



A comparative study on the dissolution and solubility of hydroxylapatite and fluorapatite at 25 °C and 45 °C

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ABSTRACT

Dissolution of the synthetic hydroxylapatite (HAP) and fluorapatite (FAP) in pure water was studied at 25 °C and 45 °C in a series of batch experiments. The XRD, FT-IR and SEM analyses indicated that the synthetic, microcrystalline HAP and FAP with apatite structure used in the experiments were found to have no obvious variation after dissolution except that the existence of OH groups in FT-IR spectra for FAP after 2880 h dissolution was observed. During the HAP dissolution (0–4320 h), the aqueous calcium and phosphate concentrations reached the maxima after 120 h and then decreased slowly with time. For the FAP dissolution in pure water, after a transient time of 1440 h (<60 d), element concentrations and pH became constant suggesting attainment of a steady-state between the solution and solid. During early stages of the FAP dissolution reaction (<72–120 h), mineral components were released in non-stoichiometric ratios with reacted solution ratios of dissolved Ca:P, Ca:F and P:F being lower than mineral stoichiometric ratios of $\text{Ca}_5(\text{PO}_4)_3\text{F}$, i.e., 1.67, 5.0 and 3.0, respectively. This indicated that F were preferentially released compared to Ca from the mineral structure. The mean K_{sp} values were calculated by using PHREEQC for HAP of $10^{-53.28}$ ($10^{-53.02}$ – $10^{-53.51}$) and for FAP of $10^{-55.71}$ ($10^{-55.18}$ – $10^{-56.13}$) at 25 °C, the free energies of formation ΔG_f° [HAP] and ΔG_f° [FAP] were calculated to be –6282.82 kJ/mol and –6415.87 kJ/mol, respectively.

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1. Introduction

Apatites [$\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH})$] play important roles in many environmental, industrial and medical processes (Bengtsson et al., 2009). Apatite is the most common phosphate mineral and the main source of the phosphorus required by plants, and because phosphorus is a growth limiting nutrient for all living organisms, the release of phosphorus from apatite dissolution controls the productivity on many ecosystems (Schlesinger et al., 1998; Bengtsson et al., 2009). Apatite is essential raw material in the manufacture of phosphate fertilizers, and is very important in the chemical and pharmaceutical industries (Skarstila and Spanos, 2007; Becker, 1989).

The apatite minerals occur as accessory minerals in almost all igneous rocks, in metamorphic rocks, in veins and other ore deposits; and most commonly as fine-grained and often impure masses as the chief constituent of phosphate rock (Dorozhkin, 1997). The mineral apatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) is one of the major reservoirs of both phosphorous and fluorine in the Earth's crust. As such apatite plays a critical role in a number of geochemical processes. Apatite influences strongly the concentration of surface, ground, and ocean water including their REE content (Harouiyi et al., 2007; Godderis et al., 2006; Köhler et al., 2005). The hard tissues in animal and human bones

and teeth consist of the so-called biological apatite (Skarstila and Spanos, 2007; Tseng et al., 2006). Hydroxylapatite (HAP) has also received much attention in medical sciences as material for artificial bone and teeth implants (Schlesinger et al., 1998).

Apatite may be used in the remediation of metal-contaminated soils and apatite precipitation has been proposed as an effective means for remediating polluted wastewaters. There are many reports on using HAP to stabilize a variety of metals, such as Co, Pb, Cu, Zn, Cd, Sb, and Cr (Zhu et al., 2008; Gómez del Río et al., 2006; Harouiyi et al., 2007), due to its capacity to retain durably a large variety of trace elements (Skarstila and Spanos, 2007).

The importance of apatite in a great variety of fields therefore calls for an understanding of their fundamental chemical properties, especially the dissolution mechanism and solubility at a variety of conditions. A number of investigations devoted to apatite dissolution kinetics and mechanisms in water, buffers, and acidic media have already been made (Harouiyi et al., 2007; Skarstila and Spanos, 2007; Tseng et al., 2006; Fulmer et al., 2002; Dorozhkin, 2002; Valsami-Jones et al., 1998; Dorozhkin, 1997). However, there always exists a controversy about whether apatite dissolves stoichiometrically/congruently (Harouiyi et al., 2007; Chairat et al., 2007b) or non-stoichiometrically/incongruently (Dorozhkin, 1997). The mechanism and surface processes of apatite dissolution are not completely understood. On the other hand, although FAP is less soluble than HAP, literature values of the solubility products vary considerably for both minerals. Values for FAP vary between 10^{-70} (Valsami-Jones et

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al., 1998) and $10^{-58.13}$ (Jaynes et al., 1999) while those for HAP exhibit an even greater variation between $10^{-88.5}$ (McDowell et al., 1977) and $10^{-55.9}$ (Snoeyink and Jenkins, 1980). These discrepant solubility products can be due to differences between the minerals in the different studies, but also due to differences in the way the experiments in the studies have been conducted (Bengtsson, 2007). Inconsistency in data presented in literature could be due to the failure to achieve equilibrium, even though some mineral suspensions were equilibrated for as long as 6 weeks (Valsami-Jones et al., 1998) or 120 hours (Fulmer et al., 2002) before being analyzed.

The goal of this study is the improved and complemented understanding of apatite dissolution mechanism. In the present study, hydroxylapatite and fluorapatite were prepared by precipitation and characterized by various techniques. The dissolution mechanism and rate of the synthetic solids have been studied at temperatures 25 °C and 45 °C. Moreover, the aqueous concentrations from the batch dissolution permit estimation of the solubility and free energy of formation of hydroxylapatite and fluorapatite.

2. Experimental methods

2.1. Solid preparation and characterization

The experimental details for the preparation of the samples by precipitation were based on the following equation: $5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{X}^- = \text{Ca}_5(\text{PO}_4)_3\text{X}$. Where $\text{X} = \text{OH}^-$ or F^- . Hydroxylapatite [$\text{Ca}_5(\text{PO}_4)_3\text{OH}$] was synthesized by controlled mixing of a slurry of 100 mL 0.5 M $\text{Ca}(\text{OH})_2$ and a solution of 60 mL 0.5 M H_3PO_4 ; fluorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$] was synthesized by controlled mixing of a solution of 100 mL 0.5 M $\text{Ca}(\text{NO}_3)_2$ and a solution of 60 mL 0.5 M Na_3PO_4 and a solution of 20 mL 0.5 M NaF, so that a Ca/P molar ratio in the mixed solution was 1.67. Reagent grade chemicals and ultrapure water were used for the synthesis and all experiments. The initial solutions were slowly mixed in a covered beaker in a course of 10 minutes at room temperature (23 ± 1 °C). The pH values of the synthesis media were adjusted to be 7–8 by using 1 M KOH solution. The resulting solution was kept at 70 °C and stirred at a moderate rate (100 rpm) using a stirrbar. After a week, the precipitates were allowed to settle. The resultant precipitates were then washed thoroughly with ultrapure water and dried at 110 °C for 24 h.

The composition of the sample was determined. The residual Ca^{2+} , Na^+ , F^- , NO_3^- and PO_4^{3-} concentrations in the decanted solutions were analyzed to calculate the compositions of the precipitates. In addition, approximately 10 mg of sample was digested in 20 mL of 1 M HNO_3 solution, and then diluted to 100 mL with ultrapure water. It was analyzed for Ca using a Perkin Elmer Model AAnalyst 700 atomic absorption spectrometer (AAS), PO_4^{3-} , F^- , Na^+ and NO_3^- using an ion chromatography (Dionex ICS-1000). The synthetic solids were characterized by powder X-ray diffraction (XRD) with an X'Pert PRO diffractometer using $\text{Cu K}\alpha$ radiation (40 kV and 40 mA). Crystallographic identification of the synthesized apatite was accomplished by comparing the experimental XRD pattern to standard compiled by the International Center for Diffraction Data (ICDD), which were card #00-009-0432 hydroxylapatite and card #00-015-0876 fluorapatite. The morphology was analyzed by scanning electron microscopy (SEM, Joel JSM-6380LV). Infrared transmission spectra (KBr) were recorded over the range of $4000\text{--}400\text{ cm}^{-1}$ using a FT-IR spectrophotometer (Nicolet Nexus 470 FT-IR).

2.2. Dissolution experiments

The dissolution and solubility experiments were conducted in much the same manner as those used for determining the solubility of magnesite [MgCO_3] by Kittrick and Peryea (1986) and for determining the solubility of barium arsenate by Essington (1988).

0.5 g of the synthetic solid was placed in 250 mL polypropylene bottle. 150 mL of ultrapure water was added into each bottle. The

bottles were capped and placed in a temperature-controlled water bath (25 °C and 45 °C). Water samples (3 mL) were taken from each bottle on 17 occasions (1 h, 3 h, 6 h, 12 h, 1 d, 2 d, 3 d, 5 d, 10 d, 15 d, 20 d, 30 d, 45 d, 60 d, 90 d, 120 d, and 180 d). After each sampling, the sample volume was replaced with an equivalent amount of ultrapure water. The samples were filtered using 0.20 μm pore diameter membrane filters and stabilized with 0.2% HNO_3 in 25 mL volumetric flask. Ca was analyzed by using an atomic absorption spectrometer and PO_4^{3-} and F^- using an ion chromatography. After 2880 h dissolution, the solid samples were taken from each bottle, washed, dried and characterized using XRD, SEM and FT-IR in the same manner as described above.

2.3. Thermodynamic calculations

Associated with each dissolution is an assemblage of solid phases, a solution phase containing dissolved calcium, phosphate and fluor, and a pH value. Assuming equilibrium has been reached, the thermodynamic data can be calculated using established theoretical principles (Bothe and Brown, 1999). In this study, the simulations were performed using PHREEQC (Version 2.15) together with its minteq.v4.dat database, which bases on the ion dissociation theory. The input is free-format and uses order-independent keyword data blocks that facilitate the building of models that can simulate a wide variety of aqueous-based scenarios (Parkhurst and Appelo, 1999).

3. Results and discussion

3.1. Solid characterizations

The composition of the synthetic solid depends on the initial Ca:P or Ca:P:F mole ratio in the starting solution. To ensure that hydroxylapatite or fluorapatite were formed, the precipitation was conducted by mixing phosphate solution, calcium solution and fluoride solution at low rate. Results suggest that the crystal was the intended composition of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ or $\text{Ca}_5(\text{PO}_4)_3\text{F}$. The atomic Ca/P ratio was 1.67 which is a stoichiometric ratio of apatite. No Na^+ and NO_3^- were detected in the prepared solid (Zhu et al., 2009, in press).

XRD, FT-IR and SEM analyses were performed on the solids before and after the dissolution experiments (Figs. 1, 2 and 3). As illustrated in the figures, the results of the analyses on materials before the dissolution were almost indistinguishable from the following reaction. No evidence of secondary mineral precipitation was observed in the dissolution experiment.

The hydroxylapatite and fluorapatite were observed by SEM to have a platy morphology with very fine particles on the crystal surface

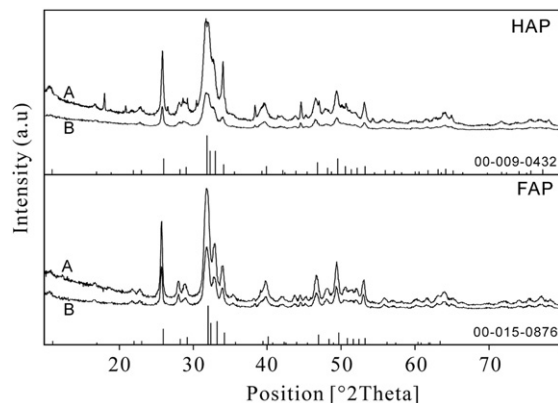


Fig. 1. XRD patterns of the synthetic hydroxylapatite and fluorapatite before (A) and after (B) dissolution at 25 °C for 120 d.

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