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Regulating fluoride uptake by calcium phosphate minerals with polymeric additives

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ABSTRACT

The fluoride uptake by various calcium phosphate minerals is reported. Hydroxyapatite (HA), octacalcium phosphate (OCP), and dicalcium phosphate dihydrate (DCPD) were individually exposed to fluoride, and they absorbed fluoride through fluorapatite formation. The fluorapatite formation was through dissolution-and-recrystallization, and the kinetics was in the order, DCPD > OCP > HA. Polymeric additives, such as poly(ethylene imine), poly(acrylic acid), and poly(ethylene glycol), significantly affected the fluoride uptake and the fluorapatite formation. Especially, the positively charged poly(ethylene imine) inhibited the formation of fluorapatite almost completely for all calcium phosphates, and ultrasound could neutralize the inhibitory effect. The inhibition was attributed to the adsorbed poly(ethylene imine) that reduced the rate constant of the reactions probably through the increased thickness of the boundary layers and/or reduced diffusion coefficients, which could be counterbalanced by ultrasound. The kinetic regulation could have broad implications in the fields of biomedical mineralization as well as the fluoride-rich wastewater treatment.

1. Introduction

Calcium phosphates encompass some of the more important minerals in the biological sphere. Carbonate-rich hydroxyapatite is the main inorganic component of the endoskeleton of vertebrates [1]. Octacalcium phosphate is involved in the formation of the apatite as the possibly initial precipitate that could act as the apatite-nucleating template [1]. Dicalcium phosphate dihydrate, also known as brushite, is often implicated in the human kidney stone formation [2,3]. Also, fluoride tends to interact with these minerals in such a way that its incorporation induces their phase transformation in the presence of water. When fluoride is present in the controlled range of concentrations as in dental treatments, the subsequent phase transformation could be beneficial by reconfiguring the apatite of teeth into less soluble fluorapatite [4]. However, fluoride in excess amounts could cause serious harm, inducing a chronic condition known as fluorosis [5–7].

Fluoride of high concentrations in ground water can be caused by both natural and man-made reasons. Some regions possess a large amount of geological minerals, such as fluorite, biotite, and topaz, which can release fluoride into ground water [8]. Representative areas include North Africa, Middle East, China, and India [8]. Also, fluoride-containing wastewater is generated from industries manufacturing semiconductor, glass, aluminum, fertilizer, and so on [9–11].

Wastewater containing fluoride has been mainly treated via adsorption and precipitation, while ion exchange and membrane filtration are also available [9,12,13]. Adsorbents utilizing rare earth elements have been getting attentions because of their efficacy in fluoride removal, while the increasing price seems problematic [14,15]. Precipitation methods using calcium salts have been industrially utilized with formation of calcium fluoride [9]. Still, the equilibrium fluoride concentration without an excess amount of calcium would be ca. 8 mg/L, which is fairly high, since the solubility product constant (K_{sp}) of calcium fluoride is 3.45×10^{-11} at 25 °C [16]. Notably low K_{sp} of ca. 10^{-120}–10^{-123} is possessed by fluorapatite ($Ca_{10}(PO_4)_6F_2$) [17,18], which makes it an interesting target for fluoride removal. In fact, the practical aspect of brushite usage has been studied in combinations of calcium hydroxide, calcite, and hydroxyapatite to reduce fluoride concentration in water [19–21].

In the present study, we investigated the kinetics of fluoride reactions with hydroxyapatite (HA), octacalcium phosphate (OCP), and brushite (DCPD). This was both to understand the process of phase transformation and to search for an inexpensive and optimized method of fluoride removal from wastewater. Also, practical sources of reaction retardation and acceleration were studied by means of polymeric additives and ultrasound. The effects of some polymeric additives were especially studied in detail also because

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of their implication in biomineralization. The regulation of inorganic phases by organic macromolecules is the hallmark of the biomineralization, because it is responsible for the controlled phase transformation of biominerals and the unusually intricate crystal morphology [22], both of which have been observed in our investigation.

2. Experimental

2.1. Materials

Calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$, 99.0%), calcium chloride dihydrate ($CaCl_2{\cdot}2H_2O$, 99+%, ACS reagent), urea ($CO(NH_2)_2$, 99.0%), and sodium fluoride (NaF, 99.0%) were purchased from Sigma–Aldrich. Gelatin (bovine skin, ~75 Bloom) was obtained from Sigma, and agarose (low melt) was from Pierce. Sodium dihydrogen phosphate dihydrate ($NaH_2PO_4{\cdot}2H_2O$, 99.0%) and potassium dihydrogen phosphate (KH_2PO_4, 99.99%) were purchased from Fluka. Poly(ethylene glycol) (PEG: $[CH_2CH_2O]_n$, M_w 8000 and 100,000), poly(acrylic acid) (PAA: $[CH_2CH(COOH)]_n$, sodium salt, 35 wt% solution in water, M_w 1800 and 15,000), and poly(ethylene imine) (PEI: $[CH_2CH_2NH]_n$, M_w 2000 and 25,000) were obtained from Aldrich. Distilled and deionized water (DDW) (resistivity >17 MΩ cm) was from Thermolyne D2622 (Barnstead, Dubuque, IA).

2.2. Preparation and characterization of calcium phosphates

OCP and HA were prepared by employing an existing method, known as single-crystal-to-single-crystal transformation [23]. Calcium nitrate tetrahydrate (20 mM) and sodium dihydrogen phosphate dihydrate (20 mM) were dissolved in 500 mL DDW. The pH was initially 4.5, and it was raised via thermal decomposition of urea (40 mM) by placing the solution in a closed container into a 100 °C convection oven. OCP was obtained after 6 h (pH 6.0), and HA was formed after 24 h (pH 7.5) via transformation of OCP phase. The desired crystal phase was filtered and thoroughly washed with DDW. It was dried in a 60 °C convection oven for 48 h before further use.

DCPD was prepared by utilizing a recipe known as the ion diffusion method [24]. A gelatin matrix (10%, w/v, 50 mL) containing NaH_2PO_4 (1.1 M) was prepared by heating the solution at 70 °C and subsequently cooling at room temperature for 6 h. Then, the same volume of 2.7 M $Ca(NO_3)_2$ (aq) was placed on top of the gelatin matrix to initiate calcium diffusion into the gel. DCPD crystals started to form within an hour, and more crystals formation, as a band of white powder at the interface, was accompanied by the local disintegration of gelatin matrix. The reaction was stopped after ca. 24 h when the crystal phase was precipitated at the bottom of the reaction vessel (pH 5). The crystals were filtered and thoroughly washed with DDW. The product was dried at room temperature for 48 h before further use.

DCPD single crystal was also prepared by the ion diffusion method but with a different gel matrix [25]. Agarose gels (1 wt%, 2 mL) containing 0.1 M KH_2PO_4 were permeated by 0.1 M $CaCl_2$ (aq, 2 mL) placed on top of the gels. Before ion diffusion, the gels were allowed to set for 24 h, and all reagent solutions were clarified through 0.2 μm poly(tetrafluoroethylene) (PTFE) filters. After 2–3 weeks, single crystals were harvested and washed with DDW. The product was dried at room temperature for at least 48 h before further use.

Morphology of the calcium phosphate crystals was observed via scanning electron microscopy (SEM, JEOL JSM-6360A) after thin Au coating (Cressington Sputter Coater 108) to minimize surface charging. Ca/P ratios of the crystals were measured by energy dispersive X-ray spectroscopy (EDS, JEOL EX-54175 JMU). The crystal phases were confirmed by wide-angle X-ray diffraction using a Bruker D8 Advance General Area Detector Diffraction System (GADDS) with Cu K_α ($\lambda = 0.154$ nm) radiation generated at 40 kV and 45 mA. A frame of diffraction data (4–40°) was collected with a Hi-Star multi-wire 2D area detector for 300 s by placing the detector at the center of the 2θ range. Data was integrated to display a typical 2θ plot vs. intensity. Spectral data were analyzed by using EVA 9.0.0.2 software containing references from the Joint Committee on Powder Diffraction Standards (JCPDS).

Surface areas of HA, OCP, and DCPD were measured using methylene blue (MB) as a molecular probe for adsorption area [26–28]. Each solid powder (100 mg) was individually placed in a 0.10 mM MB aqueous solution (3 mL). UV absorbance was measured after 24 h at 665 nm (Jasco V-560 UV/Vis Spectrophotometer, Japan), and the remaining MB concentration was calculated against a pre-obtained calibration curve. (Note that the MB adsorption reached equilibrium stages before 24 h, showing the same UV absorbance at 24, 48, and 72 h.) From the average of 5 measurements, the surface area was calculated using 1.3 nm^2 of occupying area per MB molecule [26,27].

Zeta-potential measurement was performed using a Malvern zetasizer 2000 (Malvern Instrument, U.K.). HA, OCP, or DCPD powders (20 mg) were dispersed in DDW (20 mL) at neutral pH. After 1–2 min of shaking, 2–3 mL of each solution was used for the measurement at 25 °C. When polymeric additives were present (0–10 μM), it was solubilized in the water part before adding particles. For each condition, 3 independent solutions were prepared, and each solution was measured 5 times.

2.3. Fluoride uptake by calcium phosphates

The calcium phosphate crystals were reacted with fluoride ions for 24 h. Each phase was placed in an aqueous solution of 50-ppm fluoride (2.63 mM NaF (aq), 20 mL) at room temperature under vigorous stirring (110–120 rpm) with a Teflon-coated magnetic stir bar (rod-shaped: length 14 mm, diameter 5 mm). The reaction vessel (diameter 27 mm, height 61 mm) was made with isotactic polypropylene. The amount of each crystal phase was to set $Ca/F \approx 5{:}1$ (HA, 26.4 mg; OCP, 35.2 mg; DCPD, 45.3 mg). Variation of the fluoride concentration was monitored in situ with a fluoride-selective electrode (Thermo Electron Corporation, an Orion 4-Star pH/ISE Benchtop meter equipped with an Orion 9609BNWP Combination fluoride electrode and an Orion 8102BNUWP ROSS Ultra glass combination pH electrode). The reaction was carried out at initial pH 3 and 7 to investigate the effect of pH on the reaction kinetics. A small amount of 1 N HNO_3 (aq) was used to adjust the pH of the NaF solution before reaction started. Drift of pH, as the reaction proceeded, was left unaltered to observe spontaneous reaction pathways. In addition, the effects of polymeric additives, such as PEG, PAA, and PEI, were studied. Polymer concentrations investigated were: 1.0 and 10 μM for PEG $M_w \approx M_n$ 8000; 10 μM for PEG M_w 100,000; 10 μM for PAA M_w 1800; 1.0 and 10 μM for PAA M_w 15,000; 1.0 and 10 μM for PEI M_w 2000 (M_n 1800); 0.010 and 0.10 μM for PEI M_w 25,000 (M_n 10,000). Each reaction was monitored at every hour, and the reported value of fluoride concentration was the average of the five independently performed experiments. After 24 hour of reactions, the solid phases were filtered, washed with DDW, and dried at 60 °C for further examination.

HA, OCP, and DCPD were also reacted with 50-ppm fluoride with application of ultrasound. Scientz-II D Ultrasonic Cell Crusher (probe size Φ6) was utilized with the pulser ratio 20% (190 W), and pulser on/off time was 0.5 s/9.9 s, where any change in the solution temperature was not observed. Each reaction was monitored at every hour, and the reported value of fluoride concentration was