Faster Synthesis of A-type Carbonated Hydroxyapatite Powders Prepared by High-Temperature Reaction

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Abstract

Synthesis of A-type carbonated hydroxyapatite (CHA) materials has typically involved heating of a hydroxyapatite composition for 24 hours or greater. In this study, a hydroxyapatite powder was heated at 800, 900 or 1000°C for 1, 8 or 16 hours in dry CO_2. Samples heated for 8 and 16 hours at 900/1000°C were fully-carbonated A-type CHAs. After only one hour at 1000°C, the carbonate content approached 95% of the theoretical maximum. Preparing compositions with more than 95% of the theoretical maximum with reduced thermal energy (1000°C for 1 hour, or 900°C for 8 hours) results in powders with higher surface areas and a reduced level of sintering, compared to powders prepared with typical thermal treatments reported for A-type CHAs, such as 1000°C for 16 hours. As far as the authors are aware, these are the shortest heating times reported for the preparation of fully-carbonated A-type CHAs which is significant for future applications of such powders, particularly in applications beyond medical devices such as chromatography, remediation and carbon capture.

1. Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) has been a cornerstone of biomaterials research for several decades. Part of the reason for this is that the HA crystal structure can accommodate a wide range of ionic substitutions, allowing for the preparation of synthetic materials with chemical compositions close to that of biological apatite (a carbonated apatite with several other trace elements also present [1,2]).

This ability for hydroxyapatite to incorporate a wide range of ionic substitutions within its structure has also led to the study of ion-substituted HA as photocatalysts [3,4]. Ion substitution of hydroxyapatites can also enhance the sorption capacity of hydroxyapatite to remove toxic species from groundwaters, for example copper-substituted HA for removal of arsenates [5]. Carbonate-substitution in HA has even been shown to result in a bifunctional catalyst with a mixture of acid and basic surface sites, and this was effective at catalysing the conversion of ethanol to hydrocarbon fuels [6]. Recently, we explored the feasibility of controlling the synthesis parameters of carbonate-substituted apatites as a method to maximise carbonate incorporation [7].

Three kinds of carbonated hydroxyapatites (CHAs) are known, with these classified according to the substitutional site of the incorporated CO_3^{2-} ions: A-type (where carbonate ions situate on OH^- sites), B-type (where carbonate ions occupy PO_4^{3-} sites) and AB-type (where carbonate ions simultaneously occupy both OH^- and PO_4^{3-} sites) [8,9].

It is widely known that A-type CHAs can be prepared by heating HA at high temperature in a CO_2 atmosphere. The reaction involved is shown in Eqn. 1, where $0 < x \leq 1$:

$$Ca_{10}(PO_4)_6(OH)_2 + xCO_2 \rightarrow Ca_{10}(PO_4)_6(OH)_{2-2x}(CO_3)_x + xH_2O \qquad \text{Eqn. 1}$$
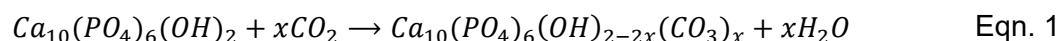
Here, two hydroxyl groups are replaced by a single carbonate ion to allow overall charge balance to be maintained. Ito *et al.* [10] prepared A-type CHAs by heating hydroxyapatite with a Ca/P molar ratio of 1.67 at 800-1000°C for 24-144 hours under a stream of CO_2 gas. The carbonate content of these materials, which ranged from 0-5.46 wt%, was determined by decomposing the synthesised apatites in an O_2 gas flow using hydrochloric acid and then measuring if this gas flow brought about a change in the pH of a solution of barium chlorate ($Ba(ClO_4)_2$) due to the precipitation of barium carbonate ($BaCO_3$). Peaks appeared in the IR spectra of the prepared materials at 1549, 1461 and 881 cm^{-1}, with none present at or near 1455, 1430 and 864 cm^{-1}, and so it was concluded that CO_3^{2-} ions had substituted onto the A-sites of the lattice alone. Tonegawa *et al.* [11] successfully synthesised an A-type carbonated hydroxyapatite in which the hydroxyl ions had been fully replaced with carbonate groups. This CHA was prepared by heating stoichiometric HA (previously synthesised by aqueous precipitation reaction using calcium hydroxide and phosphoric acid) at 1000°C for 24 hours under a dry CO_2 gas flow rate of 500 ml/min. The temperature was increased at 5°C/min and the carbon dioxide gas was thrice passed over active alumina to ensure it was dry.

The prepared apatite had a Ca/P molar ratio of 1.67 and a CO_3^{2-} content of 5.33 wt%, measured by thermogravimetry, which was close to the theoretical maximum of 5.82 wt% (i.e. when x = 1.0 in Eqn. 1). These ions situated exclusively on the A-sites, evidenced by the fact that vibrations corresponding to CO_3^{2-} ions appeared in the IR spectrum of the material at 1539, 1467 and 879 cm^{-1} only. Also, no bands attributable to the vibrational modes of hydroxyl ions were observed. Extra reflections were present in the X-ray diffraction pattern of the material at 12.86, 23.2, 26.8, 29.6, 29.9 and 35.5° 2θ, which were attributed to the carbonated HA structure having monoclinic symmetry in the space group *Pb* with unit cell constants *a* = 9.5671(2), *b* = 19.063(3), *c* = 6.8678(1) Å and β = 119.82(1)°, a doubled superstructure of the hexagonal form. This group also prepared a similar A-type CHA using another high-temperature synthesis route [12]. Synthetic HA with a Ca/P molar ratio of 1.65 was heated for 64 hours at 900°C in a CO_2 flow of 500 ml/min. The crystal structure of the carbonated hydroxyapatite was again monoclinic (space group *Pb*), with lattice constants *a* = 9.571(1), *b* = 19.085(2), *c* = 6.8755(3) Å and β = 119.847(7)°. Thermogravimetry revealed that the prepared material contained 5.45 wt% carbonate and the researchers concluded that these ions situated exclusively on the A-sites as vibrations corresponding to carbonate ions were observed in the FTIR spectrum of the apatite at 879, 1467 and 1539 cm^{-1} only. Additionally, no vibrations corresponding to hydroxyl ions were observed.

Until now the reported synthesis of these A-type CHA materials has required that HA be heated for timescales in the range of 15-144 hours [10-14]. Consequently, the aim of this study was to investigate whether fully carbonated A-type CHA powders can be prepared by heating hydroxyapatite for significantly shorter periods of time. It is important to be able to efficiently produce the end member of the composition $Ca_{10}(PO_4)_6(OH)_{2-2x}(CO_3)_x$ (i.e. x = 1) as it is then convenient to refine the conditions to produce a given composition within the range of x = 0-1 as may be required for a specific application. Reducing the time the samples are held at high temperatures would be beneficial in terms of minimising grain/crystallite growth within the powder particles, reducing energy requirements to synthesise these materials, and in the case of potential CO_2 capture applications using calcium phosphates, would provide a rapid system of maximising the amount of CO_2 captured in the A-type CHA structure in a time-scale that is feasible in terms of use.

2. Materials and methods

2.1. Sample Preparation

Stoichiometric HA was first synthesised at room temperature in ambient atmosphere by aqueous precipitation reaction. This reaction was based on an established precipitation route [15] and involved adding a phosphoric acid (H_3PO_4) solution dropwise to an aqueous suspension of calcium hydroxide ($Ca(OH)_2$). The quantity of each reactant used was calculated such that the Ca/P molar ratio of the reactants was equal to 1.67. The $Ca(OH)_2$ suspension was prepared by dispersing 0.11 moles of calcium hydroxide (98% assay, VWR, UK) in approximately 150 ml of distilled water. 30 ml of concentrated ammonium hydroxide solution was added to ensure that the pH of the suspension did not fall out with a desired range (9-11) upon the introduction of the H_3PO_4 solution and thus avoid the formation of calcium-deficient impurity phases [16,17]. The H_3PO_4 solution was then prepared by diluting 0.066 moles of phosphoric acid (Merck, 85% solution in water) with 150 ml of distilled water. This solution was added dropwise to the continuously stirred $Ca(OH)_2$ suspension over a period of about 2 hours. The reaction mixture was stirred for a further two hours and then left to age unstirred overnight. The aged reaction mixture was filtered, thoroughly rinsed with distilled water and the resultant filter-cake dried in air in an oven at 90°C overnight. The dried filter-cake was then ground to a fine powder using a mortar and pestle. Subsequently, the power was subjected to a heat treatment at 300°C in air to remove synthesis residuals such as absorbed water, using a muffle furnace (Carbolite Gero Ltd., UK) with a heating and cooling rate of 5 °C/min, and a hold for one hour. Finally, aliquots (c. 0.5 g) of this 'as-prepared' powder were subjected to a heat treatment in a tube furnace (Carbolite Gero Ltd., UK) under a dry CO_2 gas flow rate of approximately 0.5 dm^3 per minute. The temperature in the furnace was ramped from ambient up to 800, 900 or 1000°C at a rate of 5 °C/min, held there for either one, eight or sixteen hours and then cooled back to room temperature at the same rate.

2.2. Sample Characterisation

Powder X-ray diffraction (XRD) was used to assess the phase composition of samples using an X'Pert Pro diffractometer (PANalytical Ltd., UK) with Cu Kα radiation (λ = 1.5418 Å), and operated at 45 kV and 40 mA. Data were collected from either 10-40 or 15-65 °2θ with a step size of 0.013 ° and a count time per step of 900 or 96 s respectively. Crystalline phases present were identified by comparing obtained patterns with PDF files from the ICDD database. The unit cell parameters of the synthesised apatites were determined by minimised Rietveld refinement with collected XRD data using the PANalytical software package 'HighScore Plus' [18]. Whereas the refinement of the as-prepared apatite was carried out in the hexagonal space group $P6_3/m$ using HA structural data reported by Sudarsanan and Young [19], the refinements of the apatites heated in CO_2 were required to be carried out in the monoclinic space group Pb using A-type CHA ($Ca_{9.9}(PO_4)_6(CO_3)_{0.9}$) structural data reported by Tonegawa *et al.* [12] as the initial model. In each case, only the background function, scale factor, lattice parameters and peak shape functions were refined. The Ca/P molar

ratio of the as-prepared powder was analysed by energy-dispersive X-ray spectroscopy (EDX) using a Gemini SEM 300 field emission SEM (Zeiss, Germany) equipped with an X-ray detector (Oxford Instruments, UK) operating at an accelerating voltage of 15 kV. A powder compact of the powder was coated with carbon prior to analysis. Three measurements were taken and the results reported as an average alongside the standard deviation. The carbonate contents of the samples were determined by combustion analysis using a LECO CS744 carbon/sulphur analyser (LECO Instruments UK Ltd., UK). For each sample, duplicate measurements were made and the mean value reported alongside the standard deviation. It was assumed that all of the carbon detected by the equipment existed as CO_2, which was reasonable as the equipment flooded the combustion chamber with oxygen and also passed the combustion products through an oxidation catalyst. FTIR spectra of the samples were obtained using a Diamond/ZnSe ATR attached to a Spectrum Two™ spectrometer (Perkin-Elmer, UK). Absorbance spectra were collected at a 2 cm^{-1} resolution, averaging 7 scans, between 4000 and 400 cm^{-1}.

The specific surface areas, SSA (m^2/g) of the powders obtained by heating at various temperature/times in dry CO_2 were determined from nitrogen adsorption isotherms collected at liquid nitrogen temperature using a Micromeritics TriStar 3000 gas adsorption analyzer (Micromeritics Instrument Corp., USA). The SSA was determined from the data using the BET method with MicroActive software (Micromeritics Instrument Corp. 2012). Powder was accurately weighed out, degassed in nitrogen at 250°C for 5 hours, prior to nitrogen adsorption measurements.

The effect of thermal treatment (temperature/time) on the microstructure of powder particles (in the range 30-300 µm diameter) was determined using scanning electron microscopy using an EVO MA 10 SEM (Zeiss, Germany). Powders heated under various conditions were fixed to an aluminium stub using adhesive carbon tape, coated with Pd/Au and imaged with an accelerating voltage of 20 kV.

3. Results and Discussion

3.1. X-Ray Diffraction (XRD) Analysis

3.1.1. Phase composition of heated samples

XRD analysis of the synthesised powder as-prepared and after being heated in CO_2 at 900 or 1000°C in dry CO_2 is presented in Figure 1. XRD patterns of the powder after undergoing similar heat treatments at 800°C are shown in Figure S1. The position of the diffraction peaks in the pattern of the as-prepared powder all matched those of the ICDD standard for hydroxyapatite [20], with no reflections attributable to any crystalline impurity phase such as calcium hydroxide ($Ca(OH)_2$), calcium carbonate ($CaCO_3$) or calcium oxide (CaO) present. Reflections corresponding to impurity phases were also not visible in the patterns of the heated apatites and so it appeared that the heat treatment did not cause any phase decomposition, even after the apatite had been heated for 16 hours at 1000°C.

Even so, the patterns of the heated samples were very different to that of the as-prepared apatite. Extra diffraction peaks were detected in these patterns at approximately 12.9, 26.9, 29.7, 30.0, 35.4 and 35.6 °2θ after the HA material had been heated for 16 hours at 800°C and one hour at 900/1000°C. This is shown in more detail in Figure 2, which displays the XRD pattern between 10 and 40 °2θ of the apatite after it had been heated in CO_2 at 1000°C for 8 hours. These diffraction peaks have been observed in other studies of A-type CHAs [12,21,22] and are indicative of these substituted HA compositions exhibiting monoclinic symmetry (space group *Pb*) as a result of the complete replacement of linear hydroxyl groups by triangular carbonate ions. Conversely, these additional reflections were not observed when the as-prepared material was heated at 1000°C in static air for 16 hours (Figure S2). At 900 or 1000°C, the intensity of these extra reflections was positively related to the dwell time at temperature, which may have indicated that not all of the HA underwent this transition from hexagonal symmetry simultaneously. Note that the reflection at 23.2 °2θ that was observed by Tonegawa *et al.* [11] was not seen in any of these patterns, perhaps because this diffraction peak was reported to be quite weak and so may have been undetectable without XRD analysis over a smaller range. Additionally, several diffraction peaks shifted to lower angles after the material was heated, with the magnitude of these shifts increasing alongside the hold time. As such behaviour was not observed in all the reflections, these shifts indicated changes in the lattice parameters (i.e. an increase in the size of the HA unit cell) and not some experimental error such as sample displacement or instrumental misalignment.

3.1.2. Crystallite sizes

The diffraction peaks of the as-prepared apatite were quite broad, consistent with the sample being composed of very small crystallites [23]. Reflections of the heated samples were much narrower than their equivalents in the pattern of the as-prepared apatite. The mean size of these primary particles were calculated using Scherrer's equation with K=0.9 and the (002) reflection at approximately 25.8 °2θ (Table 1), confirming increasing temperature increased crystallite size. The results also demonstrated that the size of these primary particles was positively correlated to the dwell time at each temperature. For comparison, the apatite was also heated in air at 1000°C for 1, 8 or 16 hours, and similar calculation of crystallite sizes from the XRD data gave mean sizes of approximately 82, 86 and 93 nm for 1, 8 and 16 hours respectively, suggesting that the CO_2 atmosphere retarded crystallite/grain growth. This is consistent with findings for carbonate-substituted HA heated in dry or wet CO_2 atmospheres, with the densification delayed to higher temperatures in a dry CO_2 atmosphere [24]. The absence of water vapour in the heating/sintering atmosphere, and therefore the gradual loss of hydroxyl groups in the lattice, will affect the migration rate of ions during crystallite/grain growth and densification.

Table 1. The average crystallite size (in nm), calculated using Scherrer's equation and the (002) reflection at approximately 25.8 °2θ, of the HA material as-prepared and after being heated for 1, 8 or 16 hours in CO_2 at each temperature.

Temperature (°C)	Hold time	τ (nm)
AP	N/A	29 ± 1
800	1 hour	33 ± 1
	8 hours	38 ± 1
	16 hours	41 ± 1
900	1 hour	47 ± 1
	8 hours	54 ± 1
	16 hours	58 ± 2
1000	1 hour	65 ± 1
	8 hours	71 ± 4
	16 hours	75 ± 2

3.1.3. Unit Cell Determination

The unit cell parameters of the apatite material as-prepared and after being heated at 900 or 1000°C in dry CO_2 are shown in Table 2. The XRD patterns of the samples prepared at 800°C did not refine well in the monoclinic space group *Pb* (i.e better fits were achieved in the hexagonal space group *P6₃/m*) and so those materials were excluded here as they were not fully substituted A-type CHAs. Also shown are the lattice parameters of the apatite material after it had been heated at 1000°C in air for 16 hours, which was also refined in the *P6₃/m* space group.

The *a*-axis of the as-prepared apatite was slightly smaller, and the *c*-axis slightly larger, than literature reported values of stoichiometric HA (a = 9.4184 Å; c = 6.8800 Å) [25]). Comparing with the literature, these small changes suggested that there was a small degree of B-type or labile carbonate substitution present in the as-prepared material [8], which would be expected as the synthesis was performed in air and not in an inert atmosphere. In contrast, the lattice parameters of the material after a 16-hour heat treatment in air at 1000°C were very similar to the literature values of stoichiometric hydroxyapatite. After the apatite had been heated for eight hours in CO_2 at 900/1000°C, the unit cell constants of the material were very similar to those of the A-type CHAs prepared by Tonegawa *et al.*, which suggested that the hydroxyl ions had been completely substituted with carbonate ions. As a 'check', it was decided to refine the XRD data of the '8 hour' samples using structural data of another A-type CHA. Fleet and Liu previously prepared a partially carbonated A-type CHA with chemical composition $Ca_{10}(PO_4)_6(CO_3)_{0.75}(OH)_{0.25}$ by a high pressure method and reported that this material formed with trigonal symmetry in the space group $P\bar{3}$ [26]. However, the fits achieved using this model were of a significantly lower quality than those realised using the monoclinic model (weighted-profile R-value, R_{wp} = 6.9% compared to 4.6% for the sample heated at 1000°C), which added further weight to support that fully carbonated A-type CHAs had been prepared.

Table 2 Lattice parameters and unit cell volume of the HA material as-prepared (AP) and after being subjected to heat treatments at 900/1000°C in dry CO_2 for 1, 8 or 16 hours. Respective e.s.d values are presented in brackets.

Temperature (°C)	Hold time	a (Å)	b (Å)	c (Å)	β (°)	Volume (Å^3)	R_{wp} (%)
AP	N/A	9.4072(5)	N/A	6.8903(5)	N/A	528.05	4.13
1000 (AIR)	16 hours	9.4218(1)	N/A	6.8810(1)	N/A	528.98	4.08
900	1 hour	9.5320(1)	19.0490(1)	6.8732(1)	119.831(1)	1083.29	6.90
	8 hours	9.5608(2)	19.0881(5)	6.8704(2)	119.822(2)	1088.45	6.68
	16 hours	9.5741(5)	19.0769(6)	6.8696(2)	119.787(4)	1089.58	4.32
1000	1 hour	9.5546(4)	19.0693(5)	6.8692(1)	119.846(3)	1086.23	4.08
	8 hours	9.5731(4)	19.0760(5)	6.8685(1)	119.800(3)	1089.10	4.60
	16 hours	9.5726(4)	19.0749(5)	6.8680(1)	119.804(3)	1088.86	4.64

3.2. Chemical Analysis

The Ca/P molar ratio of the as-prepared apatite was determined to be 1.64 ± 0.02 using EDX. This was lower than the designed value of 1.67 that is characteristic of stoichiometric HA and so this analysis suggested that the synthesised material was slightly calcium-deficient. To try and substantiate this result, the as-prepared material was heated at 1250°C in air for two hours. At this temperature, a calcium-deficient apatite would be expected to decompose and produce a secondary phase of tricalcium phosphate [27]. However, no such phase (or any other secondary phase for that matter) was detected by XRD (Figure S3) after this heat treatment, which suggested that the Ca/P molar ratio of the material was actually closer to the stoichiometric value of 1.67. This apparent underestimation of the Ca/P molar ratio of the apatite may be a result of the analysis being performed on a simple compacted disc rather than a highly polished surface, as the accuracy of EDX analysis is inversely proportional to the surface roughness of the specimen under examination [28].

From combustion analysis a significant quantity of carbonate ions were present in the as-prepared apatite, even though carbonate-free reagents were used and the Ca/P molar ratio was calculated such that no carbonate ions should have substituted onto phosphate sites, Figure 3. Such contamination is one of the major disadvantages associated with using aqueous precipitation reactions to prepare hydroxyapatite materials [29]. These ions were likely to have been incorporated into the apatite during the precipitation reaction, as this reaction (as well as the subsequent ageing and filtering steps) was performed in air rather than a controlled inert atmosphere. This presented ample opportunity for atmospheric CO_2 to dissolve into the reaction mixture and for the resultant CO_3^{2-} ions to substitute into the apatite structure or exist as labile (non-apatitic) carbonate.

The carbonate content of the apatite samples heated in CO_2 reached 5.75 and 5.65 wt% after 8 hours at 900 and 1000°C respectively, which is very close to the theoretical maximum of 5.82 wt%. This was considerably less time to reach this degree of carbonation than each of the materials prepared by Tonegawa *et al* [11,12]. Conversely, the apatite had to be heated for 16 hours to reach this carbonate content when the heat treatment was carried out at 800°C. Another significant result was the fact that 95% of the maximum carbonate content was achieved after heating in CO_2 for only one hour at 1000°C. The results of the combustion analysis overall suggested that the carbonation of the apatite at 1000°C proceeded *via* two distinct stages. In the first stage, the CO_3^{2-} content of the apatite increased rapidly over a short period of time; this was followed by a second stage in which the rate of carbonation was much slower and little additional CO_2 was taken up by the material. The transition between these two stages seemed to occur once the carbonate content had exceeded approximately 90% of the maximum that was achieved (i.e. 5.09 wt%), although more data points would be needed to confirm this.

3.3. Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR spectra of the apatites are shown in Figure 4 & Figure 5. The spectrum of the as-prepared apatite (Figure 4) was typical of hydroxyapatite prepared using an aqueous precipitation reaction [17,30]. Each of the four IR-active phosphate vibrations that are characteristic of HA were visible. The presence of hydroxyl ions in the lattice was confirmed by bands attributable to the librational and stretching vibrations of OH^- ions at approximately 630 and 3570 cm^{-1}, respectively. In addition, a broad band attributed to the presence of absorbed water [31] was observed at approximately 1640 cm^{-1}. This band indicated that neither the oven drying nor the heat treatment in air at 300°C had fully dried the precipitated apatite. Bands corresponding to the v_2 and v_3 vibrational modes of carbonate ions were also present in this spectrum between 900-850 and 1550-1350 cm^{-1} respectively, Figure 4(B,C). This is not surprising as the aqueous precipitation reaction was carried out under ambient conditions, so atmospheric CO_2 would be dissolved in the reactant solutions and the reactant mixture. Synthesis of HA has been described in the literature with a method that removes the presence of atmospheric CO_2 from affecting the reaction by using degassed solutions and a blanket of an inert gas over the synthesis [32], but our approach was to follow more readily used and practical reaction conditions. Although these bands were broad, distinct peaks were seen in these regions at 878, 1415 and 1450 cm^{-1}. Additionally, it appeared that a contribution was also present at approximately 873 cm^{-1}. Comparing the frequencies of these vibrations to the literature suggested that carbonate ions had substituted onto both hydroxyl and phosphate sites [8]. A relatively weaker contribution was also observed in the v_3 region at 1495 cm^{-1} but this peak was not assigned to any particular vibration. It is known that a somewhat accurate estimate of the relative distribution of carbonate ions over A and B sites can be obtained by comparing the intensities of the carbonate peaks of the v_2 region (873 and 880 cm^{-1}) [33]. No attempt was made to do so, however, due to the broad nature of this band.

The heat treatments at 800, 900 or 1000°C in CO_2 altered the FTIR spectrum of the material considerably, Figure 5. Whilst the four phosphate vibrations remained visible, the appearance of these bands changed markedly. The heat treatment caused the v_1 vibration at approximately 960 cm^{-1} to become more intense and also caused the v_2 vibration that appeared in the spectrum of the as-prepared apatite at approximately 560 cm^{-1} to shift to relatively higher frequencies. Additionally, after the material had been heated for sixteen hours at 800°C, eight hours at 900°C and one hour at 1000°C, the v_3 phosphate band split into three distinct contributions at approximately 1000, 1050 and 1128 cm^{-1}, with the peak at 1000 cm^{-1} also shifting to relatively lower frequencies. The splitting of this band has been related to a lower crystal symmetry associated with a monoclinic unit cell [22]. The OH^- stretch and libration bands disappeared after the material had been heated for eight hours at 800 or 900°C and after one hour at 1000°C, a consequence of hydroxyl ions being replaced in the lattice with carbonate.

All of the heated apatites produced intense peaks attributable to A-type carbonate substitution [34] at approximately 878, 1465 and 1530 cm^{-1}. These were accompanied by the disappearance of the contributions assigned to B-type carbonate [8] that were present in the spectrum of the as-prepared apatite at 873, 1415 and 1450 cm^{-1}. From these observations, it could be deduced that the heat treatment increased the degree of A-type carbonate substitution in the material whilst simultaneously driving from the lattice carbonate ions that had substituted onto phosphate sites or labile sites during the precipitation reaction. After the material had been heated for eight hours at 900 or 1000°C, it appeared that the substituted carbonate ions had situated exclusively on the hydroxyl sites, whereas contributions corresponding to B-type carbonate substitution were still apparent (particularly at 1415 cm^{-1}) even after the apatite had been heated for sixteen hours at 800°C. This confirmed that none of the materials prepared at 800°C were fully substituted A-type CHAs but were rather AB-type carbonated hydroxyapatites. In addition, a very weak peak corresponding to the v_4 vibrational mode of carbonate ions appeared in the FTIR spectrum of the material at approximately 760 cm^{-1} after the apatite had been heated for eight hours at 900°C and one hour at 1000°C. A selection of samples were subjected to a subsequent heat treatment (1 hour at 1000°C) in an N_2/H_2O atmosphere. Carbonate bands were absent from the FTIR spectrum of the 900°C '1 hour' sample and appeared only weakly in the spectrum of the 1000°C '16 hours' sample, Figure 6. In addition, hydroxyl vibrations also appeared after this treatment at approximately 630 and 3570 cm^{-1}. These differences, corresponding to a reversal of the A-type carbonate for hydroxyl groups, is clear when compared with the data in Figure 5 of the A-type CHAs. Additionally, the XRD patterns of these twice-heated materials were almost identical to that shown in Figure S2 (i.e. they were single-phase apatites and arranged in the hexagonal space group $P6_3/m$). This meant that the A-type carbonation of these samples could be reversed, at least partially, without compromising the apatite crystal structure. When the FTIR data is taken together with the data from XRD analysis and also carbonate quantification, it is clear that fully carbonated A-type CHAs could be prepared using shorter heating times than have previously been reported (15-144 hours [10,13,14]).

3.5. Specific surface area (SSA) measurements

The specific surface areas of powders heated at 900 or 1000°C in dry CO_2 for between 1 and 16 hours were determined by the BET method and are displayed in Figure 7. Consistent with studies on undoped hydroxyapatite the surface area decreases with increased thermal treatment [35]. Prolonged dwell times at a given temperature results in a decrease in surface area, and as shown in Figure 3 the gain in A-type carbonate substitution with prolonged dwell time, particularly by increasing from 8 to 16 hours, is negligible.

3.6. Scanning electron microscopy (SEM).

The effect of the various thermal heat treatments in dry CO_2 on the microstructure of the apatite powders was studied using SEM. Representative microstructures of the surface of powder particles

heated at 900 or 1000°C for 1 hour in dry CO_2 are shown in Figure 8(A&B). Although chemical analysis showed a small increase in carbonate content when the powder was heated to 1000°C compared to 900°C for 1 hour (Figure 3), the microstructure of samples showed an increased coarsening of the primary particles as the temperature was increased. Increasing the dwell time at 900 and 1000°C to 8 (Figure 8(C&D) or 16 hours (Figure 8(E&F)) resulted in further coarsening of the microstructure with progression through early stages of sintering/densification. Although these powder particles have not undergone e.g. uniaxial compaction, they are progressing towards the formation of a typical sintered microstructure of hydroxyapatite ceramics [24,36]. The changes in microstructure, in particular the increase in primary particle/grain size is consistent with the changes in surface area described in Figure 7. A-type carbonate substitution is known to inhibit sintering of hydroxyapatite [37], so although relatively high temperatures of 900-1000°C were used here, the A-type carbonate substitution level can be used to inhibit sintering/grain growth in applications where maintaining a high surface area/small particle size/high porosity may be important, such as catalysis or remediation.

4. Conclusions

The synthesis of A-type CHA materials under different thermal treatments in dry CO_2 was motivated by a desire to investigate if fully carbonated A-type CHA powders could be prepared using shorter heating times than have previously been reported (15-144 hours). There was substantial evidence to support that the samples obtained after HA was heated for 8 hours at 900/1000°C in CO_2 were A-type carbonated hydroxyapatites in which all of the hydroxyl groups had been replaced with carbonate ions. The CO_3^{2-} content of these materials were very close to the theoretical maximum of 5.82 wt% (i.e. the carbonate content of an A-type CHA of chemical composition $Ca_{10}(PO_4)_6CO_3$). As far as the authors are aware, these are the shortest heating times that have been reported to date for the preparation of fully-carbonated A-type CHAs by high temperature reaction. Importantly, heating for only 1 hour at 1000°C resulted in approximately 95% of the theoretical carbonate substitution. The findings may be of interest to a number of research fields, where controlling the type and amount of carbonate substitution can change the properties of the resulting material, such as solubility for medical applications, or the concentration of acid surface sites for catalytic applications or for chromatography applications. Rapid A-type carbonate substitution as described here provides a method of controlling the influence of OH^- for CO_3^{2-} ion substitution on the properties of hydroxyapatite, particularly in emerging applications beyond the field of biomaterials. Although the amount of carbonate incorporated into the HA lattice is relatively low (less than 6 wt% carbonate, or 4.4 wt% CO_2), an interesting observation here is that the A-type substitution is reversible, with only a 1 hour heat treatment in an N_2/H_2O atmosphere resulting in the loss of carbonate groups and the appearance of hydroxyl groups, by FTIR analysis. This rapid carbonation/decarbonation may have potential interest in the utilisation of calcium phosphate apatites recovered from biological waste sources for applications outside medical applications.

Conflicts of Interest

The authors have no conflicts to declare.

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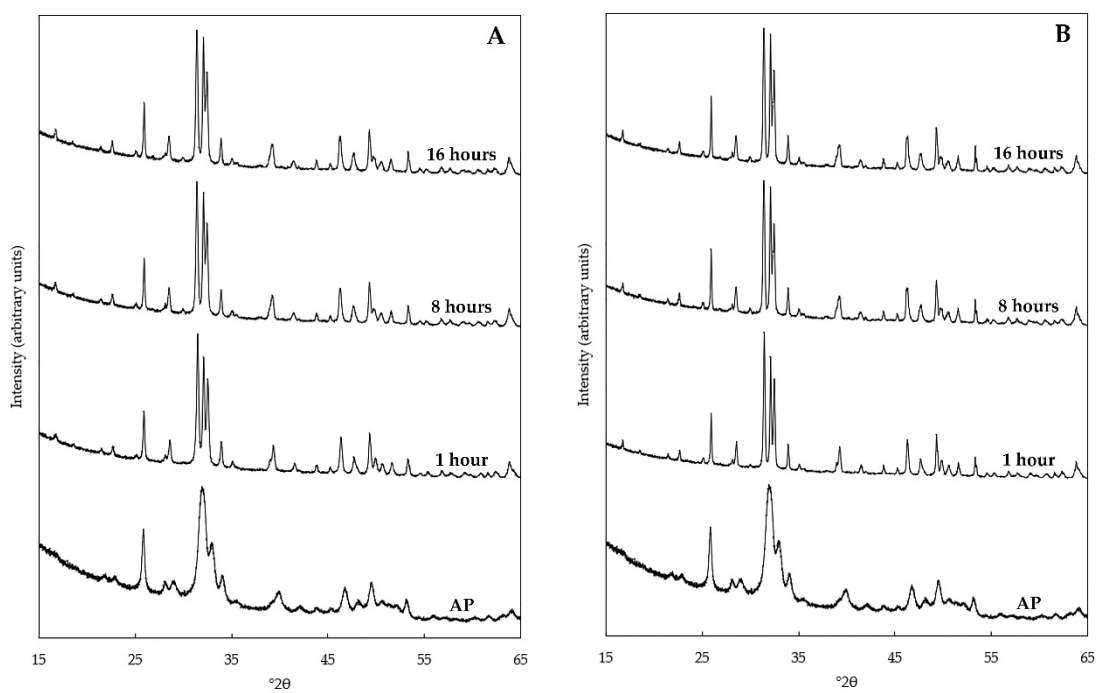
Figure 1 Normalised (I_{max} = 100) XRD patterns between 15-65 °2θ of the hydroxyapatite material as-prepared (AP) and after being heated in CO_2 for 1, 8 or 16 hours at 900 (A) or 1000°C (B).
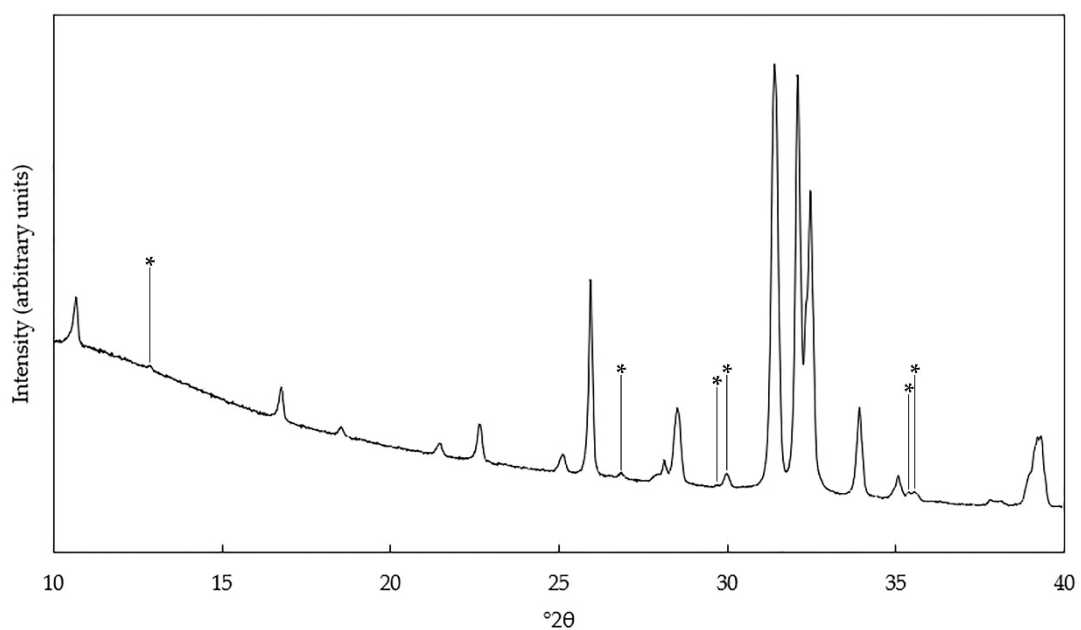
Figure 2 X-ray diffraction pattern between 10-40 °2θ of the HA material after it had been heated for 8 hours at 1000°C in CO_2. Extra reflections corresponding to monoclinic symmetry (space group Pb) are marked by asterisks.
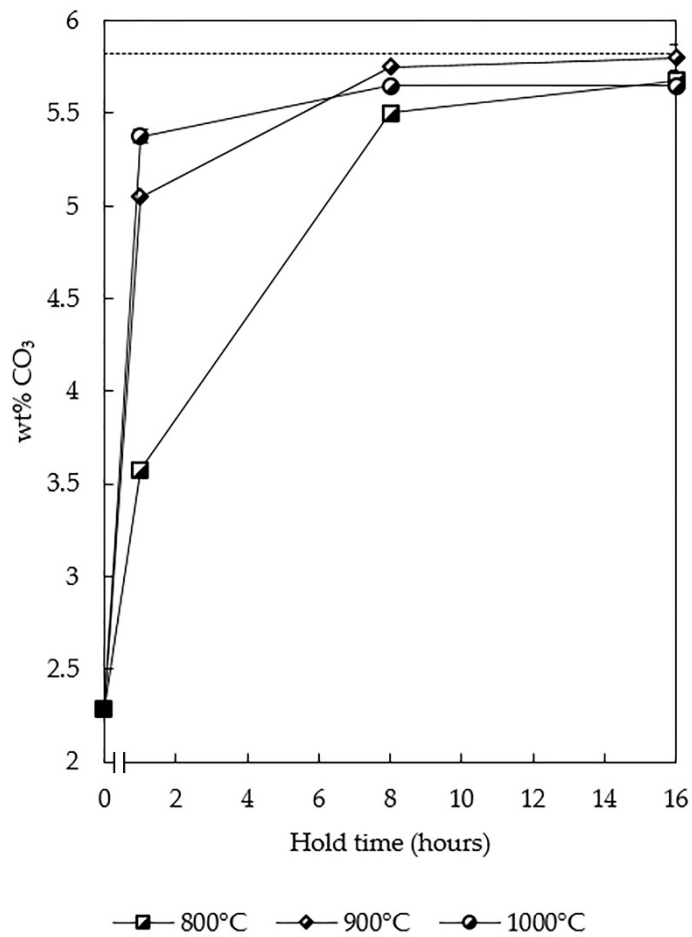
Figure 3 The carbonate content of the apatite as-prepared (i.e. when hold time = 0) and after being subjected to heat treatment in CO_2 for hold times of 1, 8 or 16 hours. The dashed line corresponds to the CO_3^{2-} content of an A-type CHA with chemical composition $Ca_{10}(PO_4)_6CO_3$ i.e. the theoretical maximum of 5.82 wt%. The lines between data points are added as a guide to the reader.
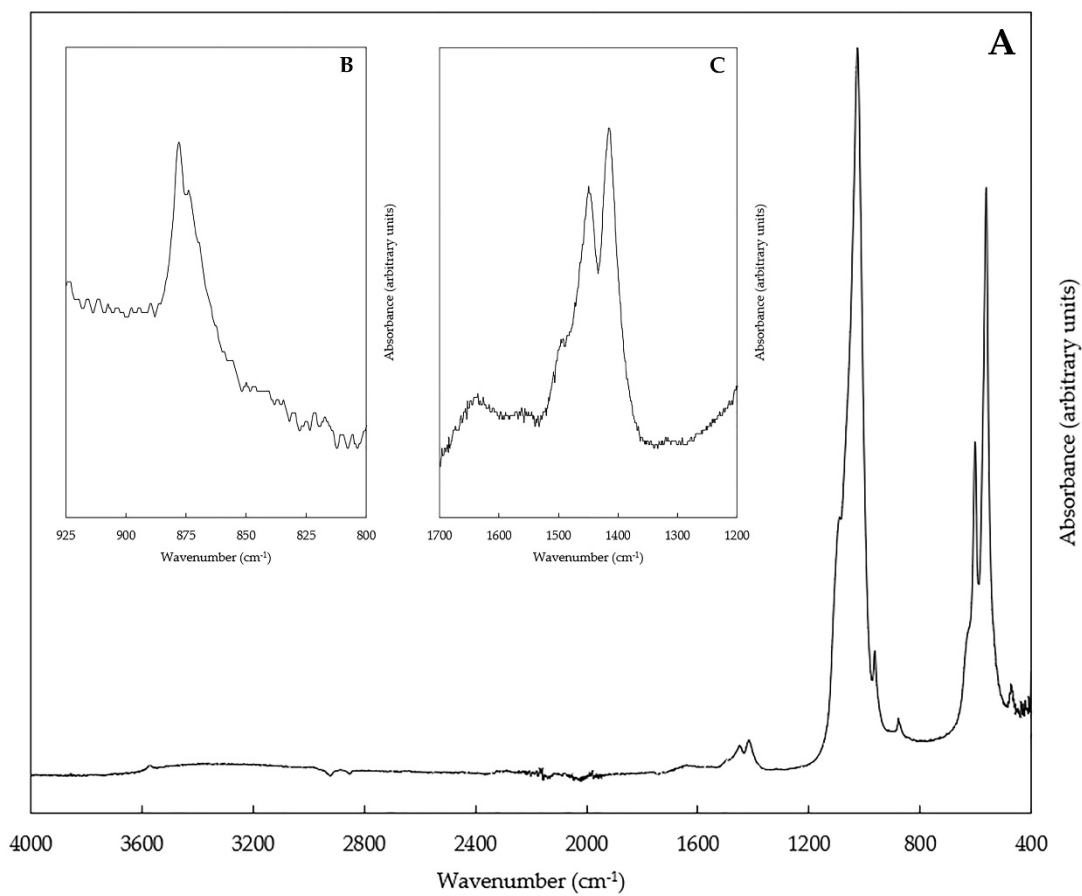
Figure 4 FTIR absorbance spectrum between 4000-400 cm^{-1} of the as-prepared apatite (A). The v_2 and v_3 carbonate regions are shown in detail in (B) and (C) respectively.
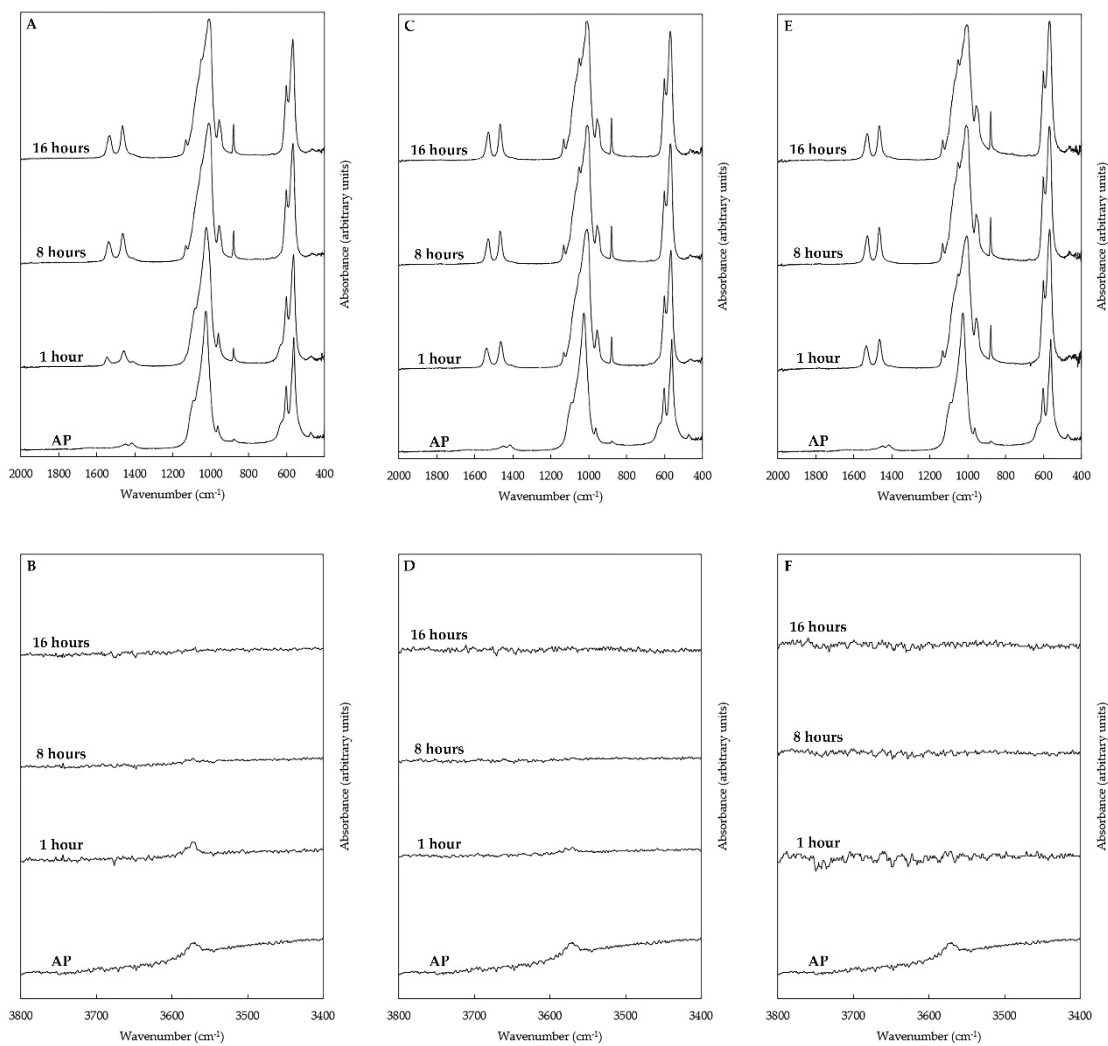
Figure 5   Normalised (A_{max} = 100) FTIR absorbance spectra between 2000-400 and 3800-3400 cm^{-1} of the apatite material as-prepared (AP) and after being heated for 1, 8 or 16 hours in dry CO_2 at 800 (A,B), 900 (C,D) and 1000°C (E,F).
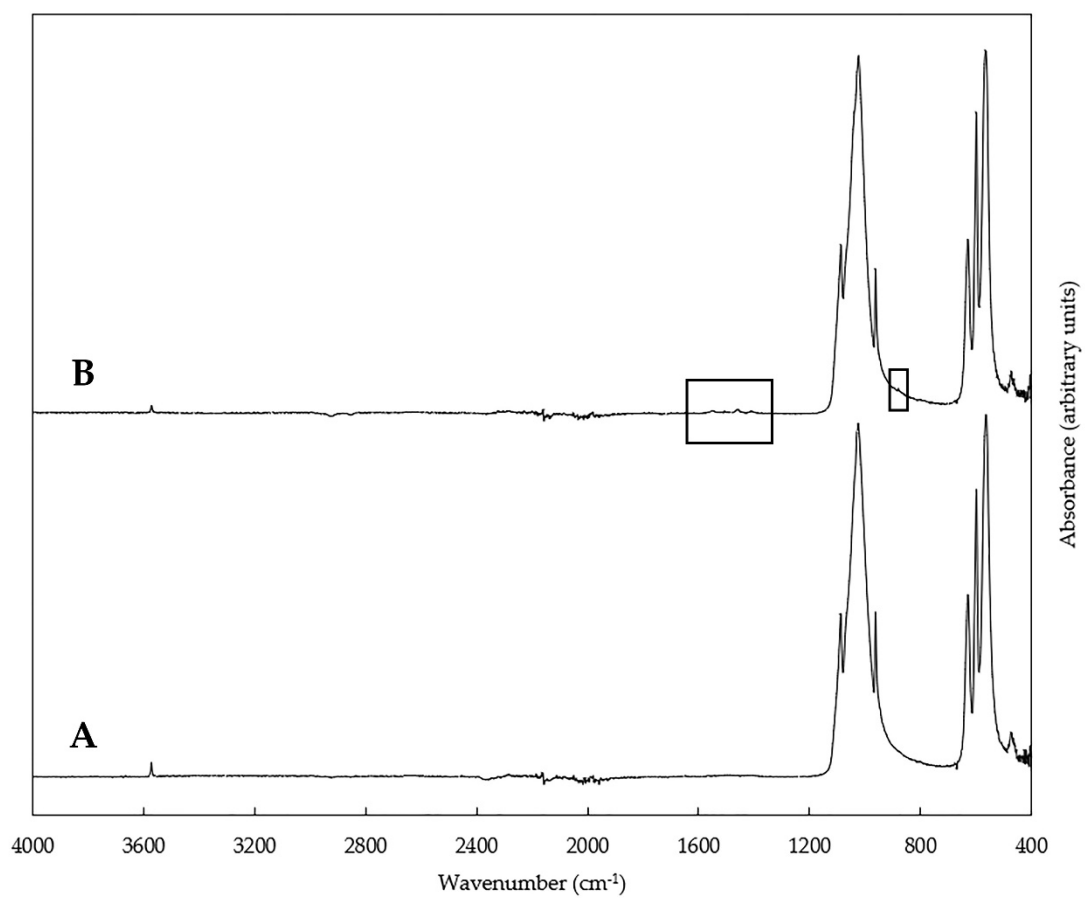
Figure 6 FTIR spectra of the 900°C '1 hour' sample (A) and the 1000°C '16 hour' sample (B) after a 1-hour heat treatment at 1000°C in an N_2/H_2O atmosphere. The v_2 and v_3 carbonate regions are outlined.
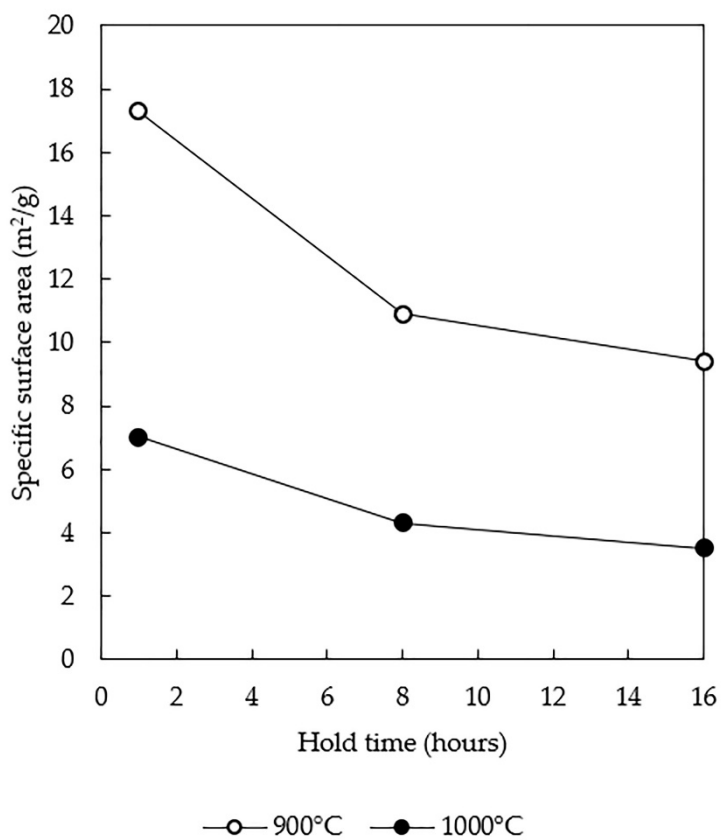
Figure 7 Specific surface area (SSA) determined by the BET method of powders heated at various times/temperatures in dry CO_2.
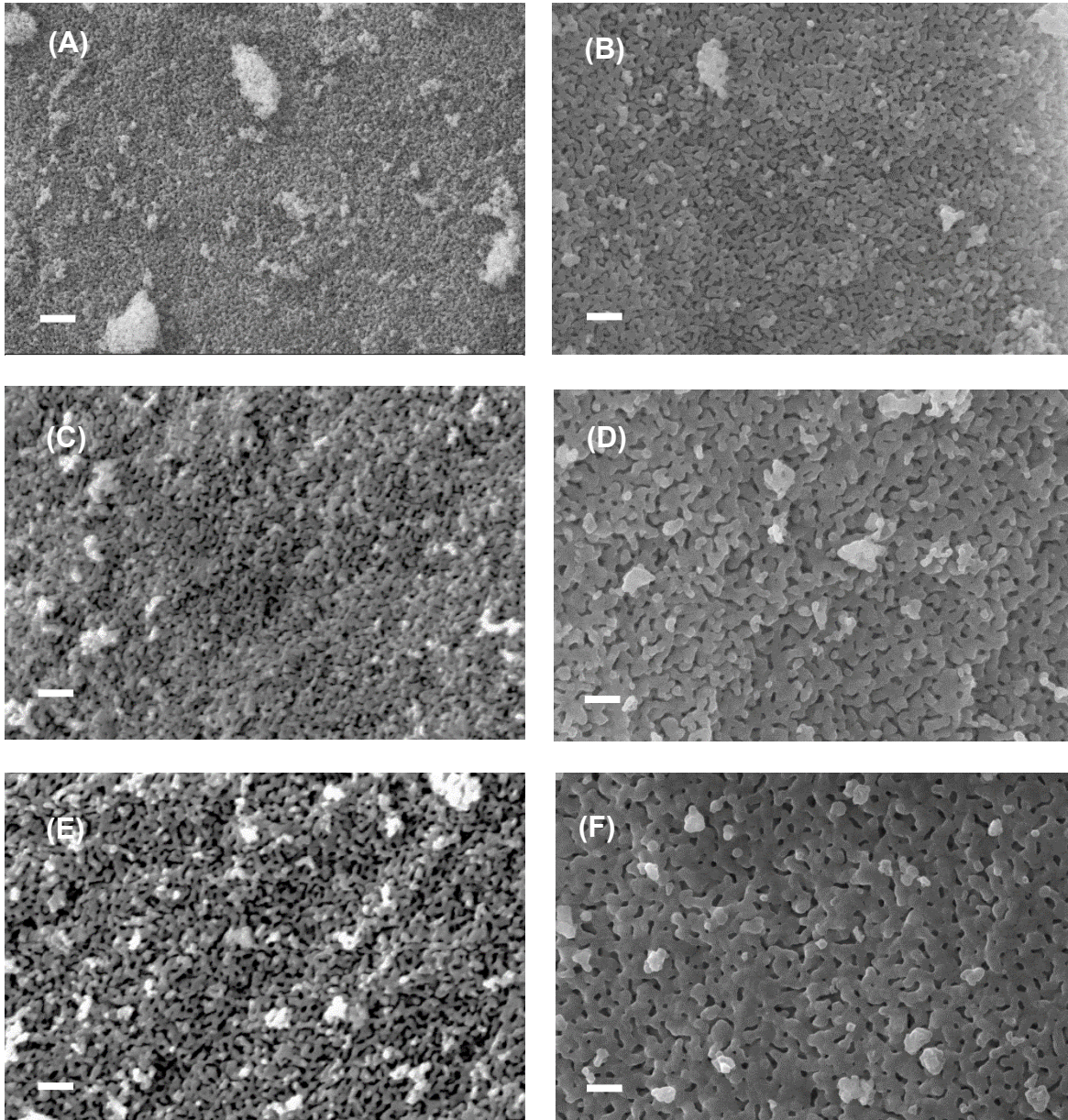
Figure 8 Scanning electron micrographs of the surfaces of powder particles of the apatite material after being heated in dry CO_2 at 900°C and 1000°C for 1 hour (A&B), 8 hours (C&D) and 16 hours (E&F) (magnification of x20k, operating voltage of 20 kV, scale bar represents 1 μm).
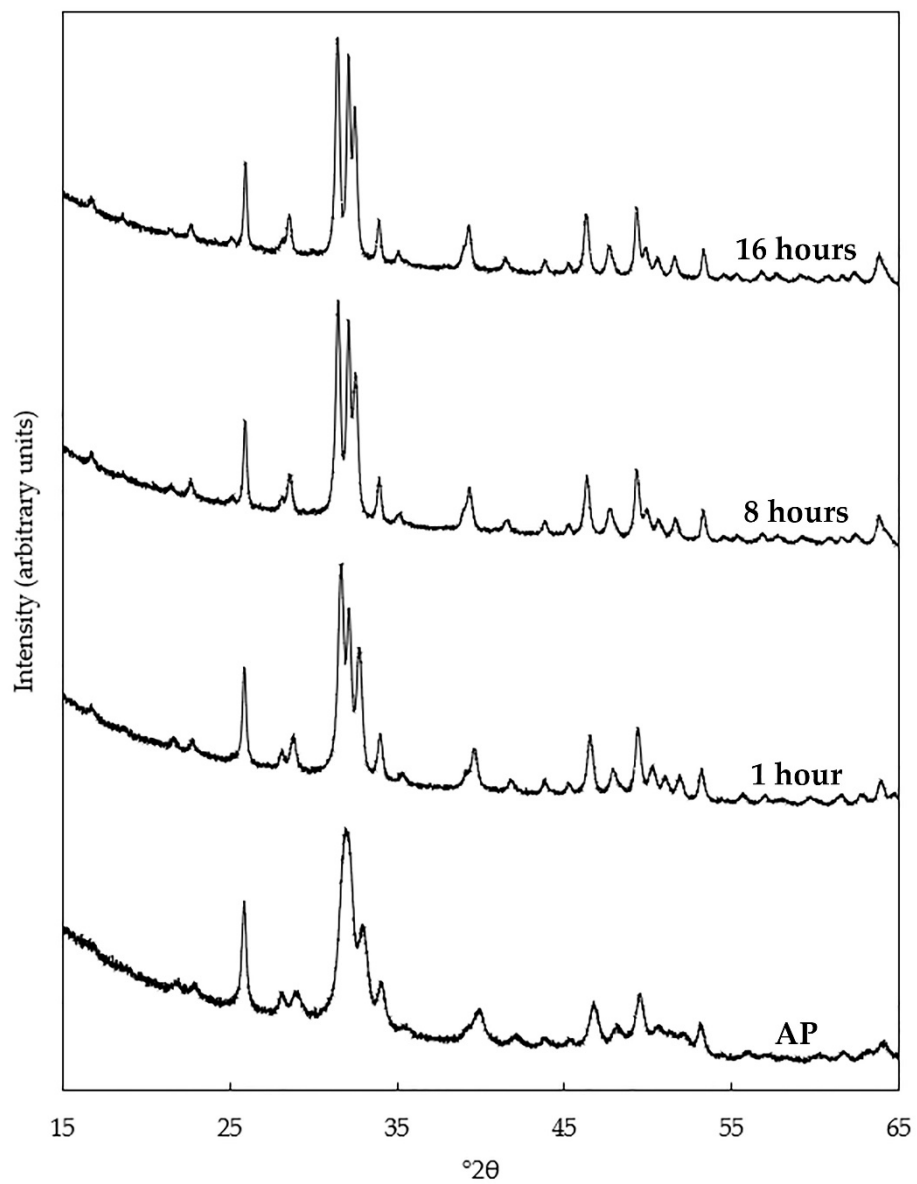
Figure S1: Normalised (I_{max} = 100) XRD patterns between 15-65 °2θ of the hydroxyapatite material as-prepared (AP) and after being heated for 1, 8 or 16 hours at 800°C in CO_2.

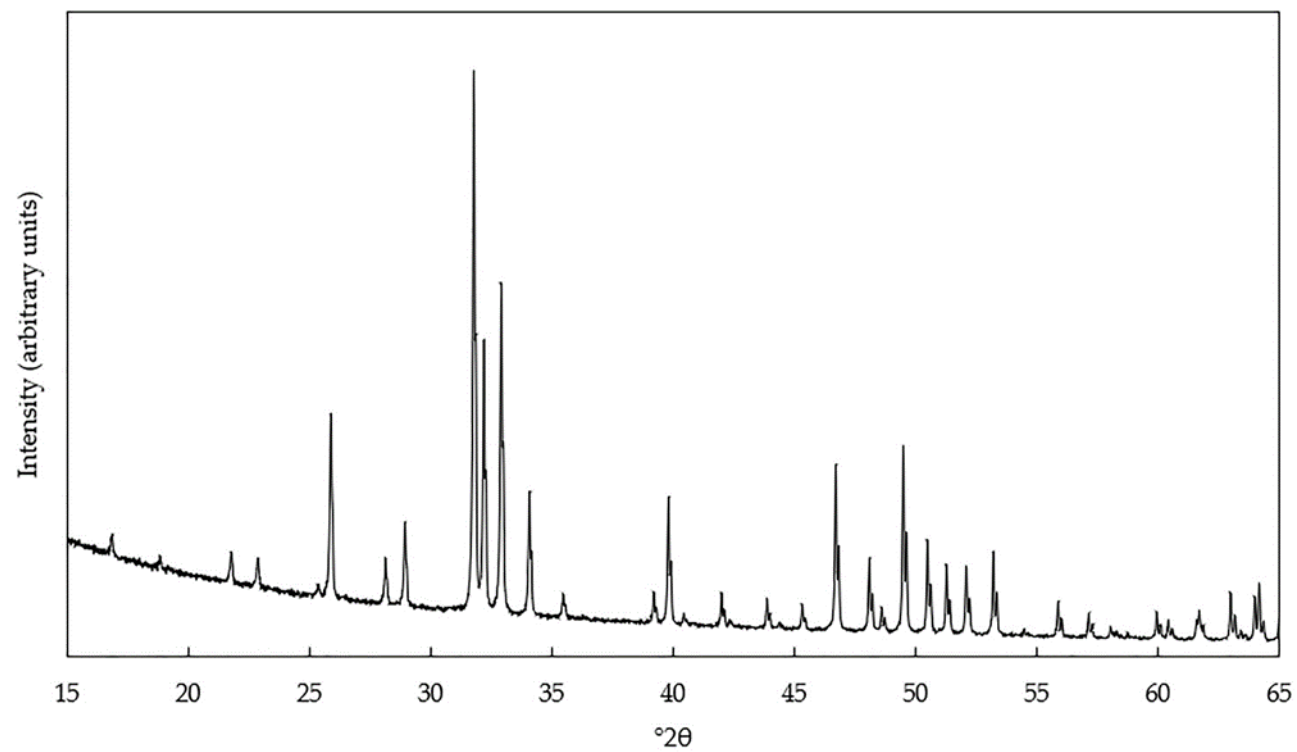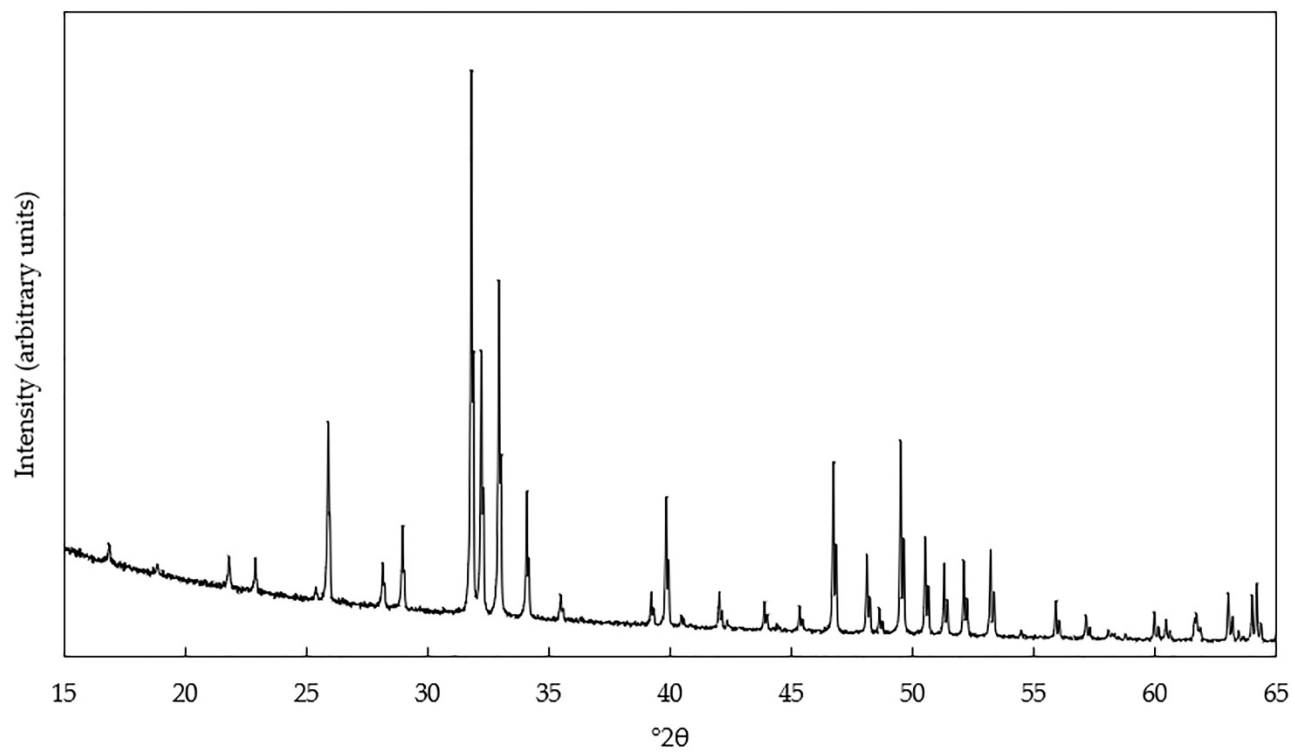Figure S2 XRD pattern between 15-65 °2θ of the hydroxyapatite material after being heated in static air for 16 hours at 1000°C.

Figure S3 XRD pattern between 15-65 °2θ of the hydroxyapatite material after being heated in static air for two hours at 1250°C.