is also somewhat higher than would be expected, slight incorporation of sodium partially accounts for this. In comparison, the buffered solution has a P/CO_3 ratio of almost nine indicating incorporation of phosphate from the buffer. The incorporation of less carbonate during reaction in the buffered solution is expected because the elevated phosphate concentration would favor phosphate incorporation. Consistent with maximizing phosphate uptake is the formation of calcium-deficient HAp even though the Ca/P ratio of the solid reactants is 1.8. The ratio of (sodium + calcium)-to-(phosphate + carbonate) is similar between the two solutions, and further indicates formation of a calcium-deficient carbonated apatite.

Combining the above-calculated ratios with assumptions regarding the crystal chemical constraints on apatites, the composition of the apatites produced can be calculated. For

Table 1 Calculated ratios of ions in the solids formed after 7 days of reaction in solutions with $NaHCO_3$-to-$CaHPO_4$ ratios of 1, with and without NaH_2PO_4 added as buffer

	Ca/P	P/CO_3	Ca/Na	(Ca + Na)/ (PO_4 + CO_3)
Unbuffered $NaHCO_3$:$CaHPO_4$ 1:1	1.80	6.15	25.36	1.61
Buffered $NaHCO_3$:$CaHPO_4$ 1:1	1.78	8.45	36.2	1.64

that formed in non-buffered solution, we can assume that Ca + Na < 10, and $PO_4 + CO_3 = 6$. Thus the amount of PO_4 incorporated is approximately 5.2 mol with 0.8 mol CO_3. To maintain a Ca/P ratio of 1.8, the calculated amount of calcium is slightly higher as well, with 9.3 mol present. The final product would be $Ca_{9.3}Na_{0.37}(CO_3)_{0.84}(PO_4)_{5.16}(OH)_{1.8}$. This is equivalent to 5.3 wt% carbonate in the apatite. This apatite composition would likely exhibit substantial bioactivity.

For the buffered solution, the amount of phosphate incorporated is increased due to the presence of sodium phosphate. Assuming that all 6 "phosphate" sites are filled, these will be occupied by approximately 5.4 mol of phosphate and 0.6 mol of carbonate. The proportion of calcium is calculated to be 9.55 mol with 0.27 mol sodium. The overall HAp composition is then $Ca_{9.55}Na_{0.27}(CO_3)_{0.63}(PO_4)_{5.37}(OH)_2$. This is equivalent to 3.9 wt% carbonate in the apatite. Thus, the buffer increases the rate of HAp formation, reduces the amount of carbonate incorporation, and produces an apatite composition that would likely be bioactive.

The variations in pH were also measured to determine whether stirring had significant effects. During the first 8 h, the pH values are highest in the unbuffered solution and lowest in water. The unbuffered solution plateaus around 9.75 for the first 16 h, then plateaus at 12 for 24 h and beyond. These variations are similar to those observed in Fig. 2, except over a longer period of time. The buffered solution reaches a maximum at 16 h and decreases, variations also similar to those shown in Fig. 2. Excepting an anomalous data point at day 3, pH variations are similar to those shown in Fig. 2. Taken together, these data suggest that pH changes in stirred and quiescent slurries are similar thus indicating it is appropriate to generalize these observations to pastes.

Calorimetric analyses established the heat evolution characteristics during the first 24 h of HAp formation in water or in a $NaHCO_3$ solution where the $NaHCO_3$:$CaHPO_4$ molar ratio is 0.5, 1.0 or 1.5. Heat evolution curves during the first 12 h are shown in Fig. 5a. Hydrolysis in water shows an initial peak associated with mixing of the reactants followed by a second peak that initiates after about 3 h. There is a period of low heat evolution between these distinct peaks. The presence of $NaHCO_3$ changes the heat evolution characteristics during the first several hours. Heat evolution in the $NaHCO_3$ solutions occur at descending rates that are proportional to its concentration. When reaction occurs at a $NaHCO_3$:$CaHPO_4$ molar ratio of 1.5, no second peak appears. These data indicate a mechanistic shift that depends on the proportion of $NaHCO_3$ present. Figure 5b shows the total heat evolution curves for the first 12 h of reaction. In spite of the mechanistic differences observed in Fig. 5a, there is no systematic trend to the total heat evolution. Previous authors have observed a decrease in crystal size with increasing bicarbonate concentration in solution [15, 16]. Thus the lack of a second reaction peak at higher concentrations of carbonate is likely related to this decreased growth.

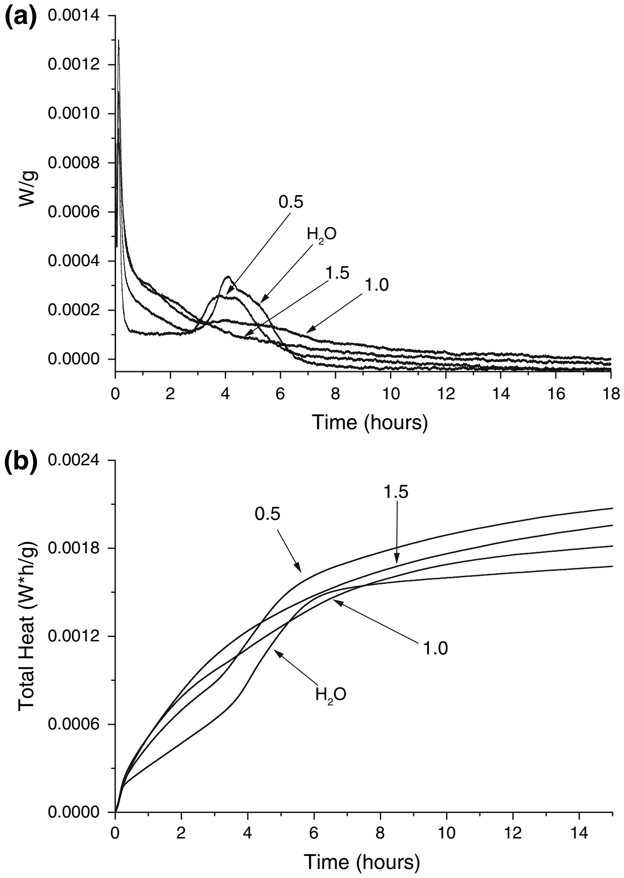

Fig. 5 **a** Rates of heat evolution during the reaction of TetCP/DCP with various $NaHCO_3$ solutions and water. **b** Total heat evolved during the formation of carbonated apatite

Figure 6 compares the heat evolution characteristics during the first 12 h of hydrolysis in buffered and unbuffered solutions where the $CaHCO_3$:$CaHPO_4$ molar ratio is 0.5 or 1.0. Although the time to complete reaction differs substantially, the bases for these differences are not apparent in the heat evolution characteristics during this period. Rather, these data suggest that rates of hydrolysis, during the period when the conversion kinetics are considered to be diffusion controlled, exhibit compositionally-dependent differences. In both cases, this may be due to addition of the phosphate group provided by the buffer. The phosphate group may not only lower reaction pH by decreasing NaOH formation, but also permit congruent dissolution of the DCPA increasing reaction rate [17].

The infrared spectra were obtained for solid samples formed after hydrolysis. All spectra are characteristic of calcium phosphates, exhibiting a broad band from 1,100 to

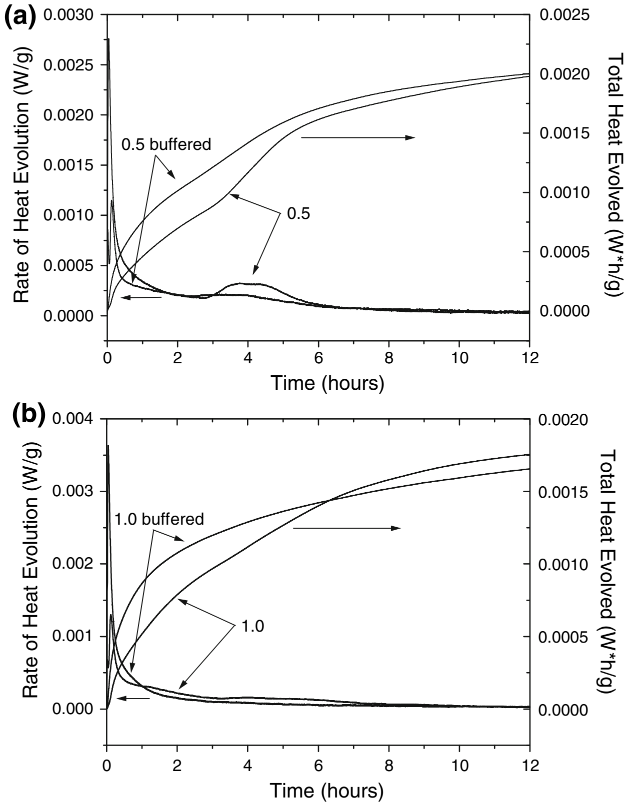

Fig. 6 Rates of heat evolution (*left axis*) and total heat evolved (*right axis*) for $NaHCO_3$ solutions in $NaHCO_3$-to-$CaHPO_4$ ratios of **a** 0.5 and **b** 1.0 and solutions with the corresponding equimolar amount of NaH_2PO_4

1,000 cm^{-1}. Figure 7 shows spectra of samples after reaction for 7 days in water or 1.0 mol ratio $NaHCO_3$-to-CaHPO4 solutions with and without buffer. The sample hydrolyzed in water contains carbonate due to reaction in air and incorporation from the milling process, as even unreacted powder shows weak carbonate bands. As expected, HAp formed in carbonate solutions contain more carbonate as indicated by increased intensities of peaks at 873, 1,423, and 1,473 cm^{-1} in comparison to powder reacted in water. The locations of these bands indicate formation of predominantly type-B carbonated apatite. The high pH of the preparation conditions likely precludes significant type-A incorporation [18]. However, Barralet et al. [15] have seen some degree of type-A substitution at low carbonate concentrations even when synthesis was carried out at a high pH, and this may explain a weak peak at 1,558 cm^{-1} seen in the present study.

Thermogravimetric analyses were performed on the aforementioned 7 day samples. The weight loss above 400°C in each apatite corresponded closely with the calculated carbonate uptake. For apatite formed in unbuffered carbonate solution, the loss was 6.5 wt%. Apatite formed in the buffered carbonate solution lost 4 wt%. Apatite formed in water lost approximately 2 wt%. As these values are higher than the amount calculated from the solution chemistry data, some of the weight loss must be due to other species. Loss of lattice water at temperatures above 400°C has been proposed to account for this discrepancy [19].

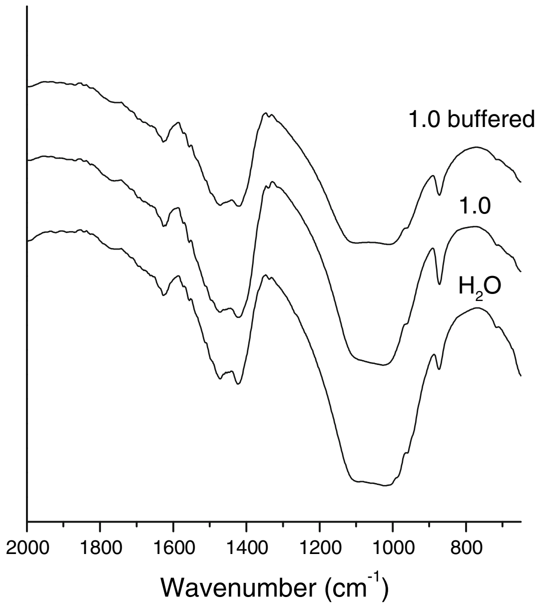

Fig. 7 FT-IR spectra of samples reacted in water or 1.0 mol ratio $NaHCO_3$-to-$CaHPO_4$ with and without buffer for 7 days

4 Conclusions

Formation of essentially phase-pure, calcium-deficient carbonated apatite was realized by combining TetCP and DCPA at Ca/P ratio of 1.8 and reacting in sodium bicarbonate solutions. Use of a sodium dihydrogen phosphate buffer to counteract NaOH formation was found to decrease the pH and increase the reaction rate, but to decrease the carbonate content of the apatite formed. Optimum reaction occurred when the $CaHPO_4$:$NaHCO_3$ ratio was 1; at values above and below this, TetCP persisted regardless of whether the system was buffered. Calorimetry indicated more rapid reaction with lower $CaHPO_4$:$NaHCO_3$ ratios. Similarly, the presence of phosphate buffer appears to accelerate the reaction by simultaneously decreasing the reaction pH and providing phosphate groups for the formation of a more stable apatite phase.

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