SOLUBILITY AND SURFACE COMPLEXATION
STUDIES OF APATITES

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Akademisk avhandling
Som med tillstånd av rektorsämbetet vid Umeå universitet för avläggande av filosofie
doktorsexamen vid Teknisk–Naturvetenskapliga fakulteten, framlägges till offentlig
granskning vid Kemiska institutionen, sal KB3B1, KBC, fredagen den 16 november
2007, kl. 10.00.
Fakultetsopponent: Professor Laurent Charlet, Observatory for Earth and Planetary
Sciences (OSUG), LGIT University of Grenoble I, CNRS, France

Department of Chemistry
Umeå University, Umeå, Sweden, 2007
Apatites are a diverse class of phosphate minerals that are important in a great variety of natural and industrial processes. They are, for example, used as raw material in fertilizer production and in the remediation of metal-contaminated soils. Hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, (HAP) and fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$, (FAP) are similar to the biological apatite that is the main constituent of mammalian bone and teeth, and they are therefore promising materials for artificial bone and tooth implants.

This thesis is a summary of four papers with focus on dissolution and surface complexation reactions of HAP and FAP in the absence and presence of both organic ligands and the natural and commonly occurring iron oxide goethite ($\alpha$-FeOOH).

The dissolution and surface complexation of HAP and FAP was investigated with a combination of different techniques. Potentiometric acid/base titrations and batch experiments were combined with X-ray Photoelectron Spectroscopy (XPS) and Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) Spectroscopy to generate dissolution and surface complexation models for both apatites. The results from these studies showed that both apatites form surface layers that are different from their bulk compositions when equilibrated in aqueous solutions. The modeling efforts predicted speciation of these surfaces as well as the concentration of the dissolution products in the solution.

The interaction between organic ligands and the apatite surfaces was also investigated and the results from this study show that the organic ligands form outer-sphere complexes on the apatite surfaces over a large pH interval, and that this adsorption enhances the dissolution of apatites.

The presence of goethite also enhances the dissolution of FAP as it acts as a sink for the phosphate released from FAP. Phase transformation in this system was detected using ATR-FTIR as the phosphate adsorbed to the goethite surface precipitates as FePO$_4$ (s) after approximately 15 days of reaction time. This changes the speciation, and possibly also the bioavailability of phosphate in this two-mineral system.

Keywords: apatite, dissolution, calcium, phosphate, fluoride, goethite, surface complexation, speciation, outer-sphere complexation, FTIR, XPS, potentiometry.
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Doctoral Thesis
2007

Department of Chemistry
Umeå University
Umeå
Sweden, 2007
Title: Solubility and Surface Complexation Studies of Apatites
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Abstract

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ISBN: 978-91-7264-425-0  56 pages and 4 papers
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1. **List of Papers**

This thesis is based on the papers listed below, which will be referred to in the text by the corresponding Roman numerals (I-IV).

I. **Dissolution, Adsorption and Phase Transformation in the Fluorapatite – Goethite System.**

   Å. Bengtsson, M. Lindegren, S. Sjöberg, P. Persson
   *Applied Geochemistry.* 9, 2016-2028,

II. **A Solubility and Surface Complexation Study of a Non-Stoichiometric Hydroxyapatite.**

   Å. Bengtsson, A. Shchukarev, P. Persson, S. Sjöberg
   Submitted to *Geochimica et Cosmochimica Acta*

III. **Solubility and Adsorption Characteristics of Non-Stoichiometric Surface Layers of Hydroxyapatite with some Organic Carboxylic Acids: An ATR-FTIR Spectroscopic and Thermodynamic Modeling Study**

   Å. Bengtsson, S. Sjöberg, P. Persson
   Submitted to *Geochimica et Cosmochimica Acta*

IV. **Phase Transformations, Ion-Exchange, Adsorption, and Dissolution Processes in Aquatic Fluorapatite Systems**

   Å. Bengtsson, A. Shchukarev, P. Persson, S. Sjöberg
   *Manuscript*
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>AAS</td>
<td>Atomic Absorption Spectroscopy</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated Total Reflectance – Fourier Transform Infrared</td>
</tr>
<tr>
<td>e.m.f</td>
<td>Electromotive force</td>
</tr>
<tr>
<td>FAP</td>
<td>Fluorapatite</td>
</tr>
<tr>
<td>HAP</td>
<td>Hydroxyapatite</td>
</tr>
<tr>
<td>IC</td>
<td>Ion Chromatography</td>
</tr>
<tr>
<td>i.e.p</td>
<td>Isoelectric Point</td>
</tr>
<tr>
<td>p.z.c</td>
<td>Point of Zero Charge</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Powder Diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>CCM</td>
<td>Constant Capacitance Model</td>
</tr>
<tr>
<td>Mal</td>
<td>Malonate</td>
</tr>
<tr>
<td>Cit</td>
<td>Citrate</td>
</tr>
<tr>
<td>Mel</td>
<td>Mellitate</td>
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3. Introduction

Apatites (Ca$_3$(PO$_4$)$_3$(F,Cl,OH)) are the most commonly occurring phosphate minerals on Earth, and consequently the primary natural sources of phosphorous [1]. Because phosphorous is an essential element in all living cells and a key nutrient in all ecosystems, the release of phosphorous from apatite dissolution controls the productivity of these ecosystems. In soils, phosphorous is released from apatite by several different processes, such as the reduction of pH and ion exchange with organic ligands (proton and ligand promoted dissolution).

Apatites are important raw material in the production of fertilizers, detergents and phosphoric acid. In addition, hydroxyapatite is compositionally similar to the calcium-deficient carbonate-hydroxyapatite found in human bones and teeth and has consequently been defined as a good candidate as material for artificial orthopedic and dental implants. Given the widespread uses of apatites in a diversity of fields, a detailed knowledge of the chemical properties of the minerals, and especially of their surfaces, becomes essential. Interactions with soils, body fluids and microorganisms inhabited within these systems can affect minerals, as well as their dissolution products. The present work has therefore been devised to resolve some of these issues, focusing on surface complexation reactions at the HAP-water and FAP-water interfaces, and their impact and relationship to mineral dissolution.

This thesis contains four papers. In Paper I the effects of goethite-promoted dissolution of FAP are described by means of dissolution experiments and thermodynamic modeling. Paper II is focused on the dissolution of HAP particles suspended in aqueous media and shows the importance of surface layers in this process. Paper III extends the efforts of Paper II by documenting the coordination of organic ligands adsorbed on the HAP surface and their effects on dissolution. Finally Paper IV consists of a FAP dissolution study paralleling the efforts of Papers II and III on HAP, and discusses the role of the fluoride ion, as well as organic ligands, in controlling dissolution.
4. **Aim of the Thesis**

The general aim of this thesis is to gain insight into the chemical properties of synthetic hydroxyapatite (HAP) and fluorapatite (FAP) particles. Four dominant aims include:

a) To characterize the surface composition using surface sensitive methods like XPS and ATR-FTIR;

b) To characterize the reactivity of apatite minerals with respect to their acid/base properties and to generate a model for the dissolution and surface complexation reactions;

c) To provide a description of the influence of organic acids on the dissolution of both hydroxyapatite and fluorapatite;

d) To predict the role of goethite (α-FeOOH) on the dissolution of fluorapatite.
5. **Phosphorous – Geochemical Cycle**

The cycling of phosphorous in soils and sediments has been the object of many studies in the contexts of fertilization and also, more lately, eutrophication [2]. As already mentioned, apatites are the primary natural source of phosphate, and weathering of apatites is the initial source of phosphorus to the global system. Human impact has increased this input of phosphorus by applying fertilizers to fields to increase crop yields. However, as phosphate is very immobile in most soils it is not necessarily bioavailable for plant uptake. Phosphate is very reactive and can precipitate with, for example, calcium, magnesium, iron and manganese in soils. It can also strongly adsorb to different metal hydroxide surfaces like goethite (α-FeOOH), gibbsite (α-Al(OH)$_3$) and alumina (Al$_2$O$_3$), as well as to organic matter in soils.

Plants and microorganisms have developed different strategies to increase their supply of phosphorous. They can for example secrete an enzyme, phosphatase, which cleaves inorganic phosphates from organophosphates. They can also exude small organic acids such as malonic acid and citric acid [3]. These acids can affect the amount of bioavailable phosphate in several different ways. i) they cause a decrease in pH which enhances the dissolution of minerals like apatite, ii) they take part in processes such as complexation with e.g. calcium, iron and aluminium, and iii) the acids can also out-compete phosphate that is adsorbed to different mineral surfaces.

6. **Phosphorous – in Teeth and Bones**

Apatite is the most important calcium phosphate mineral occurring in the human body. A carbonate-containing calcium deficient apatite is a major component of bones and teeth and as HAP is very similar to this component, synthetic HAP is a promising material for artificial bone and teeth implants [4].

Bones are always in contact with surrounding extracellular fluid and are therefore very susceptible to the content of the fluid. For example, toxic elements like cadmium and lead that are introduced to extracellular fluids can potentially accumulate in bones. Bones also provide a reservoir of calcium,
phosphate and carbonate ions to the extracellular fluids and the solubility of the bone mineral controls the concentration of these ions [5]. Dallemagne and Richelle [6] discovered that bones contain 0.8 – 0.9 wt % citrate that is likely to be adsorbed onto apatite crystals of bones. This citrate most likely influences the solubility of the bone mineral and therefore also changes the composition of the extracellular fluid.

Bacteria in the mouth produce acids that attack the teeth and cause tooth decay. Fluoridation of apatite in teeth is believed to suppress tooth decay and the role of the fluoride ions in this process has been the subject of numerous investigations [7, 8, 9]. Precipitation of less soluble FAP, formation of a protective surface layer of fluoride ions, and inhibition of acid generation from oral bacteria are some suggestions to why fluoride suppresses dental decay. The role of fluoride ions in enamel caries however seems to be far from understood.

7. Apatites – General Chemistry

Pure apatites defines three unique minerals; fluorapatite \([\text{Ca}_5(\text{PO}_4)_3\text{F}]\), chlorapatite \([\text{Ca}_5(\text{PO}_4)_3\text{Cl}]\), and hydroxyapatite \([\text{Ca}_5(\text{PO}_4)_3\text{OH}]\). These minerals lack chemical substitutions and belong to the space group \(P6_3/m\) and have a formula unit \((Z)\) of 2 [10].

The phosphorous in apatites are in tetrahedral coordination to four oxygen atoms, which are coordinated to two different types of calcium atoms. Ca1 is coordinated to nine oxygen atoms and has \(z\) values of 0 and \(\frac{1}{2}\). This calcium atom does not coordinate to \(F, Cl\) or \(OH\). The Ca2 ion is coordinated to six oxygen atoms and one anion, i.e. \(F, Cl\) or \(OH\). It forms layers of triangles on the planes \(z = \frac{1}{4}\) and \(z = \frac{3}{4}\) and in the middle of these triangles a column of anions builds up (Figs. 1 and 2). Here a difference between the three apatites takes place. The OH ion and especially the Cl ion are too big to fit in the same plane as the three surrounding calcium atoms, and are therefore placed above or below the plane. This causes a disturbance in the \(P6_3/m\) symmetry of the crystal. The F ion in fluorapatite, however, is small enough to fit in the same plane as the three calcium atoms and does not cause this disturbance of the symmetry.
Figure 1. The atomic arrangement of hydroxyapatite projected on the \{001\} plane (green = F; red = Ca\(^{2+}\); black = P\(^{5+}\); blue = O\(^{2-}\)). The black triangles mark the position of the column of fluoride ions surrounded by Ca\(^{2+}\) atoms.

Figure 2. Depiction of possible anion positions in the hexagonal apatite structure. This figure is adapted from Hughes et al. [8].
Pure apatites do exist in nature but more commonly occur as solid solutions with a wide range of composition. The anions in the column along the z-axis can hold a combination of Cl, F, and OH. Calcium can be substituted with a number of different cations (e.g. Cu$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Zn$^{2+}$) while phosphate can be replaced by a range of anions (e.g. SO$_4^{2-}$, AsO$_4^{3-}$, CO$_3^{2-}$, SiO$_4^{4-}$).

The apatite crystal can exhibit many different forms, but most apatite crystals are needle-shaped and only bound by the \{100\} and the \{001\} planes [11] (Fig. 3), and according to Kukura et al. [12], the \{100\} is the dominant plane. Crystallographic data of apatites show that there are roughly 12 sites / nm$^2$ on this plane but some studies [12, 13] suggest that only a fraction of these sites is chemically active.

Figure 3. Schematic picture of (left) the stoichiometric composition, and (right) example of a calcium and fluoride/hydroxide depleted composition of the \{100\} surface of FAP/HAP. The solid lines represent the unit cell.
7.1. HAP and FAP

HAP and FAP have molecular masses of 502.29 g/mol and 504.98 g/mol, respectively. Although FAP is less soluble than HAP, literature values of the solubility products according to reactions (1) and (2) vary considerably for both minerals. Values for FAP vary between $1 \times 10^{-70}$ [14] to $1 \times 10^{-58.13}$ [15] while those for HAP exhibit even greater variation between $1 \times 10^{-88.5}$ [16] and $1 \times 10^{-55.9}$ [17]. 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. When working with minerals like apatites, one has to consider a myriad of factors that can affect the outcome of the experiments, and one very important factor seems to be the equilibration period prior the experiments. Previous studies [18] have shown that 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 30 days before being analysed.

Apatites are complex minerals and when investigating their dissolution a number of possible reactions must be taken into account. The dissolution according to reactions (1) and (2) are strongly pH dependent and coupled with protonation and complexation reactions like those of (3) and (4). For FAP, complexation reactions involving the fluoride ion (5) and (6), as well as the formation of a secondary precipitate at low pH (7), also have to be considered:

\[
\begin{align*}
\text{Ca}_5(\text{PO}_4)_3\text{OH} & \rightleftharpoons 5 \text{Ca}^{2+} + 3 \text{PO}_4^{3-} + \text{OH}^- \quad (1) \\
\text{Ca}_5(\text{PO}_4)_3\text{F} & \rightleftharpoons 5 \text{Ca}^{2+} + 3 \text{PO}_4^{3-} + \text{F}^- \quad (2) \\
\text{PO}_4^{3-} + n\text{H}^+ & \rightleftharpoons \text{H}_n\text{PO}_4^{(3-n)-} \quad (n = 1, 2, 3) \\
\text{Ca}^{2+} + \text{PO}_4^{3-} + n\text{H}^+ & \rightleftharpoons \text{CaH}_n\text{PO}_4^{(n-1)+} \quad (n = 1, 2) \\
\text{Ca}_5(\text{PO}_4)_3\text{F} + 6 \text{H}^+ & \rightleftharpoons \text{CaF}^+ + 4 \text{Ca}^{2+} + 3 \text{H}_2\text{PO}_4^- \quad (5) \\
n\text{F}^- + \text{H}^+ & \rightleftharpoons \text{HF}_n^{(2n-1)+} \quad (n = 1, 2) \\
\text{Ca}^{2+} + 2 \text{F}^- & \rightleftharpoons \text{CaF}_2 \text{ (s)} \quad (7)
\end{align*}
\]
It has been suggested that apatites form surface layers of different compositions than the bulk when they get in contact with an aqueous solution [12, 19, 20] but the composition of these surface layers is not fully understood. What is clear is that the formation of a surface layer would affect the solubility of the mineral and that the solubility would reflect the composition of the surface layer and not the apatite in the bulk. One process that has been suggested to be responsible for the formation of this non-stoichiometric surface layer on HAP is the creation of vacancies on Ca and OH sites and the protonation of phosphate groups. The range of composition may be expressed as \( Ca_{(10-x)}(HPO_4)_{x}(PO_4)_{(6-x)}(OH)_{(2-x)} \) but the limiting composition of this non-stoichiometric HAP is somewhat uncertain. Limiting values of \( x = 1 \) (\( Ca(HPO_4)(PO_4)OH \), with \( Ca/P = 1.5 \)) [8] as well as \( x = 2 \) (\( Ca(HPO_4)2(PO_4)4 \) with \( Ca/P = 1.33 \)) [21] have been suggested. In addition, Meyer and Fowler [22] claim the existence of a limiting value of 1.4. (\( Ca_{8-d}(HPO_4)1,d(PO_4)4,d(OH)0,d \) \\

Another process that has to be taken into account when discussing the dissolution of apatites is the formation of surface complexes. The two surface sites that can take part in surface complexation reactions are believed to be \( \equiv CaOH \) and \( \equiv OPO_3H_2 \) [23]. The complexation reactions that have been considered in the model presented within this work are shown in reaction (8)-(13).

\[
\begin{align*}
\equiv CaOH + nH^+ &\rightleftharpoons \equiv CaOH_n^{n+} & (n = -1, 1) & (8) \\
\equiv OPO_3H_2 &\rightleftharpoons \equiv OPO_3H_{2-n}^{n-} + nH^+ & (n = 1, 2) & (9) \\
\equiv CaOH_2^{+} + H_2PO_4^- &\rightleftharpoons \\
&\equiv CaOPO_3H_{n}^{(n-2)-} + (2-n)H^+ + H_2O & (n = 0, 1, 2) & (10) \\
\equiv OPO_3^{2-} + Ca^{2+} + nH^+ &\rightleftharpoons \equiv OPO_3Ca_n^{n+} & (n = 0, 1, 2) & (11) \\
\equiv F + H_2O &\rightleftharpoons \equiv OH + H^+ + F^- & (12) \\
\equiv CaOH_2^{+} + F^- &\rightleftharpoons \equiv CaF + H_2O & (13)
\end{align*}
\]
The number of reactions presented above demonstrates the complexity of apatite dissolution, and due to this complexity it is crucial to make use of a wide range of analytical techniques when trying to elucidate these processes. Most studies on this subject have however only analysed ions dissolved from the apatites and not investigated mineral surfaces. In this work we have used batch experiments, potentiometric titrations, zeta-potential measurements, XPS and ATR-FTIR spectroscopy and combined the results from these analyses to create one complete model of the dissolution of HAP and FAP over a large pH interval.

8. Organic Ligands

Organic acids exuded from plants and microorganisms are present in all natural soils and waters. They are very important in the process of bringing sparingly soluble phosphate minerals like apatite into solution. Little is however known quantitatively on the effects of microbial products on apatite dissolution, nor on the mechanisms responsible for the release of phosphate from minerals like apatite [24].

The organic acids used in Papers III and IV, are malonic, citric and mellitic acid (Fig. 4). Malonic acid and citric acid are known exudates from roots and microorganisms [3] and mellitic acid serves as a model substance for

![Figure 4. Structural formula of the organic ligands.](image-url)
organic acids with a high density of carboxylate groups present in soils. Citric acid has also been found in the human plasma where it can interact with the apatite surfaces in bone and teeth. 

Carboxylic acids generally bind to mineral surfaces as inner- or outer-sphere complexes. Inner-sphere complexation is a specific adsorption involving a direct bond between the ligand and the metal ion(s), i.e. calcium at the apatite surface:

\[
\equiv \text{SOH}^2 + \text{L}^- \rightleftharpoons \equiv \text{SL} + \text{H}_2\text{O} \quad (14)
\]

\[
\equiv \text{SOH} + \text{M}^{z+} \rightleftharpoons \equiv \text{SOM}^{(z-1)} + \text{H}^+ \quad (15)
\]

Outer-sphere complexation can involve: (1) direct hydrogen bonding of carboxylic groups to surface hydroxyl groups or, (2) electrostatic stabilisation with one or a concerted array of oppositely charged surface sites. The latter type of adsorption involves at least one water molecule interposed between the ligand and the mineral surface.

\[
\equiv \text{SOH}_2^+ + \text{L}^- \rightleftharpoons \equiv \text{SOH}_2^+\text{L}^- \quad (16)
\]

Vibration spectroscopy has been successfully used in deciphering binding modes of carboxylic and amino acids adsorption to a range of mineral surfaces [25, 26, 27, 28, 29, 30]. These efforts will be extended to three carboxylic acids of the apatite surfaces.
9. Experimental Procedures and Techniques

A variety of experimental techniques have been used for this work to obtain information on processes occurring both in solution and on the surfaces of the HAP and FAP minerals.

9.1. Mineral Synthesis

All minerals used for this work were synthesized in the laboratory using the methods of Hayek et al. [31] for HAP and Penel et al. [32] for FAP.

HAP was synthesised by the drop-wise addition of a 1600 mL solution of 0.37 M \((\text{NH}_4)_2\text{HPO}_4\) at pH 12 to 1200 mL of 0.83 M \(\text{Ca(NO}_3)_2\cdot4\text{H}_2\text{O}\) (also adjusted to pH 12 by additions of \(\text{NH}_3\)). The product was matured for 1 hour at approximately 80 ºC and then cooled to room temperature. The precipitate was washed several times with deionised and boiled water and then dialysed in Millipore 12-14000 D tubes for about three months. The precipitate was then dried at room temperature, gently mortared, and stored in polyethene bottles.

FAP was synthesised by the drop-wise addition of 1000 mL of 0.4 M \(\text{Ca(NO}_3)_2\cdot4\text{H}_2\text{O}\) (Scharlau) to a boiling solution of 1000 mL 0.24 M \((\text{NH}_4)_2\text{HPO}_4\) (Merck) and 0.18 M \(\text{NH}_4\text{F}\) (Merck) over a 1 hour period. pH was kept to a value of about 9 by addition of small aliquots of 25 % \(\text{NH}_3\) (Scharlau). The product was matured for an additional hour at 80 ºC and then cooled to room temperature. It was then washed with deionised and boiled water and dialysed in Millipore 12-14000 D tubes for about three months. The product was dried at room temperature, gently mortared, and then stored in polyethene bottles.

In both syntheses the long-term dialysis procedures had at least three possible effects on the maturation of the precipitates. The first one consisted of removing all excess ions from the suspension, yielding a resulting suspension of low ionic strength, which was necessary for the experiments of this study. The second effect includes a long-term maturation of the bulk solid. Finally, the third effect, which is one of the central themes of this work, involves an equilibration
between the surfaces of HAP and FAP and water. This equilibration is found to have induced the formation of a surface layer that is compositionally different than the bulk. This surface layer is expected to control the surface chemistry of the HAP and FAP particles by impacting both dissolution and well as organic acid adsorption reactions.

9.2. Batch Experiments

Batch experiments are very useful for quantifying amounts of ions dissolved from a mineral, as well as substances adsorbed to a mineral surface. The technique of batch experiments was therefore used to investigate the dissolution and acid-base properties and the determine the adsorption of organic ligands to the two apatites, and to investigate the influence of the presence of goethite on dissolution of fluorapatite.

9.2.1. Dissolution of Fluorapatite in the Presence of Goethite

To investigate how the presence of goethite could influence the dissolution of fluorapatite, series of batch experiments were prepared. The experimental procedure is described in detail in Paper I. Briefly, three series of batch experiments containing both goethite and fluorapatite were prepared. Aliquots of acidified goethite suspensions with three different concentrations were added to 15 mL test tubes. A dialysis tube containing an acidified fluorapatite suspension was added to each test tube and the test tubes were put on an end-over-end rotator to equilibrate for 2 h, 4 h, 24 h, 72 h, 7 days, 15 days, 21 days, 42 days, or 129 days. Four of the test tubes in each series were prepared as three identical replicates. After equilibration, the dialysis tubes were removed, pH was measured and the test tubes were centrifuged at 5000 rpm for 20 minutes. The goethite pastes and small volumes of the supernatants were immediately analysed by means of ATR-FTIR spectroscopy. The supernatants were filtered and analysed for calcium, phosphate, fluoride and iron in solution. One series containing only fluorapatite and one series containing only goethite were also prepared as control series.
9.2.2. **Dissolution of Hydroxy- and Fluorapatite**

The dissolution of hydroxyapatite and fluorapatite was studied in series of batch experiments. Aliquots of the mineral suspensions and appropriate volumes of acid or base to cover a large pH interval were added to 15 mL test tubes. Three of the batches in each series were prepared as three individual replicates. The test tubes were left to equilibrate on an end-over-end rotator for 3.5 months. After equilibration, pH was measured and the test tubes were centrifuged at 4000 rpm for 20 minutes. The paste obtained was analysed with X-ray Photoelectron Spectroscopy (XPS) and Attenuated Transform Reflectance Fourier Transfrom InfraRed (ATR-FTIR) spectroscopy. The remaining supernatant was filtered through a 22 µm filter and analysed for dissolved calcium, phosphate and, in the batches with fluorapatite, also for fluoride. Details for these analyses are described in Papers II and IV.

9.2.3. **Dissolution of Hydroxyapatite and Fluorapatite in the Presence of Organic Ligands**

The procedure for studying the influence of organic acids of the dissolution of hydroxyapatite and fluorapatite is described in Papers III and IV. Briefly, aliquots of apatite suspension and appropriate amounts of acid or base were mixed together with a solution of malonate, citrate or mellitate in 15 mL test tubes. The test tubes were equilibrated on an end-over-end rotator and after 3.5 months pH were measured and the test tubes were centrifuged at 4000 rpm for 20 minutes. The obtained pastes and a small volume of the supernatants were analysed immediately with ATR-FTIR and the remaining supernatants were filtered and analysed for dissolved calcium, phosphate, and fluoride in the case of fluorapatite, as well for remaining organic ligands in solution.

9.3. **Potentiometric Titrations**

Potentiometric titrations are very useful for monitoring acid-base reactions in aqueous solutions. The titrations presented in this work were performed with an automatic system designed and built at the department of Chemistry, Umeå University and thoroughly described in the literature [33, 34, 35, 36]. In short, it consists of a cell arrangement immersed in an oil thermostat to maintain constant...
temperature. The titration vessel is purged with a low flow of humidified N\textsubscript{2} gas during the experiments to avoid any interference from CO\textsubscript{2} and O\textsubscript{2}. A small propeller is used to continuously stir mineral suspensions and the use of a propeller, as an alternative to the more common magnetic stirrer, is chosen to avoid possible grinding of the mineral particles in the suspensions. The HCl and NaOH used in the titrations were prepared in a total ionic strength of 0.1 M Na(Cl), and as constant ionic medium is used, the free H\textsuperscript{+} concentration can be determined by measuring the emf (E) of the cell:

- Ag, AgCl(s) | ionic medium || equilibrium solution | glass electrode +

The E of the cell is measured and the free H\textsuperscript{+} concentration calculated with:

$$E = E_0 + g \log [H^+] + E_j$$

(17)

$E_0$ (in mV) is an apparatus constant for the cell, and it is determined from a number of titrations of hydrochloric acid with known concentration, before and directly after the titrations. $g = RT \ln 10 / nF = 59.16$ mV at 25 °C and when $n = 1$. The liquid junction potential $E_j$ (in mV), is the potential that arises at the interface between the analyte solution and the salt bridge, and is calculated according to Sjöberg et al. [35].

9.4. **Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy**

Infrared spectroscopy is used to study vibrational motions of atoms in a molecule. When subjecting a molecule to infrared radiation it absorbs a portion of the radiation at specific wavelengths, and this gives rise to vibrational excitations of the molecule. Different molecules absorb different wavelengths of the radiation and produce absorption spectra characteristic for that specific molecule.

Attenuated total reflectance (ATR) spectroscopy, is used for samples that are too strongly absorbing for conventional transmittance measurements.
The ATR cell consists of a crystal of a material with a high refractive index, in this study a diamond, and the sample is placed on top of the crystal. The crystal transmits infrared radiation and enables the IR light to be reflected at the interface between the crystal and the sample. This light penetrates only a few micrometers into the sample, giving a small analysis depth optimal for strongly absorbing samples like mineral pastes and making it more sensitive to molecules at the mineral surface.

The ATR-FTIR spectra presented in Papers I-IV were collected using a Bruker IFS 66v/s spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector. The spectra were recorded with a horizontal ATR accessory and a diamond crystal as the reflection element (SensIR Technologies). The sample cell was kept under vacuum throughout the analysis to exclude interference from carbon dioxide. The angle of incidence for this setup is approximately 45°, which is far from the critical angle at approximately 30°. Solutions and pastes were applied directly to the diamond crystal surface and covered with a vacuum-proof lid to protect the samples from vacuum and subsequent drying. 500 scans were recorded in about 7 minutes in the range 370 – 7500 cm⁻¹, with a resolution of 4 cm⁻¹. Spectra of the empty cell, supernatant, and the wet paste were collected for each sample. The spectrum of the empty cell was automatically subtracted from the two latter spectra by the OPUS software (Bruker Inc.), which also was used to control the spectrometer and in all data treatment. Sample spectra were then interpreted after subtracting the spectrum of supernatant from the spectrum of the corresponding paste. In the spectra of organic ligands adsorbed to HAP (Paper III), and the spectra of phosphate adsorbed to goethite (Paper I) a second subtraction was also executed. In Papers III and IV, spectra from the HAP and FAP series without any organic ligands present were subtracted from the series containing citrate or mellitate. The same kind of subtraction was made in Paper I, were a spectrum from the blank goethite series were subtracted from the spectrum of adsorbed phosphate on goethite. These subtractions were made to increase the signal from the adsorbed organic ligands and phosphate.

In the HAP series without organic ligands present (Paper II) the 2D correlation coefficient method [37] was used to find the subtle changes taking place at the surface of HAP. A 2D evaluation can show IR signals induced by an
external perturbation, in this case the change in pH, and it gives an enhanced spectral resolution compared to conventional IR spectra. The 2D correlation calculations were made with the OPUS software.

9.5. **X-ray Diffraction**

X-ray diffraction (XRD) is used to identify crystalline structures. The method is based on the model by Bragg, and according to this model the crystal structure consists of planes that reflect X-rays. The wavelength of the X-ray is of the same order of magnitude as the bond distances between the atoms in the crystal and therefore produces a pattern unique for the atomic arrangement in the sample. The diffraction pattern is dependent on the angle of incident radiation and the distance between the planes:

\[ 2d \sin \theta = n \lambda \]  \hspace{1cm} (18)

where \( d \) is the distance between imaginary planes within the crystal, \( \theta \) the angle of incident radiation, \( n \) the order of reflection and \( \lambda \) the wavelength of the X-ray radiation. XRD can also provide additional information about the sample, e.g. if it consists of very small particles and if there is any amorphous material present in the sample. No identification of amorphous structures is however possible using this technique.

In this study XRD was used to identify the outcome of the HAP and FAP synthesis (Paper II and IV), as well as to verify for possible phase transformations of the synthesised minerals after being equilibrated in ionic medium. The analyses were conducted using a Bruker D8 Advance instrument and Cu K\( \alpha \) radiation. The obtained diffraction patterns were compared to reference pattern in a database and the structures of HAP and FAP were confirmed. The analysis did not show any indications of phase transformations of neither HAP nor FAP after being equilibrated in ionic medium.
9.6. **X-ray Photoelectron Spectroscopy**

X-ray photoelectron spectroscopy (XPS) measures the core electron binding energies and can be used to determine and quantify the chemical composition of a sample surface. As a sample gets bombarded with high energy X-rays, it emits inner level electrons, and by measuring the kinetic energy of those electrons and by knowing the energy of the X-ray beam, the electron binding energy can be calculated according:

\[ E_b = h \nu - E_k - \Phi \]  \hspace{1cm} (19)

Where \( E_b \) is the binding energy, \( h \) Planck’s constant, \( \nu \) the frequency, \( E_k \) the kinetic energy of photoelectron and \( \Phi \) the spectrometer work function (constant for the instrument).

The information of the sample is based on the principle that the binding energy for core level electrons is specific for each element and orbital. A change in oxidation state, coordination and electronegativity of a ligand would cause a shift in binding energies, making it possible to distinguish between different chemical forms of the element of interest.

The depth of analysis using XPS is approximately 3 – 10 nm depending on sample density, kinetic energy of the measured photoelectron, as well as on which elements are present in the sample. The major part of the signal is originated from a layer about 1/3 of the analysis depth which makes XPS a surface sensitive technique. The detection limit is approximately 0.1 atomic %. The centrifuged pastes from the HAP and FAP series (Papers II and IV) were analysed with a Kratos Axis Ultra electron spectrometer using a monochromatic Al Kα source operated at 150 W, hybrid lens system with magnetic lens, and charge neutraliser. To keep the HAP-water interface unchanged in vacuum, the samples were pre-cooled using liquid nitrogen. This procedure [38] involves pre-cooling in the end of the sample transfer rod (20 min at -170 ºC) and then waiting 45 s after loading the wet paste before pumping the introducing chamber. After pumping to 10⁻⁵ Pa, the frozen paste was transferred to the pre-cooled (-160 ºC) manipulator where it was kept until a base vacuum of 2 - 4 (10⁻⁷) Pa in the analysis chamber was reached. Wide spectra (pass energy 160 eV) and the narrows scans of all detected elements (pass energy 20 eV)
were acquired. The temperature of the manipulator did not exceed -150 °C during the whole experiment, and there were no detectable increases in pressure in the analysis chamber. The wide spectrum taken in the end of experiment was, in addition, identical to the one taken at the beginning. After the measurements at liquid nitrogen temperature, the sample was kept in the analysis chamber overnight to warm to room temperature in order to remove water from the interface. All XPS experiments were repeated the next day to follow the changes at the HAP surface caused by water loss. The binding energy (BE) scale was referenced to the C1s line of aliphatic carbon, set at 285.0 eV. Processing of the spectra was accomplished with Kratos software and CasaXPS program package.

9.7. Ion Chromatography

Ion chromatography was used to analyse anions in supernatants from the batch experiments (Papers I-IV). An eluent consisting of a mixture of NaCO₃ and NaOH was pumped through an injection valve where exactly 20 µL of the sample was injected into the system. The eluent composition was optimised for ionic strength and pH. The sample was then carried by the eluent to the separation column where the anions separate due to their interaction with cations fixed on particles inside the column. Depending on the anions capacity to interact with the column material, they are slowed down to an extent characteristic for each ion. The ions are consequently separated and carried to the suppressor where they, as well as the eluent, get protonated. The protonation of CO₃²⁻ and OH⁻ in the eluent decreases the background signal when the eluent enters the conductivity detector, and this increases the systems sensitivity for the sample ions. To further increase this sensitivity, the eluent was passed through a CO₂-suppressor prior entering the detector. Inside the CO₂-suppressor the eluent is passed through a gas-permeable capillary where the CO₂ is removed by applying vacuum. Finally the eluent and the sample enter the conductivity detector which consists of a flow cell with two electrodes between which an electronic (AC) potential is applied. The anions in the sample increase the current in the cell and this increase is proportional to the increase in conductivity. The concentration of the anions can then be evaluated from a calibration curve.
When analysing both fluoride and phosphate from the FAP samples a gradient system was used. Due to the size and charge of the fluoride ion it is hardly retained in the separation column and elutes rapidly even when a very weak eluent is used. Phosphate, however, interacts more strongly to the positive packing material inside the separation column, and when using a weak eluent it is retained there for a long time, causing band broadening of the peak and thereby also lowering the detection limit. To be able to analyse both fluoride and phosphate, a gradient system with two eluent pumps was utilized. One pumping water and the other one the mixture of NaCO$_3$ and NaOH. In the beginning of the analysis the eluent consists of ~90% of water to be able to separate fluoride and the chloride used as ionic medium, and after the fluoride and chloride were eluted, the strength of the eluent was gradually increased to be able to elute the phosphate ions. The detection limit for both fluoride and phosphate was 2.5 µM.

### 9.8. Electrokinetics

To evaluate adsorption processes on a mineral surface, knowledge of the surface charge and potential is crucial. Electrophoretic mobilities of particles can be used to determine the electric (Zeta) potential at the shear plane of mineral particles suspended in aqueous media. The principles for this is based on the fact that charged particles move in an electric field, and by applying an electric field to a very dilute particle suspension and measuring the direction and velocity of the particle motion, the zeta potential can be calculated using the Smoluchowski equation [39].

The Zetasizer 4 (Malvern) was used to determine zeta potentials of HAP and FAP in 0.1 M Na(Cl) ionic medium in the pH range 3 – 10 (Papers II and IV), from which the isoelectric points (iep) were determined.

### 9.9. Modeling

Surface complexation models can be used to describe reactions taking place at the interface between a mineral and a solution. The acid/base properties of HAP and FAP presented in Papers II and IV in this thesis, the speciation in the FAP-Goethite system (Paper I), and the speciation of organic ligands (Paper III) were
described with Constant Capacitance Model (CCM). Even though more sophisticated models could be built, we chose to work with the simpler CCM model due to the complexity of these multi-component systems. In this model adsorbed ions are assumed to be directly bound to the surface and no distinction is made between inner sphere and outer sphere complexes, and this approach has been successfully used in other studies on apatites [40].

The model is developed assuming a constant capacitance for the electrical double layer at the charge surface [41]:

\[ \Psi = T_\sigma F/(s \cdot A \cdot C) \tag{20} \]

where \( \Psi \) is the surface potential (V), \( C \) is a constant with the dimensions of specific capacitance (CV\(^{-1}\)/m\(^2\)), \( T_\sigma \) is the molarity of total surface charge (mol/L), \( s \) is the specific surface area (m\(^2\)/g), and \( A \) is the solid concentration (g/L).

The activity coefficients of the different species in solution are controlled by an ionic medium of constant ionic strength (I = 0.1 M). In addition the activity coefficients of the surface species were assumed to be constant. When necessary, the individual activity coefficients \( \gamma_i \) of an ionic species were recalculated to an ionic strength (I) of 0.1 utilizing Davis equation [42], where \( z_i \) denotes the ionic charge number.

\[ \log \gamma_i = -0.509 z_i^2 (I^{1/2}/(1+I^{1/2}) - 0.31) \tag{21} \]

In all papers of this thesis the equilibrium calculations were accomplished by the means of WinSGW [43] which is a computer code based on the SOLGASWATER algorithm [44].
10. The Chemistry of Aqueous Suspensions of HAP and FAP

10.1. Dissolution, Adsorption and Phase Transformation in the Fluorapatite – Goethite System

Phosphate released from apatites is not readily bioavailable as it is adsorbed to soil mineral and organic particle surfaces, or even precipitated as secondary metal-phosphates. Goethite, a commonly-occurring iron oxide, represents a notably strong sink for phosphate in soils. In this section we present results from a study (Paper I) investigating how the strong affinity of goethite for phosphate drives the dissolution of FAP and thereby alters the phosphate speciation in this two-mineral system. This constitutes the first study of this thesis and makes use of a simpler dissolution model of FAP than the one presented in Section 10.4 and Paper IV.

The experimental data of Fig. 5 provide compelling evidence for a strong dependence of FAP/Goethite concentration ratios on the dissolution of FAP. The inverse correlation between soluble phosphate and goethite concentrations (Fig. 5b) is a direct consequence of the high affinity of phosphate for the goethite surface, which enhances the extent of FAP dissolution. This enhancement is however partially hindered by the concomitant increase in pH (Fig. 5a) that results from the adsorption of phosphate. The overall reaction for this system can therefore be written as:

\[
\text{Ca}_5(\text{PO}_4)_3\text{F} + 3 \equiv \text{FeOH} + (3+3n) \text{H}^+ \\ 3 \equiv \text{FeH}_n\text{PO}_4^{(n-2)} + 3 \text{H}_2\text{O} + 5 \text{Ca}^{2+} + \text{F}^- \quad (22)
\]
Figure 5. Variation of (a) pH and (b) phosphate concentration in solution as a function of time in the presence of (•) 0 g/L goethite, (○) 2.9 g/L goethite, (●) 6.1 g/L goethite, and (■) 12.2 g/L goethite.

The ATR-FTIR spectra of Fig. 6 confirm that complexes of phosphate are formed on the goethite surface. There are, however, differences in the IR features of the adsorbed phosphate between the experimental series. For the samples with reaction times shorter than 15 days these differences are attributed to differences in surface speciation due to differences in pH and in total surface coverage. Similar effects have been identified by Tejedor-Tejedor and Anderson [45].
Figure 6. ATR-FTIR spectra of a) AG-12.2, b) AG-6.1, c) AG-2.9. Ref A is a spectrum of phosphate adsorbed at the goethite surface at pH 5.9 and Ref B is at pH 5.3. In c) spectrum attained after 72 h, is omitted due to experimental problems causing poor data quality.

The series with the highest FAP/Goethite ratio (AG-2.9) also exhibited a gradual appearance of a very broad feature over an equilibration period longer than 15 days. After a spectral subtraction procedure (described more in detail in Paper I), spectra similar to the reference spectrum of a freshly precipitated iron phosphate were obtained (Fig. 7). This result indicates that FePO$_4$ (s) precipitates after approximately 15 days of reaction time and thereby further alters the speciation of phosphate in this system. This is in very good agreement with the calculated speciation of phosphate (Paper I).

The sum of phosphate in solution, adsorbed to the goethite surface and precipitated as FePO$_4$ (s), is higher when more goethite is present in the system (Fig. 8). This highlights the importance of surface complexation and the presence of available surface sites for promoting the dissolution of apatite.
Figure 7. ATR-FTIR spectra of the remaining features for the samples equilibrated for 24 h, 15 days, 21 days, and 129 days after subtracting the spectrum of the experimental point withdrawn after 4 h (spectrum not shown). Ref C is the spectrum of a precipitated iron phosphate phase.

Figure 8. The sum of phosphate in solution, adsorbed onto goethite, and precipitated iron phosphate in the presence of (+) 0 g/L goethite, (○) 2.9 g/L goethite, (●) 6.1 g/L goethite, and (●) 12.2 g/L goethite.

The other two ions released from FAP during dissolution, calcium and fluoride, showed slightly different dissolution behaviour compared to phosphate.
The concentration of calcium released to the solution was dependent on both the goethite suspension density and on reaction time. However, in agreement with previous findings [46], there was most likely no or very little amounts of calcium adsorbed at the water-goethite interface. The time dependency for fluoride differed somewhat from that of calcium and phosphate. Initially the series with lowest FAP/Goethite ratio gave the lowest fluoride concentration in solution, but after approximately 7 days this series instead gave the highest concentration. This could be explained by the adsorption of fluoride to goethite in the early stages of the experiments, promoted by the abundance of surface sites, and by the release of fluoride due to competitive adsorption of phosphate in the later stages.

The modeling efforts presented for this system (Paper I), explained the experimental concentrations of calcium and phosphate in solution, but were not able to explain the high concentrations of fluoride due to a limited representation of the dissolution mechanisms. More accurate models for the dissolution of apatite should in fact also take into account surface complexation as well as ion-exchange reactions. The following sections and Papers II-IV address these issues by providing experimental and modelling evidence for these simultaneously-occurring reactions.

### 10.2. Surface Composition of HAP and FAP

Apatites have been shown to form surface layers that are compositionally different than the bulk [19, 47]. This was also noted in the experiments of the mixed fluorapatite-goethite system (Section 10.1). These surface layers formed in response from interfacial reactions with aqueous solutions during the dialysis procedure after the synthesis. As the solubility of mineral is reflected by the properties of surface layer(s) it becomes imperative that the composition of the surface layer(s) is known. In this section we present some of the results from two studies (Paper II and IV) investigating the composition of the surface layers of the synthetic HAP and FAP. This information was then taken into account when calculating the dissolution and surface complexation behaviour of the two apatites.
XPS was used to determine the composition of the surface layers formed on the HAP and FAP particles. The results from the XPS measurements (Fig. 9) confirm that the surfaces of the two minerals have a different composition than their bulk compositions. For both the minerals, the Ca/P ratios have decreased relative to the bulks. The HAP surface showed the composition with a Ca/P ratio of ~1.4 compared to the bulk ratio of ~1.6, while the FAP surface showed the composition with a Ca/P ratio of ~1.5 compared to its bulk with a ratio of 1.7. The Ca/P ratios on the two apatite surfaces were quite stable over a large pH interval, and the only major change was for the FAP surface at low pH where a precipitation of CaF$_2$ (s) occurs.

Figure 9. Atomic ratios at the surfaces of (a) HAP and (b) FAP as a function of pH.
In contrast to XPS, a major portion of the signal in the ATR-FTIR analyses arises from the bulk of the minerals. The ATR-FTIR spectra of the wet HAP and FAP pastes obtained from the batch experiments (Fig. 10) show that there was no or very little protonated phosphate present in the bulk, and that changes in pH had very little effect on these phosphate bands.

An attempt to increase the resolution of the ATR-FTIR spectra was made to provide information of the speciation of the surface of the apatites. The asynchronous 2D correlation map of ATR-FTIR spectra (Fig. 11) provides a better resolution and can therefore make it possible to detect subtle changes arising from variations in pH. Unfortunately the specific surface area of FAP (10.7 m²/g) was not large enough to detect any bands arising from protonation of surface phosphate groups. The 2D correlation map for HAP (with a specific
surface area of 80.5 m\(^2\)/g), on the other hand, revealed bands not detectable in Fig. 10. The most important of these was the band at 1130 cm\(^{-1}\), which arises from protonated phosphate groups [45] on the surface of HAP. These observations are in very good agreement with the findings of Jarlbring et al. [48] who found evidence for protonated phosphate groups on the surface of FAP by \(^1\)H and \(^{31}\)P MAS NMR.

Given the findings presented within this section, the XRD measurements confirming the apatite structures of the bulk, and the dissolution data that will be presented in Section 10.3, the two apatites are proposed to have surface layers with the compositions: \(\text{Ca}_{8.4}(\text{HPO}_4)_{1.6}(\text{PO}_4)_{4.4}(\text{OH})_{0.4}\) for HAP and \(\text{Ca}_9(\text{HPO}_4)_{2}(\text{PO}_4)_{4}F_2\) for FAP.
10.3. Solubility and Surface Complexation of HAP and FAP

The solubility of a mineral depends on several different factors, including the energetic cost of dissociating atoms as well as the reactivity of the surface.

The lattice energy of an ionic crystal is defined as the energy cost to convert one mole of its chemical unit into free ions [50]. To find out how much energy that is stored in a unit volume of the crystal the term lattice energy density is used. The lattice energy is therefore divided by the molar volume (cm$^3$/mole) of a formula unit of the crystal, and this calculation can be used to compare how strongly the atoms bind to each other in two comparable minerals like HAP and FAP. The lattice energy values for HAP (34092 kJ/mole) and FAP (34118 kJ/mole) have been used to determine the Gibbs free energy of dissolution [51]. These values already suggest that HAP is intrinsically more soluble. However, it has been suggested that fluorhydroxy apatites with variable F/OH ratios are even less reactive than pure fluor- and hydroxyapatites due to the existence of strong F-OH hydrogen bonding in the structure [52].

Surface reactivity also contributes to the solubility of a mineral. As has been described in previous studies on apatites, the surface consists of different groups of varying reactivity. A simplified model can describe the surfaces with only two reactive surface sites, $\equiv$CaOH and $\equiv$OPO$_3$H$_2$ [23]. These two sites can undergo a number of protonation and deprotonation steps, as well as take part in surface complexation reactions with different ions (e.g. phosphate, calcium, fluoride, organic ligands, etc…) An ion exchange reaction between fluoride and hydroxide on the surface of FAP will also be presented in this section.

The data presented in Fig. 12 clearly show the differences in the dissolution between the two apatites. The concentration of calcium in solution is higher for HAP compared to FAP at pH values below 9, and the same relationship is valid for phosphate below pH 7. Above these pH values the calcium and phosphate concentrations are comparable for both minerals. These results indicate that different processes are predominant under different pH conditions.
Figure 12. Dissolution of HAP and FAP illustrated by (a) calcium and (b) phosphate in solution. Lines are derived from model calculations (Paper II and IV).

The predominating process in the most acidic suspensions is dissolution causing the concentrations of calcium and phosphate to amount up to 50 and 40 mM respectively. These values were used to calculate preliminary formation constants for the two surface layers:

\[
8.4 \text{Ca}^{2+} + 6 \text{HPO}_4^{2-} + 0.4 \text{H}_2\text{O} \rightleftharpoons \text{Ca}_{8.4}\text{(HPO}_4\text{)}_{1.6}\text{(PO}_4\text{)}_{4.4}\text{(OH)}_{0.4}(s) + 4.8 \text{H}^+ \quad (23)
\]

\[
9 \text{Ca}^{2+} + 6 \text{HPO}_4^{2-} + 2 \text{F}^- \rightleftharpoons \text{Ca}_9\text{(HPO}_4\text{)}_3\text{(PO}_4\text{)}_4\text{F}_2(s) + 4 \text{H}^+ \quad (24)
\]

In the higher pH range the predominating processes are surface complexation reactions and they were investigated by potentiometric acid/base
titrations of the minerals (Fig. 13). The results from the titrations were used to elucidate the complexation reactions taking place at the surface of HAP and the calculations provide support for the surface reactions:

\[ \equiv \text{CaOH} + \text{H}^+ \rightleftharpoons \equiv \text{CaOH}_2^+ \quad (25)\]

\[ \equiv \text{OPO}_3\text{H}_2 \rightleftharpoons \equiv \text{OPO}_3\text{H}^- + \text{H}^+ \quad (26)\]

Even after including these reactions at high pH increasing residuals were found in the calculations at pH above 10 for both minerals and the best fit was obtained for the species \( \equiv \text{OPO}_3\text{Na}^- \) which also was included in the models.

\[ \equiv \text{OPO}_3\text{H}_2 + \text{Na}^+ \rightleftharpoons \equiv \text{OPO}_3\text{Na}^- + 2\text{H}^+ \quad (27)\]

The formation constants for (25)-(27) were assumed to be the same for both systems.

In the calculation for the FAP surface we had to include additional reactions to get a good fit between experimental and calculated data:

\[ \equiv \text{F} + \text{H}_2\text{O} \rightleftharpoons \equiv \text{OH} + \text{F}^- + \text{H}^+ \quad (28)\]
Figure 13. Results of titration data of (a) HAP and (b) FAP suspensions. The solid concentration and method of titrant addition (coulometric, HCl, or NaOH) is specified in the legend.

After including reaction (24) to explain the high fluoride concentrations found in solution, we realised that we had to include a re-adsorption reaction of some of the fluoride to fit the surface potential at pH_{eq}:

\[ \text{CaOH}_2^+ + F^- \rightleftharpoons \text{CaF} + \text{H}_2\text{O} \]  

(29)

This re-adsorbed fluoride can help stabilizing the surface by forming hydrogen bonds with neighbouring protonated calcium and phosphate sites.

At near neutral pH both dissolution and surface complexation reactions had to be taken into account. Furthermore, the high Ca/P ratios in solution
indicated that there also is re-adsorption of phosphate from the solution to the positively charged surfaces of HAP and FAP (Fig. 14). This observation is in accordance with the radioisotope measurements of Kukura et al. [12]. The re-adsorption also occurs at lower pH values, but due to the high concentrations of calcium and phosphate in solution, the effect is not noticeable on the Ca/P ratio in solution. This reaction was included in both models, but due to the low specific surface area and lower solubility of FAP, the effect of the re-adsorbed phosphate on Ca/P ratios in solution is negligible in this system.

Finally, the calculations for the constants of the solubility products of the two surface layers were refined including all reactions included in this section. The modelling predictions using the refined values (Paper II and IV) reveal a good agreement between the experimental and calculated data (Figs. 12, 13 and 16). The distribution diagrams showing surface speciation of HAP and FAP (Fig. 15) predict positively charged \( \equiv \text{CaOH}_2^+ \) and negatively charged \( \equiv \text{OPO}_3^H \) sites over a large pH interval of both apatites. It is also clear that the amount of re-adsorbed phosphate is higher on the HAP surface compared to the
FAP surface which is in accordance with previous discussions on the differences in solubility and specific surface area between the two minerals.

Figure 15. The calculated surface speciation of (a) HAP and (b) FAP as a function of pH, in \( I = 0.1 \) M Na(Cl), and at \( T = 25 \) °C.
The experimental and calculated values for fluoride in solution are depicted together with the calculated values of the precipitation of CaF$_2$ (s) (Fig. 16). The fit between the calculated and experimental data is good at pH $> 5.5$, but deviates at lower pH values where CaF$_2$ (s) precipitates. This could be due to minor errors in the formation constant (which was not optimized in the calculations) but it could also be due to an epitaxial precipitation of CaF$_2$ (s), changing the surface speciation of FAP.

![Figure 16. Calculated amount of CaF$_2$ (s), and experimental and calculated concentrations of fluoride in solution as a function of pH. [FAP] = 7.7 g/L, 0.1 M Na(Cl), T = 25 ºC.](image)

Finally, the calculated values of the surface potentials including all above mentioned surface reactions resulted in $\Psi = 0$ mV with pH$_{pzc}$ = 7.9 for HAP and 5.3 for FAP. These values are in good agreement with pH$_{iep}$ = 8.1 for HAP and pH$_{iep}$ = 5.7 for FAP obtained from the electrophoretic mobility measurements.
10.4. Surface Complexation of Carboxylic acids and their Impact on HAP and FAP Dissolution

The adsorption of an organic ligand to a mineral surface is affected by a number of different factors, e.g. the degree of protonation of the ligands, the pH$_{\text{iep}}$ of the surface, as well as the ligands and the surface’s abilities to form complexes with other species present in the system.

In this section we present some of the results from two studies (Paper III and IV) investigating how the three organic ligands (malonate, citrate and mellitate) interact with the surfaces of HAP and FAP, and how these interactions affect apatite dissolution.

Simple model calculation of the three ligands in the presence of HAP gave an indication of the speciation of the ligands in these systems (Fig. 17). The models predict the formation of negatively charged species over the entire pH range. These species can be available for adsorption onto the positively charged surface sites of both apatites (Fig. 18). The calculations also show that a calcium-mellitate solid phase (Ca$_3$Mel (s)) is expected to precipitate at low pH values in the series containing mellitate.

The adsorption curves of the three ligands are somewhat similar for the two different apatite surfaces (Fig. 18). All three ligands adsorb to the surfaces over a large pH interval. In the distribution diagrams for the surface speciation of the two apatites without any ligands present (Fig. 15) we can see that there are positively charged calcium surface sites (=CaOH$_2$`) present in the pH range of adsorption, and these sites are suggested to be the adsorption center for the ligands. This is also corroborated by the fact that the amount of ligands adsorbed to the FAP surface is more affected by the decrease in availability of these sites, rather than the repulsion of the negatively charged surface above pH$_{\text{iep}}$ 5.7.
Figure 17. Calculated speciation of (a) malonate, (b) citrate, and (c) mellitate in the presence of 7.7 g/L of HAP, in 0.1 M Na(Cl). The total ligand concentration was 1.49 mM which represents 2.4 μmoles/m² of HAP. F denotes the fraction of ligand in the system, either precipitated or in solution.
Figure 18. Adsorption of malonate, citrate, and mellitate on (a) HAP and (b) FAP surfaces as a function of pH. $I = 0.1$ M Na(Cl), $T = 25$ °C. [Ligand] = 2.4 µmoles/m$^2$ of HAP or FAP. The solid lines were generated as a visual aid.

Above pH 8-9, the adsorption curves show a correlation between the extent of adsorption and the charge of the ligand. Mellitate (Mel$^6$), adsorbs quite extensively, barely affected by the repulsion of the increasingly negative surface. The adsorption of citrate (Cit$^-3$), however, decreases drastically at these pH values and malonate (Mal$^2$) barely adsorbs at all.
Below pH 8, this relationship is reversed and this trend is especially pronounced in the FAP system. This effect could partly be explained by the repulsion between the charged ligands on the surface. The repulsion between the highly charged mellitate ions would be larger compared to citrate, which in turn would show more repulsion than malonate. An additional explanation to this trend is surface saturation. If all carboxylate groups interact with the surfaces, which is shown for citrate in the ATR-FTIR spectra (Fig. 20), the bulkiness of citrate and especially mellitate would cause a lower ligand to surface ratio compared to malonate. The 100 % adsorption of mellitate in the HAP system at pH 4.6 is due to precipitation of Ca₃Mel (s) which will be discussed in the end of this section.

ATR-FTIR spectra of the wet pastes in these experiments can show how the ligands adsorb onto the apatite surfaces. The signal-to-noise in the spectra for malonate and citrate onto FAP were, however, too low and no spectra will therefore be shown from these two series.

The ATR-FTIR spectrum of malonate adsorbed onto HAP (Fig. 19) is comparable to its non-protonated aqueous counterpart with asymmetric ($\nu^{as}_{\text{C-O}}$) and symmetric ($\nu^{s}_{\text{C-O}}$) stretching vibrations at 1580 and 1362 cm⁻¹, respectively. These spectra are in agreement with those of a previously identified hydrogen-bonded malonate complexes on goethite ($\alpha$-FeOOH) [29]. They do however differ considerably from those of a chelating inner sphere complex and we can therefore conclude that the predominant malonate surface complex is stabilized by electrostatic and hydrogen bonding interactions. We assume that this is also true for the adsorption of malonate onto the FAP surface.
Figure 19. ATR-FTIR spectra of (a) malonate adsorbed onto HAP at pH 7.30 and [Malonate] = 2.4 µmol / m² of HAP, and (b) non-protonated malonate in aqueous solution.

The ATR-FTIR spectra of citrate adsorbed onto HAP show practically no variations with respect to peak positions or relative intensities as a function of pH (Fig. 20). This indicates the predominance of one surface species. A comparison of the spectra of this surface complex and those of aqueous Cit³⁻ and HCit²⁻ shows that it is the non-protonated Cit³⁻ that interacts with the surface. The spectral characteristics of this surface complex suggest that it is bonded to the surface through electrostatic and hydrogen bonding interactions. Further analyses of the ATR-FTIR spectra (Paper III) indicates that all three carboxylate groups interact with the HAP surface.
The ATR-FTIR spectra of mellitate adsorbed onto HAP and FAP are depicted together with the spectra of aqueous, non-protonated mellitate (Mel\textsuperscript{6–}) and a precipitated calcium mellitate phase (Fig. 21). Pronounced peaks are detected in all spectra indicating adsorption over the entire pH range investigated in accordance with the adsorption data of Fig. 18. The spectra in the HAP system display pH-dependent features which indicate the presence of at least two surface species. At pH 7.2 and above, all spectra are nearly identical showing peaks at 1337, 1432 and 1579 cm\textsuperscript{-1}, which are in good agreement the peaks of aqueous mellitate at 1334, 1426, and 1577 cm\textsuperscript{-1}. These peaks are also detected in the FAP system but in this system the signal-to-noise ratio is lower than in the HAP system due to the low surface area of FAP. The strong resemblance between the surface and solution spectra shows that there is very little structural change when mellitate is transferred from solution to an adsorbed state at the water-apatite interfaces, and this implies that adsorption at pH > 7.2 occurs via a deprotonated outer sphere complex. This is corroborated by comparing spectra of samples prepared in H\textsubscript{2}O and D\textsubscript{2}O. As demonstrated previously [28] the upward shift of ν\textsuperscript{as}\textsubscript{C–O} by 13 cm\textsuperscript{-1} in D\textsubscript{2}O (Fig. 21) is a result of the atomic-mass
effect, shifting the bending mode to lower frequency which then decouples from $\nu_{\text{C-O}}$. As only one broad $\nu_{\text{C-O}}$ peak appears also in D$_2$O, the carboxylate groups of adsorbed mellitate should interact with water molecules at the interface and is not directly coordinated to surface calcium ions.

In the HAP spectrum at pH 4.9 peaks at 1348, 1449, 1540 and 1570 cm$^{-1}$ are detected and these are almost identical to those of precipitated Ca$_3$Mel (s). The HAP spectrum at pH 6.2 also shows these four peaks as well as the three shoulders at 1337, 1430 and 1580 cm$^{-1}$, indicating that at this pH value mellitate surface complexes coexist with precipitated Ca$_3$Mel (s). This is in very good agreement with the distribution diagrams calculated from the thermodynamic model presented in the beginning of this section. We found no spectral evidence for the Ca$_3$Mel (s) precipitation in the spectra of samples equilibrated at low pH in the FAP system. This is probably due to the lower solubility of FAP causing less calcium in solution, but also to the lower total concentration of mellitate in the FAP system.

![Figure 21. The ATR-FTIR spectra of a precipitated calcium mellitate and mellitate adsorbed to HAP (left) and FAP (right). $I = 0.1$ M Na(Cl). $T = 25$ °C. [Mellitate] = 2.4µmol / m$^2$ of HAP and FAP.](image)

A comparison between the amounts of calcium released from HAP with and without ligands present show a slight decrease of calcium in the near neutral pH range when citrate and mellitate are present in the system (Fig. 22a). This is most likely due to interactions between the outer-sphere bound citrate or mellitate on the surfaces of the apatites and the calcium in solution. The model
calculations predict the formation of negatively-charged calcium complexes in both these systems (CaCit\(^{-}\) and CaMel\(^{4-}\)). However, as the spectroscopic data do not confirm any ternary surface complexes we instead suggest that the enhanced calcium uptake arises from cooperative electrostatic effects with the outer-sphere complexes of citrate and mellitate on the apatite surfaces.

In the comparison of phosphate concentration in solution for the same systems (Fig. 22b), the effect of citrate and mellitate is even more pronounced than for calcium. At pH > 6 the concentrations of soluble phosphate are higher in these two series than in both the inorganic control series and the series containing malonate. This is a further indication that the charge of a ligand plays an important role in on its interaction with a mineral surface. The effect of the ligands is highest at near-neutral pH values where phosphate is re-adsorbed to the HAP surface (Fig. 22). Ligand adsorption out-competes this re-adsorbed phosphate, thereby increasing the concentration of phosphate in solution. This is also evidenced by the solution Ca/P ratios (Fig. 22c) where the high ratios of the organic-free system are suppressed by the presence of organics, and most particularly by citrate and mellitate. Malonate has, on the other hand, a weaker but nonetheless measurable effect on the Ca/P ratios.
Figure 22. (a) Calcium, (b) phosphate in solution in the HAP suspensions with; (O) no ligand, (●) malonate, (△) citrate, and (■) mellitate, and (c) the ratios between Ca and P in these suspensions as a function of pH.
At pH > 8, where there is no re-adsorbed phosphate, the adsorption of ligands still enhances the concentration of phosphate in solution, which probably is due to an exchange mechanism between the ligand and the bulk phosphate on the surface of the apatite.

The same comparisons were also made for the FAP systems but no effect on the concentrations of calcium and phosphate in solution could be found. This is probably due to the low surface area of the FAP, the lower solubility of FAP, and of course the lower total concentration of ligands in the system (as the ligand concentrations were normalized against the total surface area).

11. Conclusions

The dissolution of HAP and FAP has been studied under several different experimental conditions with a range of techniques to achieve understanding in how these two abundant minerals may interact with their natural surroundings, e.g. body fluids and soil environments. It has been shown that the dissolution processes are very complex and the approach throughout this study has therefore been to quantitatively measure the dissolution products in solution, but also using spectroscopical techniques to find out how the different experimental conditions affect the surfaces of the minerals and thereby also the dissolution (Fig. 23).

One of the most important findings in this thesis was that both apatites had formed surface layers different than the bulk when they were equilibrated in aqueous solutions. As the surface governs the solubility of a mineral it was of great importance to find out the composition of the surface before performing additional experiments on these minerals. Batch experiments, potentiometric titrations together with XPS and ATR-FTIR measurements provided the information required to calculate thermodynamic models of the dissolution reactions of the two apatites. The calculations required the addition of surface complexation and ion exchange reactions to fully describe the dissolution behaviour of the apatites to get good fits between experimental and calculated
data. The modeling efforts gave insight in the surface speciation partially responsible for the lower solubility of FAP as the fluoride ions released from the FAP during dissolution re-adsorbed to positively charged calcium sites, thereby stabilizing the FAP surface. The calculated model also predicted re-adsorbed phosphate on both apatite surfaces, but the amount of this species was higher on the HAP surface due to the larger surface area and the higher solubility causing higher concentration of phosphate in solution of this mineral.

ATR-FTIR measurements revealed that organic ligands adsorb to apatite surfaces as outer-sphere complexes over a large pH interval. This adsorption enhances the dissolution of apatites as it can out-compete adsorbed phosphate on the apatite surfaces, or even take part in ion exchange reactions with the phosphate surface sites. The presence of a mineral that acts as a sink for the phosphate or the other dissolution products of apatites can also enhance the apatite dissolution. This mechanism is of course affected by the affinity of the mineral surface for the dissolution products.

Figure 23. Overview of the reactions of HAP and FAP presented in this thesis.
Although the dissolution of HAP and FAP has been thoroughly investigated in this study, there are certain aspects of these systems that are not fully understood and a deeper understanding can be gained by designing new experiments. The formation of the surface layers of the apatites occurs already under the dialysis step after the syntheses, and performing a long-time study on this formation to see if there will be a full phase-transformation of the mineral would be interesting.

It should also be of interest to further investigate the adsorption mechanisms of organic ligands as well as their effects on mixed FAP-Goethite suspensions. The organic ligands have a strong affinity for both surfaces and as it has been shown that the ligands can out-compete phosphate adsorbed to the goethite surface, the adsorption of the ligands on both minerals would enhance the amount of phosphate release to solution.

Such investigations will require a multi-technique approach to fully be able to understand the processes occurring both in solution and on the surfaces of the minerals.
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13. Acknowledgements

Under min doktorandtid är det många personer varit delaktiga i mitt liv och i det här kapitlet får jag en möjlighet att tacka alla er som funnits där för mig och som på olika sätt hjälpt mig igenom de här åren. Jag skriver dock detta kl 23.50 kvällen innan avhandlingen ska tryckas, så om det är någon jag glömmer så vill jag redan här passa på att säga förlåt.

Tack till:

Min handledare Staffan Sjöberg för att du tog dig an mig som doktorand, för att du funnits där, stöttat mig och för att du tålmodigt svarat på mina ändlösa frågor om modellering och minerałytor. Du har lärt mig så otroligt mycket.

Min biträdande handledare Per Persson. Tack för att du har funnits där och stöttat mig när jag behövt det som mest.

Lars Lövgren, min biträdande handledare som gav mig möjligheten att doktorera på denna fantastiska avdelning.

Georange för finansiering av mina första doktorandår.

Ted och Birgit på Metrohm för all hjälp med IC-systemet.
Alla kollegor på ’fd oorganisk kemi’, jag kommer nog aldrig att uppleva en sådan otrolig stämning på en arbetsplats igen. Jag vill speciellt nämna Ingegärd för att du alltid fått allting att flyta, både ute på lab och under alla fester vi haft på avdelningen; Andrei för din hjälp med XPS-mätningarna; Gun-Britt för att du alltid hittar lösningar på alla problem; Gun för att du fått undervisningen att flyta så bra; samt Dan för hjälp med XRD-analyserna av mina apatiter.


Malin, tack för din vänskap och ditt stöd under de senaste åren. Jag tror ärligt talat att jag inte hade klarat det här utan dig. Kommer verkligen att sakna dig!!
(Jag ser fram emot New York)

Hanna, tack för din vänskap, ditt stöd och för all hjälp med både avhandlingen och lägenheten.

Julia och Jörgen. Tack för att ni alltid finns där för mig trots att vi inte längre bor i samma land. Jag saknar er otroligt mycket. Hoppas att vi snart kan komma och hälsa på er (och grilla ☺) i Bristol igen!

Tove, Katarina, Madeleine, Elisabet, Elinor, Ola, Rickard, Laura, Dip, John, Matthias och Frida ☻. Det har varit fantastiskt roligt att ha er som (jobbar)kompisar.

Anna N, för din vänskap och ditt stöd, både i och utanför träningslokalerna. Nu kanske jag får mera tid att träna så att jag i alla fall kan bli starkare än dig i någon övning på gymmet…


Lotta, Cissi, Carin och Veronica. Ni är helt underbara och ni är beviset på att en familj inte behöver ha blodsband för att räknas. Det kommer att bli otroligt svårt att flytta ifrån Umeå...

Calle. Tack för att du alltid finns där. Tycker så mycket om dig!


Eva och Anna med familjer. Mina underbara systrar som visat mig hur man kan vara så lika och så olika på samma gång. Jag älskar er.

Mamma och pappa. Tack för all kärlek och allt stöd ni gett mig. Ni har verkligen lärt mig allt som är viktigt i livet. Ni är helt underbara föräldrar och jag älskar er så mycket!