Polyhedron 44 (2012) 143–149

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis, structure, and solubility of carbonated barium chlor- and hydroxylapatites

Claude H. Yoder [a,*], Jill D. Pasteris [b], Katherine A. Krol [a], Victoria L. Weidner [a], Richard W. Schaeffer [c]

[a] Department of Chemistry, Franklin & Marshall College, Lancaster, PA 17603, USA
[b] Department of Earth and Planetary Sciences and The Center for Materials Innovation, Washington University in St. Louis, St. Louis, MO 63130-4899, USA
[c] Department of Chemistry and Biochemistry, Messiah College, Grantham, PA 17027, USA

ARTICLE INFO

Article history:
Received 18 April 2012
Accepted 19 June 2012
Available online 28 June 2012

Dedicated to Alfred Werner on the 100th Anniversary of his Nobel Prize in Chemistry in 1913.

Keywords:
Carbonated barium apatite
XRD
Raman
IR
Cell parameters
Structure

ABSTRACT

Two series of carbonated barium apatites [BaApZ = $Ba_{10}(PO_4)_6Z_2$] were prepared in aqueous solution. Carbonated barium hydroxylapatites (CBaApOH) were prepared by mixing solutions of $Ba(NO_3)_2$ with $(NH_4)_2HPO_4$ and $(NH_4)_2CO_3$ at pH 12. Carbonated barium chlorapatites (CBaApCl) could only be prepared by stirring barium chlorapatite with $(NH_4)_2CO_3$ at pH 10 for 1 week. Powder X-ray diffraction showed no evidence of the presence of $BaCO_3$ or other possible impurities such as $BaHPO_4$ in the carbonated products. Variations in carbonate content of the apatites had little effect on the width of peaks in their XRD patterns. The cell parameters determined by full pattern analysis were also relatively independent of the carbonate content of the apatites, although CBaApCl showed a slight decrease in *a*-axis length with increasing carbonate content. The slight decrease in the *a*-axis length, the amount of carbonate incorporated in the apatites, and the specific IR absorbances in the carbonate spectral regions support the mechanism of carbonate substitution for phosphate (B-type). In contrast, the barium:phosphate ratio determined for several apatites of different carbonate concentrations suggests carbonate substitution for the monovalent anion (A-type). Raman spectroscopy of CBaApOH confirmed that carbonate incorporation causes atomic disorder within the structure and that apparently carbonate-saturated CBaApOH still contains appreciable hydroxyl. Activity-based K_{sp} values were determined for both series of carbonated apatites and show that the solubilities of both CBaApCl and CBaApOH remain almost constant at low carbonate concentrations but increase at higher carbonate values (assuming B-type substitution). The K_{sp} values for uncarbonated BaApCl and BaApOH were determined by extrapolation to 0% carbonate (10^{-103} and 10^{-107} for BaApCl and BaApOH, respectively).

1. Introduction

Although carbonated calcium hydroxylphosphate (hydroxylapatite = CaApOH = $Ca_{10}(PO_4)_6(OH)_2$) has been studied for many years, the effects of carbonate on the structure and properties of apatite are still not well understood [1]. In our current study we continue our program of modeling the effects of carbonate incorporation on members of the apatite group through the use of apatites containing cations other than calcium. We have recently reported on lead apatites [2], and we here report on our studies of the heavy-metal apatites, barium hydroxylapatite (BaApOH) and barium chlorapatite (BaApCl). Barium chlorapatite is found in nature as the mineral alforsite; the hydroxyl derivative does not occur naturally.

While BaApCl can be synthesized in aqueous solution from $BaCl_2$ and a soluble source of phosphate [3], BaApOH forms with greater difficulty [4,5], generally at pH 12 upon heating for extended periods [3]. The structures of both alforsite [6] and the hydroxyl derivative [7,8] have been determined to have $P6_3/m$ symmetry, typical of most members of the apatite family Fig. 1.

The incorporation of carbonate into the apatite structure can occur by substitution for the monovalent anion (A-type substitution of one CO_3^{2-} for two X^-) or by substitution for phosphate (B-type substitution), the latter of which entails loss of both monovalent anions and cations to maintain charge neutrality [9,10]. B-type substitution or a combination of A- and B-type substitution is observed for calcium apatite in aqueous syntheses [1,9–12]. B-type substitution is also most likely for the lead hydroxyl- and chlorapatites under aqueous conditions [2]. The incorporation of carbonate in barium apatites has been addressed only by solid-state, high-temperature synthesis in which substitution involved dehydration of hydroxyl to oxide to produce phases of the type

* Corresponding author.
E-mail addresses: claude.yoder@fandm.edu (C.H. Yoder), pasteris@levee.wustl.edu (J.D. Pasteris), rschaeff@messiah.edu (R.W. Schaeffer).

0277-5387/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.poly.2012.06.039

$Ba_5(PO_4)_{3-x}(CO_3)_x(OH)_{1-x}O_x$ [12], and by adsorption of CO_2 during the synthesis of barium hydroxylapatite at high pH [13].

In the present study, the objectives were to prepare carbonated barium hydroxylapatite (CBaApOH) and carbonated barium chlorapatite (CBaApCl) by aqueous synthesis, to determine the mechanism of carbonate substitution at 60 or 90 °C through IR and X-ray analysis, and to determine the effect of carbonate on the solubility of the apatites.

2. Materials and methods

2.1. Syntheses

All water was Milli-Q doubly deionized water that was purged with nitrogen gas to remove carbon dioxide.

Barium chlorapatite was obtained in 150 mL of water heated to 60 °C with pH adjusted to 10 using 6 M ammonia. A solution containing 0.00409 mol of $BaCl_2{\cdot}2H_2O$ (Fisher Scientific Company, 99.4%) and a solution containing 0.00246 mol of $NH_4H_2PO_4$ (Sigma–Aldrich, 98+%) were then slowly (ca. 1 mL/min) and simultaneously titrated into the bath. The reaction mixture was then stirred and heated for 4 h at pH 10 and a temperature of 60 °C. The mixture was filtered by suction through a medium filter crucible. The product was washed two times with a total of 40 mL of warm water and then air-dried overnight and finally in vacuo for 1 h. The product ($Ba_5(PO_4)_3Cl$) was obtained in 80–95% yield.

Barium hydroxylapatite was synthesized in aqueous solution using $Ba(NO_3)_2$ (Sigma–Aldrich, 99+%) and $(NH_4)_2HPO_4$ following the conditions outlined by Flora et al. [3]. A 20 mL portion of water was adjusted to a pH of 12 through dissolution of approximately 550 mg of sodium hydroxide (Acros, 97+%) before any reagents were added. A solution containing 0.00383 mol of $Ba(NO_3)_2$ and a solution containing 0.00230 mol $(NH_4)_2HPO_4$ were added alternately in small portions. The pH was adjusted back to 12 using 6 M NaOH, and the reaction mixture was heated and stirred for 5 days at 90 °C. The cooled reaction mixture was then filtered by suction, washed at least twice with a total of 40 mL of warm water, air-dried overnight and then in vacuo for 1 h. The product ($Ba_5(PO_4)_3OH$) was obtained in 50–70% yield.

Carbonated apatites were prepared by two different experimental approaches. In the first approach the apatites were synthesized as discussed above but with NH_4HCO_3 (Sigma–Aldrich, $\geqslant$99.0%) dissolved in the bath. The amount of NH_4HCO_3 added was varied based on the desired carbonate to phosphate ratio in the solution (generally less than 1:1). In the second approach, approximately 0.20 g of the already synthesized, uncarbonated barium apatite was stirred in a 0.01 M $(NH_4)_2CO_3$ solution for 1 week. The volume of the $(NH_4)_2CO_3$ solution used depended on the desired carbonate to phosphate ratio in the bulk system. The pH of the solution was adjusted to 10 (periodically during the week) using 6 M NH_3 for BaApCl and to a pH of 12 using 6 M NaOH for the BaApOH. All samples were collected by suction filtration in a medium filter crucible, washed, and dried as described above.

2.2. Analyses

Weight percent carbon was determined by Schwarzkopf Microanalytical Laboratories, Woodside, NY, using a C-, H-, N-elemental analyzer after combustion at 1000 °C in a stream of oxygen. The reported carbonate concentrations have an experimental error of ±0.2 wt%. Barium, phosphorus, and chlorine analyses were obtained with ICP-OES and ion chromatography (chloride) (Galbraith Laboratories, Knoxville, TN) and have a relative uncertainty of ca. 5%. The uncertainty in the carbonate values was obtained from the standard deviation based on triplicate analyses of one sample.

2.3. XRPD

Powder X-ray diffractograms were obtained with a Phillips 3520 X-ray diffractometer using Cu Kα radiation in conjunction with a monochromator. A step size of 0.02° 2-theta and dwell times of 1–5 s were used over the range 2–60° 2-theta. The instrument was calibrated regularly using a quartz standard. Each line pattern was carefully scrutinized for traces of barium carbonate, barium hydrogen phosphate, barium phosphate, and starting materials. Cell parameters were determined using the program Unit Cell (Cambridge Earth Sciences, Holland and Redfern, 2007), assuming a hexagonal crystal system. Cell parameters of many samples were checked using a PANalytical X'Pert PRO MPD (Multi-Purpose Diffractometer) Theta–Theta System with Cu Kα radiation (λ = 1.54060 Å). Instrumental settings included a step size of 0.02° 2-theta and dwell times of 1–5 s over the analysis range of 2–60° 2-theta. Based on repeated analyses of specific samples, the standard deviation of the cell parameters is estimated to be 0.002 Å.

2.4. IR Analysis

Infrared spectra were obtained with a Bruker Tensor 37 spectrometer using a ZnSe ATR accessory. Analyses were based on 256 scans from 600 to 4000 cm^{-1} with a resolution of 2 cm^{-1}.

2.5. Raman microprobe spectroscopy

Raman spectra were obtained on three CBaApOH samples to further characterize the phosphate phase and to detect contaminating phases at a lower concentration than that detected by powder X-ray diffraction. The confocal Raman system used in this study is an integrated, fiber-optically coupled microscope-spectrometer-detector from Kaiser Optical (Ann Arbor, Michigan). The HoloLab Series Research Raman Spectrometer configured for 532-nm laser excitation simultaneously records the spectral range of 0–4300 Δ cm^{-1}. The Andor high-resolution, thermoelectrically cooled CCD array detector provides a resolution of 2.5 cm^{-1}. Analyses of powders were made using an Olympus 80× objective with an N.A. of 0.75. Each Raman analysis represents the average of 32 acquisitions of 4 s each. Every sample underwent at least six analyses. The laser power was 10 mW at the sample surface, and the diameter of the beam was about 1 μm at the sample surface. The focus was optimized so as to obtain the maximum signal:noise ratio.

2.6. Solubility measurements

Finely ground 10 mg samples were equilibrated at 25 ± 1 °C in a shaker bath for 6 days in 50 mL of 1.71×10^{-3} M ammonium phosphate buffer. The ammonium phosphate buffer consisted of 97 ppm phosphate and 18 ppm ammonium ion. The resulting mixtures were centrifuged and filtered using a 45 μm disc to remove any residual solid. The barium concentrations were determined using a Spectro Ciros CCD ICP-AES (at 230.424 nm). The relative uncertainties in the barium concentrations are estimated to be ±5%. Activities of each species were calculated using Visual MINTEQ (Version 3.0) from experimental values of barium and phosphate concentrations and pH values at the conclusion of each equilibration period. Additional solubility trials were conducted for up to 2 weeks to confirm that equilibrium was established.