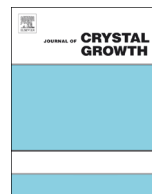




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Strontium hydroxyapatite and strontium carbonate as templates for the precipitation of calcium-phosphates in the absence and presence of fluoride



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ABSTRACT

The heterogeneous precipitation of calcium-phosphates on calcium hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ or HAP) in the presence and absence of fluoride is important in the formation of bone and teeth, protection against tooth decay, dental and skeletal fluorosis and defluoridation of drinking water.

Strontium hydroxyapatite ($\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$ or SrHAP) and strontium carbonate (SrCO_3) were used as calcium-free seed templates in precipitation experiments conducted with varying initial calcium-to-phosphate (Ca/P) or calcium-to-phosphate-to-fluoride (Ca/P/F) ratios. Suspensions of SrHAP or SrCO_3 seed templates (which were calcium-limited for both templates and phosphate-limited in the case of SrCO_3) were reacted at pH 7.3 (25 °C) over 3 days. The resulting solids were examined with Scanning Transmission Electron Microscopy (STEM), X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR), and X-ray Photoelectron Spectroscopy (XPS), X-ray Absorption Near Edge Structure (XANES), and Extended X-ray Absorption Fine Structure spectroscopy (EXAFS).

Calcium apatite was the predominant phase identified by all techniques independent of the added Ca/P ratios and of the presence of fluoride. It was not possible to make an unambiguous distinction between HAP and fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, FAP). The apatite was calcium-deficient and probably contained some strontium.

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1. Introduction

The heterogeneous precipitation of calcium hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ or HAP) on bones and teeth (as templates) is a process of primary importance in vertebrate physiology [1]. The uptake of fluoride into HAP and the precipitation of fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ or FAP) can protect teeth from caries, but at higher exposure, may lead to discoloration of teeth or even crippling bone weakness [2]. Medical and dental applications have motivated studies of HAP and FAP precipitated under highly-controlled and non-

physiological conditions (e.g., hydrothermal synthesis [3,4] or aerosol deposition onto titanium [5] or after calcination [6,7]) complementing earlier studies on the precipitation of a variety of calcium phosphate solids [8–14]. In most studies, HAP and FAP (in the presence of dissolved fluoride, F) have been the thermodynamically-favored phases, but the formation of other calcium phosphate solids, particularly as intermediates, has also been reported depending on reaction time, solution conditions including the degree of super-saturation, initial calcium-to-phosphate (Ca/P) ratios, pH and ionic strength, temperature and surface area of HAP added as a seed template. Studies of F-substituted apatites have suggested that more crystalline apatites are formed at higher temperatures (over the range of 3–90 °C) [15,16] and that fluorite (CaF_2) may be formed as an intermediate during FAP precipitation in aqueous solution [17]. Carbonate minerals have been used as either a seed or sacrificial template; overgrowth of octacalcium phosphate (OCP) has been observed on both calcite and mixed calcite-aragonite crystals [18] and complete dissolution of

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biogenic aragonite (cuttlefish bone) was observed in association with the formation of apatite [19], calcium phosphates [20] or fluoride-substituted hydroxyapatite [21].

Fluoride uptake by HAP and precipitation of FAP are also relevant to the defluoridation of drinking water [22–26]. Bone char (predominantly HAP) is being used for this purpose in rural Kenya; filters are amended with pellets containing calcium phosphates and calcite (CaCO_3) to improve performance [27]. The composition of pore fluids in the filters can be highly variable due to variability in the composition of source waters, intermittent supply of water to the filters and physico-chemical reactions occurring in the filter bed.

Here, we use strontium carbonate (SrCO_3) and strontium hydroxyapatite ($\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$ or SrHAP) as Ca-free templates for the precipitation of calcium phosphate phases. This study focused on distinguishing between calcium apatites and other calcium phosphate phases precipitated under ambient conditions (pH 7.3, 25 °C) after the addition of solutes with varying initial calcium-phosphate (Ca/P) ratios in the presence and absence of dissolved F. The intention of using Sr-based seed templates was to distinguish the newly-precipitated phases from the seed phases. Solute were added in Ca/P ratios corresponding to the stoichiometry of various possible products: 1.0 for brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), 1.50 for β -tricalcium phosphate ($\beta\text{-Ca}_3(\text{PO}_4)_2$ or $\beta\text{-TCP}$), and 1.67 for HAP and FAP. When fluoride was added, the initial Ca/P/F ratios were either stoichiometric for FAP, F-limited for FAP or P-limited for FAP with excess Ca and F in the stoichiometric ratio for CaF_2 . Solute were added at concentrations relevant for filter systems used for defluoridation of drinking water. The composition of the solids produced after 3 d was characterized using scanning transmission electron microscopy (STEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy, and X-ray diffraction (XRD). The stoichiometry of precipitated solids was calculated based on the removal of the constituent ions from solution.

2. Materials and methods

2.1. Chemicals and materials

All chemicals used (excluding FAP and SrHAP reference samples) were of at least “pro analysi” grade (p.a., from Merck and Fluka). Solutions were prepared in nanopure water (Barnstead NANOpure Diamond UV, resistivity > 18 $\text{M}\Omega\text{-cm}$) in polyethylene vessels washed with acid (0.65% HNO_3) and rinsed at least 3 times with nanopure water. Solid reference samples were obtained from

commercial suppliers (brushite and monetite (CaHPO_4) from Fluka, fluorite (CaF_2) from AlfaAesar, SrCO_3 from Merck, $\beta\text{-TCP}$ from Cerros and HAP from Budenheim) or synthesized (SrHAP and FAP) as described elsewhere [28].

2.2. Batch experiments

Experiments were performed in duplicate in open systems (atmospheric pCO_2) at 25 ± 1 °C with 2 g SrHAP or SrCO_3 in 1 L nanopure water. Suspensions were stirred by a suspended magnetic stirrer to avoid sample grinding. Solution pH was controlled over the duration of the experiment at 7.3 ± 0.5 with 0.1 M HNO_3 and 0.1 M NaOH, using titration units as in [26,28]. After dispersion for 10 min, dissolved Ca and PO_4 were added to the SrHAP/ SrCO_3 suspensions from 0.5 M $\text{Ca}(\text{NO}_3)_2$, 0.3 M $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, 0.3 M Na_2HPO_4 , and 0.4 M NaF stock solutions (accommodating changes in volume due to pH-adjustment and sampling prior to solute addition) to achieve target initial solute concentrations (1–6 mM Ca, 2–5 mM PO_4 , 0–3 mM F, Table 1). After 3 d, solids were collected on cellulose-nitrate filters (0.45 μm , Sartorius), air-dried and stored at room temperature for further analysis. Filtrates for solute analysis were collected by filtration through nylon filters (0.2 μm , PALL) and analyzed for major cations (Na, Ca and Sr) and anions (chloride and phosphate) as well as for total dissolved inorganic carbon as described previously [26]. Reported concentrations were corrected to account for dilution during pH adjustment.

2.3. Solid characterization

Analyses by XPS, XRD and FTIR were performed for all precipitates and for the reference samples HAP, FAP, SrHAP, SrCO_3 and CaF_2 as described previously [26] except for modification of the FTIR analysis parameters as follows: spectra recording velocity 10 kHz; filter 1.2 kHz, undersampling ratio (UDR) 2, resolution 2 cm^{-1} , aperture 0.25 cm^{-1} and sensitivity 16 [–]. All FTIR data were normalized to the baseline. For STEM analysis of the precipitated sample HAP_SrHAP, about 20 mg of well-ground, air-dried sample was suspended in approximately 50 mL ethanol, sonicated in a water bath (Bioblock Scientific) for 2 min and centrifuged (UniCen MR, Herolab) at 4300 rpm for 10 min to remove large aggregates. Two drops of the supernatant were deposited on a TEM grid (Cu/holey carbon-coated; Okenshoji Co., Ltd). The microscope (Hitachi HD 2700Cs) was operated with an acceleration voltage of 200 kV in a high resolution mode. The solids were localized using a High-Angle Annular Dark Field

Table 1
Summary of samples prepared with different Ca, PO_4 (and F) concentrations and seeding templates at pH 7.3.

Sample name	Seed	Added Ca: PO_4 (:F) concentrations [mM]	Molar Ca/P		
			ideal ^a	added ^b	precipitate ^c
brushite_SrHP	SrHAP	5:5 stoichiometric for brushite	1.00	0.98	1.51
$\beta\text{-TCP}$ _SrHAP	SrHAP	5:3.33 stoichiometric for $\beta\text{-TCP}$	1.50	1.44	1.46
HAP_SrHAP	SrHAP	5:3 stoichiometric for HAP	1.67	1.60	1.56
non-stoich_SrHAP	SrHAP	2:4 non-stoichiometric	–	0.48	1.16
FAP- CaF_2 _SrHAP	SrHAP	6:3:3 PO_4 -limited for FAP	–	1.97	1.90
FAP- CaF_2 _SrCO ₃	SrCO ₃	6:3:3 PO_4 -limited for FAP	–	2.00	1.71
FAP_SrHAP	SrHAP	5:3:1 stoichiometric for FAP	1.67	1.62	1.66
FAP_SrCO ₃	SrCO ₃	5:3:1 stoichiometric for FAP	1.67	1.67	1.49
FAP-HAP_SrHAP	SrHAP	5:3:0.5 F-limited for FAP	1.67	1.62	1.52
FAP-HAP_SrCO ₃	SrCO ₃	5:3:0.5 F-limited for FAP	1.67	1.67	1.49

Note: ^b and ^c are averaged values based on duplicate experiments.

^a for solid shown as stoichiometric.

^b corrected for partial dissolution of SrHAP during 10 min pre-dispersion.

^c based on the decrease in dissolved concentrations observed after 3 d.

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