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Optimization of co-precipitation processes in apatite-based filter materials for the removal of fluoride from drinking water

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Abstract

Drinking water with elevated fluoride (F) concentrations affects the health of millions of people world-wide. Several techniques have been developed to remove F from drinking water. One viable, effective and inexpensive option, particularly for developing countries, is filtering using bone char. Fluoride uptake on bone char is primarily controlled by the main compound of bones, calcium hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAP), which forms fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, FAP) in presence of F. The addition of solid calcium-phosphate pellets to the bone char filter media has significantly improved the F uptake capacity in these contact precipitation filters. The pellets dissolve, releasing calcium (Ca) and phosphate (PO_4) to solution, which then can precipitate as a new phase incorporating F. However, these filters could still be optimized to improve their efficiency.

This thesis investigates the uptake of F in apatitic systems under environmentally relevant conditions. The main aim of this work is to gain insights into the predominant processes controlling F uptake in bone char and contact precipitation filter systems to provide a basis for filter optimization.

Fluoride uptake on synthetic HAP, as a proxy for bone char, was investigated under constant conditions over 28d as function of solution pH and initial F concentration, in presence and absence of the anions bicarbonate, sulfate and chloride. The F uptake was found to be predominantly controlled by adsorption processes onto the HAP surface, which allowed a subsequent substitution of OH by F within the HAP crystal structure. The F uptake increased with decreasing solution pH that controlled the surface sites species on the HAP crystals. The result of F uptake was the formation of an FAP-like surface layer on the nanosized HAP crystals. It was further observed that chloride, sulfate and bicarbonate did not affect F uptake capacity. Rapid decreases were observed

in the initial dissolved concentrations of Ca and F but not of PO_4 . This indicated the initial precipitation of fluorite (CaF_2), which subsequently dissolved to reprecipitate as the thermodynamically most stable phase FAP.

In a further approach, the method of contact precipitation was modelled in batch studies. Dissolved Ca and PO_4 (and F) were added independently to apatitic suspensions in various stoichiometric ratios corresponding to different calcium-phosphate phases in order to investigate whether or not these phases were formed in heterogeneous systems. The solutions were initially saturated with respect to brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), β -tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$, β -TCP), octacalcium phosphate ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, OCP), HAP, FAP, and CaF_2 or with respect to brushite, β -TCP, OCP and HAP. The final phases were intensively investigated by various solid characterization techniques. Phase distinction was facilitated by the use of Ca-free seeding templates, strontium hydroxyapatite ($\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$, SrHAP) and strontium carbonate (SrCO_3). After 3d reaction time at neutral pH conditions, the final precipitate was found to be the thermodynamically most stable phase FAP when F was initially added, and HAP in the absence of added F. Thus, phase formation was independent of both added Ca/P or Ca/P/F ratios and the type of seeding template used. X-ray Absorption Spectroscopy indicated either the precipitates to be Ca-deficient (non-stoichiometric) HAP or to be mixtures of HAP and brushite and/or β -TCP. These phases were probably precipitated as intermediate phases, since solutions did not reach complete equilibrium conditions after 3d. Precipitates obtained in fluoridated systems, where solution composition was initially PO_4 -limited for stoichiometric FAP and excess Ca and F were stoichiometric for CaF_2 , showed shifts of atomic binding energies towards energy levels of CaF_2 in X-ray Photoelectron Spectroscopy (XPS). Moreover, it was observed that Ca/P ratios

estimated from elemental loss from solution do not necessarily provide sufficient identification of the final precipitate.

Zusammenfassung

Erhöhte Fluoridkonzentrationen in Trinkwasser gefährden weltweit die Gesundheit von Millionen von Menschen. Viele Technologien wurden entwickelt, um das Fluorid (F) aus dem Trinkwasser zu entfernen. Eine praktikable, effektive und gleichzeitig relativ kostengünstige Methode ist die Nutzung von Knochenkohle als Filtermaterial, welche besonders für Entwicklungsländer interessant ist. Die Fluoridaufnahme auf Knochenkohle wird vorrangig durch den Hauptbestandteil der Knochen bestimmt, dem Calciumphosphat-Mineral Hydroxyapatit ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAP), welches sich in Anwesenheit von Fluoridionen zu Fluorapatit ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, FAP) umwandelt. Die Ergänzung von Calciumphosphat-Pellets zur Knochenkohle als Filtermaterial verbessert signifikant die Fluoridaufnahme in diesen *Contact Precipitation* Filtern. Die Pellets lösen sich auf, geben Calcium (Ca) und Phosphat (PO_4) in Lösung, so dass diese Ionen als neue Mineralphasen ausfallen und dabei F binden können. Jedoch können diese Filter noch bezüglich ihrer Fluoridaufnahmekapazität optimiert werden.

Diese Arbeit untersucht die Aufnahme von F in apatitischen Systemen unter Umweltbedingungen. Das Hauptziel der Arbeit ist der Einblick in die dominierenden Prozesse, welche die Aufnahme von F auf Knochenkohle und in *Contact Precipitation* Filtersystemen kontrollieren, um eine Basis zur Filteroptimierung zu schaffen.

Die Fluoridaufnahme auf synthetischen HAP, als Ersatz für Knochenkohle, wurde unter konstanten Bedingungen über 28 Tage als Funktion von Lösungs-pH und Anfangskonzentration von F, in und ohne die Gegenwart von den Anionen Bikarbonat, Sulfat und Chlorid untersucht. Die Fluoridaufnahme wurde überwiegend durch Adsorptionsprozesse an der Oberfläche von HAP kontrolliert. Die Adsorption ermöglichte eine anschließende Substitution von Hydroxid (OH)-Ionen für F-Ionen

innerhalb der HAP Kristallstruktur. Die Fluoridaufnahme stieg mit sinkendem pH-Wert der Lösung, wobei der pH die Oberflächenspezies auf den HAP-Kristallen bestimmt. Das Ergebnis der Fluoridaufnahme war die Bildung einer FAP-ähnlichen Oberflächenschicht auf den nanogrossen HAP-Kristallen. Des Weiteren hatten Chlorid, Sulfat und Bikarbonat keinen Einfluss auf die Fluoridaufnahmekapazität. Ein schneller Abfall der Anfangskonzentrationen von Ca und F, aber unveränderte PO_4 Konzentrationen deuteten auf eine Ausfällung von Fluorit (CaF_2) hin, welches sich anschliessend löste und als das thermodynamisch stabilste Mineral FAP neu ausfiel.

Im weiteren Ansatz wurde die Methode der *Contact Precipitation* in Batchversuchen simuliert. Gelöste Ca und PO_4 (und F) wurden unabhängig und in verschiedenen stoichiometrischen Verhältnissen entsprechend verschiedener Calciumphosphate in apatitische Suspensionen gegeben, um zu untersuchen, ob die entsprechenden Phasen sich in heterogenen Systemen bilden. Die Lösungen waren anfänglich übersättigt im Hinblick auf die Minerale Calcium Hydrogenphosphat ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), β -Tricalciumphosphat ($\text{Ca}_3(\text{PO}_4)_2$, β -TCP), Octacalciumphosphat ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, OCP), HAP, FAP und CaF_2 bzw. für Calcium Hydrogenphosphat, β -TCP, OCP und HAP. Die Endprodukte wurden mittels verschiedener Charakterisierungstechniken intensiv untersucht. Eine Phasenunterscheidung wurde durch die Nutzung von Ca-freien Fällungshilfsmitteln, wie Strontium Hydroxyapatite ($\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$, SrHAP) and Strontium Carbonat (SrCO_3) ermöglicht. Wenn F anfänglich in Lösung gegeben wurde, bildete sich nach drei Tagen Reaktionszeit bei neutralem pH-Wert FAP als thermodynamisch stabilste Phase. Ohne Einfluss von F bildete sich HAP. Daher war die Mineralbildung unabhängig von den zugegebenen Ca/P oder Ca/P/F Verhältnissen sowie von der Art des genutzten Fällungshilfsmittels. Röntgen-Absorptions-Spektroskopie deutete entweder auf die Bildung von Ca-armen (nicht-

stoichiometrischen) HAP oder darauf, dass HAP Beimischungen von Calcium Hydrogenphosphat und/oder β -TCP enthielt. Diese Minerale könnten sich als Zwischenphasen bei den Ausfällungsprozessen bilden, da die Suspensionen nach drei Tagen noch kein Gleichgewicht erreicht hatten. Ausfällungsprodukte aus fluoridierten Systemen, in denen die Lösungen anfänglich für stoichiometrischen FAP PO_4 -limitiert waren und überschüssiges Ca und F stoichiometrisch für CaF_2 war, zeigten in Röntgenphotoelektronenspektroskopie (XPS) Verschiebungen von atomaren Bindungsenergien zu Energieniveaus die charakteristisch für CaF_2 sind. Des Weiteren wurde beobachtet, dass Ca/P Verhältnisse, berechnet basierend auf den Elementverlust in Lösung, nicht unbedingt ausreichen, um Ausfällungsprodukte zu identifizieren.

Da SrHAP in den oben genannten Versuchen zur heterogenen Ausfällung von Calciumphosphaten genutzt wurde und da es käuflich nicht erwerblich ist, wurde es im Rahmen dieser Arbeit synthetisiert. Das Ausfällungsprodukt wurde umfassend mittels verschiedener Techniken untersucht. Das Produkt war kristallin, aber angereichert mit Strontium (Sr). Die Strontiumanreicherung basierte auf Ausfällungen kleiner Mengen von Strontium Hydroxid ($\text{Sr}(\text{OH})_2$) und SrCO_3 .

Bis heute konzentriert sich die Optimierung der DefluoridierungsfILTER auf die Suche nach einem idealen Verhältnis von Knochenkohle zu Calciumphosphat-Pellets zur Bildung von FAP. Da diese jedoch unabhängig von den Ca/P Verhältnissen ist, kann der Schwerpunkt der Filteroptimierung neu auf die Kontaktzeit des zu filternden Wassers mit dem Filtermaterial, auf die Pelletauflösung und auf eine Vor- und Nachbehandlung des Wassers gelegt werden. Auch steht der Austausch von Knochenkohle mit synthetischem HAP zur Diskussion.

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Chapter

1

General Introduction

1.1 Fluoride in groundwater

Fluoride (F) is a common element in the earth's crust¹ and is present in various minerals, such as fluorite (CaF_2 , fluorspar), fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, FAP), biotite, cryolite, hornblende and topaz. Depending on climatic conditions (e.g. precipitation and evapotranspiration) and hydrogeology (e.g. water-mineral contact time), which influence weathering processes and groundwater recharge, the F-bearing minerals can release F to the environment and further into groundwater.

In groundwaters that contain calcium (Ca), dissolved F concentrations are predominantly controlled by the precipitation of CaF_2 . As a consequence, elevated F concentrations often occur in groundwaters where dissolved Ca concentrations are fairly low.² Geological settings of F-bearing and Ca-poor minerals are volcanic (extrusive), granitic (magmatites) and gneissic (metamorphites) rocks and sediments of marine origin.² Groundwaters in arid regions, which experience low recharge and that are predominantly sodic (dominated by NaHCO_3), or geothermal waters can also contain elevated F concentrations.² Amini et al. (2008)³ developed a model to predict the probability of F-enriched groundwaters on a global scale Figure 1.1. This model is based on a database of over 60'000 F measurements and statistically analyses the relationship of elevated F concentrations to geospatial proxies including geological settings, climatic conditions, topography, and soil properties. The results show that less developed countries in arid climates are predominantly affected.

Apart from groundwaters, surface waters can also contain F, though F concentrations are usually lower (0.5 mg L^{-1} for freshwaters).² One examples for F-rich surface waters is Lake Elementaita, Kenya, where a F concentration of 162.5 mg L^{-1} has been found.⁴ This lake has geothermal springs.

The predominant concern of F-rich waters is that when groundwaters and surface waters are used for drinking water supply, the ingestion of elevated F concentration can pose serious health risks for humans.

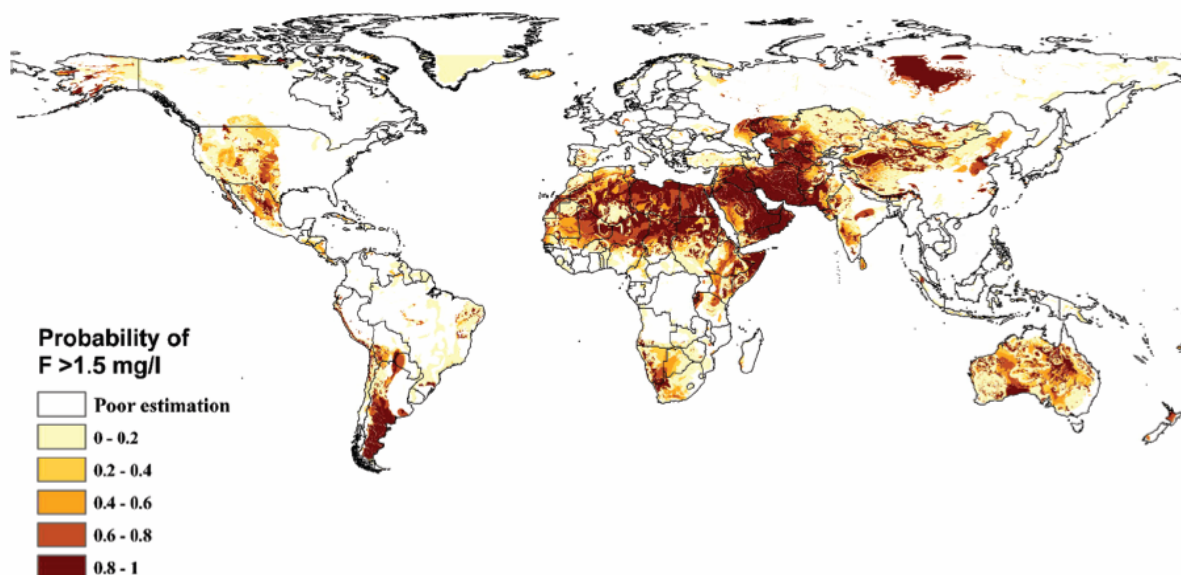


Figure 1.1 Modelled probabilities of F concentrations in the groundwater exceeding the WHO guideline value of 1.5 mg L^{-1} from Amini et al. (2008) ³

1.2 Fluoride related health effects

Health effects related to F uptake in the human body can be positive or negative. At concentrations below 1 mg L^{-1} , F is known to have a protective effect against tooth decay.⁵ Therefore, it has been added to drinking water in Switzerland (1950s to 1980s)⁶ and is still added in some parts of the USA^{7, 8} where geogenic F concentration in drinking water is relatively low. For the same reason F is an ingredient in tooth paste, mouth wash and table salt.

Negative health effects are caused by the ingestion of elevated F concentrations. Once the F enters the blood circulation, it is retained in Ca-rich areas such as bone and teeth.⁷ Two different kinds of health effects are caused by elevated F uptake. *Dental fluorosis* (Figure 1.2 a) affects the tooth development. The effects range from white line striations through to brown patches, malformed teeth and early tooth loss. Affected

people may also suffer from social stigmatisation. *Skeletal fluorosis* (Figure 1.2 b) is caused by an increased bone density due to F incorporation in the bones⁹ and calcification of joints and ligaments.¹⁰ People suffer from aches in joints, while stiffness and even bone deformation can occur.



Figure 1.2 (a) Typical teeth motteling caused by dental fluorosis and (b) bone deformation of skeletal fluorosis

Fluorosis is irreversible. There is thus a need to reduce the F uptake in the human body. Depending on F-levels in drinking water, this can be achieved by either of two ways. One option is a change of diet, including Ca-rich food/drink/medicals. The Ca forms poorly absorbed compounds and thus decreases the bio availability of F.¹¹ Another option is the removal of F from drinking water prior to consumption.

1.3 Hydroxyapatite - the main compound in bones and teeths

The positive health effects of tooth strengthening by F treatment is related to the main compound in teeth and bones, which is hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAP). In comparison to other calcium-phosphate minerals, HAP has a relatively complex crystal structure. The smallest repeating unit of the hexagonal HAP crystal (unit cell), consists of six Ca atoms (*Ca I*), which are associated to two hydroxyl ions and to six phosphate groups, forming a channel in which the hydroxyl ions are located. The other four Ca atoms (*Ca II*) are coordinated to the oxygen (O) atoms of the phosphate groups outside of the channel (Figure 1.3 a). The six *Ca I* atoms form triangles perpendicular to

the screw axis of the hydroxyl ions, but the hydroxyl ions do not necessarily lie in the centre of the plane formed by three calcium atoms;¹² the hydrogen ion faces away from the calcium plane, but the O-H bond never cuts across the plane¹³ (Figure 1.3 b). This is different for fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, FAP), where the hydroxyl group is substituted by F. In this case the F ion lies symmetrically in the plane of the *Ca I* triangles, which results in a higher crystallinity and stability of FAP in comparison to HAP.

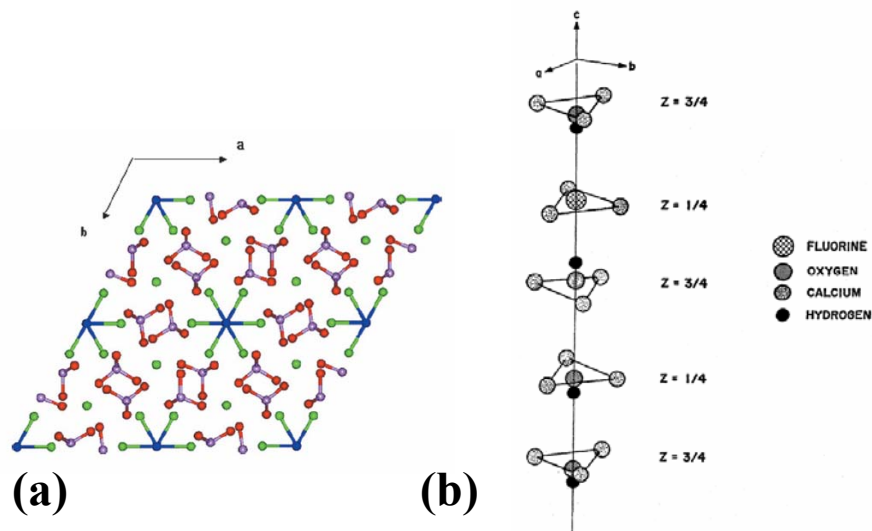


Figure 1.3 (a) Plan view of a FAP surface, showing F atoms in the hexagonal channels surrounded by *Ca I* atoms, followed by the phosphate groups and *Ca II* atoms (Ca: green; F: blue; O_{phosphate}: red; P: purple) (from DeLeeuw, 2004);¹⁴ (b) Placement of OH and F within the *Ca I* triangle planes (from Young and Elliot, 1966).¹⁵

1.4 Fluoride removal from drinking water

In response to the recognition that high F in drinking water can have negative health effects, several techniques for the removal of F from drinking water were developed. Reverse osmosis¹⁶⁻¹⁸ and membrane filtration¹⁹ are very efficient technologies and are mainly used in industrialized countries. These techniques require maintenance skills and are relatively expensive. Filtration with activated alumina is applied in the USA,²⁰ but the filter material is relatively expensive to produce.

Less developed countries have a need for low-cost material that is easy to use, socially accepted and can be locally produced. Two methods have been successfully implemented to date. The Nalgonda technique, which is applied in India and in some areas of East Africa, is based on co-precipitation of F with aluminium hydroxide produced by mixing of alum and lime.²¹ Another efficient method to remove F from drinking water is the use of bone char filters, which is outlined in the following paragraph.



Figure 1.4 Filter media (a) of bone char and (b) calcium-phosphate pellets, both are used in household filter units (c) and in community filters (d).

1.5 The use of bone-char-based filter materials for fluoride removal from drinking water

Bone char was first used in the 1930s in the USA to remove F from drinking water.²² Though its use has been superseded by activated alumina in industrialized countries,²³ it

has found application in a number of less developed countries including Kenya, Tanzania and Thailand.^{24, 25, 26}

Bone char is produced by incineration at a controlled temperature of 400 – 500°C for around 10 days followed by washing with sodium hydroxide to remove organic residues, neutralisation and rinsing. Then the bones are crushed to granules (Figure 1.4 a) that are used in filter units of different dimensions. Household filters (Figure 1.4 c) are in bucket form and appear to be a status symbol for families that are able to own a filter. Community filters (Figure 1.4 d) serve an entire village and are usually run by local authorities that charge small amounts for treated waters. Depending on the volume of water consumed and on the water composition such as pH and dissolved F concentration, filter lifetime can vary significantly. Once the filter media is saturated with F, the material needs to be replaced or regenerated.

The F uptake on bone char is associated with the HAP crystal structure and several studies, which are cited in Chapter 2, have been performed to investigate the mechanisms controlling F uptake on HAP. The three potential processes of adsorption, substitution and precipitation are summarized in Figure 1.5 and are discussed in detail in Chapter 2. Although these studies have contributed to a general understanding of F uptake on HAP, they were mainly carried out under physiological rather than under environmentally relevant conditions.

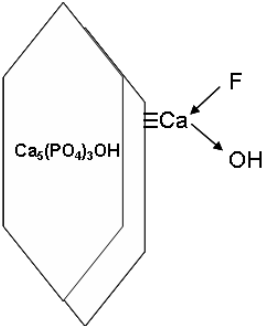
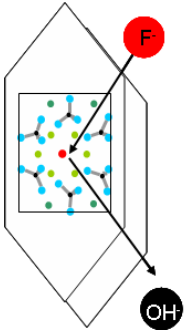
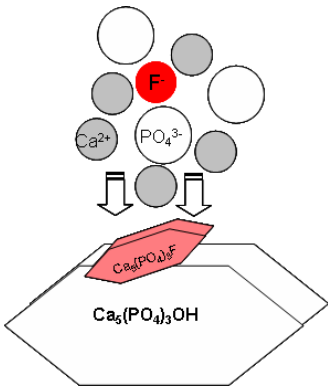
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| <p>ADSORPTION</p>  | <p>The crystal surface sites of HAP have specific groups (e.g. $=\text{CaOH}$ and $=\text{OPO}_3\text{H}_2$). Bengtsson et al. (2009)²⁷ conducted surface complexation modelling based on the assumption that F can sorb to $=\text{CaOH}$. Depending on solution pH, adsorption would result in the release of protons or water, while F is removed from solution.</p> |
| <p>SUBSTITUTION</p>  | <p>Once F is sorbed to the HAP surface, it could substitute for the OH ions within the HAP crystal structure, forming FAP. A complete substitution of all OH groups within the HAP crystal might require long equilibration times. From a kinetic perspective, the formation of FAP as a less soluble phase on the surface of HAP decreases HAP solubility.¹⁴</p> |
| <p>PRECIPITATION</p>  | <p>If dissolved Ca, PO_4 and F concentrations exceed saturation levels, FAP could also precipitate as a new solid. This process can occur as a homogeneous precipitation in solution or as a heterogeneous surface precipitation process in presence of a seeding template like HAP. Further information about precipitation processes of calcium-phosphate phases are provided in 1.7.</p> |

Figure 1.5 Mechanisms of F uptake on HAP

1.6 Contact precipitation method for improving bone char filters

In order to enhance the F uptake capacity of bone char filters, the *contact precipitation* method has been developed and implemented after rudimentary testing.^{25,}

^{28, 29} The Non-Government Organisation, the Catholic Diocese of Nakuru, Kenya, has developed solid calcium-phosphate pellets (Figure 1.4 b), which they add to the bone

char media in the ratio 3 parts of pellets to 1 part of bone char. These pellets slowly dissolve, releasing Ca and PO₄ to solution that should then precipitate as FAP, which incorporates F directly, or as HAP, which would allow F-adsorption and substitution reactions to take place. Precipitation of CaF₂ could also occur. The formation of any of these three minerals would enhance F removal.

Indeed a significant improvement in contact precipitation filters relative to bone char units has been observed.^{25, 28} Elevated dissolved Ca and PO₄ concentrations influence precipitation processes and thus filter function. From laboratory experiments it is known that the calcium-phosphate pellets release Ca and PO₄ in ratios that vary significantly and are mostly below the ideal stoichiometric ratio for HAP and FAP.³⁰ What is not known is to what extent the different dissolved Ca/P ratios affect mineral formation and thus F uptake capacity. Information about phase formation can be used to optimize these filter systems for a maximal F removal capacity and regeneration procedures of the spent filter media.

1.7 Potential mechanisms for fluoride removal in surface precipitation of HAP/FAP

Insights into heterogeneous precipitation processes on apatite surfaces can be provided by dental research. Though, experimental procedures varied, making it difficult to compare the outcomes, it was found that precipitation processes at the HAP surface depend on several conditions (saturation degree, pH, added Ca/P, co-presence of dissolved F, seed concentration and reaction time), as outlined below. From a thermodynamic perspective, the final product at equilibrium is expected to be the thermodynamically most stable phase, which is HAP in calcium-phosphate systems or FAP in calcium-phosphate-fluoride systems. However, until equilibrium is achieved, more soluble intermediate phases can form (according to the Ostwald Step Rule)³¹,

which then dissolve and re-precipitate as the more stable phase. The formation of intermediates may hinder the precipitation of the thermodynamically most stable phase, e.g. of HAP, and could consequently affect F uptake.

Experiments for F removal in apatite-based systems in the past have focused on solution composition and effects of Ca/P ratios, which were equal or greater than the stoichiometric ratio for HAP/FAP of 1.67. Fluoride removal at pH 7 was increased relative to the use of bone char alone when the added dissolved Ca/P ratio was more than twice the stoichiometric ratio for FAP; under alkaline pH conditions, a stoichiometric ratio was sufficient to achieve the same F removal.²⁸ However, the solid precipitates were not investigated in detail for confirmation of phase formation,^{32, 25, 24, 28, 29} which is essential for a better understanding of the processes in contact precipitation systems. As the dissolution of pellets is limited, a lower degree of supersaturation could result in calcium-phosphates other than FAP.

In the field of medical research, Nancollas and co-workers (references are provided in the following paragraphs) applied constant composition studies (continuous addition of Ca and PO₄ to achieve constant concentration in solution and constant pH) in order to investigate intermediate phases formed during the precipitation of HAP. Solutions were initially supersaturated with respect to one or more of the phases brushite (CaHPO₄*2H₂O), β -tricalcium phosphate (Ca₃(PO₄)₂, β -TCP), octacalcium phosphate (Ca₈H₂(PO₄)₆*5H₂O, OCP) and HAP.

Brushite

In acidic systems with pH 5-6 at 37°C with an initial Ca/P ratio of 1.0 (Ca 0.63-15 mM) and if the surface area of the apatitic seed ranged between 0.5-170 m² L⁻¹, brushite was found to be the final product after about 2-7h.³³⁻³⁶ The phase was identified by the

final precipitated Ca/P of around 1.0, by X-ray Diffraction (XRD) and by platelets identified in Secondary Electron Microscopy (SEM) images. If in the same systems the seed concentration was 10-fold, the precipitated Ca/P increased to 1.50 and the formation of a “basic calcium-phosphate phase” was suggested, which was not clearly defined and potential partial seed dissolution was not considered.³⁴ If F was added in concentration up to 0.05 mM, FAP was identified.³³

OCP

At pH 7.4 at 25°C or 37°C with an initial Ca/P ratio of 1.33 (0.16-1.6 mM Ca) and HAP seed surface areas of 612-10'000 m² L⁻¹, OCP was found as an intermediate at a timescale of 10 min to 3h after which HAP was observed. The phases were determined by XRD, Fourier Transform Infrared Spectroscopy (FTIR) and precipitated Ca/P at around 1.45.³⁶⁻³⁸ In presence of dissolved F (up to 1.4 mM), OCP formation was not observed.³⁹

TCP

Although some of the systems mentioned above resulted in precipitates with a Ca/P ratio of around 1.5, the formation of TCP was not considered. Instead this observation was attributed to mixtures between OCP and HAP or precipitation of a Ca-deficient HAP.^{33, 37}

HAP

In systems at pH 7.4 at 25°C and 37°C, with an initial Ca/P ratio (0.16-1.56 mM Ca) ranging between 1.67 to 1.50 and the surface area of apatitic seeds (HAP and FAP) of 2'700-10'000 m² L⁻¹, HAP was found as the final product after at least 3h. The Ca/P ratio of the precipitates was 1.56-1.95, and for Ca/P ratios greater than 1.67 the co-

existence of other calcium-phosphate phases was assumed. Apart from the precipitated Ca/P ratios indications for HAP were provided by XRD, FTIR and SEM.^{39, 36-38}

FAP

In presence of 0.25 mM F (1:1 or 5:1 Ca/F) with the same conditions as described for HAP, FAP was formed instead of HAP;^{40, 36} in acidic conditions the formation of brushite as an intermediate was suggested.⁴¹ The later reaction was reported to be faster than the transformation to FAP via HAP and the formation of FAP over CaF₂ would be favoured in presence of brushite.⁴¹ Further the rate of FAP crystal growth was greater on FAP than on HAP seeds.⁴² This observation was attributed to oriented crystal growth on perfectly oriented crystal surfaces.⁴² Also it was observed that crystallization occurred more readily in the presence of sodium than of potassium ions.³⁷

1.8 Seeding template in heterogeneous precipitation processes

The precipitation processes mentioned above were performed in apatitic systems, containing seeds of HAP, FAP or related material, such as enamel. Surface characterizations of the precipitate solids were limited for two reasons: i) it might have been difficult to differentiate the new precipitate from the seed surface of similar composition; ii) the seed surface might have undergone partial transformation and/or dissolution, which could have changed its surface composition and thus affected the evaluation of the final precipitate.

In Albertus (2000)³² it is stated that the use of an apatitic seeding template is essential as a catalyst to precipitate F. Therefore, the use of an apatite with a composition different from the expected precipitates might facilitate the differentiation of the new phase from the seed. One possible mineral is strontium hydroxyapatite (Sr₁₀(PO₄)₆(OH)₂, SrHAP).

1.9 Strontium hydroxyapatite

Strontium hydroxyapatite has not been investigated in nearly as much detail as HAP, primarily since it has fewer applications. There has been some interest in SrHAP in the context of treatment for osteoporosis, where strontium (Sr) is used as a substitute for Ca. Some solid-solution studies have been performed to evaluate potential bone stabilities as function of the degree of Sr substitution within the HAP crystal structure.⁴³

As for HAP, the crystal structure of SrHAP is hexagonal, while its unit cell has the dimensions of $a=b$: 9.745 Å and c : 7.265 Å.⁴⁴ The SrHAP crystal unit cell is slightly greater than for HAP, since Sr has a greater atomic radius leading to an increased atomic distance within the crystal structure. Since SrHAP is not a commercial product, each publication dealing with SrHAP has utilised its own freshly synthesized product, which has generally not been well characterized. In most cases strontium hydrogen phosphate (SrHPO_4) was detected, which indicated the formation of non-stoichiometric SrHAP.⁴⁵⁻⁴⁷ Kim and Park (2005)⁴⁸ showed phase formations of different strontium phosphates (tristrontium phosphate ($\text{Sr}_3(\text{PO}_4)_2$) and collin salt ($\text{Sr}_6\text{H}_3(\text{PO}_4)_5 \cdot 2\text{H}_2\text{O}$)) for different pH conditions. Since these pH conditions occur in SrHAP syntheses, formation of by-products could affect the production of pure SrHAP. It is therefore necessary to evaluate the best method producing pure, crystalline SrHAP. This is discussed in more detail in Chapter 4.

1.10 Open research questions

Based on the introduction above, some research questions remained that need to be clarified for a better understanding of the function of HAP-based fluoride removal filters:

- What is the predominant process responsible for F uptake on HAP under controlled environmentally-relevant conditions?

- Is it possible to quantify the F uptake on HAP by solid characterization techniques?
- To what depth is F incorporated into the HAP crystal?
- What kind of calcium-phosphate phases precipitate in presence of an apatitic seeding template as function of different Ca/P and Ca/P/F ratios?
- Is it possible to distinguish clearly between new Ca-containing precipitates and a Ca-free seed surface by use of surface and bulk sensitive techniques?
- Filter systems contain calcite. Do the same calcium-phosphate phases precipitate if a carbonated seed is used instead of an apatitic template?
- Is it possible to synthesize pure, crystalline SrHAP?

1.11 Thesis outline

The introduction above has shown that key processes responsible for F uptake in apatite-based systems under environmentally relevant conditions are linked to the surface properties and crystal structure of HAP as well as to the precipitation of F-bearing minerals. This study has aimed to answer several research questions that are stated in 1.10. The results of this work are presented in the form of papers, which were published in peer-reviewed journals (Chapter 2) or will be submitted in the near future (Chapter 3 and 4).

Chapter 1 has introduced the issue of F in groundwater as a geogenic element, which can cause irreversible health effects in humans. These health effects are associated with the main compound in bones and teeth, the calcium-phosphate mineral hydroxyapatite (HAP). Based on the crystal structure of HAP, the knowledge of F uptake on bones is also relevant to the removal of F from drinking water. Deliberately-induced precipitation of calcium-phosphate minerals, where apatite is used as a seed to stimulate the precipitation process, enhances F removal in filter systems. The precipitation processes depend on several factors, which influence each other. Furthermore the use of a seeding template with a composition similar to that of the new precipitate makes it difficult to characterize the main phase formation. This difficulty can be avoided by the use of a seeding template with a different composition from that of the expected precipitate. Once the chemical mechanisms and phase formations are understood, apatite-based filter systems could be optimized for enhanced efficiency in F removal from drinking water.

Chapter 2 focuses on the uptake of F from aqueous solution on nanosized synthetic HAP that was investigated under environmentally relevant pH conditions and as

function of various initial F concentrations. Solution data presented was based on 28-day-equilibration and was compared with results of an intensive solid characterization. Bulk compositions of the solids were evaluated by Transmission Electron Microscopy (TEM), and Fourier Transform Infrared Spectroscopy (FTIR) and surface compositions by X-ray Photoelectron Spectroscopy (XPS) and Nano Secondary Mass Spectroscopy (NanoSIMS) analyses for phase identification and to quantify the uptake of F on HAP.

Chapter 3 presents the results of an investigation into phase formation in calcium-phosphate systems. Different Ca/P and Ca/P/F ratios were used to precipitate calcium-phosphate phases on seeding templates. The initial Ca/P ratios were chosen to correspond to brushite (1.0), β -TCP (1.5), HAP (1.67) or were non-stoichiometric (0.5) or Ca/F ratios corresponded to FAP (5.00) or FAP with CaF_2 (2.00) in order to investigate whether or not these solids are formed. To facilitate the phase examination, Ca-free seeding templates were used. Strontium hydroxyapatite (SrHAP) seeds were used to provide an apatitic surface. In comparison, strontium carbonate (SrCO_3) was applied to model a carbonate seeding surface and a carbonate solution. The precipitates were intensively investigated by surface and bulk analyses using X-ray Diffraction (XRD), FTIR, XPS, X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure spectroscopy (EXAFS).

Chapter 4 describes the synthesis of SrHAP, which was employed as a seeding template in chapter 3. The synthesized product was characterized for its purity by XRD, FTIR, XPS, TEM, and by Thermogravimetric Analysis (TGA). In addition, the solubility constant was determined over an equilibration of 91 days.

Chapter 5 presents a general conclusion and an outlook of possible optimization procedures for the removal of F from drinking water based on apatitic-filtration systems.

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Chapter

2

Uptake of Fluoride from Aqueous Solution on Nano-Sized Hydroxyapatite: Examination of a Fluoridated Surface Layer

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Abstract

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAP), both as a synthetic material and as a constituent of bone char, can serve as an effective and relatively inexpensive filter material for fluoride (F) removal from drinking water in low-income countries. Fluoride uptake on HAP can occur through different mechanisms, which are, in principle, influenced by solution composition. Suspensions of HAP (2 g L^{-1}) were equilibrated under controlled pH conditions (pH 6.5, 7.3, 9.5) at 25°C for 28d after the addition of different F concentrations (0.5–7.0 mM). The reacted HAP solids were examined with Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), and Nano Secondary Ion Mass Spectroscopy (NanoSIMS). Fluoride uptake on HAP was dependent on pH, with the highest capacity at pH 6.5; the lowest uptake was found at pH 9.5. Under all experimental conditions, the thermodynamically stable mineral phase was fluorapatite, ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, FAP). Fluoride uptake capacity was quantified on the basis of FTIR and XPS analysis, which was consistent with F uptake from solution. The results of XPS and NanoSIMS analyses indicate that a fluoridated surface layer with a thickness of several nanometers is formed on nanosized HAP.

2.1 Introduction

The ingestion of elevated fluoride (F) concentrations via drinking water affects the health of several million humans worldwide, particularly in less developed countries.¹ Fluoride has a protective effect against tooth decay at low doses, but elevated uptake can cause dental and skeletal fluorosis.¹ The therapeutic dose and harmful levels are relatively close; the reported optimum value in drinking water to prevent tooth decay² is only 0.5 mg L^{-1} below the maximum guideline value of 1.5 mg L^{-1} recommended by the

World Health Organization.¹ Elevated F concentrations are naturally present in some groundwater sources that are used for drinking water supply, for example in East Africa,^{3,4} India,⁵ China,⁶ Mexico,⁷ and Argentina.⁸

Both harmful and therapeutic health effects of F are related to its uptake by hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAP), the main constituent of bones and teeth.⁹ Due to the propensity of HAP to take up F, the mineral, in the form of bone char or as a synthetic material, has been used in water treatment for F removal.^{10, 11} In industrial countries, F removal is accomplished by more efficient but relatively expensive technologies, such as activated alumina and reverse osmosis.¹² In developing countries, bone char is still a viable option.^{10, 13} The F uptake capacity of HAP is a key criterion for implementation as it directly affects the lifetime and cost of filter media. Fluoride removal efficiency can be influenced by HAP morphology and water composition, such as pH and potentially competing anions (e.g., chloride, sulfate, and carbonate).^{14, 15} In order to predict the HAP filter performance, it is important to identify and quantify the contributions of possible mechanisms for F uptake on HAP: (i) adsorption on the surface, (ii) substitution into the crystal lattice, and (iii) (dissolution-) precipitation.

(i) Surface Adsorption. In this mechanism, F forms surface complexes with reactive sites on HAP, such as $\equiv\text{CaOH}$. The surface charge is controlled by the chemisorption and release of protons at this site and also on $\equiv\text{OPO}_3\text{H}_2$.¹⁶ The high affinity of F for the HAP surface leads to exchange of water (at acidic pH) or hydroxide ions (at neutral pH) at $\equiv\text{CaOH}$ sites. A comprehensive overview of the surface species distribution of FAP as function of pH is provided by Bengtsson et al. (2009).¹⁶

(ii) Substitution in the HAP Crystal Lattice. Fluoride ions sorbed onto the HAP surface can substitute for hydroxide (OH) within the HAP crystal structure.¹⁷ This substitution

is favored because F, with its smaller ionic radius (F: 0.133 nm, OH: 0.137 nm), fits better into the crystal structure of apatite yielding the more thermodynamically stable fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, FAP).¹⁸⁻²⁰ This substitution process is independent of and does not affect surface charge. It is kinetically controlled primarily by diffusion of fluoride from the HAP surface into the crystal. The formation of several nm thick surface layers of FAP on bulk HAP has been observed after 5 min²¹ or 1h²² equilibration in F solutions and may hinder further incorporation of F into the bulk HAP.²³

(iii) (Dissolution-)Precipitation. HAP dissolution, particularly under acidic conditions, can result in an increase of calcium (Ca^{2+}) and (total, dissolved) phosphate (PO_4) concentrations in solution. If the solution becomes supersaturated with respect to solids such as FAP or fluorite (CaF_2), the precipitation of these phases can result in a decrease in dissolved solute concentrations. Such precipitation has been observed to occur either homogeneously in solution or heterogeneously on a pre-existing surface when fluoride is added to HAP suspensions.^{24, 22, 25} Less stable intermediates such as CaF_2 may dissolve in favor of reprecipitation of the most thermodynamically stable phase, FAP.²⁶

Although many different studies have contributed to a general understanding of the reactions between F and HAP, they are difficult to compare because either HAP surface area was not reported,^{27, 28} the pH was not controlled,^{24, 11} or the equilibration times varied from minutes^{29, 30} to months.¹⁷ Furthermore, most studies were conducted at pH 4–7, which is relevant for dental care,^{31, 25} rather than for environmental groundwater conditions (pH 5–9).

The aim of the present study was to determine the predominant mechanisms of F uptake on synthetic HAP as function of F concentration at environmentally relevant pH

values. A combination of microscopic and spectroscopic techniques was applied to examine the surfaces of the solid products to qualitatively and quantitatively evaluate the F uptake capacity on nanosized HAP. The outcome provides an insight into surface reactions on HAP-based filter media during F removal from drinking water and might support optimization potentials of such filter systems.

2.2 Experimental Section

Chemicals and Materials

Powdered HAP was obtained from Budenheim GmbH, Germany. Its characterization as well as the synthesis of FAP as a solid reference sample is provided in the Supporting Information (2.S1–2.S2).

All other chemicals used were of at least “pro analysi” grade (p.a., from Merck and Fluka). Nanopure water (Barnstead NANOpure Diamond UV, resistivity $>18\text{M}\Omega\text{-cm}$) was used for rinsing and solution preparations. Acid-washed (0.65% HNO_3 followed by ≥ 3 rinses with nanopure water) polyethylene (PE) vessels were used for solution preparation and storage.

Influence of pH on the Fluoride Uptake Capacity

Fluoride uptake capacity of HAP was determined in duplicate in open systems (atmospheric p_{CO_2}) with nanopure water at $25 \pm 1^\circ\text{C}$. Suspensions (2g HAP L^{-1}) were mixed by a suspended magnetic stirrer to avoid sample grinding. Prior to F uptake investigations, two experiments were conducted without pH adjustment to determine the equilibration time and equilibrium pH, in addition to solution equilibrium composition within 26d.

For all following F uptake experiments, the suspension was pH controlled (6.5 ± 0.5 , 7.3 ± 0.5 , 9.5 ± 0.5) with 0.1 M HNO_3 and 0.1 M NaOH , using titration units (665, 725,

and 842 with Metrohm software Tiamo 1.2.1) coupled to pH meters (Metrohm 691 and 713) and electrodes (Metrohm 6.0259.100 and 6.0258.010). Electrode two-point calibrations were performed at the start of each experiment by using Titrisol buffers (pH 4 and 9) and checked by measuring buffer of pH 7 (Titrisol). After equilibration for 3d, F was added to HAP suspensions from a 0.5 M NaF stock solution to achieve initial dissolved concentrations of 0.5, 0.9, 2.0, 3.3, 5.0 and 7.0 mM. For F and elemental analysis (details in 2.S3–2.S5, Supporting Information), filtered (0.2- μ m nylon, PALL) samples (10 mL) were taken over 28d, with more intensive sampling in the initial 24h. It should be noted that potential effects from particles $<0.2 \mu\text{m}$ and therefore not retained by the filter were not investigated in detail; these could have the effect of increasing the elemental concentrations in the solutions.

Samples (20 mL) for total dissolved inorganic carbon (DIC) analysis were taken prior to the addition of F and at the end of the 28d-equilibration time. For cation analysis, samples were acidified with 1% suprapure HNO_3 and stored at 4°C until analysis. Measured elemental concentrations were corrected for the solution volume and solid loss. A 28d-equilibration period was chosen because F concentrations did not vary more than 5% within the final week. The remaining solid material was collected on a 0.45- μm cellulose-nitrate filter (Sartorius), air-dried, and stored at room temperature for further analysis.

Influence of Different Anions on the Fluoride Uptake Capacity at Fixed pH

The effect of competing anions on F uptake on HAP was assessed in duplicates using the same setup as described above, at pH 7.3 and 0.5 mM initial F, but with a shortened equilibration time of 7d (when 80–90% of the initial F was taken up from solution in batches without anion addition). Chloride (Cl^-) and sulfate (SO_4^{2-}) were added from stock solutions (5.0 mM and 2.5 M NaCl and 5.0 mM and 1.5 M Na_2SO_4 , respectively)

to achieve total dissolved concentrations of 0.5, 5.0, and 50 mM simultaneously with the addition of F.

To assess the influence of 5.0 and 50 mM HCO_3^- , the system was covered with a septum lid, and a N_2 -gas mixture containing $16,100 \pm 2,000$ ppm CO_2 (PanGas) and a 10-fold higher concentration respectively, was bubbled directly into the suspension at a rate of approximately $0.05\text{--}0.10 \text{ L min}^{-1}$. The gas mixture, together with 0.1 M NaOH, was used for pH adjustment throughout the experiment, including a 3d-pre-equilibration. The DIC was monitored during the experiments.

Solid Characterization

Transmission Electron Microscopy (TEM, Tecnai, F30ST, FEI) was performed on pure unreacted HAP and FAP and on solids of 28d-reacted HAP from batches conducted at pH 6.5 with 7.0 mM initial F (highest F uptake from solution) and at pH 9.5 with 2.5 mM initial F (low F uptake from solution). An acceleration voltage of 300 kV was used. The microscope was operated in the scanning mode and the solids were localized using a High-Angle Annular Dark Field (HAADF) detector and analyzed with an Energy Dispersive X-ray (EDX) system (EDAX).

Fourier Transform Infrared Spectroscopy (FTIR, FTS 575C, Portman Instruments AG, Software BIO-RAD Win-IR, version 4.14) measurements were conducted on air-dried solids of 28d-reacted HAP from batches conducted at pH 6.5, 7.3, and 9.5 with initial F of 3.3, 3.3, and 2.5 mM, respectively (errors for pH 9.5 with 3.3 mM F were too high for further consideration of this data). The spectra were compared with those of pure unreacted HAP and FAP and ground mixtures of the two (1:3, 1:1, and 3:1). To differentiate the spectral intensities for the 630 cm^{-1} peak, all data were normalized to the baseline and to unity for the P—O peak at 600 cm^{-1} .

X-ray Photoelectron Spectroscopy (XPS, Quantum 2000, Physical electronics) was performed on air-dried pure unreacted HAP and FAP, and CaF₂ (rock mineral, AlfaAesar), and on solids obtained from batches conducted at pH 6.5, 7.3 and 9.5 with 7.0, 3.3, and 2.5 mM initial F. The XPS analysis employed monochromatic Al K α radiation and was conducted under constant neutralization using an electron flood gun and very low energy Ar⁺ ions (10 eV). Binding energy calibration was carried out using adventitious carbon, setting the binding energy of C(1s) to 284.8 eV. Spectra were obtained from the untreated surface and after sputter cleaning using an analysis spot with a diameter of 150 μ m.

Secondary Ion Mass Spectroscopy (NanoSIMS50, Cameca, Courbevoie, France) was performed on the solid obtained from the batch conducted at pH 6.5 with 7.0 mM initial F. Carbon (¹²C⁻), fluorine (¹⁹F⁻), phosphorus (³¹P⁻), oxygen (¹⁶O⁻), and nitrogen (¹²C¹⁴N⁻) were detected simultaneously. The analysis was conducted with a lateral dimension of approximately 200 nm \times 200 nm and the surface layers were sputtered to a depth of 20 planes corresponding to a maximum depth of 60–90 nm.

Experimental set-ups and sample preparations for all solid characterization methods are provided in the Supporting Information (2.S7–2.S10).

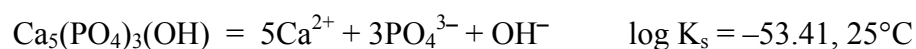
2.3 Results and Discussion

When HAP is (pre)equilibrated in water, the concentrations of Ca and PO₄ increase toward their pH-dependent equilibrium values. The presence of these ions in solution will then influence the mechanism(s) by which added F is taken up by the solid. Different effects on the solution composition are expected for the various possible mechanisms. In the case of F adsorption (mechanism (i)) and/or substitution into the lattice (mechanism (ii)), an increase in the hydroxide (OH) concentration, and hence pH,

would be expected. If precipitation occurs (mechanism (iii)), decreases in the concentrations of both Ca and PO₄ should be observed for FAP precipitation. In the case of CaF₂ precipitation, the PO₄ concentration would be unaffected. Of course, mechanism (iii) can only occur if the prior dissolution of HAP produces sufficiently high concentrations of Ca and/or PO₄ that the solutions are supersaturated with respect to a solid phase at a given F concentration and pH. In addition to the observed changes in solution composition, evidence for or against the presence of FAP and CaF₂ in the reacted solids was obtained by TEM, FTIR, and XPS analyses. The surface enrichment of F in the reacted solids was examined by XPS and NanoSIMS.

HAP Dissolution as a Precondition for Fluoride Uptake Experiments

Dissolution of HAP without pH adjustment (or F addition) was observed over 26d and resulted in an average pH of 7.3 ± 0.1 . This equilibrium pH is close to literature values of 7.05³² and 7.13³³ for the pzc in HAP systems open to the atmosphere. The ionic strength of 2.1 mM was dominated by Ca, PO₄, HCO₃⁻, K⁺, and Cl⁻, the latter two diffusing out of the pH electrode. The Ca and PO₄ concentrations at 26d were 0.09 and 0.08 mM respectively, which corresponds to a saturation index of 0.37 ± 0.21 according to the following reaction



(See ref³⁴). A lower solubility for HAP ($\log K_s$ of -58.52) has also been reported.³⁵

Uptake of Fluoride from Aqueous Solution

For F uptake experiments, HAP suspensions were pre-equilibrated with water for 3d, allowing the solutions to reach saturation with respect to HAP at pH 7.3 and 9.5. Upon addition of F, immediate sharp increases in pH were observed in experiments conducted at pH 6.5 and 7.3, and the pH stat systems required 5–15 min to readjust the pH to the

target values (data not shown). Simultaneous with the pH increases, the F concentration decreased. For initial F <2 mM at pH 7.3, Ca and PO₄ concentrations remained relatively constant, whereas for initial F >2 mM, the concentration of Ca decreased rapidly and that of PO₄ increased slowly over the 28d-equilibration period (Figure 2.1a). Calcium and F concentrations decreased faster at pH 6.5 than at 7.3 for initial F >2 mM (Figure 2.1a and b). All suspensions at pH 6.5 and those with initial F >3.3 mM at pH 7.3 were initially supersaturated with respect to CaF₂ (Table 2.1) and saturation decreased over 28d; note that the Ca concentration after pre-equilibration was highest at pH 6.5. At pH 9.5, there was an initial increase in pH and concurrent decreases in F and Ca concentrations were less pronounced, but PO₄ concentrations increased significantly with time (Figure 2.1a).

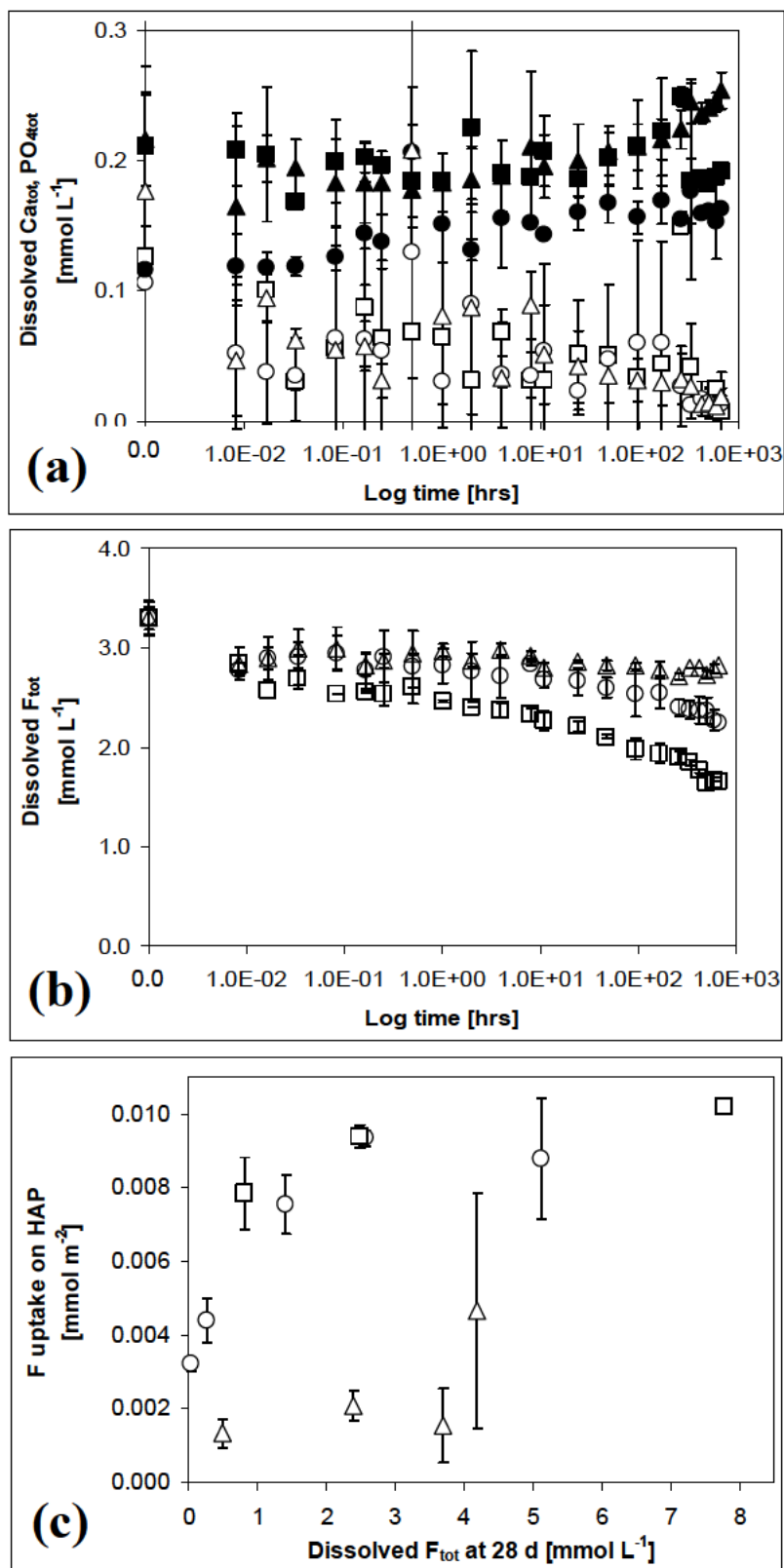


Figure 2.1 (a) Total dissolved Ca concentrations at pH 6.5 (\square), 7.3 (\circ), and 9.5 (Δ), and PO_4 concentrations (filled symbols) from batches with 3.3 mM initial F at 25°C and $[\text{HAP}] = 2 \text{ g L}^{-1}$. (b) Total dissolved F concentration. (c) Fluoride uptake (mmol m^{-2}) on HAP. All data points are based on averages ($n = 2$). Error bars present the standard deviation and are sometimes smaller than the symbols.

Table 2.1 Averaged Total Dissolved Concentrations (n = 2) of F, Ca and PO₄ and Saturation Indices for Relevant Solids for Batches Conducted at pH 6.5, 7.3, and 9.5 with Initial F of 2.5–7.0 mM a) after 3d-Pre-Equilibration before F Addition (Potential Saturation Indices for CaF₂ and FAP) and b) after 20-28d Equilibration in F Solution^a

| Sample | | F _{tot} [mM] | Ca _{tot} [mM] | PO ₄ _{tot} [mM] | Saturation Index | | | |
|--------|---|--------------------------|---------------------------|--|-------------------|------------------|--------------------|------------------|
| | | | | | HAP | CaF ₂ | FAP | β-TCP |
| pH6.5 | a | | 0.13±0.01 | 0.21±0.06 | -5.61±-5.67 | 0.88±0.08 | 2.16±2.11 | -4.10±-4.32 |
| 3.3mM | b | 1.67±0.05 | 0.02±0.01 | 0.19±0.004 | -9.84±-9.86 | -0.60±-0.93 | -2.40±-2.43 | -6.71±-6.80 |
| pH6.5 | a | | 0.34±0.005 | 0.20±0.01 | -2.35±-3.48 | 2.11±0.57 | 5.79±4.77 | -2.06±-3.32 |
| 7.0mM | b | 5.09±0.20 | 0.03±0.02 | 0.24±0.02 | -8.53±-8.16 | 0.56±0.41 | -0.51±-0.14 | -6.03±-5.77 |
| pH7.3 | a | | 0.21±0.06 | 0.12±0.03 | 0.08±-0.44 | 1.08±0.56 | 7.04±6.52 | -0.88±-1.41 |
| 3.3mM | b | 2.29±0.11 | 0.01±0.01 | 0.16±0.01 | -5.63±-5.53 | -0.46±-0.81 | 1.12±1.22 | -4.45±-4.43 |
| pH9.5 | a | | 0.01±0.001 | 0.13±0.01 | 2.39±2.22 | -0.67±-1.40 | 7.07±6.89 | -0.29±-0.68 |
| 2.5mM | b | 2.23±0.09 | 0.03±0.01 | 0.28±0.02 | 5.67±5.72 | -0.07±-0.53 | 10.27±10.33 | 1.56±1.48 |

^aSaturation indices were calculated according to $S = \log(IAP / K_{s0})^{\frac{1}{\eta}}$, where IAP is the ion activity product, K_{s0} is the solubility product and η is the number of ions in the formula unit of the considered mineral.⁴¹ The IAP was adjusted for each individual sample; K_{s0} was corrected according to Davies for the individual activity coefficients. Hydroxyapatite (HAP): $5Ca^{2+} + 3PO_4^{3-} + OH^-$; $\log K_{s0HAP} = -53.28$;³⁴ fluorite (CaF₂): $Ca^{2+} + 2F^-$; $\log K_{s0CaF2} = -10.50$;⁴⁹ fluorapatite (FAP): $5Ca^{2+} + 3PO_4^{3-} + F^-$; $\log K_{s0FAP} = -56.12$;³⁴ β-tricalciumphosphate (β-TCP): $3Ca^{2+} + 2PO_4^{3-}$; $\log K_{s0TCP} = -28.92$.⁵⁰ Bold numbers indicate saturation of the specific phase; (-) DIC not measured.

Under all conditions, the suspensions were initially supersaturated with respect to FAP. The degree of saturation was lower at pH 6.5 than at pH 9.5 and, in all cases, generally decreased over 28d. At pH 9.5, the suspensions were also supersaturated with respect to β-tricalciumphosphate (β-Ca₃(PO₄)₂, β-TCP). After 28d, suspensions at pH 9.5 were close to saturation with CaCO₃.

The initial sharp pH increases with unchanged Ca and PO₄ concentrations in experiments with initial F concentrations <2 mM suggest the exchange of F for OH ions through adsorption (mechanism (i)) and/or substitution (mechanism (ii)). The adsorption mechanism is consistent with the observation of a plateau in F uptake as a

function of equilibrium F concentration at pH 7.3 after 28d (Figure 2.1c). The maximum uptake of $0.009 \text{ mmol m}^{-2}$ (0.58 mmol g^{-1}) at pH 7.3 corresponds to 25% of the initial F of 5 mM. The results agree well with those obtained by Bregnhøj (1995),¹⁰ who found a maximum F uptake of approximately $0.006 \text{ mmol m}^{-2}$ on bone char, in which HAP is the main mineralogical component, after a 3week-equilibration. White et al. (1988)³⁶ found $0.004 \text{ mmol m}^{-2}$ F uptake on HAP with 1h equilibration at pH 7.0, 37°C and 100 mM initial F, whereas Lin et al.²² obtained an uptake capacity of $0.003 \text{ mmol m}^{-2}$ on HAP with a reaction time of 2-3h at pH 7.1–7.3, 37°C (initial F concentration not reported). In the present study, F uptake within 3h reached ~40% of the maximum uptake for initial F <1 mM and ~20% for initial F >1 mM.

The F uptake capacity at pH 6.5 of 0.01 mmol m^{-2} (although based on only three data points) was slightly enhanced relative to that at pH 7.3 (Figure 2.1c). This trend of higher F uptake at lower pH is in agreement with the results of other studies.^{22, 37} At pH 9.5, no plateau was observed, and the maximum noted F uptake was only $0.005 \text{ mmol m}^{-2}$. This is consistent with the observation of fewer available F adsorption sites on the HAP/FAP surface at alkaline pH as reported by Bengtsson et al. (2009).¹⁶

If the observed uptake of F is attributed to the substitution of F for OH (mechanism (ii)), the corresponding extent of conversion of HAP to FAP would be 33% at pH 6.5, 30% at pH 7.3, and 5% at pH 9.5 (assuming 1.99 mmol OH in 1g HAP). Since the substitution would be expected to occur first in the unit cells adjacent to the surface, it is useful to estimate how much F could be substituted for OH given the HAP unit cell dimensions of $a = b: 0.91466 \text{ nm}$, $c: 0.68745 \text{ nm}$ obtained from the XRD reference card.³⁸ Considering both orientations of $a \times b$ and $a \times c$ faces of the unit cell toward the solution gives a range of 0.002 to $0.0058 \text{ mmol m}^{-2}$ based on exchange of either one or both OH within the unit cell. The observed uptake at pH 6.5 (0.01 mmol m^{-2}) and pH

7.3 (0.009 mmol m⁻²) exceeded the estimated range, which suggests either that both adsorption (mechanism (i)) and substitution of F for OH (mechanism (ii)) in the first unit cell layer contribute to the observed F uptake and/or that F diffuses further into the crystal allowing substitution within the bulk. The latter process is likely to be kinetically limited.

In the substitution mechanism, FAP is formed by transformation of HAP rather than by HAP dissolution and subsequent FAP precipitation (mechanism (iii)). As previously noted, the PO₄ concentration in solution (which derives from the HAP pre-equilibration) did not decrease over 28d but rather increased. This suggests that FAP is not directly precipitated from solution (mechanism (iii)). If, however, HAP dissolution proceeds throughout the 28d-equilibration, FAP precipitation might limit the accumulation of phosphate in solution, thus it may not be possible to exclude this mechanism entirely.^{39,40}

At pH 9.5, solutions were also supersaturated with respect to β -TCP (Table 2.1), but again, it would be expected that its formation would be accompanied by removal of PO₄ from solution, which was not observed. The observed decreases in Ca could be related to precipitation of CaCO₃, which would in turn decrease the level of saturation with respect to HAP and promote HAP dissolution and the accumulation of PO₄ in solution.

Over the course of the 28d-equilibration, unstable solid phases formed as intermediates or, in the case of HAP, present initially would be expected to undergo dissolution in favor of forming FAP as the most thermodynamically stable phase.²⁶

Although formation of FAP through (dissolution-)precipitation (mechanism (iii)) seems less likely to control F uptake than adsorption and/or substitution (mechanisms (i) and (ii)), the concurrent decrease in Ca and F at pH 6.5 and 7.3 (with initial F >2

mM) is indicative of the precipitation of CaF_2 , which is initially oversaturated in these systems. The maximum amount of CaF_2 that could be formed in these systems can be estimated based on the removal of Ca from solution to be approximately 4mg. Diluted into about 2g of HAP, this amount of CaF_2 would be below the detection limit for XRD analysis ($\sim 1\text{--}5\%$ by mass).

Influence of Anions on Fluoride Uptake

The anions Cl^- , SO_4^{2-} , and HCO_3^- in excess of F^- (up to 100-fold) had no significant effect on the F uptake on HAP during 7d-equilibration (Figure 2.2). Nor was the uptake affected by the ionic strength (average range: 3–350 mM), which is consistent with F adsorption on HAP through an inner-sphere binding mechanism.⁴¹

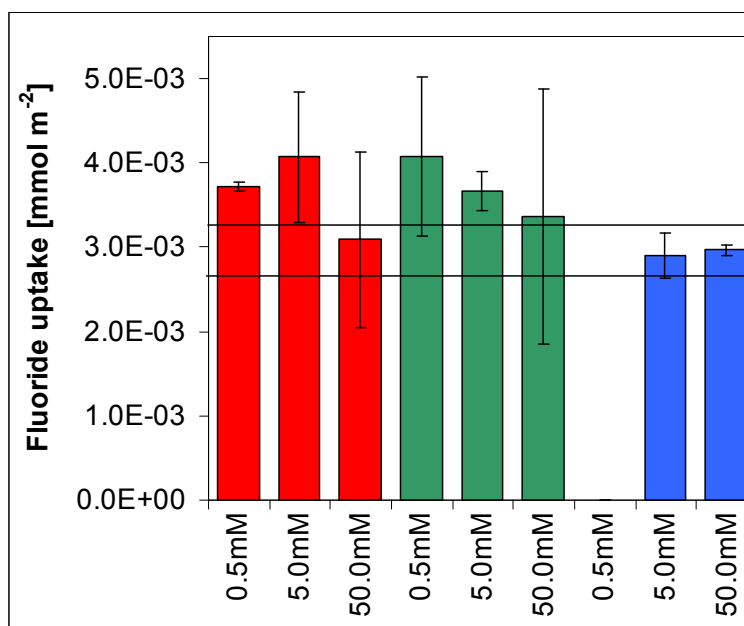


Figure 2.2 Average F uptake ($n = 2$) obtained in HAP suspensions [2 g L^{-1}] with 0.5 mM initial F at pH 7.3 and 25°C: red: sulfate (0.5 ± 0.05 , 5 ± 0.5 , and $50 \pm 5 \text{ mM}$); green: chloride (0.5 ± 0.05 , 5 ± 0.5 , and $50 \pm 5 \text{ mM}$); and blue: bicarbonate (5 ± 0.2 and $50 \pm 12 \text{ mM}$). Error bars present the standard deviation; solid lines present F uptake \pm standard deviation without any anion addition. The average background electrolyte composition had an ionic strength of 3–350 mM as a result of pH adjustment (as NaNO_3), dissolution of HAP and addition of sodium salts, including NaF .

The relative affinity of HAP for F as compared to other ions is likely to be related to the size of the ions (F^- : 0.133 nm; OH^- : 0.137 nm;²⁰ CO_3^{2-} : 0.178 nm;⁴² Cl^- : 0.181 nm;²⁰ SO_4^{2-} : 0.230 nm⁴²) particularly for the substitution mechanism (ii). Substitution of F for OH would result in the least perturbation of the HAP crystal lattice,¹⁸ while Cl^- and SO_4^{2-} are too large to be easily accommodated. Carbonate is known to substitute into HAP, and this has been found to be associated with release of PO_4 and decreased stability of the HAP crystal structure.⁴³ Although this would be expected to decrease F uptake, no such effect was observed in this study.

TEM

Transmission micrographs (Figure 2.S1 a–d, Supporting Information) showed typical needle-shaped crystals (dimensions of 50–100 nm) for the standard samples of pure, unreacted HAP and FAP, which readily aggregated to form globular particles with dimensions of 1–20 μm . The habitus of the crystals remained the same when HAP was equilibrated with F at pH 9.5, but at pH 6.5, the equilibrated crystals were generally smaller in size (20–80 nm) and appeared irregularly shaped. Similarly shaped crystals have been observed previously⁴⁴ and their habitus attributed to incomplete F substitution in HAP. The appearance of the crystals obtained in the present study at pH 6.5 might also reflect partial dissolution of the original HAP.

FTIR

Previous FTIR studies, such as those by Elsami et al. (2009),⁴⁵ used the O–H stretching mode at around 3570 cm^{-1} to distinguish qualitatively between HAP and FAP. In the present study, the O–H libration mode at 630 cm^{-1} (which is present in HAP but absent in pure FAP)^{46, 47} was used to quantify F uptake on HAP. The libration mode corresponds to an infinitely long chain of OH ions located in the calcium-phosphate

channels of the HAP crystal.⁴⁸ This chain decreases in length if F substitutes for OH, which results in a decrease of the O—H-libration intensities.⁴⁸ With increased F substitution, the libration peak shifts to higher wavenumbers.⁴⁸ The appearance of OH and F related peaks at around 713, 735, and 747 cm^{-1} have been reported for fluoridated HAP samples that were calcined after reaction with F,^{48, 44} but these were not observed in the present study (Figure 2.S2 a—e, Supporting Information).

The extent of F exchange for OH was estimated by comparing the FTIR spectra of the pure solids and homogenized mixtures of HAP and FAP (1:3, 1:1, 3:1) with the spectra of solids collected after 28d-equilibration at pH 6.5, 7.3 and 9.5 with initial F concentrations of 3.3, 3.3 and 2.5 mM, respectively (Figure 2.3). On the basis of a linear interpolation of the normalized absorbance at 630 cm^{-1} between pure HAP (0% F), the homogenized HAP—FAP mixtures, and pure FAP (100% F), the extent of substitution of F for OH is 32% at pH 6.5, 20% at pH 7.3 and 2% at pH 9.5, which is in reasonable agreement with the values calculated based on the uptake of F from solution. In addition, slight peak shifts to higher wavenumbers relative to that for HAP were observed with increased F uptake (HAP: 628.81 cm^{-1} ; pH 9.5: 630.01 cm^{-1} ; pH 7.3: 630.01 cm^{-1} , pH 6.5: 630.74 cm^{-1} ; Figure 2.3).

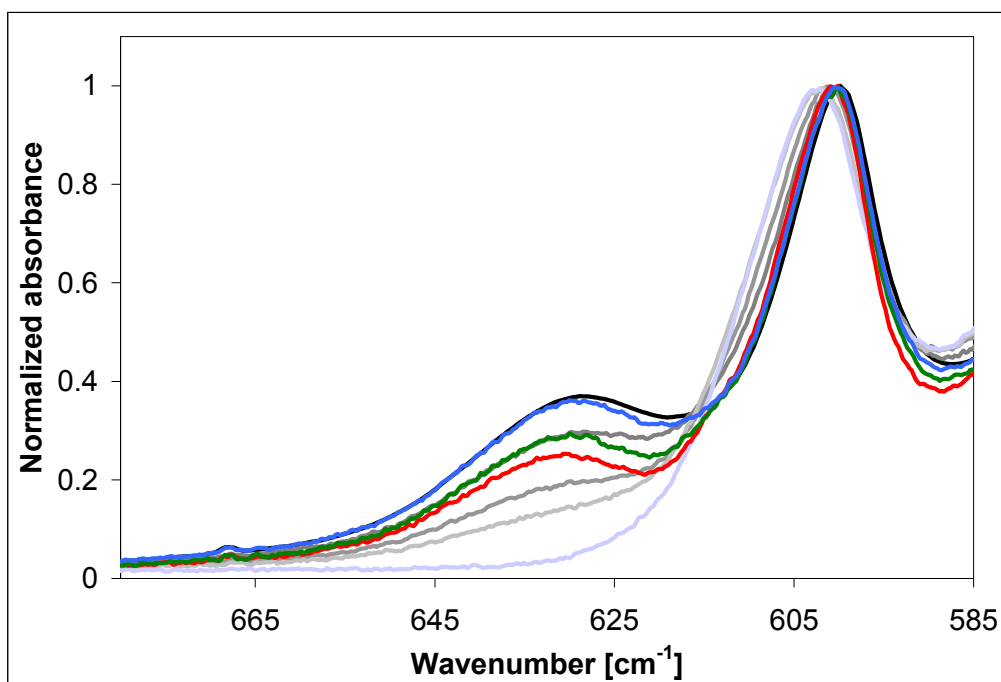


Figure 2.3 FTIR absorbance spectra for the following phases: 100% HAP (black), 3 HAP : 1 FAP (dark grey), 1 HAP : 1 FAP (medium grey), 1 HAP : 3 FAP (light grey), 100% FAP (pale grey), solids from batch pH 6.5 (red), pH 7.3 (green), and pH 9.5 (blue) with initial F of 3.3, 3.3 and 2.5 mM, respectively. The data shown were normalized to the baseline and to 1.0 for the P—O peak at 600 cm^{-1} .

XPS

The surface-sensitive technique of XPS was used to compare the surface composition of the reacted solids with pure unreacted HAP and FAP. Surface sputtering to a depth of approximately 5 nm decreased the average carbon (C) signal from 9.0 ± 2.0 to 3.8 ± 1.6 ($n = 5$) atm% with the C signal assigned mainly to C—C bonds. This signal was thus attributed to surface contamination, and therefore carbon was excluded from the compositional analysis presented in Table 2.2. A surface excess of about 6atm% was observed for oxygen (O) for both HAP and FAP before sputtering; after sputtering, this surface excess was eliminated for HAP and slightly reduced for FAP. The elemental ratios of Ca/P in the sputtered samples of HAP (1.82) and FAP (1.53) were in reasonable agreement with the nominal value of 1.67.

The data for F abundance in the reacted solids decreased with increasing pH of the equilibration reaction. This trend was observed both before and after sputtering; a slight increase in the F atm% in the sputtered samples likely reflects the removal of some excess O. The %substitution of FAP for HAP in the reacted samples after sputtering were 71% at pH 6.5, 49% at pH 7.3, and 22% at pH 9.5. These values are considerably higher and spread over a more narrow range than those obtained from FTIR and the changes in solution composition but may also be influenced by the lower than nominal atm% of Ca and P observed in the XPS (after sputtering) of the reacted solids.

One other key finding from the XPS analysis was that the observed Ca(2p) binding energy in the reacted samples corresponds to that of apatite rather than CaF_2 (Figure 2.S3 a–b, Supporting Information). Since CaF_2 is not infrared active, this solid could not be excluded from the FTIR analysis. The XPS data indicate that F is incorporated into the reacted solids in a FAP-like phase, which persists at depths of more than 5nm into the solid.

Table 2.2 Surface Composition [atm%] of Pure Unreacted HAP and FAP, CaF₂ and of Solids Collected from Batches Conducted at pH 6.5, 7.3 and 9.5 with 7.0, 3.3, 2.5 mM Initial F, Respectively Obtained from XPS Analysis^a

| | O(1s) | F(1s) | P(2p) | Ca(2p) | Ca/P | Ca/F | O/P | F/O | F/P |
|----------------------------|-------|-------|-------|--------|------|------|-----|-------|-----|
| HAP (nominal) | 61.9 | 0.0 | 14.3 | 23.8 | 1.67 | | 4.4 | | |
| FAP (nominal) | 57.1 | 4.8 | 14.3 | 23.8 | 1.67 | 4.8 | 4.1 | 0.087 | 0.4 |
| CaF ₂ (nominal) | 0.0 | 66.7 | 0.0 | 33.3 | | 0.5 | | | |
| before sputtering | | | | | | | | | |
| HAP | 65.7 | 0.0 | 14.1 | 20.2 | 1.43 | | 4.7 | | |
| FAP | 60.8 | 4.0 | 14.2 | 21.0 | 1.47 | 5.2 | 4.3 | 0.066 | 0.3 |
| CaF ₂ | 0.0 | 63.7 | 0.0 | 36.3 | | 0.6 | | | |
| pH6.5-7.0 | 61.7 | 3.0 | 14.1 | 21.3 | 1.51 | 7.2 | 4.4 | 0.048 | 0.2 |
| pH7.3-3.3 | 62.8 | 2.3 | 14.2 | 20.7 | 1.46 | 9.1 | 4.4 | 0.036 | 0.2 |
| pH9.5-2.5 | 64.7 | 1.2 | 13.4 | 20.8 | 1.55 | 17.6 | 4.8 | 0.018 | 0.1 |
| after sputtering | | | | | | | | | |
| HAP | 61.8 | 0.0 | 13.5 | 24.5 | 1.82 | | 4.6 | | |
| FAP | 59.8 | 4.5 | 14.1 | 21.5 | 1.53 | 4.8 | 4.2 | 0.075 | 0.3 |
| CaF ₂ | 0.0 | 64.8 | 0.0 | 35.1 | | 0.5 | | | |
| pH6.5-7.0 | 59.0 | 3.6 | 13.7 | 23.8 | 1.73 | 6.7 | 4.3 | 0.060 | 0.3 |
| pH7.3-3.3 | 60.6 | 2.4 | 13.7 | 23.2 | 1.69 | 9.5 | 4.4 | 0.040 | 0.2 |
| pH9.5-2.5 | 63.2 | 1.1 | 13.6 | 22.2 | 1.63 | 20.0 | 4.7 | 0.018 | 0.1 |

^a Upper section: nominal values. Middle section: values obtained before sputtering. Lower section: values obtained after sputtering

NanoSIMS

Additional information on surface composition was obtained using NanoSIMS. While XPS samples a relatively large area (0.02 mm²), the area sampled by NanoSIMS is much smaller (0.04 μm²). Thus NanoSIMS has a better chance of sampling individual particles (note that every attempt was made to disperse the particles on the sample holder).

The depth profiles of individual anions ($^{31}\text{P}^-$, $^{12}\text{C}^-$, and $^{16}\text{O}^-$) exhibited maxima at around 18 nm (Figure 2.S4, Supporting Information). This might be related to an increase in the sampled volume with depth (assuming a spherical particle). Since the intensity of the signals reflect the electronegativity of the analytes and provides information only on relative abundance, signals for $^{19}\text{F}^-$, $^{12}\text{C}^-$, and $^{16}\text{O}^-$ were normalized to the signal for $^{31}\text{P}^-$ to account for instrumental and matrix effects.

The normalized profile $^{19}\text{F}/^{31}\text{P}$ (Figure 2.4) of the solid reacted at pH 6.5 with 7.0 mM initial F revealed a sharp decrease within the first 6–12 nm (3–4 ablation planes) corresponding to a decay length ($1/e$) of about 4.5–6.5 nm. This sharp initial decrease suggests a relative enrichment of fluoride on the sample surface. A similar trend was observed for $^{16}\text{O}/^{31}\text{P}$ with a relatively enrichment of $^{16}\text{O}^-$ corresponding to a decay length of 3.8–5.7 nm, which probably resulted from sorbed H_2O molecules on the apatite surface. With increased sputtering of the sample, the data become less reliable with increasing sample depth. In general, the findings are consistent with literature values for a fluoridated surface layer of 3–4 nm (neutral pH, 1h exposure to an undefined concentrated fluoride solution)²² and of 6 nm (pH 6.2, 5 min exposure to 1.3 mmol NaF).²¹ Further, they agree with molecular dynamic models,²³ which suggested a partial F incorporation into the HAP crystal

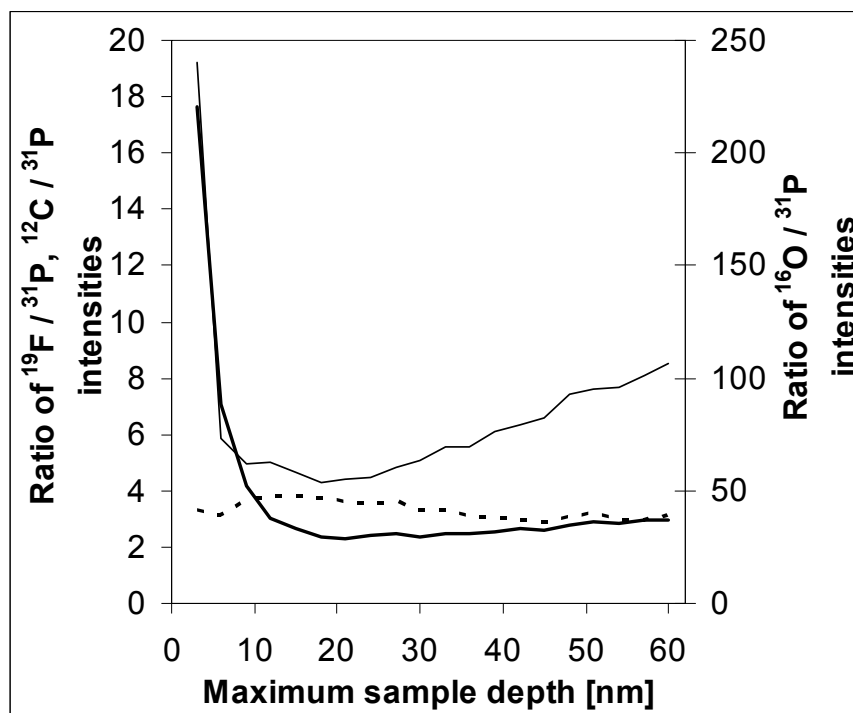


Figure 2.4 NanoSIMS measurements of the ratios $^{19}\text{F}/^{31}\text{P}$ (thick solid line, scale on the left y-axis), $^{12}\text{C}/^{31}\text{P}$ (dotted line, scale on the left y-axis) and $^{16}\text{O}/^{31}\text{P}$ (thin solid line, scale on the right y-axis). The analyzed solids were collected from the batch at pH 6.5 with 7.0 mM initial F.

Comparison of Interrogation Methods and Implications for Field Applications

Assessment of F uptake on HAP through observations of changes in solution chemistry, FTIR and XPS provided reasonably consistent estimates of the uptake capacity of nanosized HAP. The surface sensitive methods, XPS and NanoSIMS, provided strong evidence for a fluoridated surface layer though NanoSIMS showed a decrease in F abundance with depth that was not evident in XPS. It is, however, likely that XPS, since it samples a larger area, averages a signal over more particles than NanoSIMS.

The analytical approaches used could not distinguish unambiguously among the possible F uptake mechanisms of adsorption, substitution, and (dissolution)-precipitation but suggest the presence of FAP-like phases in all reacted solid products. The evolution of the PO_4 concentrations in solutions equilibrated with HAP and F do not support the (dissolution)-precipitation mechanism but cannot entirely exclude it. The changes in solution chemistry do indicate that CaF_2 is precipitated initially, but the XPS results indicate that any precipitated CaF_2 is replaced by FAP over the 28d-equilibration.

In the experimental systems studies here, HAP was equilibrated with F over 28d. This long equilibration time is not representative of how HAP-based filters would be deployed in the field. Shorter equilibration times would tend to limit the accumulation of Ca and PO_4 (i.e., by HAP dissolution) in the pore spaces of the filter. The adsorption mechanism would be more likely to predominate under these conditions and, in the case of alkaline water, F uptake might be very low. This could be offset by pH adjustment to increase F uptake, but this may be logistically difficult in developing countries. Another option would be to mix a relatively soluble Ca- and PO_4 -containing mineral into the filter material. This would provide ions for precipitation reactions and thus enhance the F uptake capacity on HAP-based filters.

2.4 Acknowledgements

We thank Stephan Hug for valuable discussions on FTIR analysis and Hermann Moench for the assistance and advice in various laboratory works. VS thanks Claire Farnsworth for fruitful discussions. Also, two anonymous reviewers (R1 and R2) are acknowledged for their constructive feedback. We acknowledge funding from the Swiss National Science Foundation (200021-117992).

2.5 Supporting Information for Chapter 2

2.S1 Characterization of unreacted HAP

The specific density of pure unreacted HAP was determined by pycnometry with cyclo-hexane at 20°C and was found to be $2.19 \pm 0.16 \text{ g cm}^{-3}$. The specific surface area of $64 \pm 3 \text{ m}^2 \text{ g}^{-1}$ was analyzed by BET-N₂ surface adsorption (Carlo Erba Sorptomatic 1900). A total of 0.65% inorganic carbon was found by catalytic combustion (CNS 1118, Carlo Erba). The solid was crystalline, and its diffraction pattern agreed with that for synthetic HAP (International Centre for Diffraction Data card 01-084-1998).

2.S2 Synthesis of FAP

In order to provide a solid standard sample, pure FAP was synthesized in batch at pH 7 by the simultaneous addition of Ca(NO₃)₂, NaHPO₄, NaH₂PO₄, and NaF to 1L nanopure water to achieve total initial concentrations of 5mM, 3mM, and 1mM for Ca, PO₄ and F, respectively. The PO₄ solutions were added at a 1:1 ratio to buffer the system around pH 7. Additionally, pH adjustment was conducted via titration units as described before. After 3d, the solid material was collected on 0.45-μm cellulose-nitrate filters (Sartorius), air-dried, and stored at room temperature for further analysis. The specific surface area determined by BET-N₂ was $34 \pm 2 \text{ m}^2 \text{ g}^{-1}$ and the purity was confirmed by XRD, where the diffraction pattern agreed with that for synthesized FAP (01-071-5051).

2.S3 Fluoride measurement

Fluoride was measured potentiometrically using Metrohm ion-specific (6.0502.150) and Ag/AgCl reference (6.0726.100) electrodes and pH meter (692). Total ionic strength adjusting buffer (TISAB) was prepared as follows: ammonium acetate (77.1g), ammonia chloride (26.8g), and Titriplex IV (4.0g) were dissolved in a 1L flask,

followed by the addition of 96% acetic acid (59 mL) and volume adjustment to 1L. Total solution volume for F^- analysis was 40 mL consisting of 2 mL of TISAB and an adequate dilution of the sample to lie within the seven point calibration range of 0.025 to 1.0 mg L^{-1} . Once stable for 1min, values were recorded. The calibration curve was analyzed according to Gran.⁵¹

2.S4 Cation and anion analysis

Major elements, such as potassium, sodium, and sulphate were analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES; Smart Analyzer SpectroCirosCCD, Version 3.3 Spectro A.I. GmbH). Standard solutions were prepared using CertiPur ICP anion multi element standard I and II (1000 mg L^{-1}) and ICP multi element standard IV (1000 mg L^{-1}). The elements calcium and magnesium were determined by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS; 7500cx, Agilent Technologies) in He-H mode. Internal standards for ICP-MS were 0.2 ppm Indium, 0.2 ppm Lutetium and 2 ppm Scandium. Prior to analysis, the ICP-MS system performance was verified by analysis of diluted Merck X and XX standard solutions. Twelve-point calibration curves were used for ICP-OES and ICP-MS analysis. All samples, including blanks of nanopure water for measurement verification, were acidified with 1% suprapure HNO_3 .

Chloride concentrations were determined by ion chromatography (IC; Dionex ICS-2100, software Chromeleon 7). Standard solutions were prepared from CertiPur ICP anion multi-element standards I and II (1000 mg L^{-1}) in concentration range of 0.1–100 mg L^{-1} ; samples were not acidified prior analysis. The linearized values of the F measurements, as well as the calibration curves of ICP-OES, ICP-MS and IC

measurements were calculated with the analytical program SQS2000 (Lernhardt, Kleiner, Wachter, 2000).

2.S5 DIC

The total dissolved inorganic carbon was analyzed (Shimadzu TOC - V CPH) with a six-point calibration in the range of 0–100 mg C L⁻¹.

2.S6 XRD

Powder X-ray Diffraction (XRD; X'Pert PRO) with Cu K α radiation (45 kV and 40 mA) was used to determine the purity of compacted powdered solids of unreacted HAP and synthesized (unreacted, pure) FAP. The obtained XRD patterns were compared to standards compiled by the International Centre for Diffraction Data (ICDD). The program HighScorePlus 2.2 provided by PANalytical was used for data evaluation.

2.S7 TEM

Approximately 5 mg of each solid was suspended in 15 mL ethanol, sonicated for 5 min with a microtip (*Bandelin Sonoplus MS75*; the amplitude used was 302 μm_{ss} with a pulse level of 25%) and finally diluted 1:20 with ethanol. Each suspension was added to a TEM grid (Cu PK/100, formvar-carbon coated, 200 mesh, SPI, USA) and air dried.

2.S8 FTIR

A small amount of dried and ground material was added onto the diamond internal reflection element (SensIR Technologies). Spectra were recorded at velocity 10 kHz, filter 1.2 kHz, UDR 2, resolution 2, aperture 1 cm⁻¹, and sensitivity 16; the signal was approximately -8.8 counts. A background scan was taken before and after measurements and was subtracted from each sample scan.

2.S9 XPS

A very small amount of powdered material was pressed into an Indium foil. Sputtering was conducted for 240–260 sec using 1keV Ar⁺ rastered over a 2 × 2 mm² area to remove most surface contaminants to a depth of about 5 nm. Sample composition calculated using standard sensitivity factors provided by the instrument manufacturer.

2.S10 NanoSIMS

Approximately 5 mg of the air-dried and ground material (solid obtained after 28d-equilibration at pH 6.5 with 7.0 mM initial F) were sonicated with a microtip (*Bandelin Sonoplus MS75*) in 20 mL ethanol for 6 min (the amplitude used was 302 μm_{ss} with a pulse level of 25%). A drop of this suspension was pipetted onto a 5 × 5 mm Si-wafer (Plano GmbH, Germany) and air-dried.

A Cs⁺ (8 keV, 1.5 pA) primary beam was rastered over a 0.2 × 0.2 μm² area on the sample surface at normal incidence and with a spatial resolution of 50 nm (spot size). The analysis was aborted after 20 ablation planes, because the ¹²C¹⁴N turned off. The ¹²C¹⁴N cluster allowed estimation of potential contaminations from exposure to atmosphere (CO₂, N₂) within the matrix. A depth profile was calculated from 3-dimensional images.

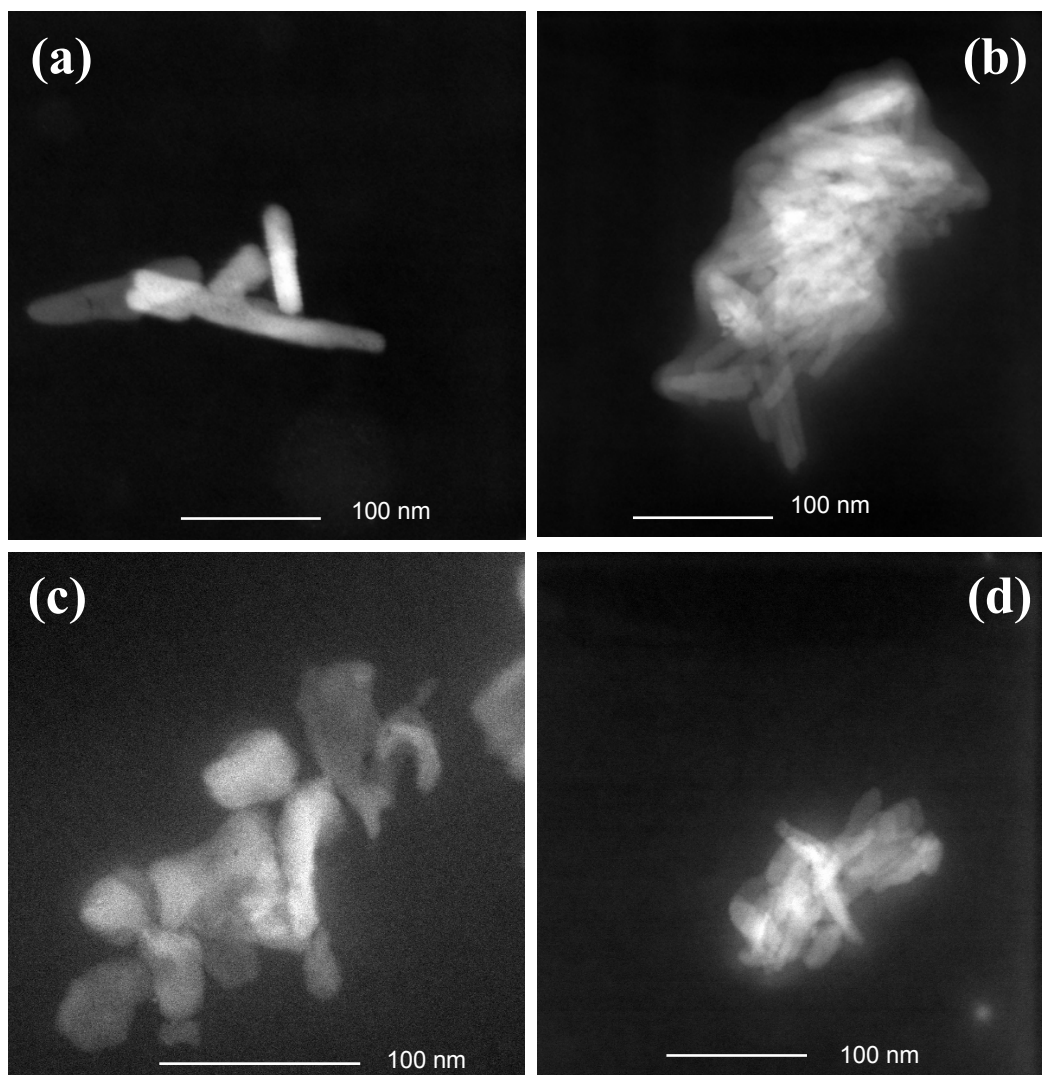
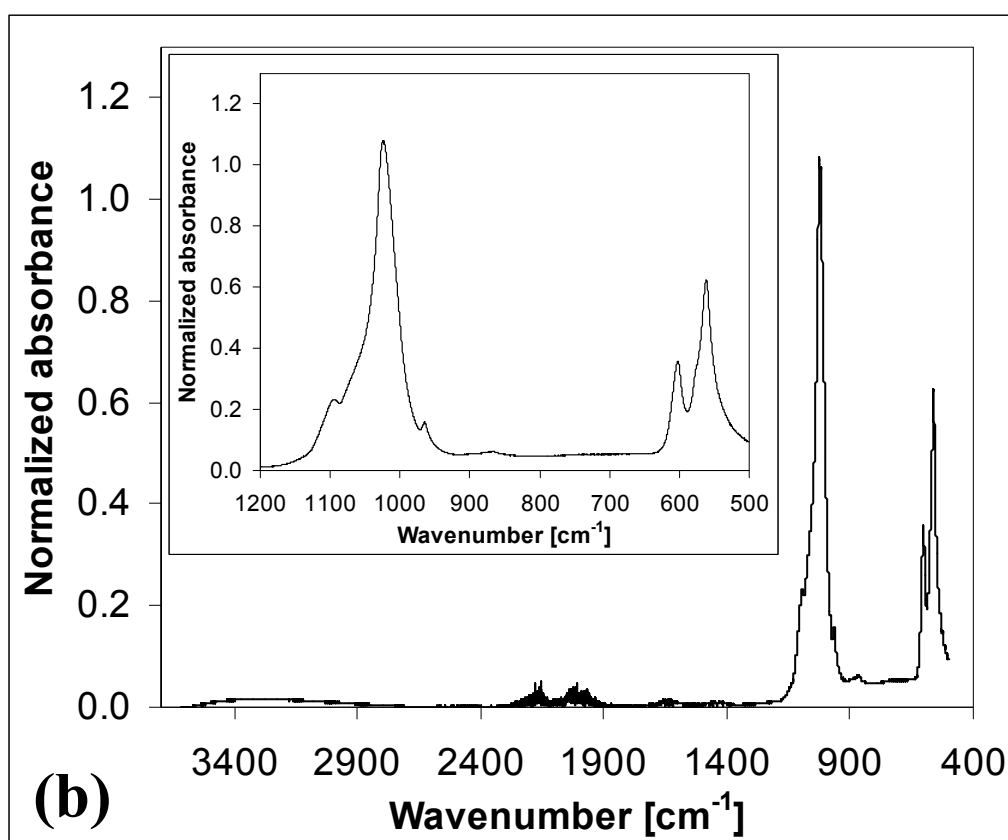
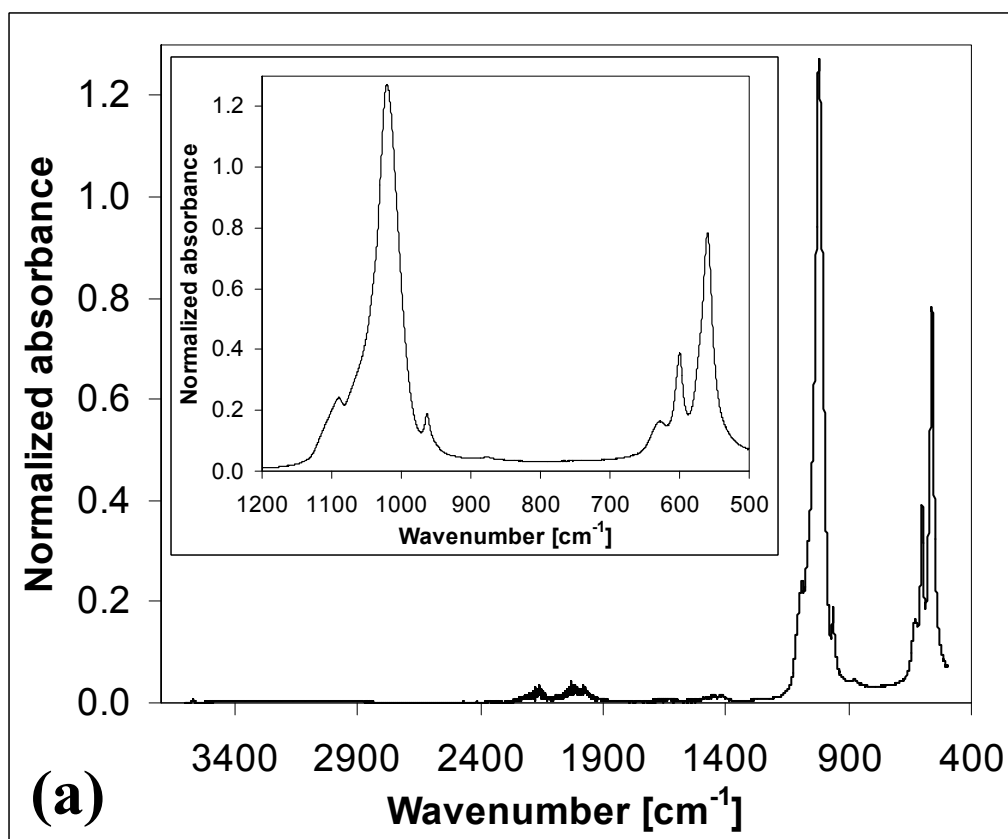
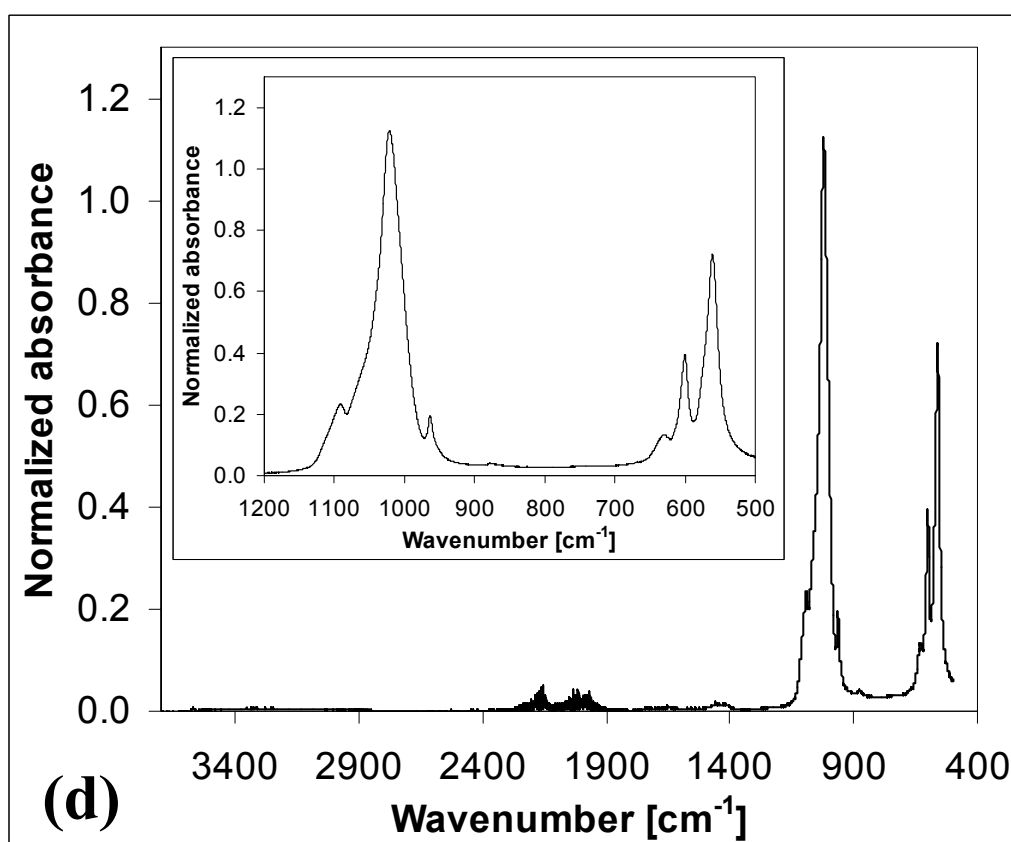
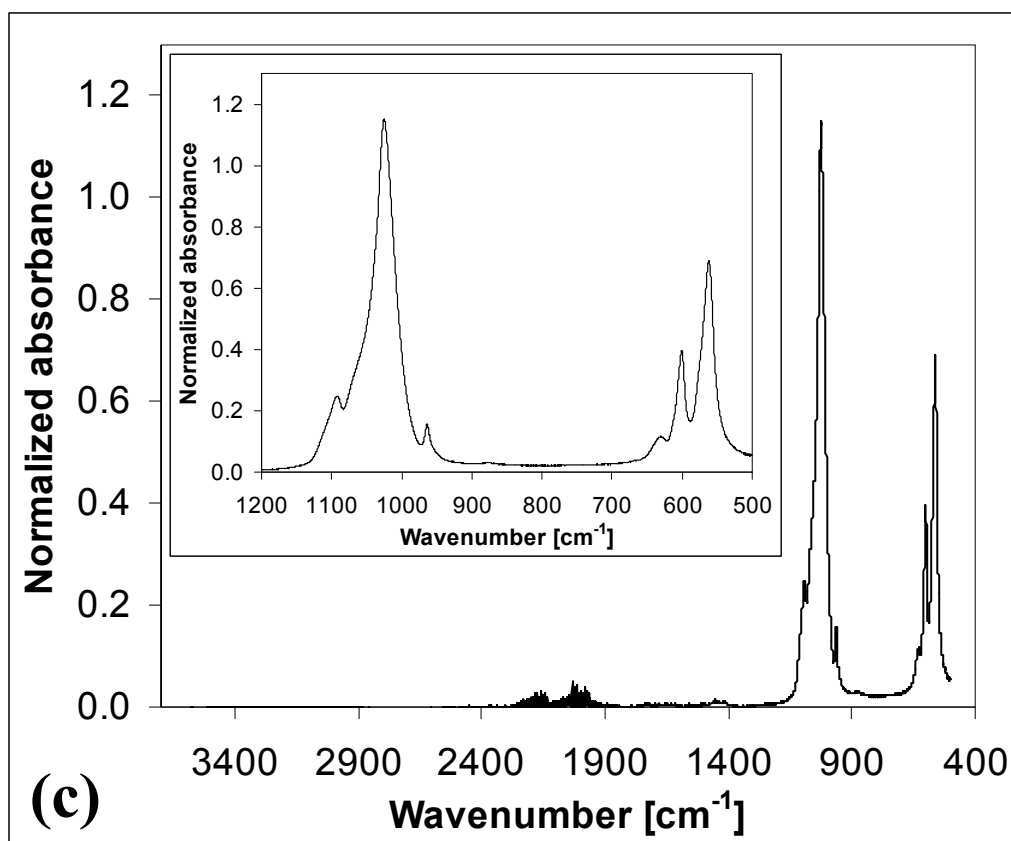


Figure 2S1 TEM images of pure unreacted HAP (a), pure unreacted FAP (b), and of the reacted material obtained after 28d-equilibration at pH 6.5 with 7.0 mM initial F (c), and at pH 9.5 with 2.5 mM initial F (d). The Ca/P atomic ratios obtained by EDX analysis were as follows: a) 1.60 ± 0.08 ; b) 1.70 ± 0.22 ; c) 1.32 ± 0.36 ; and d) 1.61 ± 0.08 .





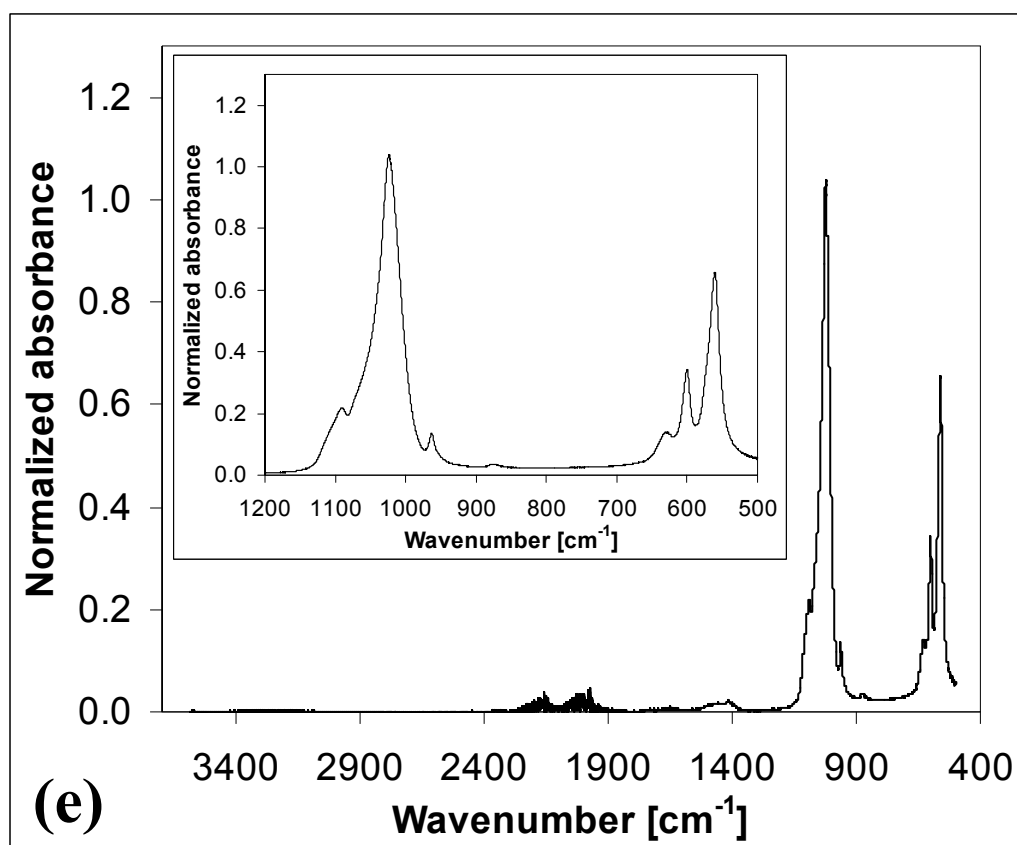


Figure 2S2 Full FTIR spectra showing the similarity of pure unreacted HAP (a), pure unreacted FAP (b), pH 6.5 with 3.3 mM initial F (c), pH 7.3 with 3.3 mM initial F (d), and pH 9.5 with 2.5 mM initial F (e), each normalized to the baseline. Apatite characteristic absorbance bands for the P—O stretching appeared at 1090, 1025, and 963 cm^{-1} and bending modes were detected at 600 and 561 cm^{-1} .⁴⁶ Carbonate assigned modes were detected at 670, 879, and 1450 cm^{-1} , which are assigned to OH substitution,^{52, 53} whereas the peaks assigned to the same substitution at 1545 and 757 cm^{-1} did not appear. In comparison, only one mode that is assigned to a phosphate substitution at 1415 cm^{-1} was detected, while to this mode related peaks at 1465, 873 cm^{-1} were not noticeable. Solids obtained from batches for bicarbonate influence did not show increased intensities of any carbonate attributed peak (data not shown).

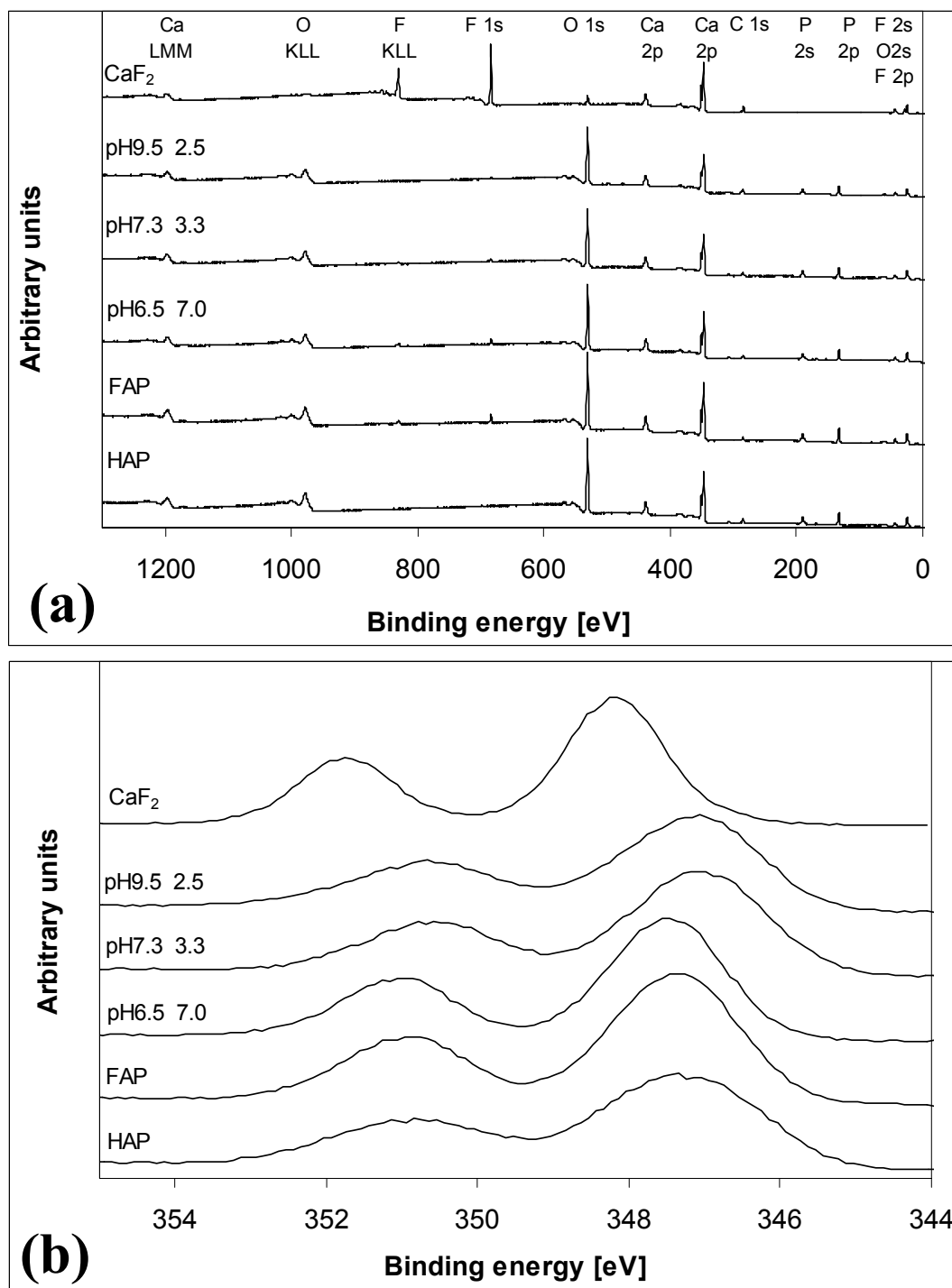


Figure 2S3 XPS survey spectra of untreated surface (bottom to top) of pure unreacted HAP, pure unreacted FAP, from samples obtained at pH 6.5, 7.3 and 9.5 with 7.0, 3.3 and 2.5 mM initial F, respectively, and of CaF_2 . (b) Normalized Ca(2p) intensities of untreated surfaces of the same samples listed in (a).

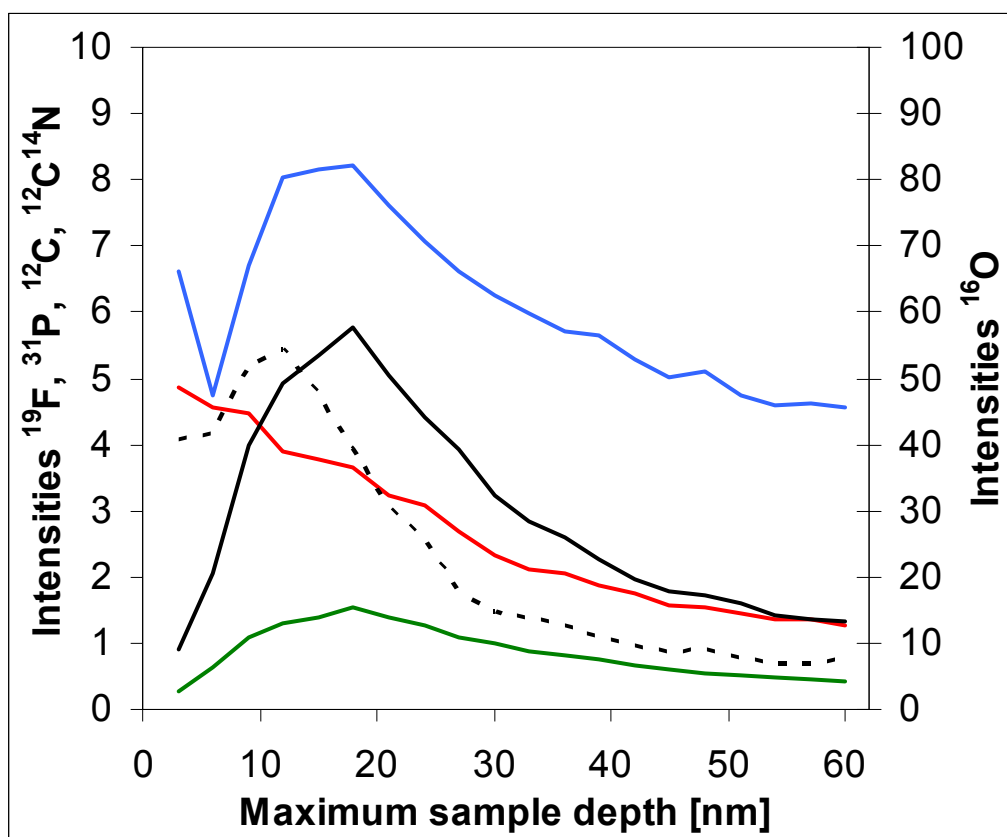


Figure 2S4 NanoSIMS raw intensities of $^{19}\text{F}^-$ (red), $^{31}\text{P}^-$ (green), $^{16}\text{O}^-$ (blue), ^{12}C (black solid line), $^{12}\text{C}^{14}\text{N}$ (black dotted line) as function of maximum sample depth.

Table 2S1 Total dissolved Ca, PO₄ and F concentrations, pH and added acid and base as function of sampling times for all conducted F uptake experiments at pH 6.5, 7.3 and 9.5

| pH 6.5 - 2 mM F initial | | | | | | | |
|-------------------------|--------------|-----------------|-----------------------------|------------------------|-------------------------|--------------------------------------|--|
| time hrs | pH | 0.1M NaOH mL | 0.1M HNO ₃ mL | F _{tot} mM | Ca _{tot} mM | PO ₄ _{tot} mM | |
| | | | | 1.97 ± 0.05 | | | |
| | | | | | 0.67 ± 0.53 | 0.37 ± 0.29 | |
| 0.00 ± 0.00 | 6.81 ± 0.27 | 0.00 ± 0.00 | 0.37 ± 0.53 | 1.50 ± 0.02 | 0.14 ± 0.03 | 0.18 ± 0.02 | |
| 0.02 ± 0.00 | 6.47 ± 0.03 | 0.00 ± 0.00 | 0.31 ± 0.43 | 1.37 ± 0.12 | 0.16 ± 0.08 | 0.20 ± 0.04 | |
| 0.04 ± 0.01 | 6.46 ± 0.03 | 0.10 ± 0.13 | 0.29 ± 0.40 | 1.43 ± 0.02 | 0.12 ± 0.04 | 0.18 ± 0.03 | |
| 0.08 ± 0.00 | 6.47 ± 0.01 | 0.38 ± 0.54 | 0.30 ± 0.42 | 1.43 ± 0.00 | 0.10 ± 0.03 | 0.17 ± 0.02 | |
| 0.17 ± 0.00 | 6.46 ± 0.004 | 0.38 ± 0.54 | 0.30 ± 0.41 | 1.42 ± 0.01 | 0.08 ± 0.01 | 0.16 ± 0.01 | |
| 0.25 ± 0.00 | 6.46 ± 0.01 | 0.43 ± 0.61 | 0.30 ± 0.42 | 1.36 ± 0.05 | 0.08 ± 0.02 | 0.16 ± 0.01 | |
| 0.50 ± 0.00 | 6.47 ± 0.01 | 0.43 ± 0.61 | 0.30 ± 0.42 | 1.33 ± 0.06 | 0.08 ± 0.03 | 0.16 ± 0.02 | |
| 1.02 ± 0.02 | 6.49 ± 0.01 | 0.43 ± 0.61 | 0.32 ± 0.44 | 1.28 ± 0.09 | 0.11 ± 0.09 | 0.18 ± 0.05 | |
| 2.00 ± 0.00 | 6.51 ± 0.03 | 0.43 ± 0.61 | 0.42 ± 0.34 | 1.26 ± 0.10 | 0.54 ± 0.71 | 0.43 ± 0.40 | |
| 4.00 ± 0.00 | 6.50 ± 0.03 | 0.43 ± 0.61 | 0.55 ± 0.15 | 1.27 ± 0.04 | 0.14 ± 0.13 | 0.20 ± 0.08 | |
| 8.01 ± 0.01 | 6.51 ± 0.02 | 0.43 ± 0.61 | 1.01 ± 0.25 | 1.24 ± 0.01 | 0.05 ± 0.01 | 0.15 ± 0.01 | |
| 11.03 ± 0.05 | 6.51 ± 0.02 | 0.43 ± 0.61 | 1.20 ± 0.27 | 1.26 ± 0.05 | 0.05 ± 0.002 | 0.15 ± 0.003 | |
| 24.03 ± 0.04 | 6.51 ± 0.01 | 0.43 ± 0.61 | 1.75 ± 0.17 | 1.18 ± 0.03 | 0.35 ± 0.44 | 0.33 ± 0.25 | |
| 47.95 ± 0.09 | 6.51 ± 0.03 | 0.43 ± 0.61 | 2.45 ± 0.17 | 1.09 ± 0.01 | 0.05 ± 0.01 | 0.16 ± 0.01 | |
| 96.36 ± 0.91 | 6.51 ± 0.02 | 0.43 ± 0.61 | 3.24 ± 0.07 | 0.99 ± 0.06 | 0.04 ± 0.002 | 0.15 ± 0.001 | |
| 167.97 ± 0.35 | 6.51 ± 0.03 | 0.43 ± 0.61 | 4.25 ± 0.05 | 0.90 ± 0.06 | 0.04 ± 0.01 | 0.16 ± 0.003 | |
| 263.88 ± 0.18 | 6.49 ± 0.05 | 0.43 ± 0.61 | 5.22 ± 0.20 | 0.80 ± 0.05 | 0.05 ± 0.001 | 0.16 ± 0.001 | |
| 336.39 ± 0.91 | 6.50 ± 0.01 | 0.43 ± 0.61 | 5.63 ± 0.18 | 0.74 ± 0.08 | 0.05 ± 0.01 | 0.16 ± 0.001 | |
| 432.13 ± 0.53 | 6.49 ± 0.01 | 0.76 ± 1.08 | 6.43 ± 0.25 | 0.70 ± 0.06 | 0.05 ± 0.0004 | 0.16 ± 0.004 | |
| 515.92 ± 17.09 | 6.49 ± 0.005 | 0.76 ± 1.08 | 7.09 ± 0.39 | 0.67 ± 0.11 | 0.06 ± 0.003 | 0.16 ± 0.004 | |
| 599.96 ± 0.29 | 6.50 ± 0.04 | 1.87 ± 0.48 | 7.57 ± 0.08 | 0.62 ± 0.09 | 0.05 ± 0.01 | 0.16 ± 0.0001 | |
| 683.92 ± 17.09 | 6.48 ± 0.02 | 2.20 ± 0.01 | 8.01 ± 0.11 | 0.57 ± 0.10 | 0.10 ± 0.03 | 0.17 ± 0.03 | |

| pH 6.5 - 3.3 mM F initial | | | | | | | | | | | | |
|---------------------------|--------------|-----------------|-----------------------------|------------------------|---------------|------|-------------------------|--------------|--|--------------------------------------|--|--|
| time hrs | pH | 0.1M NaOH mL | 0.1M HNO ₃ mL | F _{tot} mM | | | Ca _{tot} mM | | | PO ₄ _{tot} mM | | |
| | | | | 3.30 | ± | 0.01 | | | | | | |
| | | | | | | | 0.13 ± 0.01 | | | 0.21 ± 0.06 | | |
| 0.00 ± 0.00 | 6.99 ± 0.37 | 0.00 ± 0.00 | 0.08 ± 0.11 | 2.84 ± 0.16 | 0.21 ± 0.25 | | | 0.21 ± 0.03 | | | | |
| 0.02 ± 0.01 | 6.46 ± 0.00 | 0.00 ± 0.00 | 0.83 ± 0.25 | 2.41 ± 0.72 | 0.17 ± 0.05 | | | 0.23 ± 0.07 | | | | |
| 0.03 ± 0.00 | 6.75 ± 0.13 | 1.61 ± 2.28 | 0.67 ± 0.89 | 2.57 ± 0.17 | 0.10 ± 0.12 | | | 0.20 ± 0.05 | | | | |
| 0.05 ± 0.02 | 6.62 ± 0.00 | 0.00 ± 0.00 | 0.07 ± 0.02 | 2.69 ± 0.81 | 0.01 ± 0.003 | | | 0.17 ± 0.05 | | | | |
| 0.08 ± 0.00 | 6.60 ± 0.005 | 1.61 ± 2.28 | 1.52 ± 1.96 | 2.61 ± 0.11 | 0.03 ± 0.02 | | | 0.19 ± 0.03 | | | | |
| 0.17 ± 0.00 | 6.51 ± 0.06 | 1.61 ± 2.28 | 1.74 ± 2.07 | 2.54 ± 0.003 | 0.08 ± 0.02 | | | 0.20 ± 0.01 | | | | |
| 0.25 ± 0.00 | 6.54 ± 0.01 | 1.97 ± 2.79 | 1.95 ± 2.18 | 2.56 ± 0.01 | 0.08 ± 0.04 | | | 0.20 ± 0.001 | | | | |
| 0.50 ± 0.00 | 6.51 ± 0.02 | 1.97 ± 2.79 | 2.04 ± 2.05 | 2.59 ± 0.12 | 0.08 ± 0.01 | | | 0.19 ± 0.01 | | | | |
| 1.02 ± 0.02 | 6.52 ± 0.03 | 1.97 ± 2.79 | 2.12 ± 1.94 | 2.53 ± 0.01 | 0.07 ± 0.004 | | | 0.19 ± 0.002 | | | | |
| 2.03 ± 0.05 | 6.51 ± 0.03 | 1.97 ± 2.79 | 2.28 ± 1.86 | 2.38 ± 0.01 | 0.03 ± 0.03 | | | 0.22 ± 0.06 | | | | |
| 4.00 ± 0.00 | 6.52 ± 0.03 | 1.97 ± 2.79 | 2.43 ± 1.65 | 2.42 ± 0.00 | 0.07 ± 0.02 | | | 0.19 ± 0.01 | | | | |
| 8.00 ± 0.00 | 6.51 ± 0.03 | 1.97 ± 2.79 | 2.68 ± 1.59 | 2.35 ± 0.07 | 0.04 ± 0.03 | | | 0.19 ± 0.001 | | | | |
| 11.08 ± 0.11 | 6.51 ± 0.03 | 1.97 ± 2.79 | 2.89 ± 1.44 | 2.30 ± 0.07 | 0.03 ± 0.003 | | | 0.21 ± 0.03 | | | | |
| 24.02 ± 0.02 | 6.51 ± 0.03 | 1.97 ± 2.79 | 3.37 ± 1.48 | 2.26 ± 0.09 | 0.05 ± 0.0004 | | | 0.18 ± 0.004 | | | | |
| 48.09 ± 0.06 | 6.51 ± 0.03 | 1.97 ± 2.79 | 4.15 ± 1.62 | 2.12 ± 0.05 | 0.05 ± 0.01 | | | 0.20 ± 0.02 | | | | |
| 84.00 ± 16.97 | 6.51 ± 0.02 | 1.97 ± 2.79 | 4.95 ± 1.99 | 2.06 ± 0.02 | 0.04 ± 0.01 | | | 0.21 ± 0.03 | | | | |
| 168.00 ± 0.00 | 6.51 ± 0.02 | 1.97 ± 2.79 | 6.27 ± 1.99 | 1.97 ± 0.11 | 0.04 ± 0.004 | | | 0.22 ± 0.04 | | | | |
| 252.22 ± 16.78 | 6.51 ± 0.04 | 1.97 ± 2.79 | 6.83 ± 1.86 | 1.89 ± 0.10 | 0.03 ± 0.03 | | | 0.20 ± 0.01 | | | | |
| 336.00 ± 0.00 | 6.50 ± 0.03 | 1.97 ± 2.79 | 7.38 ± 1.74 | 1.87 ± 0.06 | 0.18 ± 0.17 | | | 0.24 ± 0.08 | | | | |
| 420.04 ± 17.03 | 6.49 ± 0.00 | 2.25 ± 3.18 | 8.19 ± 1.85 | 1.81 ± 0.03 | 0.02 ± 0.01 | | | 0.19 ± 0.003 | | | | |
| 504.04 ± 0.06 | 6.50 ± 0.02 | 2.30 ± 3.25 | 8.75 ± 1.98 | 1.70 ± 0.02 | 0.02 ± 0.01 | | | 0.18 ± 0.002 | | | | |
| 588.03 ± 16.97 | 6.49 ± 0.02 | 4.47 ± 6.32 | 11.26 ± 4.97 | 1.65 ± 0.09 | 0.02 ± 0.001 | | | 0.19 ± 0.01 | | | | |
| 672.00 ± 0.00 | 6.50 ± 0.02 | 5.94 ± 8.41 | 13.13 ± 7.16 | 1.64 ± 0.02 | 0.02 ± 0.01 | | | 0.19 ± 0.005 | | | | |

| pH 6.5 - 7.0 mM F initial | | | | | | | | | | | | |
|---------------------------|-------------|-----------------|-----------------------------|------------------------|----------------|--|-------------------------|---------------|--|--------------------------------------|--|--|
| time hrs | pH | 0.1M NaOH mL | 0.1M HNO ₃ mL | F _{tot} mM | | | Ca _{tot} mM | | | PO ₄ _{tot} mM | | |
| | | | | 6.90 ± 0.36 | | | 0.34 ± 0.005 | | | 0.20 ± 0.01 | | |
| | | | | | | | | | | | | |
| 0.00 ± 0.00 | 6.62 ± 0.17 | 0.00 ± 0.00 | 0.00 ± 0.00 | 6.06 ± 0.12 | 0.08 ± 0.001 | | | 0.21 ± 0.004 | | | | |
| 0.02 ± 0.00 | 6.66 ± 0.13 | 0.00 ± 0.00 | 0.20 ± 0.18 | 5.93 ± 0.25 | 0.07 ± 0.01 | | | 0.21 ± 0.003 | | | | |
| 0.03 ± 0.00 | 6.57 ± 0.10 | 0.00 ± 0.00 | 0.30 ± 0.27 | 5.83 ± 0.23 | 0.06 ± 0.01 | | | 0.21 ± 0.003 | | | | |
| 0.08 ± 0.00 | 6.54 ± 0.06 | 0.00 ± 0.00 | 0.35 ± 0.20 | 5.89 ± 0.26 | 0.05 ± 0.003 | | | 0.21 ± 0.0004 | | | | |
| 0.19 ± 0.04 | 6.53 ± 0.02 | 0.00 ± 0.00 | 0.42 ± 0.10 | 5.93 ± 0.44 | 0.08 ± 0.05 | | | 0.23 ± 0.03 | | | | |
| 0.27 ± 0.02 | 6.53 ± 0.00 | 0.00 ± 0.00 | 0.48 ± 0.01 | 5.81 ± 0.14 | 0.04 ± 0.001 | | | 0.20 ± 0.01 | | | | |
| 0.50 ± 0.00 | 6.52 ± 0.03 | 0.00 ± 0.00 | 0.60 ± 0.06 | 5.94 ± 0.33 | 0.04 ± 0.00001 | | | 0.21 ± 0.01 | | | | |
| 1.00 ± 0.00 | 6.51 ± 0.04 | 0.00 ± 0.00 | 0.75 ± 0.07 | 5.76 ± 0.22 | 0.04 ± 0.003 | | | 0.21 ± 0.01 | | | | |
| 2.00 ± 0.00 | 6.52 ± 0.03 | 0.00 ± 0.00 | 0.92 ± 0.06 | 5.79 ± 0.04 | 0.03 ± 0.003 | | | 0.20 ± 0.001 | | | | |
| 4.03 ± 0.04 | 6.51 ± 0.03 | 0.00 ± 0.00 | 1.15 ± 0.09 | 5.72 ± 0.34 | 0.04 ± 0.02 | | | 0.22 ± 0.02 | | | | |
| 8.08 ± 0.11 | 6.51 ± 0.03 | 0.00 ± 0.00 | 1.46 ± 0.15 | 5.53 ± 0.19 | 0.07 ± 0.06 | | | 0.23 ± 0.03 | | | | |
| 17.67 ± 9.43 | 6.52 ± 0.03 | 0.00 ± 0.00 | 2.12 ± 0.57 | 5.61 ± 0.21 | 0.04 ± 0.02 | | | 0.23 ± 0.03 | | | | |
| 36.56 ± 17.71 | 6.50 ± 0.02 | 0.00 ± 0.00 | 2.84 ± 0.62 | 5.54 ± 0.13 | 0.05 ± 0.04 | | | 0.25 ± 0.05 | | | | |
| 60.33 ± 16.92 | 6.51 ± 0.03 | 0.00 ± 0.00 | 3.39 ± 0.17 | 5.54 ± 0.17 | 0.02 ± 0.0002 | | | 0.23 ± 0.01 | | | | |
| 83.87 ± 16.92 | 6.51 ± 0.04 | 0.00 ± 0.00 | 3.86 ± 0.16 | 5.47 ± 0.24 | 0.02 ± 0.003 | | | 0.23 ± 0.01 | | | | |
| 167.96 ± 0.06 | 6.51 ± 0.03 | 0.00 ± 0.00 | 4.68 ± 0.16 | 5.34 ± 0.31 | 0.02 ± 0.002 | | | 0.23 ± 0.01 | | | | |
| 252.21 ± 17.27 | 6.50 ± 0.00 | 0.00 ± 0.00 | 5.46 ± 0.31 | 5.32 ± 0.30 | 0.02 ± 0.001 | | | 0.23 ± 0.01 | | | | |
| 336.02 ± 0.02 | 6.51 ± 0.03 | 0.00 ± 0.00 | 6.03 ± 0.13 | 5.14 ± 0.18 | 0.04 ± 0.03 | | | 0.26 ± 0.04 | | | | |
| 420.00 ± 16.97 | 6.51 ± 0.05 | 0.52 ± 0.74 | 6.94 ± 0.79 | 5.28 ± 0.32 | 0.02 ± 0.001 | | | 0.24 ± 0.01 | | | | |
| 504.00 ± 0.00 | 6.51 ± 0.04 | 0.90 ± 1.27 | 7.64 ± 1.15 | 5.18 ± 0.13 | 0.02 ± 0.002 | | | 0.24 ± 0.01 | | | | |
| 588.00 ± 16.97 | 6.51 ± 0.03 | 0.90 ± 1.27 | 8.02 ± 1.36 | 5.10 ± 0.27 | 0.02 ± 0.004 | | | 0.24 ± 0.01 | | | | |
| 672.01 ± 0.01 | 6.49 ± 0.06 | 0.90 ± 1.27 | 8.40 ± 1.14 | 5.00 ± 0.29 | 0.04 ± 0.03 | | | 0.25 ± 0.04 | | | | |

| pH 7.3 - 0.5 mM F initial | | | | | | | | | | | | |
|---------------------------|--------------|-----------------|-----------------------------|------------------------|---------------|---------------|-------------------------|--|--|--------------------------------------|--|--|
| time hrs | pH | 0.1M NaOH mL | 0.1M HNO ₃ mL | F _{tot} mM | | | Ca _{tot} mM | | | PO ₄ _{tot} mM | | |
| | | | | 0.43 | ± | 0.03 | 0.00 ± 0.00 | | | | | |
| | | | | | | | | | | | | |
| 0.00 ± 0.00 | 7.32 ± 0.03 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.32 ± 0.06 | 0.15 ± 0.11 | 0.13 ± 0.04 | | | | | | |
| 0.02 ± 0.00 | 7.34 ± 0.01 | 0.00 ± 0.00 | 0.17 ± 0.15 | 0.30 ± 0.06 | 0.09 ± 0.10 | 0.11 ± 0.07 | | | | | | |
| 0.03 ± 0.00 | 7.36 ± 0.01 | 0.00 ± 0.00 | 0.35 ± 0.43 | 0.29 ± 0.05 | 0.09 ± 0.11 | 0.11 ± 0.08 | | | | | | |
| 0.08 ± 0.00 | 7.38 ± 0.05 | 0.00 ± 0.00 | 1.36 ± 0.59 | 0.29 ± 0.05 | 0.02 ± 0.01 | 0.07 ± 0.02 | | | | | | |
| 0.17 ± 0.00 | 7.39 ± 0.07 | 0.00 ± 0.00 | 3.30 ± 0.59 | 0.28 ± 0.05 | 0.02 ± 0.0002 | 0.07 ± 0.01 | | | | | | |
| 0.25 ± 0.00 | 7.36 ± 0.05 | 0.00 ± 0.00 | 4.56 ± 0.04 | 0.28 ± 0.06 | 0.02 ± 0.004 | 0.08 ± 0.01 | | | | | | |
| 0.50 ± 0.00 | 7.34 ± 0.004 | 0.00 ± 0.00 | 5.92 ± 0.98 | 0.26 ± 0.06 | 0.06 ± 0.05 | 0.10 ± 0.04 | | | | | | |
| 1.00 ± 0.00 | 7.32 ± 0.001 | 0.00 ± 0.00 | 6.48 ± 1.04 | 0.24 ± 0.06 | 0.10 ± 0.09 | 0.12 ± 0.04 | | | | | | |
| 2.00 ± 0.00 | 7.30 ± 0.01 | 0.00 ± 0.00 | 6.48 ± 1.04 | 0.22 ± 0.06 | 0.11 ± 0.12 | 0.13 ± 0.08 | | | | | | |
| 4.00 ± 0.00 | 7.30 ± 0.03 | 0.00 ± 0.00 | 6.48 ± 1.04 | 0.20 ± 0.06 | 0.11 ± 0.13 | 0.14 ± 0.09 | | | | | | |
| 8.04 ± 0.06 | 7.33 ± 0.02 | 0.00 ± 0.00 | 6.78 ± 1.46 | 0.19 ± 0.05 | 0.02 ± 0.0001 | 0.08 ± 0.01 | | | | | | |
| 11.00 ± 0.00 | 7.28 ± 0.01 | 0.00 ± 0.00 | 7.05 ± 1.84 | 0.18 ± 0.05 | 0.02 ± 0.003 | 0.08 ± 0.01 | | | | | | |
| 24.00 ± 0.00 | 7.28 ± 0.004 | 7.50 ± 3.54 | 9.17 ± 1.17 | 0.14 ± 0.04 | 0.02 ± 0.01 | 0.09 ± 0.01 | | | | | | |
| 48.00 ± 0.00 | 7.32 ± 0.01 | 10.00 ± 7.07 | 12.17 ± 3.59 | 0.12 ± 0.03 | 0.02 ± 0.001 | 0.09 ± 0.0004 | | | | | | |
| 96.00 ± 0.00 | 7.31 ± 0.001 | 29.00 ± 26.87 | 21.54 ± 1.30 | 0.10 ± 0.03 | 0.02 ± 0.01 | 0.09 ± 0.003 | | | | | | |
| 168.00 ± 0.00 | 7.33 ± 0.003 | 37.60 ± 28.85 | 34.50 ± 4.18 | 0.07 ± 0.02 | 0.03 ± 0.003 | 0.09 ± 0.01 | | | | | | |
| 264.02 ± 0.00 | 7.31 ± 0.03 | 50.74 ± 31.48 | 39.84 ± 6.92 | 0.05 ± 0.02 | 0.03 ± 0.001 | 0.09 ± 0.001 | | | | | | |
| 336.00 ± 0.00 | 7.31 ± 0.01 | 59.51 ± 32.36 | 47.71 ± 7.39 | 0.04 ± 0.01 | 0.03 ± 0.0004 | 0.09 ± 0.002 | | | | | | |
| 432.08 ± 0.12 | 7.31 ± 0.01 | 70.93 ± 36.30 | 54.09 ± 4.37 | 0.04 ± 0.01 | 0.07 ± 0.07 | 0.12 ± 0.03 | | | | | | |
| 504.00 ± 0.00 | 7.29 ± 0.02 | 77.16 ± 33.17 | 62.63 ± 2.43 | 0.03 ± 0.01 | 0.03 ± 0.01 | 0.09 ± 0.003 | | | | | | |
| 600.02 ± 0.02 | 7.31 ± 0.01 | 90.23 ± 25.13 | 75.93 ± 16.39 | 0.03 ± 0.01 | 0.04 ± 0.01 | 0.10 ± 0.01 | | | | | | |
| 672.00 ± 0.00 | 7.32 ± 0.02 | 101.85 ± 29.92 | 84.77 ± 15.50 | 0.02 ± 0.01 | 0.05 ± 0.02 | 0.10 ± 0.01 | | | | | | |

| pH 7.3 - 0.9 mM F initial | | | | | | | | | |
|---------------------------|--------------|-----------------|-----------------------------|------------------------|---------------|----------------|-------------------------|--|--|
| time hrs | pH | 0.1M NaOH mL | 0.1M HNO ₃ mL | F _{tot} mM | | | Ca _{tot} mM | | |
| | | | | 0.89 ± 0.04 | | | | | |
| | | | | | | | 0.04 ± 0.05 | | |
| 0.00 ± 0.00 | 7.50 ± 0.02 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.70 ± 0.01 | 0.02 ± 0.01 | 0.07 ± 0.04 | | | |
| 0.02 ± 0.00 | 7.43 ± 0.04 | 0.00 ± 0.00 | 0.31 ± 0.38 | 0.69 ± 0.03 | 0.02 ± 0.01 | 0.07 ± 0.04 | | | |
| 0.03 ± 0.00 | 7.41 ± 0.12 | 0.17 ± 0.23 | 0.44 ± 0.49 | 0.69 ± 0.07 | 0.07 ± 0.03 | 0.11 ± 0.02 | | | |
| 0.09 ± 0.01 | 7.42 ± 0.13 | 0.17 ± 0.23 | 0.51 ± 0.40 | 0.68 ± 0.06 | 0.03 ± 0.01 | 0.09 ± 0.03 | | | |
| 0.17 ± 0.00 | 7.39 ± 0.13 | 0.17 ± 0.23 | 0.65 ± 0.27 | 0.66 ± 0.05 | 0.02 ± 0.01 | 0.08 ± 0.04 | | | |
| 0.28 ± 0.04 | 7.39 ± 0.10 | 0.17 ± 0.23 | 0.77 ± 0.14 | 0.66 ± 0.08 | 0.02 ± 0.01 | 0.08 ± 0.03 | | | |
| 0.50 ± 0.00 | 7.37 ± 0.03 | 0.17 ± 0.23 | 1.06 ± 0.17 | 0.64 ± 0.08 | 0.09 ± 0.11 | 0.12 ± 0.09 | | | |
| 1.00 ± 0.00 | 7.31 ± 0.02 | 0.18 ± 0.25 | 1.33 ± 0.55 | 0.62 ± 0.09 | 0.08 ± 0.09 | 0.12 ± 0.08 | | | |
| 2.02 ± 0.02 | 7.29 ± 0.02 | 0.18 ± 0.25 | 1.36 ± 0.51 | 0.61 ± 0.08 | 0.02 ± 0.00 | 0.09 ± 0.03 | | | |
| 4.00 ± 0.00 | 7.28 ± 0.005 | 3.15 ± 4.45 | 4.36 ± 3.73 | 0.58 ± 0.08 | 0.02 ± 0.02 | 0.10 ± 0.03 | | | |
| 8.02 ± 0.02 | 7.28 ± 0.04 | 3.87 ± 5.47 | 5.01 ± 4.65 | 0.56 ± 0.08 | 0.06 ± 0.04 | 0.12 ± 0.01 | | | |
| 11.01 ± 0.01 | 7.30 ± 0.05 | 4.24 ± 6.00 | 5.16 ± 4.86 | 0.53 ± 0.05 | 0.14 ± 0.09 | 0.18 ± 0.03 | | | |
| 24.00 ± 0.00 | 7.33 ± 0.04 | 4.24 ± 6.00 | 5.24 ± 4.94 | 0.48 ± 0.03 | 0.04 ± 0.03 | 0.12 ± 0.03 | | | |
| 47.98 ± 0.02 | 7.31 ± 0.01 | 4.25 ± 6.01 | 5.42 ± 5.14 | 0.44 ± 0.02 | 0.08 ± 0.05 | 0.15 ± 0.02 | | | |
| 84.02 ± 16.95 | 7.29 ± 0.07 | 4.25 ± 6.01 | 8.31 ± 1.31 | 0.40 ± 0.01 | 0.01 ± 0.0001 | 0.11 ± 0.001 | | | |
| 168.00 ± 0.00 | 7.29 ± 0.01 | 7.28 ± 10.29 | 17.39 ± 0.96 | 0.40 ± 0.06 | 0.02 ± 0.01 | 0.12 ± 0.003 | | | |
| 252.00 ± 16.97 | 7.28 ± 0.03 | 7.44 ± 10.51 | 19.22 ± 3.19 | 0.29 ± 0.01 | 0.01 ± 0.001 | 0.11 ± 0.00005 | | | |
| 335.98 ± 0.02 | 7.36 ± 0.08 | 7.44 ± 10.51 | 20.62 ± 4.82 | 0.27 ± 0.002 | 0.01 ± 0.001 | 0.11 ± 0.003 | | | |
| 420.15 ± 16.76 | 7.21 ± 0.13 | 8.12 ± 11.48 | 24.30 ± 7.98 | 0.24 ± 0.01 | 0.01 ± 0.003 | 0.12 ± 0.004 | | | |
| 504.03 ± 0.04 | 7.21 ± 0.07 | 8.12 ± 11.48 | 25.51 ± 8.76 | 0.22 ± 0.003 | 0.01 ± 0.0005 | 0.11 ± 0.001 | | | |
| 587.96 ± 16.91 | 7.28 ± 0.10 | 12.94 ± 9.81 | 26.95 ± 6.76 | 0.20 ± 0.01 | 0.02 ± 0.01 | 0.12 ± 0.004 | | | |
| 671.97 ± 0.07 | 7.34 ± 0.06 | 18.19 ± 2.39 | 29.78 ± 10.49 | 0.19 ± 0.01 | 0.01 ± 0.002 | 0.11 ± 0.0001 | | | |

| pH 7.3 - 2.0 mM F initial | | | | | | | | | |
|---------------------------|--------------|-----------------|-----------------------------|------------------------|--------------|--------------|-------------------------|--|--|
| time hrs | pH | 0.1M NaOH mL | 0.1M HNO ₃ mL | F _{tot} mM | | | Ca _{tot} mM | | |
| | | | | 2.08 ± 0.08 | | | | | |
| | | | | | | | 0.06 ± 0.02 | | |
| 0.00 ± 0.00 | 7.55 ± 0.17 | 0.00 ± 0.00 | 0.00 ± 0.00 | 1.80 ± 0.11 | 0.02 ± 0.01 | 0.09 ± 0.04 | | | |
| 0.02 ± 0.00 | 7.55 ± 0.07 | 0.00 ± 0.00 | 0.26 ± 0.28 | 1.79 ± 0.08 | 0.01 ± 0.003 | 0.10 ± 0.03 | | | |
| 0.03 ± 0.00 | 7.47 ± 0.21 | 0.00 ± 0.00 | 0.63 ± 0.68 | 1.75 ± 0.14 | 0.03 ± 0.01 | 0.11 ± 0.04 | | | |
| 0.08 ± 0.00 | 7.57 ± 0.38 | 0.22 ± 0.30 | 0.93 ± 0.54 | 1.72 ± 0.12 | 0.02 ± 0.01 | 0.11 ± 0.03 | | | |
| 0.17 ± 0.00 | 7.59 ± 0.39 | 0.22 ± 0.30 | 1.39 ± 0.10 | 1.72 ± 0.08 | 0.01 ± 0.003 | 0.11 ± 0.02 | | | |
| 0.25 ± 0.08 | 7.33 ± 0.00 | 0.43 ± 0.13 | 1.31 ± 0.39 | 1.60 ± 0.48 | 0.01 ± 0.003 | 0.12 ± 0.04 | | | |
| 0.50 ± 0.00 | 7.50 ± 0.29 | 0.22 ± 0.30 | 3.12 ± 2.38 | 1.68 ± 0.10 | 0.02 ± 0.01 | 0.12 ± 0.02 | | | |
| 0.75 ± 0.23 | 7.59 ± 0.00 | 0.00 ± 0.00 | 6.56 ± 1.97 | 1.73 ± 0.52 | 0.02 ± 0.005 | 0.11 ± 0.03 | | | |
| 1.00 ± 0.00 | 7.41 ± 0.13 | 0.22 ± 0.30 | 4.64 ± 4.53 | 1.62 ± 0.11 | 0.03 ± 0.01 | 0.13 ± 0.02 | | | |
| 2.00 ± 0.00 | 7.33 ± 0.02 | 0.22 ± 0.30 | 5.92 ± 6.32 | 1.66 ± 0.07 | 0.01 ± 0.01 | 0.12 ± 0.01 | | | |
| 4.00 ± 0.00 | 7.31 ± 0.04 | 0.22 ± 0.30 | 8.36 ± 9.63 | 1.56 ± 0.12 | 0.01 ± 0.01 | 0.13 ± 0.002 | | | |
| 8.00 ± 0.00 | 7.32 ± 0.02 | 0.22 ± 0.30 | 10.48 ± 12.61 | 1.53 ± 0.05 | 0.01 ± 0.004 | 0.14 ± 0.001 | | | |
| 11.07 ± 0.09 | 7.30 ± 0.01 | 0.22 ± 0.30 | 11.51 ± 13.70 | 1.51 ± 0.06 | 0.01 ± 0.002 | 0.14 ± 0.01 | | | |
| 24.05 ± 0.07 | 7.32 ± 0.03 | 0.22 ± 0.30 | 14.23 ± 16.84 | 1.46 ± 0.01 | 0.01 ± 0.002 | 0.14 ± 0.01 | | | |
| 48.08 ± 0.12 | 7.31 ± 0.01 | 0.22 ± 0.30 | 16.65 ± 20.26 | 1.38 ± 0.05 | 0.02 ± 0.01 | 0.15 ± 0.01 | | | |
| 84.19 ± 16.70 | 7.31 ± 0.01 | 0.22 ± 0.30 | 21.19 ± 25.58 | 1.34 ± 0.02 | 0.00 ± 0.001 | 0.15 ± 0.01 | | | |
| 168.03 ± 0.07 | 7.31 ± 0.03 | 24.19 ± 34.21 | 49.59 ± 3.92 | 1.19 ± 0.04 | 0.01 ± 0.01 | 0.14 ± 0.01 | | | |
| 252.01 ± 16.96 | 7.31 ± 0.02 | 26.43 ± 37.38 | 55.21 ± 0.01 | 1.14 ± 0.03 | 0.01 ± 0.004 | 0.15 ± 0.02 | | | |
| 336.03 ± 0.04 | 7.30 ± 0.01 | 34.87 ± 49.31 | 66.01 ± 7.66 | 1.08 ± 0.01 | 0.01 ± 0.001 | 0.15 ± 0.00 | | | |
| 420.02 ± 16.95 | 7.32 ± 0.02 | 36.49 ± 51.60 | 70.56 ± 6.36 | 1.03 ± 0.01 | 0.01 ± 0.001 | 0.15 ± 0.01 | | | |
| 504.00 ± 0.00 | 7.30 ± 0.004 | 37.30 ± 52.32 | 72.71 ± 6.21 | 1.03 ± 0.01 | 0.02 ± 0.003 | 0.15 ± 0.01 | | | |
| 588.00 ± 16.97 | 7.30 ± 0.001 | 37.15 ± 52.53 | 73.57 ± 5.36 | 1.00 ± 0.04 | 0.02 ± 0.01 | 0.22 ± 0.11 | | | |
| 672.08 ± 0.12 | 7.28 ± 0.03 | 37.76 ± 53.40 | 75.01 ± 5.34 | 0.98 ± 0.03 | 0.01 ± 0.003 | 0.15 ± 0.01 | | | |

| pH 7.3 - 3.3 mM F initial | | | | | | | | | | | | | | | | | | | | |
|---------------------------|---|-------|------|---|-------|-----------------|---|------|-----------------------------|---|-------|------------------|---|------|-------------------|---|------|--------------------------------|---|--------|
| time hrs | | | pH | | | 0.1M NaOH mL | | | 0.1M HNO ₃ mL | | | F _{tot} | | | Ca _{tot} | | | PO ₄ _{tot} | | |
| | | | | | | | | | | | | mM | | | mM | | | mM | | |
| | | | | | | | | | | | | 3.42 | ± | 0.17 | | | | 0.11 | ± | 0.14 |
| 0.00 | ± | 0.00 | 7.47 | ± | 0.04 | 0.00 | ± | 0.00 | 0.00 | ± | 0.00 | 2.78 | ± | 0.11 | 0.05 | ± | 0.06 | 0.12 | ± | 0.03 |
| 0.02 | ± | 0.00 | 7.67 | ± | 0.01 | 0.00 | ± | 0.00 | 0.13 | ± | 0.10 | 2.89 | ± | 0.06 | 0.04 | ± | 0.04 | 0.12 | ± | 0.01 |
| 0.03 | ± | 0.00 | 7.72 | ± | 0.04 | 0.00 | ± | 0.00 | 0.33 | ± | 0.26 | 2.90 | ± | 0.22 | 0.04 | ± | 0.04 | 0.12 | ± | 0.01 |
| 0.08 | ± | 0.00 | 7.71 | ± | 0.14 | 0.00 | ± | 0.00 | 0.57 | ± | 0.23 | 2.95 | ± | 0.27 | 0.06 | ± | 0.08 | 0.13 | ± | 0.01 |
| 0.17 | ± | 0.00 | 7.53 | ± | 0.42 | 0.00 | ± | 0.00 | 1.26 | ± | 0.55 | 2.77 | ± | 0.17 | 0.06 | ± | 0.08 | 0.14 | ± | 0.04 |
| 0.26 | ± | 0.01 | 7.59 | ± | 0.32 | 0.29 | ± | 0.41 | 1.50 | ± | 0.21 | 2.91 | ± | 0.19 | 0.05 | ± | 0.07 | 0.14 | ± | 0.02 |
| 0.50 | ± | 0.00 | 7.55 | ± | 0.29 | 0.41 | ± | 0.58 | 2.33 | ± | 0.47 | 2.81 | ± | 0.26 | 0.13 | ± | 0.10 | 0.21 | ± | 0.05 |
| 1.00 | ± | 0.00 | 7.46 | ± | 0.24 | 0.41 | ± | 0.58 | 3.53 | ± | 1.87 | 2.82 | ± | 0.36 | 0.03 | ± | 0.04 | 0.15 | ± | 0.03 |
| 2.10 | ± | 0.14 | 7.40 | ± | 0.08 | 0.41 | ± | 0.58 | 5.33 | ± | 4.41 | 2.76 | ± | 0.18 | 0.09 | ± | 0.12 | 0.13 | ± | 0.01 |
| 4.00 | ± | 0.00 | 7.35 | ± | 0.03 | 0.41 | ± | 0.58 | 7.20 | ± | 6.78 | 2.71 | ± | 0.31 | 0.04 | ± | 0.04 | 0.16 | ± | 0.04 |
| 8.08 | ± | 0.12 | 7.29 | ± | 0.01 | 0.41 | ± | 0.58 | 9.71 | ± | 9.75 | 2.84 | ± | 0.21 | 0.04 | ± | 0.02 | 0.15 | ± | 0.002 |
| 11.01 | ± | 0.01 | 7.27 | ± | 0.001 | 0.85 | ± | 1.20 | 10.41 | ± | 9.23 | 2.68 | ± | 0.02 | 0.05 | ± | 0.07 | 0.14 | ± | 0.001 |
| 24.04 | ± | 0.06 | 7.32 | ± | 0.03 | 1.00 | ± | 1.41 | 11.47 | ± | 10.05 | 2.66 | ± | 0.08 | 0.02 | ± | 0.02 | 0.16 | ± | 0.01 |
| 48.02 | ± | 0.02 | 7.31 | ± | 0.01 | 1.60 | ± | 2.26 | 13.98 | ± | 11.14 | 2.60 | ± | 0.14 | 0.05 | ± | 0.06 | 0.17 | ± | 0.01 |
| 84.01 | ± | 16.96 | 7.28 | ± | 0.01 | 1.73 | ± | 2.45 | 18.78 | ± | 17.00 | 2.54 | ± | 0.10 | 0.06 | ± | 0.08 | 0.16 | ± | 0.01 |
| 168.04 | ± | 0.06 | 7.30 | ± | 0.01 | 3.80 | ± | 5.37 | 29.31 | ± | 25.35 | 2.55 | ± | 0.23 | 0.06 | ± | 0.08 | 0.17 | ± | 0.02 |
| 252.06 | ± | 17.01 | 7.34 | ± | 0.06 | 3.80 | ± | 5.37 | 31.84 | ± | 28.92 | 2.40 | ± | 0.16 | 0.03 | ± | 0.03 | 0.16 | ± | 0.01 |
| 336.07 | ± | 0.07 | 7.32 | ± | 0.03 | 3.80 | ± | 5.37 | 34.01 | ± | 31.23 | 2.38 | ± | 0.09 | 0.01 | ± | 0.01 | 0.18 | ± | 0.03 |
| 420.02 | ± | 16.95 | 7.26 | ± | 0.18 | 3.80 | ± | 5.37 | 38.49 | ± | 37.31 | 2.37 | ± | 0.10 | 0.02 | ± | 0.01 | 0.16 | ± | 0.001 |
| 504.00 | ± | 0.00 | 7.26 | ± | 0.11 | 4.74 | ± | 6.70 | 39.93 | ± | 37.82 | 2.37 | ± | 0.14 | 0.01 | ± | 0.01 | 0.16 | ± | 0.0003 |
| 588.00 | ± | 16.97 | 7.26 | ± | 0.06 | 7.74 | ± | 2.46 | 40.04 | ± | 37.66 | 2.27 | ± | 0.13 | 0.01 | ± | 0.01 | 0.15 | ± | 0.03 |
| 672.04 | ± | 0.06 | 7.28 | ± | 0.03 | 14.34 | ± | 5.89 | 44.85 | ± | 43.56 | 2.24 | ± | 0.11 | 0.01 | ± | 0.01 | 0.16 | ± | 0.001 |

| pH 7.3 - 5.0 mM F initial | | | | | | | | | |
|---------------------------|--------------|-----------------|-----------------------------|------------------------|---------------|---------------|-------------------------|--|--|
| time hrs | pH | 0.1M NaOH mL | 0.1M HNO ₃ mL | F _{tot} mM | | | Ca _{tot} mM | | |
| | | | | 5.02 ± 0.11 | | | | | |
| | | | | | | | 0.10 ± 0.03 | | |
| 0.00 ± 0.00 | 7.73 ± 0.09 | 0.00 ± 0.00 | 0.00 ± 0.00 | 4.76 ± 0.10 | 0.02 ± 0.01 | 0.11 ± 0.06 | | | |
| 0.02 ± 0.00 | 7.83 ± 0.13 | 0.00 ± 0.00 | 0.18 ± 0.08 | 4.68 ± 0.08 | 0.03 ± 0.01 | 0.14 ± 0.02 | | | |
| 0.03 ± 0.00 | 7.77 ± 0.19 | 0.00 ± 0.00 | 0.90 ± 0.10 | 4.64 ± 0.20 | 0.02 ± 0.01 | 0.14 ± 0.01 | | | |
| 0.08 ± 0.00 | 7.54 ± 0.41 | 0.00 ± 0.00 | 2.04 ± 0.25 | 4.63 ± 0.14 | 0.02 ± 0.01 | 0.14 ± 0.02 | | | |
| 0.17 ± 0.00 | 7.43 ± 0.21 | 0.41 ± 0.58 | 3.82 ± 2.30 | 4.67 ± 0.03 | 0.02 ± 0.01 | 0.15 ± 0.02 | | | |
| 0.25 ± 0.00 | 7.31 ± 0.08 | 0.41 ± 0.58 | 6.05 ± 5.45 | 4.65 ± 0.004 | 0.01 ± 0.004 | 0.15 ± 0.01 | | | |
| 0.50 ± 0.00 | 7.33 ± 0.08 | 0.61 ± 0.31 | 10.62 ± 11.91 | 4.55 ± 0.01 | 0.03 ± 0.01 | 0.15 ± 0.02 | | | |
| 1.00 ± 0.00 | 7.32 ± 0.01 | 2.01 ± 1.68 | 11.47 ± 13.11 | 4.49 ± 0.13 | 0.02 ± 0.005 | 0.15 ± 0.01 | | | |
| 1.97 ± 0.05 | 7.33 ± 0.09 | 2.01 ± 1.68 | 12.48 ± 14.18 | 4.50 ± 0.11 | 0.02 ± 0.01 | 0.16 ± 0.005 | | | |
| 4.00 ± 0.00 | 7.33 ± 0.02 | 2.01 ± 1.68 | 13.57 ± 15.73 | 4.37 ± 0.18 | 0.08 ± 0.02 | 0.18 ± 0.03 | | | |
| 8.00 ± 0.00 | 7.33 ± 0.02 | 2.21 ± 1.40 | 14.61 ± 16.38 | 4.47 ± 0.03 | 0.01 ± 0.004 | 0.16 ± 0.003 | | | |
| 11.03 ± 0.05 | 7.33 ± 0.02 | 2.21 ± 1.40 | 15.04 ± 16.74 | 4.43 ± 0.14 | 0.01 ± 0.003 | 0.16 ± 0.003 | | | |
| 24.02 ± 0.02 | 7.33 ± 0.004 | 2.58 ± 0.88 | 15.96 ± 16.48 | 4.29 ± 0.03 | 0.01 ± 0.004 | 0.17 ± 0.0001 | | | |
| 48.00 ± 0.00 | 7.29 ± 0.04 | 3.97 ± 0.69 | 17.46 ± 14.35 | 4.21 ± 0.18 | 0.07 ± 0.02 | 0.19 ± 0.02 | | | |
| 84.03 ± 16.92 | 7.32 ± 0.01 | 4.84 ± 0.004 | 18.19 ± 14.57 | 4.26 ± 0.01 | 0.01 ± 0.002 | 0.17 ± 0.01 | | | |
| 168.00 ± 0.00 | 7.31 ± 0.03 | 5.68 ± 0.62 | 19.06 ± 13.35 | 4.11 ± 0.04 | 0.05 ± 0.02 | 0.23 ± 0.03 | | | |
| 252.00 ± 16.97 | 7.31 ± 0.01 | 10.78 ± 7.80 | 24.96 ± 7.39 | 4.12 ± 0.09 | 0.01 ± 0.001 | 0.19 ± 0.01 | | | |
| 336.03 ± 0.01 | 7.30 ± 0.06 | 36.39 ± 44.01 | 50.55 ± 25.81 | 4.08 ± 0.13 | 0.02 ± 0.03 | 0.20 ± 0.01 | | | |
| 420.01 ± 16.96 | 7.34 ± 0.02 | 45.97 ± 57.56 | 62.02 ± 32.60 | 3.91 ± 0.22 | 0.01 ± 0.0003 | 0.19 ± 0.01 | | | |
| 504.08 ± 0.12 | 7.35 ± 0.02 | 45.97 ± 57.56 | 63.32 ± 31.37 | 3.88 ± 0.29 | 0.09 ± 0.12 | 0.24 ± 0.07 | | | |
| 588.01 ± 16.96 | 7.35 ± 0.03 | 45.97 ± 57.56 | 66.01 ± 27.94 | 3.83 ± 0.24 | 0.04 ± 0.05 | 0.22 ± 0.03 | | | |
| 672.09 ± 0.13 | 7.34 ± 0.02 | 45.99 ± 57.54 | 66.14 ± 28.06 | 3.77 ± 0.23 | 0.01 ± 0.001 | 0.19 ± 0.01 | | | |

| pH 9.5 - 0.5 mM F initial | | | | | | | |
|---------------------------|--------------|-----------------|-----------------------------|------------------------|-------------------------|---------------------------|--|
| time hrs | pH | 0.1M NaOH mL | 0.1M HNO ₃ mL | F _{tot} mM | Ca _{tot} mM | PO _{4 tot} mM | |
| | | | | 0.53 ± 0.01 | | | |
| | | | | | | | |
| 0.00 ± 0.00 | 9.69 ± 0.10 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.46 ± 0.04 | 0.01 ± 0.00 | 0.13 ± 0.01 | |
| 0.02 ± 0.00 | 9.62 ± 0.04 | 0.00 ± 0.00 | 0.05 ± 0.03 | 0.46 ± 0.03 | 0.02 ± 0.01 | 0.13 ± 0.02 | |
| 0.03 ± 0.01 | 9.53 ± 0.00 | 0.00 ± 0.00 | 0.44 ± 0.13 | 0.47 ± 0.14 | 0.00 ± 0.00 | 0.12 ± 0.04 | |
| 0.08 ± 0.00 | 9.52 ± 0.07 | 0.00 ± 0.00 | 0.29 ± 0.21 | 0.44 ± 0.02 | 0.01 ± 0.003 | 0.13 ± 0.01 | |
| 0.15 ± 0.02 | 9.52 ± 0.03 | 0.00 ± 0.00 | 0.32 ± 0.16 | 0.44 ± 0.01 | 0.00 ± 0.001 | 0.13 ± 0.01 | |
| 0.25 ± 0.00 | 9.50 ± 0.004 | 0.00 ± 0.00 | 0.36 ± 0.11 | 0.43 ± 0.03 | 0.00 ± 0.001 | 0.13 ± 0.01 | |
| 0.50 ± 0.00 | 9.47 ± 0.03 | 0.00 ± 0.00 | 0.36 ± 0.11 | 0.42 ± 0.02 | 0.01 ± 0.002 | 0.13 ± 0.01 | |
| 1.01 ± 0.01 | 9.46 ± 0.01 | 0.00 ± 0.00 | 0.36 ± 0.11 | 0.41 ± 0.02 | 0.03 ± 0.03 | 0.14 ± 0.01 | |
| 2.00 ± 0.00 | 9.49 ± 0.01 | 0.40 ± 0.12 | 0.57 ± 0.39 | 0.39 ± 0.003 | 0.01 ± 0.003 | 0.13 ± 0.01 | |
| 4.00 ± 0.00 | 9.51 ± 0.004 | 1.14 ± 0.14 | 0.79 ± 0.71 | 0.39 ± 0.01 | 0.01 ± 0.002 | 0.14 ± 0.01 | |
| 8.00 ± 0.00 | 9.48 ± 0.03 | 2.60 ± 0.52 | 1.20 ± 1.29 | 0.37 ± 0.002 | 0.02 ± 0.01 | 0.14 ± 0.02 | |
| 10.92 ± 0.12 | 9.49 ± 0.03 | 3.40 ± 1.08 | 1.70 ± 1.99 | 0.37 ± 0.005 | 0.01 ± 0.003 | 0.14 ± 0.02 | |
| 24.00 ± 0.00 | 9.49 ± 0.01 | 8.64 ± 5.91 | 3.13 ± 4.01 | 0.36 ± 0.002 | 0.01 ± 0.003 | 0.15 ± 0.02 | |
| 47.97 ± 0.16 | 9.50 ± 0.004 | 12.92 ± 5.00 | 4.17 ± 5.49 | 0.29 ± 0.07 | 1.83 ± 2.56 | 0.18 ± 0.05 | |
| 84.01 ± 16.96 | 9.48 ± 0.04 | 17.50 ± 8.44 | 5.53 ± 7.41 | 0.34 ± 0.01 | 0.01 ± 0.01 | 0.17 ± 0.01 | |
| 168.04 ± 0.06 | 9.49 ± 0.01 | 25.92 ± 7.33 | 6.03 ± 8.11 | 0.33 ± 0.02 | 0.01 ± 0.002 | 0.19 ± 0.02 | |
| 252.00 ± 16.97 | 9.03 ± 0.67 | 32.25 ± 1.29 | 6.03 ± 8.11 | 0.31 ± 0.03 | 0.00 ± 0.01 | 0.19 ± 0.04 | |
| 335.99 ± 0.15 | 9.48 ± 0.03 | 50.35 ± 4.58 | 6.18 ± 8.33 | 0.32 ± 0.03 | 0.00 ± 0.01 | 0.21 ± 0.04 | |
| 420.14 ± 17.01 | 9.48 ± 0.03 | 65.66 ± 1.60 | 6.18 ± 8.33 | 0.32 ± 0.03 | 0.00 ± 0.01 | 0.14 ± 0.16 | |
| 504.00 ± 0.00 | 9.48 ± 0.03 | 73.92 ± 2.70 | 6.18 ± 8.33 | 0.32 ± 0.02 | 0.01 ± 0.01 | 0.23 ± 0.05 | |
| 588.00 ± 16.97 | 9.48 ± 0.02 | 80.60 ± 2.81 | 6.18 ± 8.33 | 0.31 ± 0.03 | 0.01 ± 0.01 | 0.25 ± 0.02 | |
| 672.03 ± 0.04 | 9.48 ± 0.03 | 86.37 ± 4.29 | 6.18 ± 8.33 | 0.30 ± 0.02 | 0.02 ± 0.01 | 0.25 ± 0.04 | |

| pH 9.5 - 2.5 mM F initial | | | | | | | |
|---------------------------|--------------|-----------------|-----------------------------|------------------------|--------|-------------------------|--------------------------------------|
| time hrs | pH | 0.1M NaOH mL | 0.1M HNO ₃ mL | F _{tot} mM | | Ca _{tot} mM | PO ₄ _{tot} mM |
| | | | | 2.49 | ± 0.02 | | |
| | | | | | | 0.01 ± 0.00 | 0.13 ± 0.01 |
| 0.00 ± 0.00 | 9.63 ± 0.04 | 0.00 ± 0.00 | 0.00 ± 0.00 | 2.41 ± 0.10 | | 0.02 ± 0.01 | 0.16 ± 0.02 |
| 0.02 ± 0.01 | 9.59 ± 0.00 | 0.00 ± 0.00 | 0.03 ± 0.01 | 2.28 ± 0.69 | | 0.01 ± 0.00 | 0.15 ± 0.04 |
| 0.03 ± 0.00 | 9.63 ± 0.06 | 0.00 ± 0.00 | 0.07 ± 0.02 | 2.30 ± 0.01 | | 0.01 ± 0.002 | 0.15 ± 0.01 |
| 0.08 ± 0.01 | 9.62 ± 0.06 | 0.00 ± 0.00 | 0.15 ± 0.02 | 2.31 ± 0.03 | | 0.01 ± 0.002 | 0.16 ± 0.01 |
| 0.14 ± 0.04 | 9.59 ± 0.07 | 0.00 ± 0.00 | 0.28 ± 0.00 | 2.27 ± 0.005 | | 0.01 ± 0.004 | 0.16 ± 0.01 |
| 0.23 ± 0.04 | 9.55 ± 0.07 | 0.00 ± 0.00 | 0.42 ± 0.05 | 2.30 ± 0.001 | | 0.01 ± 0.002 | 0.16 ± 0.01 |
| 0.28 ± 0.09 | 9.57 ± 0.00 | 0.00 ± 0.00 | 0.60 ± 0.18 | 2.30 ± 0.69 | | 0.01 ± 0.004 | 0.17 ± 0.05 |
| 0.53 ± 0.04 | 9.47 ± 0.03 | 0.00 ± 0.00 | 0.65 ± 0.30 | 2.31 ± 0.01 | | 0.01 ± 0.004 | 0.16 ± 0.02 |
| 1.02 ± 0.02 | 9.43 ± 0.07 | 0.00 ± 0.00 | 0.65 ± 0.30 | 2.26 ± 0.03 | | 0.01 ± 0.004 | 0.16 ± 0.01 |
| 2.02 ± 0.02 | 9.49 ± 0.01 | 0.53 ± 0.21 | 0.65 ± 0.30 | 2.29 ± 0.02 | | 0.01 ± 0.003 | 0.16 ± 0.01 |
| 4.00 ± 0.00 | 9.50 ± 0.001 | 1.25 ± 0.48 | 0.65 ± 0.30 | 2.34 ± 0.06 | | 0.02 ± 0.0002 | 0.17 ± 0.01 |
| 8.01 ± 0.01 | 9.51 ± 0.001 | 1.86 ± 0.75 | 0.65 ± 0.30 | 2.22 ± 0.01 | | 0.02 ± 0.005 | 0.17 ± 0.02 |
| 11.07 ± 0.05 | 9.50 ± 0.00 | 2.44 ± 0.45 | 0.65 ± 0.30 | 2.26 ± 0.07 | | 0.02 ± 0.004 | 0.17 ± 0.01 |
| 24.02 ± 0.02 | 9.51 ± 0.01 | 6.24 ± 1.82 | 0.65 ± 0.30 | 2.20 ± 0.02 | | 0.03 ± 0.01 | 0.18 ± 0.01 |
| 47.93 ± 0.13 | 9.50 ± 0.002 | 11.77 ± 4.34 | 0.65 ± 0.30 | 2.12 ± 0.08 | | 0.02 ± 0.001 | 0.18 ± 0.02 |
| 72.03 ± 0.01 | 9.50 ± 0.001 | 16.71 ± 4.48 | 0.65 ± 0.30 | 2.13 ± 0.14 | | 0.02 ± 0.002 | 0.19 ± 0.01 |
| 96.03 ± 28.81 | 9.50 ± 0.00 | 28.23 ± 8.47 | 0.86 ± 0.26 | 2.13 ± 0.64 | | 0.02 ± 0.01 | 0.22 ± 0.06 |
| 168.04 ± 0.04 | 9.50 ± 0.001 | 37.28 ± 10.48 | 0.65 ± 0.30 | 2.15 ± 0.07 | | 0.03 ± 0.01 | 0.22 ± 0.01 |
| 252.03 ± 17.02 | 9.50 ± 0.001 | 54.88 ± 15.14 | 0.65 ± 0.30 | 2.25 ± 0.04 | | 0.05 ± 0.02 | 0.25 ± 0.01 |
| 336.07 ± 0.09 | 9.50 ± 0.001 | 69.59 ± 13.58 | 0.65 ± 0.30 | 2.16 ± 0.04 | | 0.04 ± 0.01 | 0.25 ± 0.03 |
| 420.98 ± 18.35 | 9.50 ± 0.004 | 84.65 ± 13.86 | 0.65 ± 0.30 | 2.03 ± 0.31 | | 0.04 ± 0.005 | 0.27 ± 0.03 |
| 492.13 ± 17.15 | 9.50 ± 0.001 | 97.17 ± 16.04 | 0.65 ± 0.30 | 2.21 ± 0.01 | | 0.03 ± 0.01 | 0.28 ± 0.04 |
| 588.50 ± 17.68 | 9.50 ± 0.001 | 105.50 ± 12.58 | 0.65 ± 0.30 | 2.26 ± 0.04 | | 0.04 ± 0.00 | 0.29 ± 0.03 |
| 660.17 ± 17.21 | 9.50 ± 0.001 | 114.96 ± 5.64 | 0.65 ± 0.30 | 2.23 ± 0.18 | | 0.03 ± 0.01 | 0.29 ± 0.02 |

| pH 9.5 - 3.3 mM F initial | | | | | | | |
|---------------------------|--------------|-----------------|-----------------------------|------------------------|-------------------------|--------------------------------------|--|
| time hrs | pH | 0.1M NaOH mL | 0.1M HNO ₃ mL | F _{tot} mM | Ca _{tot} mM | PO ₄ _{tot} mM | |
| | | | | 3.42 ± 0.17 | | | |
| | | | | | | | |
| 0.00 ± 0.00 | 9.63 ± 0.06 | 0.00 ± 0.00 | 0.00 ± 0.00 | 2.84 ± 0.17 | 0.01 ± 0.01 | 0.18 ± 0.09 | |
| 0.02 ± 0.00 | 9.63 ± 0.04 | 0.11 ± 0.15 | 0.27 ± 0.19 | 2.89 ± 0.10 | 0.06 ± 0.07 | 0.16 ± 0.04 | |
| 0.03 ± 0.00 | 9.52 ± 0.002 | 0.11 ± 0.15 | 0.62 ± 0.06 | 2.99 ± 0.11 | 0.03 ± 0.04 | 0.16 ± 0.03 | |
| 0.08 ± 0.00 | 9.53 ± 0.01 | 0.11 ± 0.15 | 0.63 ± 0.04 | 2.99 ± 0.06 | 0.02 ± 0.01 | 0.16 ± 0.003 | |
| 0.17 ± 0.00 | 9.54 ± 0.01 | 0.11 ± 0.15 | 0.71 ± 0.09 | 2.83 ± 0.21 | 0.04 ± 0.05 | 0.15 ± 0.01 | |
| 0.26 ± 0.01 | 9.51 ± 0.01 | 0.11 ± 0.15 | 0.73 ± 0.07 | 2.87 ± 0.11 | 0.01 ± 0.01 | 0.16 ± 0.01 | |
| 0.44 ± 0.08 | 9.50 ± 0.004 | 0.11 ± 0.15 | 0.74 ± 0.05 | 2.94 ± 0.07 | 0.19 ± 0.27 | 0.15 ± 0.01 | |
| 0.94 ± 0.08 | 9.50 ± 0.001 | 0.26 ± 0.34 | 0.81 ± 0.16 | 2.97 ± 0.005 | 0.07 ± 0.09 | 0.16 ± 0.01 | |
| 1.94 ± 0.08 | 9.47 ± 0.02 | 0.87 ± 0.72 | 1.22 ± 0.49 | 2.88 ± 0.06 | 0.08 ± 0.10 | 0.16 ± 0.01 | |
| 3.94 ± 0.08 | 9.50 ± 0.01 | 2.18 ± 1.91 | 1.58 ± 0.61 | 2.98 ± 0.07 | 0.02 ± 0.02 | 0.16 ± 0.01 | |
| 8.07 ± 0.09 | 9.51 ± 0.001 | 3.59 ± 3.57 | 2.19 ± 1.46 | 2.92 ± 0.07 | 0.04 ± 0.04 | 0.16 ± 0.01 | |
| 10.94 ± 0.08 | 9.48 ± 0.02 | 4.46 ± 4.37 | 2.49 ± 1.71 | 2.80 ± 0.04 | 0.04 ± 0.05 | 0.17 ± 0.01 | |
| 24.00 ± 0.00 | 9.47 ± 0.02 | 7.79 ± 6.15 | 3.33 ± 1.57 | 2.86 ± 0.04 | 0.04 ± 0.03 | 0.17 ± 0.01 | |
| 48.10 ± 0.14 | 9.51 ± 0.003 | 11.11 ± 7.62 | 3.58 ± 1.21 | 2.82 ± 0.02 | 0.03 ± 0.02 | 0.18 ± 0.02 | |
| 84.01 ± 16.96 | 9.49 ± 0.03 | 13.32 ± 8.17 | 3.69 ± 1.06 | 2.82 ± 0.05 | 0.03 ± 0.02 | 0.19 ± 0.01 | |
| 168.00 ± 0.00 | 9.51 ± 0.01 | 17.69 ± 6.98 | 3.69 ± 1.06 | 2.78 ± 0.03 | 0.03 ± 0.02 | 0.20 ± 0.01 | |
| 252.00 ± 16.97 | 9.49 ± 0.005 | 23.27 ± 6.29 | 3.69 ± 1.06 | 2.71 ± 0.09 | 0.03 ± 0.02 | 0.21 ± 0.01 | |
| 336.02 ± 0.02 | 9.47 ± 0.01 | 29.20 ± 4.70 | 3.69 ± 1.06 | 2.80 ± 0.03 | 0.03 ± 0.01 | 0.23 ± 0.03 | |
| 420.00 ± 16.97 | 9.48 ± 0.001 | 37.35 ± 7.02 | 3.69 ± 1.06 | 2.80 ± 0.00 | 0.02 ± 0.01 | 0.22 ± 0.01 | |
| 492.00 ± 16.97 | 9.46 ± 0.004 | 45.54 ± 4.29 | 3.69 ± 1.05 | 2.73 ± 0.00 | 0.01 ± 0.01 | 0.23 ± 0.01 | |
| 588.02 ± 16.95 | 9.47 ± 0.01 | 53.20 ± 9.27 | 3.70 ± 1.05 | 2.79 ± 0.05 | 0.01 ± 0.01 | 0.24 ± 0.01 | |
| 660.08 ± 16.86 | 9.47 ± 0.01 | 62.16 ± 10.21 | 3.70 ± 1.05 | 2.82 ± 0.05 | 0.02 ± 0.005 | 0.25 ± 0.02 | |

Table 2S 2 Total dissolved Ca, PO₄, F, Na, and anion concentrations, pH and added acid and base as function of sampling times for all conducted F uptake experiments for potential anion influence

| 0.5 mM F initial - 0.5 mM Cl | | | | | | | | | | | |
|------------------------------|--------------|------------------|------------------------------|------------------------|---|--------------|-------------------------|--------------------------------------|-------------------------|-------------------------|--|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | F _{tot} mM | | | Ca _{tot} mM | PO ₄ _{tot} mM | Na _{tot} mM | Cl _{tot} mM | |
| | | | | 0.52 | ± | 0.01 | | | | | |
| | | | | | | | | | | | |
| 0.00 ± 0.00 | 7.29 ± 0.28 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.33 ± 0.00 | | 0.10 ± 0.10 | 0.14 ± 0.07 | 1.10 ± 0.54 | 1.02 ± 0.42 | | |
| 0.03 ± 0.01 | 7.31 ± 0.17 | 0.66 ± 0.94 | 0.10 ± 0.13 | 0.32 ± 0.02 | | 0.04 ± 0.02 | 0.10 ± 0.01 | 1.11 ± 0.55 | 1.03 ± 0.44 | | |
| 0.04 ± 0.01 | 7.40 ± 0.10 | 1.17 ± 1.66 | 0.45 ± 0.20 | 0.31 ± 0.03 | | 0.05 ± 0.02 | 0.11 ± 0.02 | 1.15 ± 0.62 | 1.04 ± 0.47 | | |
| 0.08 ± 0.00 | 7.30 ± 0.02 | 1.17 ± 1.66 | 0.92 ± 0.47 | 0.27 ± 0.01 | | 1.37 ± 1.79 | 1.01 ± 1.23 | 1.24 ± 0.68 | 0.97 ± 0.61 | | |
| 0.17 ± 0.00 | 7.30 ± 0.06 | 1.49 ± 1.93 | 1.05 ± 0.66 | 0.27 ± 0.01 | | 0.20 ± 0.24 | 0.21 ± 0.16 | 1.18 ± 0.60 | 1.12 ± 0.44 | | |
| 0.25 ± 0.00 | 7.27 ± 0.01 | 1.49 ± 1.93 | 1.11 ± 0.74 | 0.24 ± 0.04 | | 0.37 ± 0.47 | 0.33 ± 0.31 | 1.19 ± 0.63 | 1.11 ± 0.48 | | |
| 0.52 ± 0.02 | 7.28 ± 0.005 | 1.72 ± 2.25 | 1.34 ± 1.07 | 0.26 ± 0.002 | | 0.04 ± 0.02 | 0.11 ± 0.02 | 1.24 ± 0.65 | 1.11 ± 0.54 | | |
| 1.03 ± 0.05 | 7.27 ± 0.02 | 1.95 ± 2.57 | 1.55 ± 1.36 | 0.21 ± 0.05 | | 0.49 ± 0.65 | 0.41 ± 0.43 | 1.29 ± 0.67 | 1.11 ± 0.63 | | |
| 2.03 ± 0.04 | 7.30 ± 0.03 | 3.52 ± 4.79 | 3.04 ± 3.46 | 0.23 ± 0.01 | | 0.03 ± 0.004 | 0.11 ± 0.01 | 1.25 ± 0.60 | 1.20 ± 0.56 | | |
| 4.00 ± 0.05 | 7.33 ± 0.02 | 6.19 ± 8.57 | 5.45 ± 6.63 | 0.21 ± 0.01 | | 0.10 ± 0.08 | 0.15 ± 0.06 | 1.48 ± 0.85 | 1.19 ± 0.61 | | |
| 8.03 ± 0.05 | 7.31 ± 0.04 | 10.43 ± 14.57 | 9.62 ± 12.51 | 0.19 ± 0.02 | | 0.16 ± 0.19 | 0.20 ± 0.12 | 1.86 ± 1.27 | 1.36 ± 0.71 | | |
| 11.00 ± 0.00 | 7.27 ± 0.02 | 12.29 ± 17.20 | 11.52 ± 14.92 | 0.18 ± 0.03 | | 0.15 ± 0.09 | 0.19 ± 0.05 | 2.14 ± 1.67 | 1.40 ± 0.88 | | |
| 24.03 ± 0.05 | 7.32 ± 0.01 | 13.47 ± 18.87 | 12.66 ± 16.53 | 0.16 ± 0.03 | | 0.05 ± 0.03 | 0.13 ± 0.01 | 2.41 ± 1.89 | 1.64 ± 1.14 | | |
| 48.19 ± 0.27 | 7.35 ± 0.03 | 14.40 ± 20.19 | 14.26 ± 18.61 | 0.14 ± 0.02 | | 0.03 ± 0.001 | 0.12 ± 0.02 | 2.52 ± 1.90 | 2.25 ± 1.89 | | |
| 84.23 ± 17.19 | 7.31 ± 0.07 | 17.35 ± 24.36 | 17.88 ± 23.56 | 0.11 ± 0.04 | | 0.15 ± 0.14 | 0.19 ± 0.06 | 2.98 ± 2.41 | 2.40 ± 1.83 | | |
| 168.29 ± 0.41 | 7.34 ± 0.03 | 27.62 ± 38.88 | 27.48 ± 36.69 | 0.07 ± 0.05 | | 0.11 ± 0.12 | 0.16 ± 0.04 | 3.67 ± 2.95 | 4.95 ± 4.70 | | |

| 0.5 mM F initial - 5.0 mM Cl | | | | | | | | | | |
|------------------------------|--------------|------------------|------------------------------|------------------------|---|-------|-------------------------|--------------------------------------|-------------------------|-------------------------|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | F _{tot} mM | | | Ca _{tot} mM | PO ₄ _{tot} mM | Na _{tot} mM | Cl _{tot} mM |
| | | | | 0.50 | ± | 0.00 | | | | |
| | | | | | | | | | | |
| 0.00 ± 0.00 | 7.38 ± 0.04 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.33 | ± | 0.01 | 0.01 ± 0.02 | 0.09 ± 0.01 | 5.26 ± 1.62 | 5.70 ± 0.52 |
| 0.02 ± 0.00 | 7.44 ± 0.08 | 0.00 ± 0.00 | 0.25 ± 0.12 | 0.32 | ± | 0.003 | 0.01 ± 0.01 | 0.09 ± 0.01 | 4.83 ± 0.79 | 5.81 ± 0.76 |
| 0.08 ± 0.00 | 7.29 ± 0.06 | 0.00 ± 0.00 | 0.68 ± 0.29 | 0.30 | ± | 0.01 | 0.02 ± 0.03 | 0.10 ± 0.01 | 4.83 ± 0.64 | 5.88 ± 0.88 |
| 0.17 ± 0.00 | 7.31 ± 0.001 | 0.55 ± 0.27 | 1.03 ± 0.78 | 0.27 | ± | 0.01 | 0.05 ± 0.07 | 0.11 ± 0.02 | 4.83 ± 0.59 | 5.89 ± 0.86 |
| 0.25 ± 0.00 | 7.29 ± 0.02 | 0.72 ± 0.51 | 1.18 ± 0.99 | 0.28 | ± | 0.01 | 0.02 ± 0.02 | 0.09 ± 0.001 | 5.09 ± 0.65 | 5.90 ± 0.85 |
| 0.50 ± 0.00 | 7.28 ± 0.02 | 1.09 ± 1.04 | 1.56 ± 1.52 | 0.26 | ± | 0.01 | 0.03 ± 0.04 | 0.11 ± 0.003 | 4.96 ± 0.44 | 6.11 ± 1.19 |
| 0.98 ± 0.02 | 7.29 ± 0.02 | 1.90 ± 2.19 | 2.38 ± 2.69 | 0.25 | ± | 0.01 | 0.01 ± 0.02 | 0.10 ± 0.005 | 5.09 ± 0.65 | 6.24 ± 1.34 |
| 2.00 ± 0.00 | 7.30 ± 0.02 | 2.89 ± 3.59 | 3.38 ± 4.10 | 0.23 | ± | 0.01 | 0.01 ± 0.02 | 0.12 ± 0.04 | 5.34 ± 0.76 | 6.38 ± 1.58 |
| 4.08 ± 0.12 | 7.30 ± 0.04 | 6.64 ± 8.90 | 7.11 ± 9.38 | 0.21 | ± | 0.02 | 0.02 ± 0.03 | 0.11 ± 0.02 | 5.74 ± 0.96 | 6.41 ± 1.55 |
| 8.16 ± 0.13 | 7.27 ± 0.01 | 7.64 ± 9.12 | 8.16 ± 9.41 | 0.19 | ± | 0.02 | 0.05 ± 0.07 | 0.12 ± 0.02 | 6.12 ± 1.10 | 3.96 ± 5.59 |
| 24.28 ± 0.08 | 7.33 ± 0.003 | 9.66 ± 10.71 | 10.08 ± 10.70 | 0.16 | ± | 0.03 | 0.01 ± 0.02 | 0.10 ± 0.01 | 6.52 ± 1.14 | 7.44 ± 2.25 |
| 47.53 ± 0.62 | 7.30 ± 0.03 | 11.26 ± 8.45 | 11.85 ± 8.23 | 0.14 | ± | 0.02 | 0.01 ± 0.01 | 0.10 ± 0.003 | 7.09 ± 0.57 | 8.55 ± 3.00 |
| 71.92 ± 0.12 | 7.30 ± 0.001 | 11.26 ± 8.45 | 11.85 ± 8.23 | 0.12 | ± | 0.02 | 0.01 ± 0.01 | 0.10 ± 0.01 | 7.00 ± 0.82 | 9.34 ± 3.22 |
| 168.28 ± 0.37 | 7.31 ± 0.01 | 17.48 ± 8.77 | 18.07 ± 7.85 | 0.08 | ± | 0.01 | 0.01 ± 0.01 | 0.10 ± 0.01 | 8.41 ± 0.59 | 13.59 ± 6.04 |

| 0.5 mM F initial - 50.0 mM SO ₄ | | | | | | | | | | |
|--|--------------|------------------|------------------------------|------------------------|---|-------|-------------------------|---------------------------|-------------------------|---------------------------|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | F _{tot} mM | | | Ca _{tot} mM | PO _{4 tot} mM | Na _{tot} mM | SO _{4 tot} mM |
| | | | | 0.50 | ± | 0.00 | | | | |
| | | | | | | | 0.08 ± 0.01 | 0.00 ± 0.00 | | |
| 0.00 ± 0.00 | 7.48 ± 0.02 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.34 | ± | 0.00 | - | 0.12 ± 0.01 | 60.88 ± 17.02 | 53.20 ± 15.96 |
| 0.03 ± 0.00 | 7.59 ± 0.02 | 0.00 ± 0.00 | 0.43 ± 0.24 | 0.30 | ± | 0.01 | - | 0.14 ± 0.03 | 60.02 ± 18.96 | 53.17 ± 15.95 |
| 0.08 ± 0.00 | 7.46 ± 0.28 | 0.00 ± 0.00 | 0.84 ± 0.95 | 0.29 | ± | 0.01 | - | 0.15 ± 0.004 | 63.20 ± 20.54 | 53.66 ± 16.10 |
| 0.13 ± 0.02 | 7.50 ± 0.21 | 0.73 ± 1.03 | 0.90 ± 0.85 | 0.28 | ± | 0.01 | - | 0.16 ± 0.01 | 63.09 ± 20.12 | 53.66 ± 16.10 |
| 0.21 ± 0.06 | 7.40 ± 0.17 | 0.73 ± 1.03 | 1.14 ± 0.96 | 0.27 | ± | 0.01 | - | 0.18 ± 0.02 | 65.11 ± 19.88 | 53.66 ± 16.10 |
| 0.38 ± 0.18 | 7.37 ± 0.15 | 0.73 ± 1.03 | 1.26 ± 0.79 | 0.25 | ± | 0.02 | - | 0.18 ± 0.003 | 65.44 ± 20.43 | 53.66 ± 16.10 |
| 0.75 ± 0.35 | 7.28 ± 0.04 | 0.73 ± 1.03 | 1.45 ± 0.52 | 0.23 | ± | 0.01 | - | 0.19 ± 0.03 | 69.57 ± 22.66 | 53.66 ± 16.10 |
| 1.48 ± 0.68 | 7.29 ± 0.01 | 0.90 ± 1.27 | 1.50 ± 0.45 | 0.21 | ± | 0.004 | - | 0.22 ± 0.05 | 68.85 ± 19.88 | 60.35 ± 18.10 |
| 2.93 ± 1.28 | 7.29 ± 0.04 | 2.11 ± 2.99 | 2.54 ± 1.90 | 0.19 | ± | 0.01 | - | 0.22 ± 0.04 | 71.81 ± 22.06 | 62.16 ± 18.65 |
| 5.94 ± 2.75 | 7.27 ± 0.07 | 2.23 ± 3.16 | 2.54 ± 1.90 | 0.17 | ± | 0.002 | - | 0.23 ± 0.06 | 71.83 ± 22.14 | 62.16 ± 18.65 |
| 11.13 ± 4.40 | 7.30 ± 0.004 | 2.67 ± 2.53 | 2.83 ± 2.32 | 0.16 | ± | 0.01 | - | 0.23 ± 0.04 | 74.74 ± 21.88 | 62.16 ± 18.65 |
| 17.45 ± 8.77 | 7.30 ± 0.005 | 3.05 ± 2.01 | 3.12 ± 2.73 | 0.14 | ± | 0.01 | - | 0.24 ± 0.04 | 76.49 ± 22.85 | 64.72 ± 19.41 |
| 36.07 ± 17.02 | 7.31 ± 0.01 | 3.34 ± 1.59 | 3.21 ± 2.85 | 0.12 | ± | 0.01 | - | 0.24 ± 0.04 | 81.22 ± 23.70 | 68.71 ± 20.61 |
| 60.23 ± 16.78 | 7.35 ± 0.03 | 3.34 ± 1.59 | 3.21 ± 2.85 | 0.11 | ± | 0.01 | - | 0.24 ± 0.03 | 81.49 ± 23.99 | 70.44 ± 21.13 |
| 107.98 ± 50.89 | 7.32 ± 0.004 | 3.64 ± 2.01 | 5.10 ± 2.61 | 0.09 | ± | 0.02 | - | 0.26 ± 0.07 | 86.47 ± 25.04 | 72.74 ± 21.82 |
| 168.07 ± 0.05 | 7.32 ± 0.01 | 3.64 ± 2.01 | 5.46 ± 2.52 | 0.07 | ± | 0.002 | - | 0.27 ± 0.04 | 92.75 ± 26.47 | 75.88 ± 22.76 |

(-) below detection limit

| 0.5 mM F initial - 0.5 mM SO ₄ | | | | | | | | | | |
|---|--------------|------------------|------------------------------|------------------------|-------------------------|--------------------------------------|-------------------------|--------------------------------------|--|--|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | F _{tot} mM | Ca _{tot} mM | PO ₄ _{tot} mM | Na _{tot} mM | SO ₄ _{tot} mM | | |
| | | | | 0.51 ± 0.02 | | | | | | |
| | | | | | | 0.12 ± 0.06 | | 0.05 ± 0.08 | | |
| 0.01 ± 0.01 | 7.33 ± 0.18 | 0.04 ± 0.06 | 0.00 ± 0.00 | 0.32 ± 0.03 | 0.90 ± 1.27 | 0.46 ± 0.50 | 1.32 ± 0.20 | 0.61 ± 0.07 | | |
| 0.03 ± 0.00 | 7.29 ± 0.12 | 0.04 ± 0.06 | 0.25 ± 0.35 | 0.31 ± 0.01 | 0.16 ± 0.22 | 0.16 ± 0.07 | 1.33 ± 0.13 | 0.61 ± 0.05 | | |
| 0.12 ± 0.00 | 7.28 ± 0.06 | 1.08 ± 1.20 | 1.10 ± 1.56 | 0.29 ± 0.005 | 0.03 ± 0.05 | 0.11 ± 0.004 | 1.38 ± 0.11 | 0.62 ± 0.03 | | |
| 0.18 ± 0.01 | 7.29 ± 0.03 | 1.12 ± 1.15 | 1.10 ± 1.56 | 0.29 ± 0.01 | 0.02 ± 0.03 | 0.11 ± 0.01 | 1.39 ± 0.15 | 0.74 ± 0.20 | | |
| 0.25 ± 0.00 | 7.31 ± 0.003 | 1.16 ± 1.09 | 1.10 ± 1.56 | 0.28 ± 0.02 | 0.09 ± 0.12 | 0.14 ± 0.02 | 1.38 ± 0.12 | 0.62 ± 0.03 | | |
| 0.50 ± 0.00 | 7.31 ± 0.03 | 1.16 ± 1.09 | 1.10 ± 1.56 | 0.27 ± 0.01 | 0.07 ± 0.10 | 0.15 ± 0.003 | 1.44 ± 0.12 | 0.61 ± 0.05 | | |
| 1.03 ± 0.04 | 7.29 ± 0.05 | 1.33 ± 1.33 | 1.10 ± 1.56 | 0.26 ± 0.003 | 0.06 ± 0.08 | 0.14 ± 0.005 | 1.44 ± 0.08 | 0.76 ± 0.14 | | |
| 1.98 ± 0.02 | 7.30 ± 0.02 | 1.60 ± 1.44 | 1.32 ± 1.86 | 0.24 ± 0.001 | 0.11 ± 0.15 | 0.15 ± 0.04 | 1.48 ± 0.03 | 0.77 ± 0.15 | | |
| 4.00 ± 0.00 | 7.30 ± 0.002 | 2.19 ± 1.47 | 1.52 ± 2.15 | 0.21 ± 0.01 | 0.75 ± 1.06 | 0.42 ± 0.36 | 1.52 ± 0.01 | 0.76 ± 0.13 | | |
| 8.03 ± 0.04 | 7.29 ± 0.04 | 5.16 ± 4.93 | 3.90 ± 5.52 | 0.20 ± 0.01 | 0.07 ± 0.10 | 0.14 ± 0.01 | 1.83 ± 0.36 | 0.63 ± 0.06 | | |
| 11.00 ± 0.00 | 7.29 ± 0.02 | 6.40 ± 6.39 | 4.90 ± 6.93 | 0.20 ± 0.01 | 0.06 ± 0.08 | 0.14 ± 0.003 | 2.05 ± 0.62 | 0.57 ± 0.19 | | |
| 23.93 ± 0.09 | 7.33 ± 0.01 | 6.65 ± 6.36 | 5.02 ± 7.10 | 0.17 ± 0.01 | 0.01 ± 0.02 | 0.14 ± 0.04 | 2.08 ± 0.60 | 0.69 ± 0.03 | | |
| 48.05 ± 0.07 | 7.29 ± 0.02 | 7.39 ± 7.00 | 6.48 ± 6.34 | 0.15 ± 0.01 | 0.08 ± 0.11 | 0.17 ± 0.01 | 2.25 ± 0.77 | 1.09 ± 0.51 | | |
| 84.21 ± 17.19 | 7.27 ± 0.04 | 7.55 ± 7.23 | 7.12 ± 6.53 | 0.13 ± 0.01 | 0.02 ± 0.03 | 0.14 ± 0.03 | 2.43 ± 0.99 | 0.78 ± 0.03 | | |
| 168.07 ± 0.09 | 7.29 ± 0.02 | 8.48 ± 8.55 | 9.59 ± 6.65 | 0.09 ± 0.01 | 0.10 ± 0.14 | 0.16 ± 0.02 | 2.88 ± 1.58 | 0.75 ± 0.04 | | |

| 0.5 mM F initial - 5.0 mM SO ₄ | | | | | | | | | | |
|---|--------------|------------------|------------------------------|------------------------|---|------|-------------------------|--------------------------------------|-------------------------|--------------------------------------|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | F _{tot} mM | | | Ca _{tot} mM | PO ₄ _{tot} mM | Na _{tot} mM | SO ₄ _{tot} mM |
| | | | | 0.50 | ± | 0.00 | | | | |
| | | | | | | | 0.07 ± 0.05 | 0.08 ± 0.01 | | |
| 0.00 ± 0.00 | 7.57 ± 0.17 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.35 | ± | 0.01 | 0.03 ± 0.02 | 0.10 ± 0.004 | 6.43 ± 1.47 | 3.57 ± 1.66 |
| 0.03 ± 0.01 | 7.60 ± 0.12 | 0.00 ± 0.00 | 0.19 ± 0.09 | 0.33 | ± | 0.02 | 0.03 ± 0.02 | 0.10 ± 0.004 | 6.40 ± 1.55 | 3.52 ± 1.59 |
| 0.05 ± 0.00 | 7.53 ± 0.14 | 0.00 ± 0.00 | 0.45 ± 0.34 | 0.32 | ± | 0.02 | 0.03 ± 0.02 | 0.10 ± 0.01 | 6.30 ± 1.65 | 3.55 ± 1.62 |
| 0.09 ± 0.01 | 7.42 ± 0.18 | 0.00 ± 0.00 | 0.69 ± 0.44 | 0.30 | ± | 0.02 | 0.05 ± 0.02 | 0.12 ± 0.01 | 6.20 ± 1.34 | 3.51 ± 1.61 |
| 0.17 ± 0.00 | 7.32 ± 0.19 | 0.00 ± 0.00 | 0.78 ± 0.31 | 0.29 | ± | 0.03 | 0.04 ± 0.01 | 0.12 ± 0.003 | 6.32 ± 1.48 | 3.55 ± 1.62 |
| 0.25 ± 0.00 | 7.45 ± 0.12 | 0.84 ± 1.18 | 1.06 ± 0.48 | 0.29 | ± | 0.01 | 0.03 ± 0.004 | 0.11 ± 0.002 | 6.30 ± 1.48 | 3.51 ± 1.54 |
| 0.50 ± 0.00 | 7.32 ± 0.02 | 1.77 ± 2.51 | 2.62 ± 2.48 | 0.27 | ± | 0.02 | 0.03 ± 0.01 | 0.12 ± 0.001 | 6.48 ± 1.25 | 3.51 ± 1.58 |
| 1.00 ± 0.00 | 7.30 ± 0.00 | 4.04 ± 5.71 | 3.79 ± 4.12 | 0.24 | ± | 0.02 | 0.04 ± 0.002 | 0.13 ± 0.01 | 6.58 ± 0.74 | 3.49 ± 1.54 |
| 2.00 ± 0.00 | 7.34 ± 0.09 | 9.65 ± 13.64 | 10.44 ± 13.44 | 0.23 | ± | 0.04 | 0.04 ± 0.01 | 0.13 ± 0.01 | 7.43 ± 0.03 | 3.47 ± 1.51 |
| 4.00 ± 0.00 | 7.30 ± 0.01 | 19.22 ± 26.51 | 19.44 ± 26.16 | 0.20 | ± | 0.04 | 0.20 ± 0.25 | 0.24 ± 0.16 | 8.30 ± 1.44 | 3.33 ± 1.68 |
| 8.36 ± 0.39 | 7.27 ± 0.01 | 34.58 ± 48.23 | 35.08 ± 47.74 | 0.18 | ± | 0.04 | 0.04 ± 0.03 | 0.13 ± 0.01 | 10.58 ± 4.47 | 3.51 ± 1.62 |
| 11.04 ± 0.06 | 7.32 ± 0.05 | 46.40 ± 64.94 | 46.47 ± 63.85 | 0.17 | ± | 0.04 | 0.04 ± 0.03 | 0.13 ± 0.004 | 11.81 ± 6.41 | 3.44 ± 1.52 |
| 24.13 ± 0.18 | 7.27 ± 0.001 | 58.10 ± 81.49 | 57.54 ± 79.36 | 0.14 | ± | 0.05 | 0.05 ± 0.04 | 0.13 ± 0.01 | 13.70 ± 8.70 | 3.35 ± 1.65 |
| 47.99 ± 0.01 | 3.64 ± 5.11 | 60.44 ± 84.80 | 61.09 ± 84.06 | 0.13 | ± | 0.04 | 0.04 ± 0.03 | 0.13 ± 0.001 | 14.29 ± 9.31 | 3.43 ± 1.79 |
| 72.03 ± 0.04 | 7.29 ± 0.004 | 62.00 ± 87.01 | 63.00 ± 86.14 | 0.11 | ± | 0.03 | 0.03 ± 0.02 | 0.12 ± 0.001 | 14.24 ± 9.42 | 3.31 ± 1.96 |
| 172.73 ± 6.69 | 7.31 ± 0.04 | 62.16 ± 87.24 | 63.28 ± 86.43 | 0.07 | ± | 0.02 | 0.03 ± 0.02 | 0.12 ± 0.01 | 14.21 ± 9.10 | 3.15 ± 2.28 |

| 0.5 mM F initial - 50.0 mM Cl | | | | | | | | | | | |
|-------------------------------|--------------|------------------|------------------------------|------------------|-------------------------|--------------------------------------|-------------------------|-------------------------|--|--|--|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | F _{tot} | Ca _{tot} mM | PO ₄ _{tot} mM | Na _{tot} mM | Cl _{tot} mM | | | |
| | | | | mM | | | | | | | |
| | | | | 0.50 ± 0.00 | | | | | | | |
| | | | | | 0.07 ± 0.001 | 0.00 ± 0.00 | | | | | |
| 0.00 ± 0.00 | 7.58 ± 0.28 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.33 ± 0.01 | - | 0.08 ± 0.01 | 35.07 ± 0.52 | 48.76 ± 2.58 | | | |
| 0.04 ± 0.01 | 7.39 ± 0.02 | 0.00 ± 0.00 | 0.18 ± 0.16 | 0.29 ± 0.03 | - | 0.09 ± 0.03 | 35.17 ± 1.03 | 48.88 ± 2.74 | | | |
| 0.09 ± 0.04 | 7.36 ± 0.10 | 0.00 ± 0.00 | 0.45 ± 0.37 | 0.28 ± 0.02 | - | 0.10 ± 0.02 | 35.55 ± 0.93 | 48.88 ± 2.74 | | | |
| 0.13 ± 0.06 | 7.31 ± 0.12 | 0.18 ± 0.25 | 0.48 ± 0.31 | 0.29 ± 0.01 | - | 0.08 ± 0.01 | 37.35 ± 1.42 | 48.88 ± 2.74 | | | |
| 0.20 ± 0.07 | 7.31 ± 0.03 | 0.29 ± 0.41 | 0.69 ± 0.54 | 0.27 ± 0.01 | - | 0.09 ± 0.01 | 38.07 ± 0.91 | 48.88 ± 2.74 | | | |
| 0.38 ± 0.19 | 7.30 ± 0.03 | 0.54 ± 0.76 | 0.91 ± 0.84 | 0.26 ± 0.02 | - | 0.11 ± 0.04 | 38.46 ± 2.94 | 48.88 ± 2.74 | | | |
| 0.75 ± 0.35 | 7.27 ± 0.01 | 0.97 ± 1.37 | 1.27 ± 1.36 | 0.24 ± 0.01 | - | 0.09 ± 0.01 | 39.95 ± 1.55 | 54.27 ± 4.09 | | | |
| 1.50 ± 0.71 | 7.29 ± 0.11 | 2.27 ± 3.08 | 2.30 ± 2.81 | 0.23 ± 0.005 | - | 0.09 ± 0.01 | 41.85 ± 1.12 | 56.00 ± 4.12 | | | |
| 3.04 ± 1.47 | 7.28 ± 0.03 | 2.78 ± 2.58 | 2.39 ± 2.93 | 0.21 ± 0.01 | - | 0.10 ± 0.01 | 41.87 ± 1.30 | 56.00 ± 4.12 | | | |
| 6.08 ± 2.95 | 7.32 ± 0.001 | 3.07 ± 2.90 | 2.39 ± 2.93 | 0.20 ± 0.002 | - | 0.11 ± 0.02 | 43.02 ± 1.14 | 56.00 ± 4.12 | | | |
| 11.26 ± 4.61 | 7.39 ± 0.05 | 3.49 ± 3.50 | 2.45 ± 2.84 | 0.18 ± 0.003 | - | 0.09 ± 0.01 | 44.15 ± 2.08 | 60.03 ± 5.10 | | | |
| 17.47 ± 9.15 | 7.32 ± 0.03 | 3.95 ± 4.15 | 2.77 ± 2.39 | 0.17 ± 0.01 | - | 0.09 ± 0.0003 | 46.47 ± 1.16 | 60.89 ± 4.81 | | | |
| 35.96 ± 17.03 | 7.31 ± 0.004 | 3.95 ± 4.15 | 3.00 ± 2.06 | 0.15 ± 0.01 | - | 0.10 ± 0.02 | 49.29 ± 1.40 | 63.15 ± 1.63 | | | |
| 60.23 ± 17.18 | 7.09 ± 0.27 | 34.26 ± 47.02 | 33.69 ± 45.31 | 0.09 ± 0.04 | - | 0.16 ± 0.10 | 51.71 ± 0.78 | 61.80 ± 3.54 | | | |
| 108.13 ± 51.09 | 7.31 ± 0.004 | 35.52 ± 48.80 | 34.61 ± 44.78 | 0.06 ± 0.03 | - | 0.10 ± 0.01 | 53.81 ± 0.87 | 61.80 ± 3.54 | | | |
| 168.12 ± 0.16 | 7.32 ± 0.04 | 35.52 ± 48.80 | 35.13 ± 44.98 | 0.05 ± 0.03 | - | 0.12 ± 0.03 | 57.81 ± 0.89 | 69.01 ± 6.67 | | | |

(-) below detection limit

| 0.5 mM F initial - 5.0 mM HCO ₃ | | | | | | | | | | | |
|--|-------------|------------------|------------------------------|------------------|-------------------|--------------|--|--------------------------------|-------------|--|-----|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | F _{tot} | Ca _{tot} | | | PO ₄ _{tot} | | | DIC |
| | | | | mM | | | | | | | |
| | | | | 0.50 ± 0.00 | 0.12 ± 0.04 | 0.00 ± 0.00 | | | | | |
| 0.00 ± 0.00 | 7.45 ± 0.02 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.37 ± 0.02 | 0.05 ± 0.01 | 0.12 ± 0.01 | | | 4.41 ± 0.54 | | |
| 0.03 ± 0.00 | 7.44 ± 0.02 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.35 ± 0.02 | 0.05 ± 0.01 | 0.12 ± 0.01 | | | 4.65 ± 0.99 | | |
| 0.08 ± 0.00 | 7.37 ± 0.03 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.34 ± 0.02 | 0.06 ± 0.01 | 0.13 ± 0.01 | | | 4.02 ± 1.68 | | |
| 0.17 ± 0.00 | 7.34 ± 0.04 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.33 ± 0.02 | 0.04 ± 0.01 | 0.13 ± 0.01 | | | 3.39 ± 2.38 | | |
| 0.25 ± 0.00 | 7.33 ± 0.05 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.32 ± 0.02 | 0.07 ± 0.01 | 0.14 ± 0.003 | | | 3.54 ± 1.56 | | |
| 0.53 ± 0.01 | 7.32 ± 0.06 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.31 ± 0.02 | 0.06 ± 0.03 | 0.14 ± 0.02 | | | 3.68 ± 0.74 | | |
| 1.09 ± 0.11 | 7.32 ± 0.05 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.29 ± 0.02 | 0.06 ± 0.02 | 0.14 ± 0.01 | | | 3.85 ± 0.95 | | |
| 2.00 ± 0.00 | 7.30 ± 0.04 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.28 ± 0.02 | 0.03 ± 0.003 | 0.14 ± 0.01 | | | 4.01 ± 1.17 | | |
| 4.12 ± 0.07 | 7.29 ± 0.01 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.26 ± 0.02 | 0.05 ± 0.02 | 0.15 ± 0.004 | | | 3.67 ± 0.07 | | |
| 24.00 ± 0.00 | 7.30 ± 0.01 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.22 ± 0.02 | 0.03 ± 0.01 | 0.15 ± 0.001 | | | 3.34 ± 1.02 | | |
| 48.03 ± 0.07 | 7.31 ± 0.03 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.19 ± 0.02 | 0.17 ± 0.21 | 0.22 ± 0.10 | | | 4.05 ± 0.10 | | |
| 119.99 ± 0.13 | 7.38 ± 0.11 | 0.02 ± 0.03 | 0.00 ± 0.00 | 0.16 ± 0.03 | 0.03 ± 0.004 | 0.17 ± 0.002 | | | 4.76 ± 1.23 | | |
| 169.63 ± 0.18 | 7.34 ± 0.05 | 0.17 ± 0.06 | 0.00 ± 0.00 | 0.15 ± 0.03 | 0.05 ± 0.02 | 0.20 ± 0.003 | | | 4.33 ± 1.29 | | |

| 0.5 mM F initial - 50.0 mM HCO ₃ | | | | | | | | | |
|---|--------------|------------------|------------------------------|------------------|-------------------|--------------------------------|---------------|--|--|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | F _{tot} | Ca _{tot} | PO ₄ _{tot} | DIC | | |
| | | | | mM | | | | | |
| | | | | 0.50 ± 0.00 | | | | | |
| | | | | | 0.16 ± 0.05 | 0.00 ± 0.00 | | | |
| 0.00 ± 0.00 | 7.36 ± 0.08 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.37 ± 0.02 | 0.14 ± 0.08 | 0.19 ± 0.05 | 21.03 ± 6.12 | | |
| 0.04 ± 0.01 | 7.33 ± 0.10 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.35 ± 0.01 | 0.08 ± 0.0002 | 0.17 ± 0.01 | 21.14 ± 6.27 | | |
| 0.08 ± 0.00 | 7.36 ± 0.03 | 0.08 ± 0.11 | 0.00 ± 0.00 | 0.35 ± 0.01 | 0.08 ± 0.001 | 0.17 ± 0.01 | 20.98 ± 6.80 | | |
| 0.17 ± 0.00 | 7.26 ± 0.02 | 0.08 ± 0.11 | 0.00 ± 0.00 | 0.33 ± 0.01 | 0.09 ± 0.002 | 0.18 ± 0.01 | 17.24 ± 1.51 | | |
| 0.25 ± 0.00 | 7.29 ± 0.02 | 0.70 ± 0.57 | 0.00 ± 0.00 | 0.33 ± 0.01 | 0.10 ± 0.03 | 0.18 ± 0.001 | 13.54 ± 3.83 | | |
| 0.52 ± 0.02 | 7.26 ± 0.01 | 1.77 ± 1.92 | 0.00 ± 0.00 | 0.32 ± 0.01 | 0.12 ± 0.06 | 0.20 ± 0.04 | 18.64 ± 3.38 | | |
| 1.03 ± 0.04 | 7.28 ± 0.001 | 3.32 ± 3.61 | 0.00 ± 0.00 | 0.30 ± 0.01 | 0.08 ± 0.02 | 0.19 ± 0.001 | 23.97 ± 10.28 | | |
| 2.05 ± 0.07 | 7.28 ± 0.01 | 3.42 ± 3.48 | 0.00 ± 0.00 | 0.29 ± 0.01 | 0.06 ± 0.01 | 0.19 ± 0.01 | 25.47 ± 12.40 | | |
| 4.26 ± 0.18 | 7.28 ± 0.01 | 7.50 ± 4.36 | 0.00 ± 0.00 | 0.27 ± 0.01 | 0.03 ± 0.04 | 0.25 ± 0.07 | 28.51 ± 12.35 | | |
| 8.03 ± 0.04 | 7.28 ± 0.01 | 11.63 ± 4.07 | 0.00 ± 0.00 | 0.25 ± 0.01 | 0.07 ± 0.01 | 0.21 ± 0.01 | 31.21 ± 16.17 | | |
| 24.54 ± 0.18 | 7.28 ± 0.03 | 17.70 ± 3.30 | 0.00 ± 0.00 | 0.23 ± 0.01 | 0.06 ± 0.00 | 0.23 ± 0.03 | 43.85 ± 5.93 | | |
| 73.03 ± 0.04 | 7.27 ± 0.01 | 19.14 ± 5.33 | 0.00 ± 0.00 | 0.20 ± 0.01 | 0.50 ± 0.63 | 0.39 ± 0.23 | 44.23 ± 6.47 | | |
| 120.05 ± 0.05 | 7.27 ± 0.001 | 19.18 ± 5.39 | 0.00 ± 0.00 | 0.18 ± 0.01 | 0.06 ± 0.002 | 0.27 ± 0.04 | 49.44 ± 0.18 | | |
| 194.93 ± 0.02 | 7.30 ± 0.01 | 19.21 ± 5.43 | 0.00 ± 0.00 | 0.17 ± 0.01 | 0.08 ± 0.04 | 0.30 ± 0.04 | 49.82 ± 0.48 | | |

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Chapter

3

Characterization of Calcium-Phosphates Precipitated in Absence and Presence of Fluoride on Strontium Hydroxyapatite and Strontium Carbonate

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Abstract

Previous studies of the heterogeneous precipitation of calcium-phosphate phases have generally used HAP as a seeding template to simulate bone or teeth surfaces. The use of a seed material with a composition similar to that of the precipitate makes it difficult to differentiate the newly-precipitated phase from the seed by solid characterization techniques. This can be facilitated by using calcium-free seeds, such as strontium hydroxyapatite ($\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$, SrHAP) or strontium carbonate (SrCO_3).

Different ratios of calcium-to-phosphate (Ca/P) were added to SrHAP suspensions and reacted at pH 7.3 (25°C) over 3d. Analogous experiments were performed with various calcium-to-phosphate-to-fluoride (Ca/P/F) ratios with SrHAP or SrCO_3 as seeding templates. The final precipitates were examined with XPS, XRD, FTIR, X-ray Absorption Near Edge Structure spectroscopy (XANES), and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy.

Independent of added Ca/P ratios, the predominant phase in the absence of F was found to be HAP, possibly in a calcium-deficient form or as a mixture with brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) or β -tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$, β -TCP). In the presence of F, fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, FAP) was found to predominate, but some evidence indicated fluorite (CaF_2) precipitation in SrCO_3 -based systems.

3.1 Introduction

Heterogeneous precipitation processes of calcium-phosphate phases, particularly of HAP, have been widely investigated because of their importance in medical bone treatment and dentistry.¹⁻³ Their potential application for the removal of elevated concentrations of fluoride from drinking water has also been explored.⁴⁻⁹ However, the identification of the precipitated solid(s) in previous studies has been complicated by

the use of HAP as the seeding template and it remains to be determined whether or not the initial dissolved calcium-to-phosphate (Ca/P) ratio affects the calcium-phosphate product formed.

Since HAP is the principal component of bones and teeth,¹⁰ it has been used as the seeding template in most prior studies of heterogeneous precipitation processes. In some of these studies, calcium (Ca) and phosphate (PO₄) were added at an initial Ca/P ratio of 1.67, stoichiometric for HAP^{11, 12} and FAP,^{13, 11} in order to induce the formation of these minerals or to investigate intermediates formed during the precipitation process in saturated solutions. In other studies, the Ca/P ratios were chosen to be stoichiometric for other solids, specifically a Ca/P ratio of 1.00 for brushite,^{2, 3, 11} 1.33 for octacalcium phosphate (Ca₈H₂(PO₄)₆*5H₂O, OCP)¹¹ and 1.50 for β -tricalcium phosphate (β -Ca₃(PO₄)₂, β -TCP).¹⁴ The elemental ratios of the precipitated solids were determined from the observed elemental losses from solution but they did not always agree with the ratios that were expected.^{2, 11, 12, 14} Potential partial seed dissolution was not considered in these studies.

In experiments carried out with Ca/P ratios of 1.67, brushite¹⁻³ or OCP¹² were observed as intermediates that subsequently dissolved and re-precipitated as the thermodynamically-stable product (HAP in calcium-phosphate systems or FAP in calcium-phosphate-fluoride systems)¹⁵ at adequate equilibration times. However, phase formation and the occurrence of intermediates appear to be dependent on the degree of supersaturation for calcium-phosphate precipitation,¹² ionic strength,¹² the presence of dissolved fluoride (F),^{1, 11, 13} surface area of seeding template,^{2, 3, 11-14} reaction time,^{3, 12, 14} and solution pH^{2, 3}, while most studies were conducted at physiological (7.4)¹¹⁻¹³ or acidic (5.0-5.5)^{1, 3} pH. The formed phases were identified with XRD,^{1, 11-14} FTIR¹¹⁻¹³ and/or Scanning Electron Microscopy (SEM).^{1-3, 11, 13, 14} However, the difficulty of

distinguishing between newly-precipitated calcium-phosphate phases and calcium-phosphate minerals used as seeding templates could be facilitated by the use of calcium-free seeding templates, specifically SrCO_3 and SrHAP.

Previous studies of SrHAP were performed in the context of treatment for osteoporosis, where strontium (Sr) is used as a substitute for Ca.¹⁶ Also some solid-solution studies have been performed to evaluate potential bone stability as function of the degree of Sr substitution within the HAP crystal structure.¹⁷ The crystal structure of SrHAP ($a=b$: 9.745 Å and c : 7.265 Å)¹⁸ is similar to that of HAP ($a=b$: 9.4166 Å and c : 6.8745 Å)¹⁹ with the slightly larger unit cell size of SrHAP resulting from the larger ionic radius of the Sr cation (Ca: 11.4 Å; Sr: 13.2 Å).²⁰ Otherwise, SrHAP has not received as much attention as HAP, primarily since it has fewer applications and, to our knowledge, it is not available as a commercial product.

The purpose of the current study was to investigate the heterogeneous precipitation of calcium-phosphate phases with different initial Ca/P ratios using Ca-free seeding templates and in presence and absence of dissolved fluoride (F) under conditions relevant for F removal from drinking water (pH 7.3, 25°C). As an alternative to SrHAP, SrCO_3 has also been used: i) to test the importance of an apatitic seeding template and ii) because calcite is commonly present in fluoride removal filter systems. Solutes were added in Ca/P ratios corresponding to the stoichiometric ratios of brushite, β -TCP, HAP or FAP. The possibility of CaF_2 precipitation was also investigated. The surface and bulk composition of the final precipitates were characterized using XPS, XRD, FTIR, XANES, and EXAFS. Filtered solutions were analyzed in order to compare elemental losses from solution with solid composition.

3.2 Experimental Section

Chemicals and Materials

All chemicals used were of at least “pro analysi” grade (p.a., from Merck and Fluka). Nanopure water (Barnstead NANOpure Diamond UV, resistivity $> 18\text{M}\Omega\text{-cm}$) was used for rinsing and solution preparations. Acid-washed (0.65% HNO_3 followed by ≥ 3 rinses with nanopure water) polyethylene (PE) vessels were used for solution preparation and storage. The solid reference samples were brushite (Fluka), FAP,²¹ fluorite (CaF_2 , AlfaAesar), HAP,²¹ monetite (CaHPO_4 , Fluka), SrCO_3 (Merck), SrHAP (Chapter 4), and β -TCP (Cerros).

Batch experiments

Batch experiments for calcium-phosphate precipitations were conducted analogous to those described in Sternitzke et al. 2012.²¹ The experiments were performed in duplicate in open systems (atmospheric p_{CO_2}) at $25 \pm 1^\circ\text{C}$ with SrHAP or SrCO_3 (2 g L^{-1}) in nanopure water. In total ten different samples were prepared (Table 3.1).

The suspensions were stirred by a suspended magnetic stirrer to avoid sample grinding. Solution pH was controlled at 7.3 ± 0.5 with 0.1 M HNO_3 and 0.1 M NaOH , using titration units (665, 725, and 842 with Metrohm software Tiamo 1.2.1) coupled to pH meters (Metrohm 691 and 713) and electrodes (Metrohm 6.0259.100 and 6.0258.010). Electrode two-point calibrations were performed at the start of each experiment by using Titrisol buffers (pH 4 and 9) and checked by measuring a pH 7 buffer (Titrisol). After dispersion for 10 min, dissolved Ca and PO_4 were added to the SrHAP/ SrCO_3 suspensions from 0.5 M $\text{Ca}(\text{NO}_3)_2$, 0.3 M $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, 0.3 M Na_2HPO_4 , and 0.4 M NaF stock solutions to achieve initial Ca, PO_4 and F concentration ratios as listed in Table 3.1. For F and elemental analysis, filtered ($0.2\text{-}\mu\text{m}$ nylon, PALL) samples of 12 mL were taken over 3d, with more intensive sampling in the

initial 24h. After 1d, dissolved concentrations did not vary more than 5% and precipitation experiments were equilibrated over 3d. (It should be noted that particles with a size of $< 0.2 \mu\text{m}$ could have passed through the filter to increase the dissolved elemental concentrations). Samples (20 mL) for total dissolved inorganic carbon (DIC) analysis were taken prior to the addition of the stock solutions and at the end of the 3d-reaction time. For Ca, P and Sr analysis, samples were acidified with 1% suprapure HNO_3 and stored at 4°C until analysis. All measured concentrations were corrected to account for volume variations due to sampling and pH adjustment. The solid material was collected on a $0.45\text{-}\mu\text{m}$ cellulose-nitrate filter (Sartorius), air-dried, and stored at room temperature for further analysis.

Elemental analysis

Methods of elemental analyses, including DIC are described in Sternitzke et al. 2012.²¹

Solid characterization

Analyses by XPS, XRD and FTIR were performed for all precipitates and for the reference samples HAP, FAP, SrHAP, SrCO_3 and CaF_2 in single measurements as described in Sternitzke et al. 2012.²¹ For FTIR analysis different parameters were used. The spectra were recorded at a velocity of 10 kHz, with a filter of 1.2 kHz, UDR 2, a resolution of 2, an aperture of 0.25 cm^{-1} and a sensitivity of 16. The signal was approximately -3.77 counts. The spectra were compared with those obtained from ground mixtures of the references HAP and SrHAP (1/3, 1/1, 3/1). All FTIR data were normalized to the baseline.

The XPS analyses were performed on the surfaces of the solids. Reference data of HAP and FAP were used from the analyses performed in Sternitzke et al. 2012.²¹

X-ray Absorption Fine Structure analyses were conducted at the Ca K-edge on the PHOENIX beamline at the Swiss Light Source (SLS, Paul Scherrer Institut PSI, Switzerland). About 70 mg of the air-dried powdered solids were pressed into discs of 10 mm diameter; the reference samples (HAP, FAP, CaF_2 , β -TCP, brushite and monetite) were diluted with cellulose powder to obtain 3% Ca in each sample. The pressed samples were glued with double-sided sticky carbon tape onto a copper sample plate, which was set at an angle of 45° with respect to the incoming beam and the fluorescence detector. The spectra were collected in an energy range between 4000 and 4760 eV with an energy step size of 2 eV in the pre-edge, 0.25 eV in the XANES and an increasing step size up to 5 eV in the EXAFS region. A dwell time of up to 6 seconds was applied for each point. A Si (111) double crystal monochromator provided an energy resolution of about 0.6 eV. The beam size was $1 \times 1 \text{ mm}^2$ and the measurements were performed at a temperature of 25°C under vacuum with a residual pressure of about 5×10^{-5} mbar. The fluorescence signal was detected by a four-element silicon drift detector and corrected for dead-time effects. A calibration of the x-ray energy used the first inflection point of a Ti K-edge spectrum and was set to 4966 eV. The data were normalized to the incoming flux by recording the total electron yield of a $0.5 \text{ }\mu\text{m}$ thick polyethylene foil covered by a 50 nm thick Ni-layer.

The IFEFFIT package was used for analysis.²² A linear pre-edge was subtracted from the data, which were then normalized to a unit step by 3rd polynomial fit to the post-edge data.

3.3 Results and Discussion

This study examined the heterogeneous precipitation of Ca-containing solids on Ca-free seeding templates of SrHAP and SrCO_3 . Dissolved Ca and PO_4 were added in different Ca/P ratios at concentrations that exceeded saturation with respect to brushite,

β -TCP, OCP and HAP. For both seeding templates, some experiments were also performed with added F; these systems were initially supersaturated with respect to brushite, β -TCP, OCP, HAP, FAP, and CaF_2 . Solutes were added in varying ratios, corresponding to the stoichiometric ratios of possible precipitates. In general, PO_4 was added at, or in excess of, the stoichiometric ratio for HAP and/or FAP precipitation. The experimental conditions can be summarized as follows (see also Table 3.1):

| | |
|---|--|
| HAP_SrHAP: | Ca/P = 5/3; PO_4 stoichiometric for HAP |
| β -TCP_SrHAP: | Ca/P = 5/3.33; PO_4 in excess for HAP, stoichiometric for β -TCP |
| brushite_SrHAP: | Ca/P = 5/5; PO_4 in excess for HAP and β -TCP, stoichiometric for brushite |
| non-stoich_SrHAP: | Ca/P = 2/4; non-stoichiometric |
| FAP_SrHAP and FAP_SrCO ₃ : | Ca/P/F = 5/3/1, stoichiometric for FAP |
| FAP-HAP_SrCO ₃ and FAP-HAP_SrCO ₃ : | Ca/P/F = 5/3/0.5, F-limited for FAP, Ca/P stoichiometric for FAP/HAP |
| FAP-CaF ₂ _SrHAP and FAP-CaF ₂ _SrCO ₃ : | Ca/P/F = 6/3/3, PO_4 -limited (based on <i>added</i> PO_4) for FAP, excess Ca/F stoichiometric for CaF_2 |

For experiments with the SrHAP template, the seed itself can also serve as a source of PO_4 to the solution. Thus, only experiment FAP-CaF₂_SrCO₃ (with the SrCO₃ template) was truly PO_4 limited.

The precipitated products were collected after 3d for solid phase analysis. Filtered solutions were analyzed so that elemental losses from solution could be compared with the detected solids.

Table 3.1 Summary of all samples: added Ca, PO₄ (and F) concentrations, ideal, added and precipitated molar Ca/P ratios, used seeding templates and saturation indices for all potential phases at pH 7.3

| sample name | | type of seed | added Ca:PO ₄ or Ca:PO ₄ :F concentrations [mM] | ideal | Molar Ca/P | | saturation indices | | | | | | | |
|---|---|-------------------|---|-------|--------------------|---------------------|--------------------|-------------------|--------------------|-------------------|-------------------|-------------------|------------------|-------------------|
| | | | | | added ^c | precip ^d | HAP | CaF ₂ | FAP | CaCO ₃ | SrCO ₃ | brushite | OCP | β-TCP |
| HAP_SrHAP | a | SrHAP | 5:3 | 1.67 | 1.60±0.01 | 1.56±0.03 | 8.01±7.65 | | | -1.69±-2.89 | -1.70±-2.08 | 0.29±-0.62 | 4.40±3.99 | 3.95±3.40 |
| | b | | stoichiometric for HAP | | | | -0.17±-0.04 | | | -2.45±-2.63 | -1.00±-1.14 | -2.15±-2.88 | -3.42±-3.46 | -1.47±-1.48 |
| β-TCP_SrHAP | a | SrHAP | 5:3.33 | 1.50 | 1.44±0.02 | 1.46±0.10 | 8.05±6.07 | | | -1.70±-4.13 | -1.74±-2.06 | 0.31±-2.08 | 4.44±2.47 | 3.98±1.84 |
| | b | | stoichiometric for β-TCP; PO ₄ in excess for HAP | | | | -2.55±-2.93 | | | -1.33±-1.89 | -1.37±-3.03 | -1.53±-1.77 | -0.34±-0.61 | |
| brushite_SrHP | a | SrHAP | 5:5 | 1.00 | 0.98±0.003 | 1.51±0.18 | 8.40±5.30 | | | -1.72±-4.54 | -1.80±-2.40 | 0.43±-2.93 | 4.78±1.75 | 4.21±1.00 |
| | b | | stoichiometric for brushite; PO ₄ in excess for HAP and β-TCP | | | | -3.15±-4.07 | | | -1.76±-2.69 | -1.36±-1.86 | -1.96±-1.99 | -0.81±-0.95 | |
| non-stoich_SrHAP | a | SrHAP | 2:1 | 0.50 | 0.48±0.0005 | 1.16±0.48 | 6.72±3.76 | | | 0.72±0.87 | 1.01±1.16 | 0.12±-3.43 | 3.48±0.48 | 3.22±0.06 |
| | b | | non-stoichiometric | | | | -0.30±-0.15 | | | 1.26±1.41 | -1.10±-1.55 | -1.23±-1.26 | -0.33±-0.48 | |
| FAP_SrHAP | a | SrHAP | 5:3:1 | 1.67 | 1.62±0.01 | 1.66±0.50 | 7.91±5.91 | 1.38±-0.47 | 14.47±12.72 | -1.70±-4.49 | -1.83±-3.29 | 0.26±-2.13 | 4.29±2.33 | 3.89±1.73 |
| | b | | stoichiometric for FAP | | | | -2.36±-2.89 | - | - | -3.00±-3.52 | -1.25±-1.80 | -2.23±-2.75 | -4.53±-5.05 | -2.50±-3.02 |
| FAP-HAP_SrHAP | a | SrHAP | 5:3:0.5 | 1.67 | 1.62±0.01 | 1.52±0.01 | 7.94±5.32 | 0.78±-1.84 | 14.19±11.46 | -1.70±-4.47 | -1.60±-2.49 | 0.27±-2.61 | 4.32±1.80 | 3.90±1.17 |
| | b | | F-limited for FAP; Ca/P stoichiometric for HAP/FAP | | | | -1.39±-1.58 | - | - | -2.57±-2.78 | -1.31±-1.70 | -2.19±-2.69 | -4.01±-5.05 | -2.02±-2.75 |
| FAP-CaF ₂ _SrHAP | a | SrHAP | 6:3:3 | 2.00 | 3.87±0.01 | 1.90±0.003 | 8.07±7.54 | 2.39±1.86 | 15.10±14.57 | -1.67±-2.19 | -1.83±-2.35 | 0.26±-0.26 | 4.37±3.85 | 3.96±3.44 |
| | b | | PO ₄ -limited for FAP (based on added PO ₄); excess Ca/F stoichiometric for CaF ₂ | | | | -5.73±-6.25 | -1.22±-1.75 | 0.13±-0.39 | -2.90±-3.42 | -1.39±-1.92 | -3.43±-3.95 | -7.96±-8.49 | -4.78±-5.31 |
| FAP_SrCO ₃ | a | SrCO ₃ | 5:3:1 | 1.67 | 1.67±0.00 | 1.49±0.03 | 7.73±4.21 | 1.36±-2.05 | 14.28±10.96 | -0.93±-5.67 | -1.31±-2.61 | 0.20±-4.66 | 4.12±0.33 | 3.77±-0.04 |
| | b | | stoichiometric for FAP | | | | -1.58±-1.44 | -1.57±-1.65 | 3.99±4.14 | -1.83±-2.22 | 0.22±-0.02 | -2.47±-2.55 | -4.33±-4.18 | -2.27±-2.14 |
| FAP-HAP_SrCO ₃ | a | SrCO ₃ | 5:3:0.5 | 1.67 | 1.67±0.00 | 1.49±0.01 | 7.75±4.38 | 0.76±-3.02 | 14.00±10.68 | -0.92±-5.22 | -1.31±-3.35 | 0.21±-3.77 | 4.14±0.70 | 3.78±0.20 |
| | b | | F-limited for FAP; Ca/P stoichiometric for FAP/HAP | | | | -1.85±-1.86 | -3.37±-3.29 | 2.79±2.88 | -1.75±-2.53 | 0.16±-0.75 | -2.47±-3.18 | -4.60±-4.70 | -2.38±-2.57 |
| FAP-CaF ₂ _SrCO ₃ | a | SrCO ₃ | 6:3:3 | 2.00 | 2.00±0.00 | 1.71±0.02 | 7.96±7.31 | 2.37±0.74 | 14.98±14.34 | -0.88±-2.26 | -1.30±-2.17 | 0.23±-0.92 | 4.27±3.61 | 3.89±3.07 |
| | b | | PO ₄ -limited for FAP; excess Ca/F stoichiometric for CaF ₂ | | | | -3.86±-3.73 | 0.32±0.46 | 1.78±1.80 | -1.65±-3.00 | 0.32±-0.56 | -3.26±-3.32 | -6.61±-6.47 | -3.78±-3.69 |

(a) after 10min suspending before ions were added (potential saturation indices for HAP, CaF₂, FAP, CaCO₃, brushite, OCP, β-TCP); (b) after 3d reaction time; (c) corrected for partial SrHAP dissolution during pre-equilibration; (d) based on removed dissolved concentrations; bold: SI values indicate achieved saturation; (-): dissolved F concentration was below detection limit (0.1 μM).

Saturation indices were calculated according to $S = \log(IAP/K_{s0})^{1/\eta}$, where IAP is the ion activity product, K_{s0} is the solubility product and η is the number of ions in the formula unit of the considered mineral.⁴⁴ The IAP was adjusted for each individual sample; K_{s0} was corrected according to Davies for the individual activity coefficients. Hydroxyapatite (HAP): 5Ca²⁺ + 3PO₄³⁻ + OH⁻; log K_{s0HAP} = -53.28;⁴⁵ fluorite (CaF₂): Ca²⁺ + 2F⁻; log K_{s0CaF2} = -10.50;⁴⁶ fluorapatite (FAP): 5Ca²⁺ + 3PO₄³⁻ + F⁻; log K_{s0FAP} = -56.12;⁴⁵ calcium carbonate (CaCO₃): Ca²⁺ + CO₃²⁻; log K_{s0CaCO3} = -8.35;⁴⁶ strontium carbonate (SrCO₃): Sr²⁺ + CO₃²⁻; log K_{s0SrCO3} = -9.96;⁴⁷ brushite (CaHPO₄*2H₂O): Ca²⁺ + PO₄³⁻ + H⁺; log K_{s0brushite} = -19.0;⁴⁸ octa-calciumphosphate (OCP): Ca₄H(PO₄)₃*2H₂O; log K_{s0OCP} = -46.6;⁴⁹ β-tricalciumphosphate (β-TCP): 3Ca²⁺ + 2PO₄³⁻; log K_{s0TCP} = -28.92.⁵⁰

XPS

The surface composition of the precipitates determined by XPS is presented in Table 3.2. Strontium hydroxyapatite-based samples clearly showed signals assigned to SrHAP, while SrCO_3 -based precipitates showed SrCO_3 -assigned signals. In all precipitates, independent of the type of seeding template, additional signals occurred at binding energies that can be assigned to HAP/FAP. While both Sr-based seeding templates (SrHAP and SrCO_3) did not exhibit any Ca(2p) signal (confirming that they were Ca-free), all precipitates showed clear Ca signals (Table 3.2). These signals were significantly lower (16 - 49%) than those of the references HAP/FAP and the Sr signals were lower than those of the SrHAP/ SrCO_3 references. The detection of Ca and Sr at the surface of the precipitates and the observation that the (Sr + Ca)/P ratios of all SrHAP-based precipitates were between 1.67 (stoichiometric for SrHAP and HAP) and 1.99 (reference SrHAP) suggest that i) the XPS averaged over an area (approximately 0.02 mm^2) containing uncoated SrHAP seed and Ca-apatite precipitates, which may or may not be surface precipitates and/or ii) the XPS signal resulted from the depth of some bulk seed as well as the Ca-apatite surface precipitate (penetration depth of the beam is approximately 5 nm) and/or iii) some Sr is adsorbed or substituted for Ca at the surface of the new precipitate.

In SrCO_3 -based precipitates, where a P-free seed was used, P(2s) signals, specific to HAP/FAP were observed, although they were of lower intensity than for the references HAP/FAP. These findings would support alternatives i) and ii) since a P substitution within the SrCO_3 crystal structure would not result in an energy level specific for an apatitic phase. It must be noted that the reference SrCO_3 also showed a P signal, but this was of significantly lower intensity than in the SrCO_3 -based precipitates and probably originated from a surface contamination caused by sample preparation.

Precipitates obtained from F-containing batches (SrHAP-based and SrCO₃-based) showed the presence of F(1s) to varying degrees. An interpretation is complicated by the observed signal for F (0.43 ± 0.11 atm%; $n = 6$) in nominally F-free seeding templates and precipitates obtained from F-free suspensions..

Table 3.2 Surface composition [atm%] of references HAP, FAP, SrHAP, SrCO₃ and CaF₂ and of all precipitates obtained from XPS analysis.

| | O(1s) | F(1s) | Ca(2p) | P(2s) ^{b)} | Sr(3p) | C(1s) | (Sr+Ca)/P | Ca/P |
|---|-------|-------|--------|---------------------|--------|-------|-----------|------|
| HAP ^{a)} | 61.90 | 0.00 | 23.80 | 14.30 | - | ni | | 1.67 |
| FAP ^{a)} | 57.10 | 4.80 | 23.80 | 14.30 | - | ni | | 1.67 |
| CaF ₂ ^{a)} | 0.00 | 66.70 | 33.30 | 0.00 | - | ni | | |
| SrHAP ^{a)} | 61.90 | 0.00 | 0.00 | 14.30 | 23.80 | ni | | |
| SrCO ₃ ^{a)} | 60.00 | 0.00 | 0.00 | 0.00 | 20.00 | 20.00 | | |
| HAP | 65.70 | 0.00 | 20.20 | 14.10 | - | ni | | 1.43 |
| FAP | 60.80 | 4.00 | 21.00 | 14.20 | - | ni | | 1.47 |
| CaF ₂ | 0.00 | 63.70 | 36.30 | 0.00 | - | ni | | |
| SrHAP | 59.23 | 0.30 | 0.00 | 13.54 | 26.93 | ni | 1.99 | |
| SrCO ₃ | 57.39 | 0.55 | 0.00 | 0.36 | 25.14 | 16.57 | 69.83 | |
| HAP_SrHAP | 60.17 | 0.47 | 4.03 | 13.56 | 21.77 | ni | 1.90 | 0.30 |
| β-TCP_SrHAP | 61.35 | 0.45 | 8.10 | 14.11 | 15.99 | ni | 1.71 | 0.57 |
| brushite_SrHAP | 61.55 | 0.52 | 7.73 | 14.42 | 15.78 | ni | 1.63 | 0.54 |
| non-stoich_SrHAP | 61.82 | 0.30 | 3.25 | 12.88 | 21.76 | ni | 1.94 | 0.25 |
| FAP_SrHAP | 59.89 | 0.97 | 3.30 | 14.14 | 21.71 | ni | 1.77 | 0.23 |
| FAP-HAP_SrHAP | 59.94 | 1.18 | 7.79 | 14.83 | 16.25 | ni | 1.62 | 0.53 |
| FAP-CaF ₂ _SrHAP | 58.89 | 2.98 | 5.28 | 14.16 | 18.69 | ni | 1.69 | 0.37 |
| FAP_SrCO ₃ | 56.79 | 2.62 | 7.95 | 7.40 | 15.09 | 10.16 | 3.11 | 1.07 |
| FAP-HAP_SrCO ₃ | 59.05 | 1.79 | 8.82 | 8.90 | 12.83 | 8.61 | 2.43 | 0.99 |
| FAP-CaF ₂ _SrCO ₃ | 54.57 | 4.58 | 10.27 | 8.46 | 12.65 | 9.48 | 2.71 | 1.21 |

(a) nominal values for example: HAP = 5Ca + 3P + 13O = 21atoms → 13O = 61.90 atm%; (b) P(2p) for HAP, FAP, CaF₂ as data originates from different analysis as the rest of the samples; (-) not detected; (ni): carbon (C1s) was not included in compositional data analysis: average C contamination was 1.23 ± 0.73 atm% ($n = 7$) in all SrHAP-based precipitates. Samples of SrCO₃-based precipitates contained an average C content of 9.42 ± 0.78 atm% ($n = 3$), which was less than for the reference SrCO₃ sample (16.57 atm%) and was included in the data presentation. The signals of FAP_SrHAP and FAP-CaF₂_SrHAP did not exhibit sufficient intensity due to insufficient solid used for sample preparation. The detection limit is approximately 1.0 atm%. For originally F-free solids (HAP_SrHAP, β-TCP_SrHAP, brushite_SrHAP, non-stoich_SrHAP) F signals were detected, most probably due to contamination during sample preparation. These findings cause a background F contamination of about 0.5 atm% and thus, makes data evaluation difficult for the other samples.

An advantage of XPS is the detection of elemental binding energies specific for each substrate. Therefore, shifts of the binding energies of the Ca(2p) signal allow a distinction between HAP/FAP and CaF_2 . While the binding energies of the F-free samples HAP_SrHAP, β -TCP_SrHAP, brushite_SrHAP and non-stoich_SrHAP were consistent with HAP, the Ca(2p) in the F-containing SrHAP-based and SrCO_3 -based precipitates exhibited a shift toward CaF_2 (right-hand side of Figure 3.1), which is best observable for FAP_SrCO₃ and FAP- CaF_2 _SrCO₃. On the left-hand side of Figure 3.1, the CaF_2 signature appears to be largest for sample FAP- CaF_2 _SrCO₃ (which has F in excess of FAP).

Consequently, the findings by XPS support the hypothesis of HAP and/or FAP precipitation in all samples. In SrCO_3 -based samples, particularly in FAP- CaF_2 _SrCO₃, indications were found for the co-precipitation of CaF_2 .

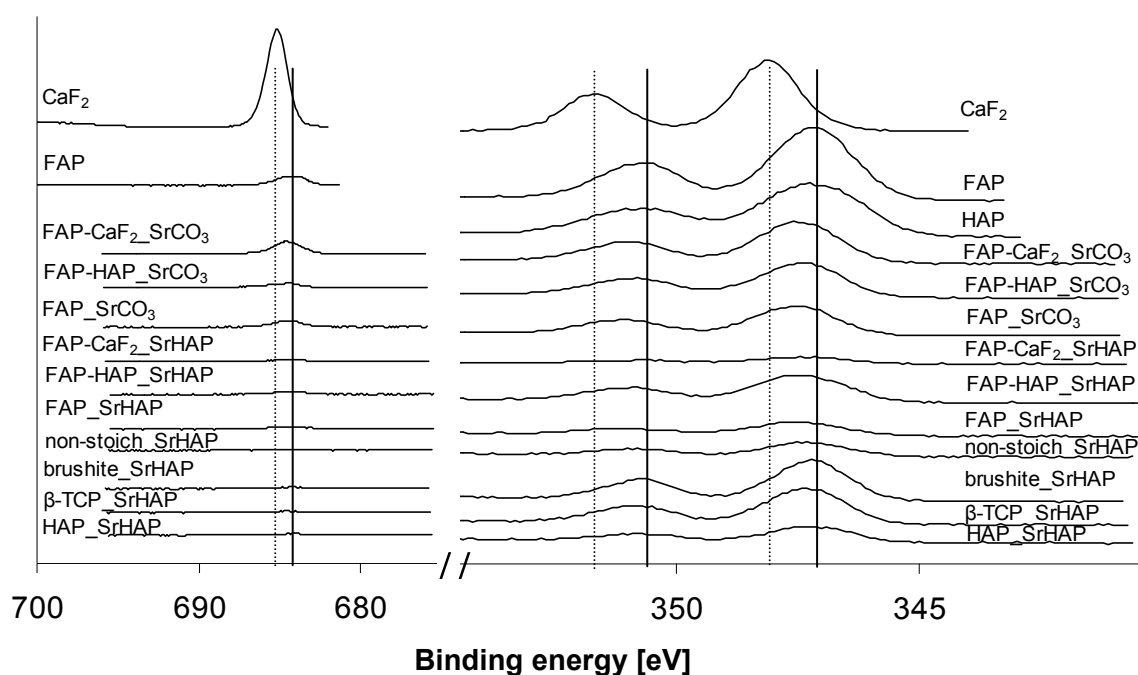


Figure 3.1 Normalized Ca(2p) intensities right and F(1s) intensities left of untreated surfaces of all precipitates compared to peak positions for HAP, FAP (highlighted by straight solid lines) and CaF_2 (straight dotted lines). The signals of FAP_SrHAP and FAP- CaF_2 _SrHAP did not exhibit sufficient intensity due to insufficient solid used for sample preparation.

XRD

The signatures of the seeding templates (SrHAP and SrCO₃) were clearly seen in the XRD patterns (Figure 3.2, 3S1 a-c). For the SrHAP-based precipitates, an additional weak peak was observed at 25.8° 2θ (Figure 3.2a and b). This corresponds with the 2θ for SrHAP. The shift to lower 2θ positions is associated with the replacement of the smaller Ca ion with the larger ion Sr ion. Normalized to the SrHAP (1 1 2) reflection at 30.6° 2θ the peak intensity corresponded to the amount of precipitate estimated by elemental loss from solution (roughly 5-11 wt% for the assumption of HAP precipitation or 11-12 wt% of FAP precipitation). The intensity may be partly influenced by the crystallinity of the precipitate, as was reported in a study of the homogeneous precipitation of HAP.²³ Although a peak for HAP at 25.8° 2θ was observed in this study, the (0 0 2) reflection for HAP has also been reported at 25.9° 2θ.^{19,24} Unambiguous assignment to HAP is further complicated by the reported reflections for β-TCP (1 0 10) at 25.8° 2θ²⁵ and 25.9° 2θ²⁶ and for OCP (2 0 0) at 25.9° 2θ.²⁷ The presence of β-TCP, however, would have resulted in the occurrence of relatively strong peaks at 10.9° (0 1 2), 13.6° (1 0 4) and 16.9° (1 1 0) 2θ (Figure 3S1d), which were not observed in any of the samples.²⁵ Since the XRD measurements were performed for 5-80° 2θ, the most intensive diffraction of OCP at 4.7° 2θ of the reflection (1 0 0) could not be detected and further peaks for OCP, particularly at 9.3 and 9.7° 2θ of the reflections (2 -1 1) and (3 0 1) were not observed (Figure 3S1a-d).²⁷

If brushite were present in the samples, a signal for the (1 4 -1) reflection would be expected at 29.3° 2θ and an appearance of the most intensive reflections ((0 2 0) and (1 2 -1)) of brushite would be expected at 11.7° and 20.9° 2θ.²⁸ These peaks were not observed even for sample brushite_SrHAP (Figure 3S1a-d).

In the samples containing F (SrHAP-based and SrCO₃-based), co-occurrence of HAP and FAP is possible that were formed separately or in solid solution, particularly for samples FAP-HAP_SrHAP and FAP-HAP_SrCO₃ in which the formation of FAP is F-limited. As the only observed peak at 25.8° 2θ is relatively broad, a clear distinction between HAP and FAP is difficult. Formation of CaF₂ might be expected for samples where FAP precipitation is PO₄ limited (FAP-CaF₂_SrHAP based on *added* PO₄ and FAP-CaF₂_SrCO₃), but overlapping peaks preclude identification of CaF₂ by XRD.

For samples precipitated on a SrCO₃ seeding template, the (0 2 1) reflection of SrCO₃²⁹ obscures any possible signal at 25.8° 2θ. The appearance of a shoulder adjacent to the (0 1 2) reflection of SrCO₃ at 31.6° 2θ²⁹ was observed in all SrCO₃-based precipitates (Figure 3.2c) consistent with the signatures of both HAP and FAP, which exhibit (2 1 1) and (1 1 2) reflections at 31.9 and 32.2° 2θ.²⁴ A similar signature could be due to formation of strontium hydrogen phosphate (SrHPO₄; (-1 2 1))³⁰, but this solid would only be expected to form under acidic conditions. Several weak peaks for OCP ((1 1 6), (1 0 6), (2 2 0), (2 2 1), and (1 3 1)) would appear at the same region.²⁷

The XRD patterns of the precipitated solids were consistent with the formation of HAP and/or FAP in all samples as found by XPS, but other solids (particularly OCP and β-TCP) would yield similar patterns. The presence of brushite could be excluded because of the absence of a peak at 25.5° 2θ, but CaF₂ could not be excluded due to spectral overlaps.

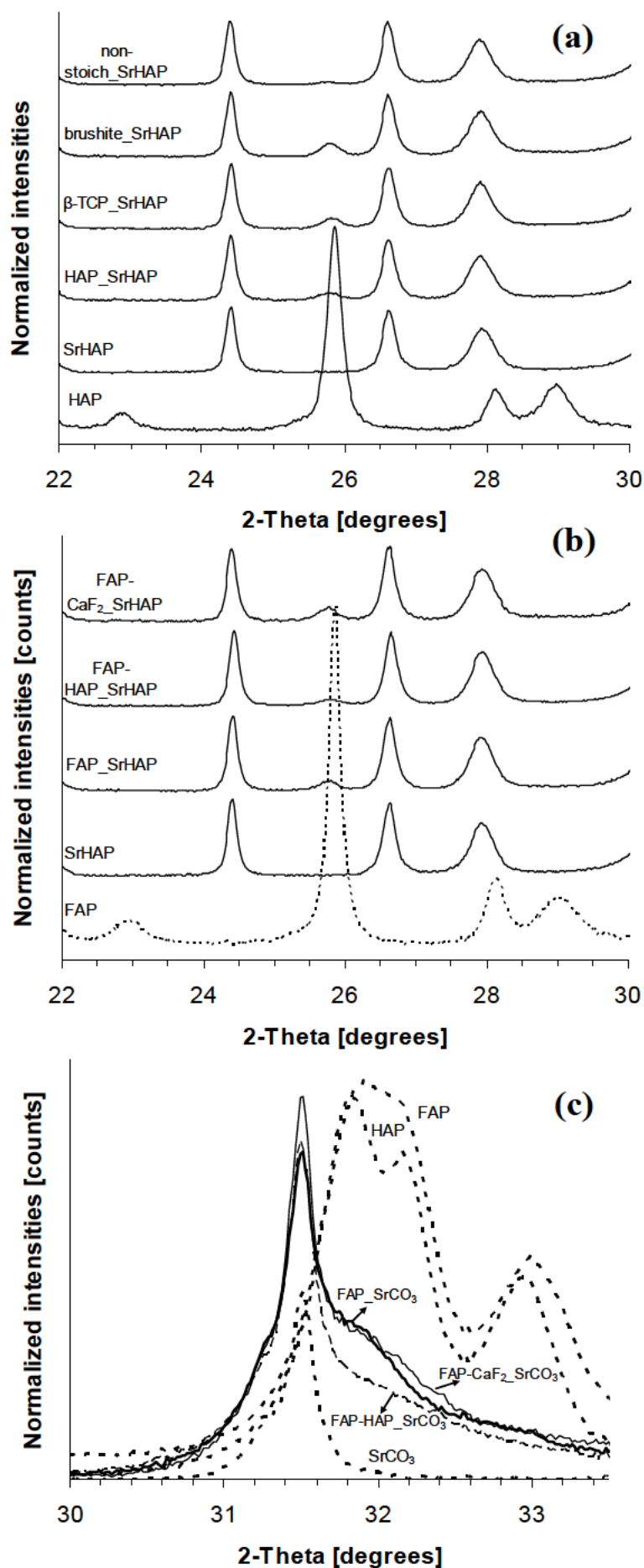


Figure 3.2 X-ray diffractograms of (a) references HAP and SrHAP compared with the SrHAP-based F-free precipitates; (b) references FAP and SrHAP with F-containing SrHAP-based precipitates; (c) diffractograms of the references FAP and SrCO₃ with all SrCO₃-based precipitates.

Diffractions of SrHAP and all SrHAP-based samples were normalized to 1 1 2 reflection of SrHAP at 30.6° 2 θ ; SrCO₃ and SrCO₃-based samples were normalized to (1 1 1) reflection at 25.1° 2 θ ; HAP and FAP were normalized to the (2 1 1) reflection at 31.8° 2 θ .

Another, more selective method to determine bulk composition of calcium-phosphates is FTIR spectroscopy. For all SrCO_3 -based precipitates a clear distinction between absorbances of carbonate³¹ and apatite³² were observed. While the carbonate-assigned absorbances decreased in intensity proportional to the amount precipitated, new absorbances of medium to strong intensity occurred at 565, 604, and 1030 cm^{-1} and a weak shoulder at 1104 cm^{-1} . At these wavenumbers PO-assigned absorbances of HAP/FAP were observed (Figure 3.3a, 3S3a, c and f) and the patterns were consistent with those obtained from physical mixtures of the references HAP and SrCO_3 in ratio 1/3, 1/1, and 3/1. In the same regions absorbances of OCP, β -TCP and brushite have been observed (Table 3S1).³² Although it is expected that strong absorbances of these phases (brushite: 525, 984, 1060, 1070, and 1132 cm^{-1} ; OCP: 1025, 1035, 1055, 1075, and 1105 cm^{-1} ; β -TCP: 972, 1041, and 1119 cm^{-1}) show patterns of at least medium intensity, it is possible that they were obscured by the broad and intense absorbances that most likely were assigned to HAP/FAP. Fowler et al. (1966)³² also observed absorbances of medium intensity for brushite at 788 and 1215 cm^{-1} and at 945 cm^{-1} for β -TCP, which were outside the regions of the absorbances observed in any of the samples. Since not even weak patterns were observed at 788, 1215 or 945 cm^{-1} , the presence of brushite and/or β -TCP is rather unlikely. The co-occurrence of OCP in SrCO_3 -based samples, however, cannot be entirely excluded.

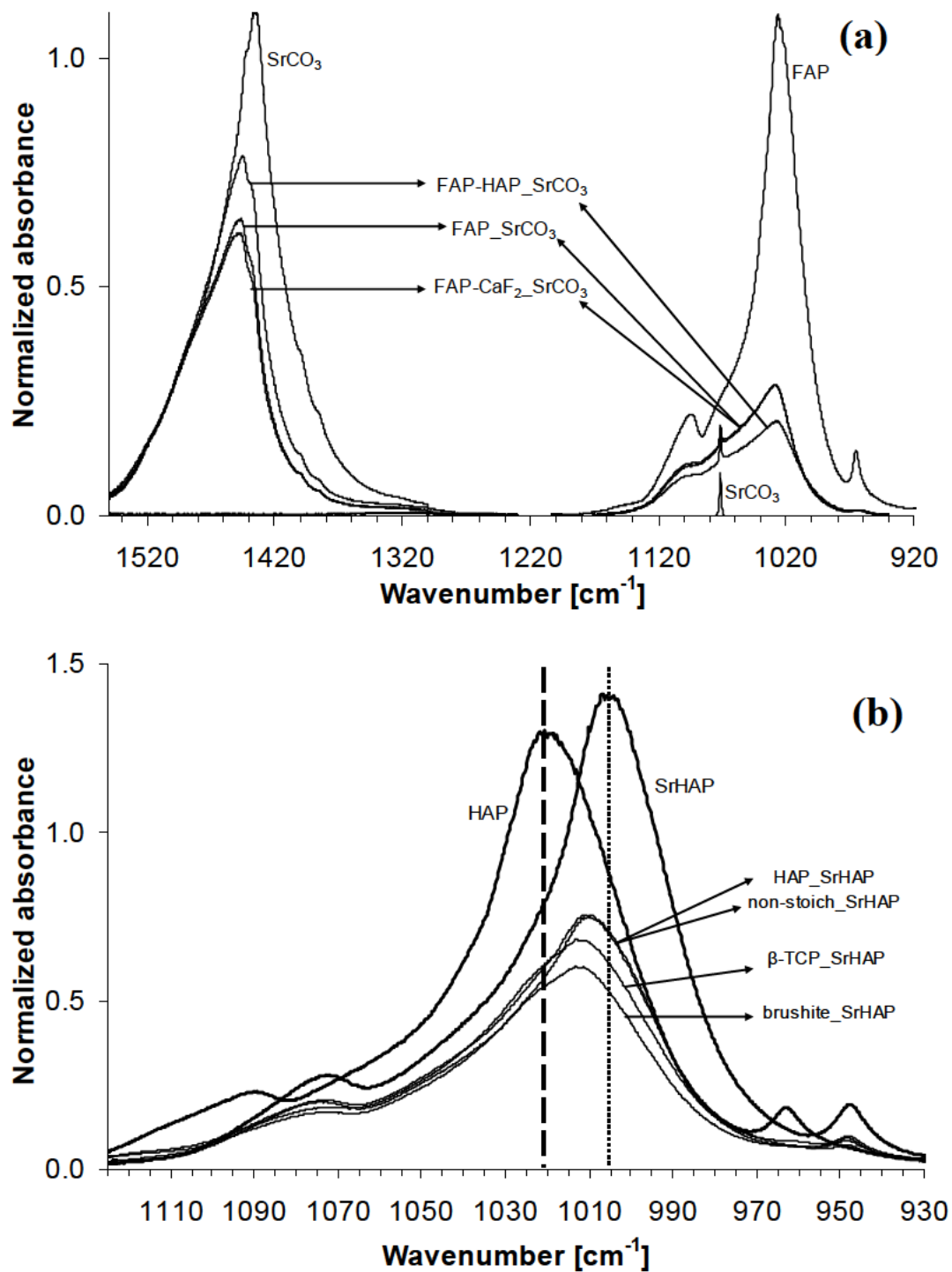


Figure 3.3 Absorbance spectra obtained by FTIR of (a) references SrCO_3 , FAP and samples of all SrCO_3 -based precipitates; spectra of FAP_SrCO_3 and $\text{FAP-CaF}_2\text{-SrCO}_3$ overlap; (b) SrHAP, HAP and F-free SrHAP-based samples; spectra of HAP-SrHAP and non-stoich_SrHAP overlap. The straight lines illustrate the peak shift of the same PO-assigned absorbance for SrHAP (dotted) and HAP (dashed) with F-free SrHAP-based precipitates in between. All spectra are normalized to the baseline.

Comparable features were observed in all SrHAP-based samples. The precipitates showed absorbances at 557, 592, 950, 1012, and 1076 cm^{-1} intermediate between SrHAP and HAP/FAP (Figure 3.3b, 3S3a, b, d, and e), which was consistent with physical mixtures of SrHAP and HAP. This might be related to the similarity of Ca- and Sr-apatites, as absorbances assigned to SrHAP exhibit a shift to lower wavenumbers due to the greater atomic radius of Sr.^{33, 34} Although it was expected that mixtures of both apatites would result in the presence of two distinct absorbances for the same PO₄ assignments, intermediate broad patterns occurred because the absorbances overlapped. One weak shoulder at 872 cm^{-1} , which was assigned to SrHAP, was also observed. At the same wavenumber the absorbance of a medium peak associated with brushite has been reported,³² but a change in intensity was not observed in any of the samples, not even for brushite_SrHAP. As postulated for SrCO₃-based precipitates, the observed patterns in the SrHAP-based samples could overlap with absorbances assigned to brushite, OCP and β -TCP, whereas absorbances of medium intensity for brushite at 788, 872, and 1215 cm^{-1} were not observed. Therefore, the co-occurrence of brushite is rather unlikely, but cannot be entirely excluded. The same is true for OCP and β -TCP. Since CaF₂ is not infrared active, this phase could not be detected by FTIR. Moreover, due to the relatively small amount precipitated (5-11 wt% assuming HAP precipitation), the OH libration mode for HAP at 630 cm^{-1} was absent, which made a distinction between HAP and FAP impossible for F-containing SrHAP-based and SrCO₃-based precipitates.

XANES

Synchrotron radiation was employed in XANES analysis in order to investigate the atomic environment of the Ca atoms in bulk of all precipitates. An advantage of this method is the possibility to detect crystalline and amorphous phases.

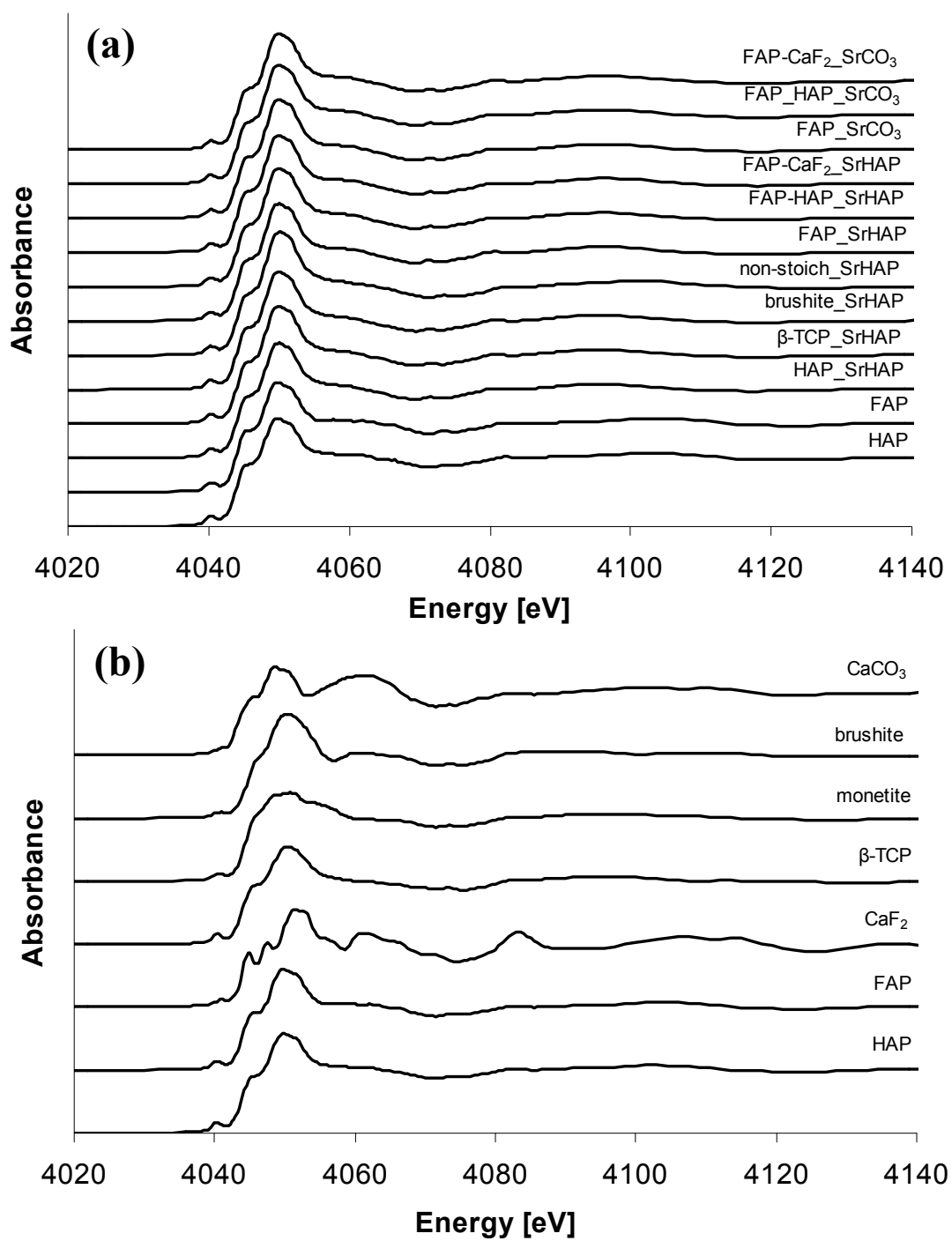


Figure 3.4 XANES obtained at the Ca-K-edge of (a) fingerprint of all precipitates with the most similar references HAP and FAP; (b) different calcium-phosphate references.

Fingerprints of all precipitates (SrHAP-based and SrCO₃-based) were consistent with the references of HAP/FAP (Figure 3.4a), though they exhibited slight differences at the white line (main peak of the spectra). In comparison to the references, the precipitates did not have a dip in between 4049.9 and 4051.5 eV. The white line peak of the F-free SrHAP-based precipitates was broader than that of the F-containing SrHAP- and SrCO₃-based samples and particularly for non-stoich_SrHAP it was more rounded in shape (Figure 3S3).

The white line dip at 4050.5 eV is caused by two different kinds of Ca atoms within the HAP and FAP crystal structure, which are coordinated in hexagonal shaped channels formed by PO₄ groups. One unit cell consists of four Ca ions (*Ca I*) located outside the PO₄ channel, while six Ca ions (*Ca II*) are located inside the PO₄ channel and are coordinated to two OH (HAP) or to two F ions (FAP).¹⁵ The white line peak at 4049.9 eV exhibits the highest absorbance, caused by *Ca I*, while the peak at 4051.5 eV is of lower intensity and originates from *Ca II*. Both peaks are separated by a slight dip at 4050.5 eV. Thus, the absence of this dip indicates a Ca-deficient apatite or the presence of another calcium phase. The crystal structures of both, brushite and β -TCP, contain one type of Ca atoms, which results in a single and round peak, while OCP exhibits a plateau-like shape as presented in Eichert et al. (2005).³⁵ In comparison, the XANES spectrum of CaF₂ is distinct from that of HAP/FAP due to its cubic crystal structure. Therefore, the co-existence of CaF₂ and OCP above detection limit in any of the samples can be excluded, while the round shaped white line for F-free SrHAP-based precipitates could result from small amounts of brushite and/or β -TCP, particularly for samples β -TCP_SrHAP and brushite_SrHAP.

For the F-containing samples (SrHAP- and SrCO₃-based) a significant distinction between HAP and FAP was as difficult as in XRD and FTIR. For the reference HAP the

pre-edge intensity was slightly higher than for FAP (Figure 3.4b), whereas the dip following the white line at around 4055.5 eV was a little more pronounced for FAP. The findings from XANES are therefore consistent with results from XPS, XRD and FTIR for the precipitation of HAP/FAP, maybe in Ca-deficient form though the co-existence of brushite and/or β -TCP cannot be entirely excluded.

EXAFS

The EXAFS spectra were obtained from the same analytical run as the XANES data and agreed with HAP/FAP as the predominate precipitate. Similarities with HAP/FAP occurred at 1.8 Å, which originates from the first O shell surrounding the two Ca atoms (*Ca I* and *Ca II*), and above 3.5 Å to about 4.0 Å (Figure 3.5a). The latter feature results from mixtures of single scattering from P and Ca accompanied by multiple scattering involving mainly O and P atoms. Differences between the HAP and FAP spectra occurred at around 3.0 Å, also resulting from an overlap of several scattering features. While HAP shows a round single peak, those of the F-free SrHAP-based precipitates appear to be split with a downward slope from about 2.8 Å toward 3.2 Å, while the feature of β -TCP_SrHAP exhibited a plateau. These differences could result from i) increased P, Ca and O scattering caused by the presence of Sr atoms, or ii) the differences indicate a co-existence of small amounts of brushite or β -TCP, since these references show similarities around 2.6-3.0 Å (Figure 3S4). However, in case of the latter, different peak shapes would have been expected for features above 3.5 Å, and these were not observed. Although the HAP EXAFS spectrum agreed with the one of Harris et al. (1986)³⁶, slight differences at around 3.0 Å could be a result of phase synthesis, since the reference was a commercial product heated to about 200°C, unlike the precipitate samples and the FAP reference sample that were air-dried solids.

The feature for FAP shows broad peaks at 3.0 and 3.6 Å (Figure 3.5b), which agreed with FAP-HAP_SrHAP and FAP-HAP_SrCO₃ (F-limited for FAP). Although this was also expected for FAP_SrHAP and FAP_SrCO₃ and FAP-CaF₂_SrHAP and FAP-CaF₂_SrCO₃ the EXAFS spectra of these samples agreed with that of HAP rather than FAP. This could possibly be explained by CaF₂ precipitation as indicated by XPS data for the presence of CaF₂ in FAP-CaF₂_SrCO₃.

Solids obtained from batches where F was added, showed increased peak intensities (e.g. FAP-HAP_SrHAP < FAP_SrHAP < FAP-CaF₂_SrHAP) proportional to the amount F precipitated, which indicates an increase of the degree of crystallinity. Incorporation of Sr into the phase crystal structure originating from the seeding templates was most likely indicated by an increased intensity of the feature at 1.3 Å in all SrHAP- and SrCO₃-based precipitates. This feature is attributed to changes in the scattering path length of the photoelectron of the O shell and exhibits only a shoulder in Sr-free reference samples.

A fitting model taking into account the structure of HAP³⁷ and one of FAP³⁸ resulted in unrealistic parameters. Similar problems occurred in the work of Harries et al. (1986)³⁶. These difficulties prevented a detailed analysis of the EXFAS data.

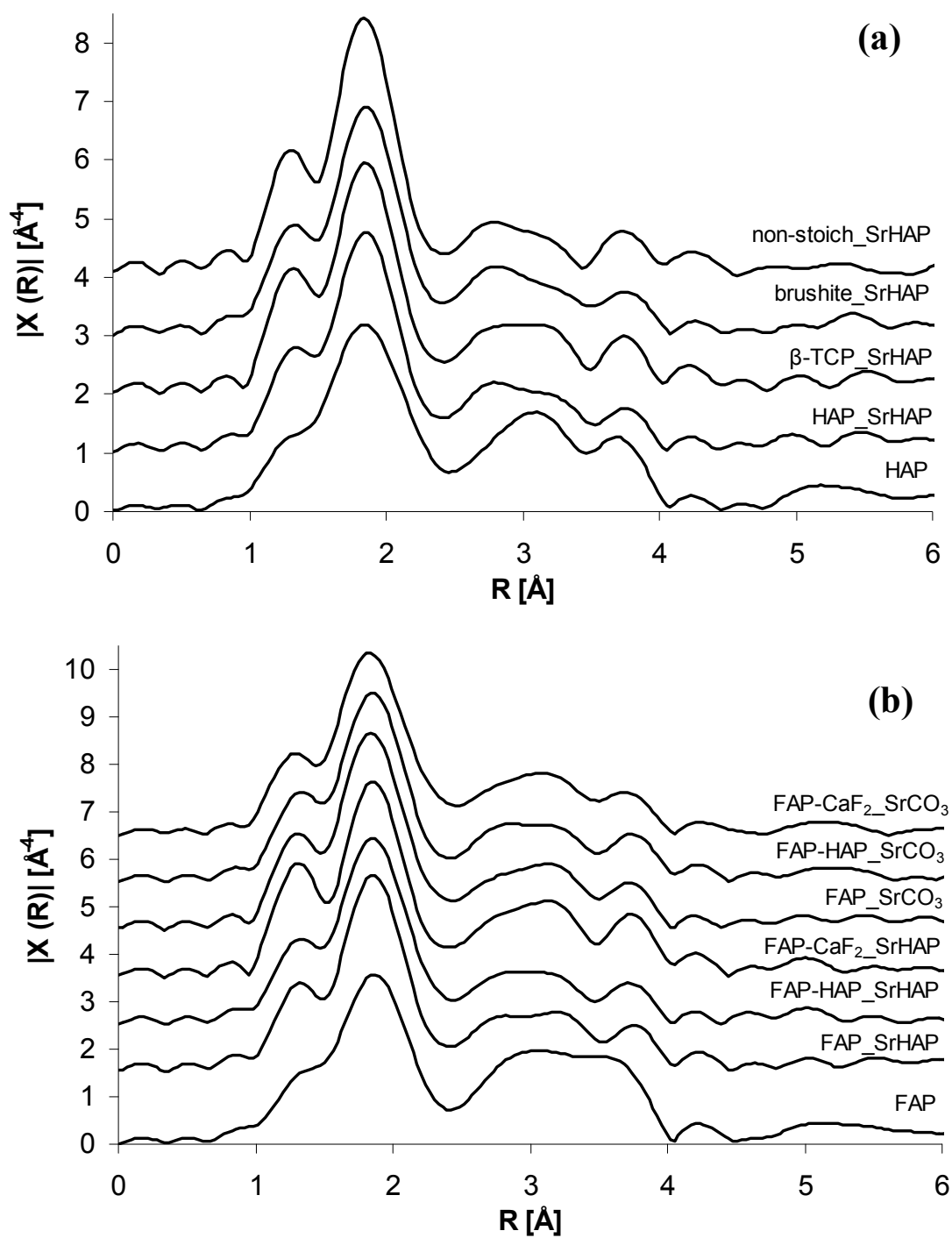


Figure 3.5 Raw EXAFS data obtained at the Ca-K-edge of (a) HAP and F-free SrHAP-based precipitates; and (b) reference FAP and all F-containing precipitates (SrHAP-based and SrCO₃-based).

In summary, phase formation seems to be independent of the stoichiometry of initially added Ca/P or Ca/P/F ratios and is also independent of the type of seeding template used, since results of all solid characterization methods were consistent for the predominant precipitates to be HAP in F-free SrHAP-based precipitates and FAP in all F-containing precipitates. From EXAFS analyses there are indications that the precipitates in samples FAP_SrHAP, FAP_SrCO₃, FAP-CaF₂_SrHAP and FAP-CaF₂_SrCO₃ were HAP rather than FAP, while XANES provided indications that all precipitates were Ca-deficient apatites. The co-existence of β -TCP, particularly in β -TCP_SrHAP and of brushite in brushite_SrHAP could not be entirely excluded. From XPS indications for CaF₂ were found for the F-containing precipitates, primarily in FAP-CaF₂_SrCO₃, which were not supported by XANES or EXAFS. Since FAP and CaF₂ exhibit different binding energies but also distinct x-ray absorptions, a detection of CaF₂ would have been expected in both techniques – XPS and XAFS. However, XPS analyzed the surface of the sample of a relatively smaller area (0.02 mm²) than XAFS (1 mm²), which is a bulk analysis. Although every attempt was made to homogenize the samples (10 wt% precipitate), it is possible that some heterogeneity occurred, so XPS was slightly more sensitive for CaF₂ detection, particularly if the crystallites are relatively small (several nm).

Solution data

Since previous studies mainly focused on solution data in order to identify phase formations the present study compares the results from solid characterization with solution data for consistency.

After 3d reaction time, all solutions where F was initially added (SrHAP- and SrCO₃-based) were highly supersaturated with respect to FAP (Table 3.1), which is consistent for the added Ca/P/F ratio to be stoichiometric for FAP. The SrCO₃-based solutions

were additionally supersaturated with respect to HAP, supporting indications by EXAFS. In sample FAP-HAP_SrCO₃ the F removal was more readily than in the FAP_SrCO₃ experiment, which indicates a more complete FAP formation in the presence of excess Ca and PO₄. The excess Ca and PO₄ removal in FAP-HAP_SrCO₃, which could not be attributed to only FAP, could therefore result from additional HAP precipitation. In contrast, FAP-CaF₂_SrCO₃ (PO₄-limited for FAP) showed significantly more F removal than could be accounted for FAP precipitation. However Ca removal was not sufficient for additional CaF₂ precipitation (please note that the Ca analysis (0.005 mM) could have been affected by relatively high (2 mM) Sr concentrations), though indications of CaF₂ in FAP-CaF₂_SrCO₃ were obtained by XPS. The greater F removal in FAP_SrHAP in comparison to FAP_SrCO₃ could result from F adsorption onto the surface of SrHAP seed and substitution of F for OH within the SrHAP crystal structure, which could have occurred in all F-containing SrHAP-based samples.

The precipitated Ca/P ratios for FAP_SrCO₃ and FAP-HAP_SrCO₃ of 1.49 indicate the formation of β -TCP (1.50) or of Ca-deficient FAP (Ca/P > 1.67), while the Ca/P of 1.71 for FAP-CaF₂_SrCO₃ would be consistent for FAP or Ca-deficient FAP plus CaF₂. Lower than expected Ca/P precipitate ratios were also found by others in heterogeneous systems using apatitic seeds.^{7, 9, 39} Although these studies do not account for partial seed dissolution, particularly if conducted at acidic pH conditions, it was assumed that the low ratios were caused by simultaneous presence of FAP, CaF₂ and brushite, while Albertus (2000)⁴⁰ assumed the precipitation of FAP was accompanied by formation of amorphous calcium phosphate.

In the absence of F, all solutions were saturated with respect to HAP. In addition the non-stoich_SrHAP was saturated with respect to SrCO₃. All F-free SrHAP-based

precipitates exhibited less Ca removal than expected, supporting indications by XANES of the formation of Ca-deficient HAP.

An evaluation of the precipitated Ca/P ratios for all SrHAP-based precipitates was less reliable since PO_4 concentrations could have been affected by partial dissolution of SrHAP.

Release of Sr and PO_4 to solution originating from SrHAP was already observed within the 10 min reaction prior the ions Ca, PO_4 (and F) were added to suspensions. Once the ions were added, dissolved Sr concentration increased rapidly by factor 2 (on average, from 0.11 mM to 0.18 mM). This was most probably induced by the addition of acidic stock solutions which resulted in a significant decrease of solution pH. A subsequently observed rapid decrease of Sr indicated a re-precipitation of Sr-containing phases, maybe as SrHAP or strontium phosphate ($\text{Sr}_3(\text{PO}_4)_2$), but possibly also of Ca-Sr apatite solid solution.^{41, 42} The amount of re-precipitated SrHAP would have been approximately 5.8 mg, which is about 0.25 wt% of the total solid mass in the batches (template plus solid calcium-phosphate precipitate). This amount is too small to be detected in any of the solid characterization techniques, though indications for solid solutions were found in EXAFS.

In contrast, the solutions of PO_4 -free SrCO_3 template showed a continuous increase of dissolved Sr concentrations (in average from 0.07 mM to 1.41 mM) indicating ongoing dissolution of SrCO_3 .

Comparison of solution data and solid phase analysis and further implications

The findings of solution data and of intensive solid characterizations are relatively consistent (Table 3.3) and showed that the thermodynamically most stable phases HAP or FAP, were formed independent of the solution stoichiometry by initially added Ca/P or Ca/P/F ratios. In fluoridated systems an initial loss of dissolved F from solution in heterogeneous systems could have also been partially caused by adsorption and substitution processes on the HAP seed surface.²¹

Table 3.3 Summary of phase identification for all precipitates (SrHAP- and SrCO₃-based) obtained by different applied solid characterization methods and from solution data.

| Sample | XRD | FTIR | XPS | XANES | EXAFS | solution data ^{a)} |
|---|---------|---------|-------------------------|--|------------------------------|--|
| HAP_SrHAP | HAP | HAP | HAP | (Ca-deficient) HAP or (brushite/ β -TCP) | HAP (brushite/ β -TCP) | HAP |
| β -TCP_SrHAP | HAP | HAP | HAP | (Ca-deficient) HAP or (brushite/ β -TCP) | HAP (brushite/ β -TCP) | HAP |
| brushite_SrHAP | HAP | HAP | HAP | (Ca-deficient) HAP or (brushite/ β -TCP) | HAP (brushite/ β -TCP) | HAP |
| non-stoich_SrHAP | HAP | HAP | HAP | (Ca-deficient) HAP or (brushite/ β -TCP) | HAP (brushite/ β -TCP) | HAP SrCO ₃ |
| FAP_SrHAP | HAP/FAP | HAP/FAP | FAP (CaF ₂) | (Ca-deficient) HAP/FAP or (brushite/ β -TCP) | HAP (CaF ₂) | - |
| FAP-HAP_SrHAP | HAP/FAP | HAP/FAP | HAP/FAP | (Ca-deficient) HAP/FAP or (brushite/ β -TCP) | FAP | - |
| FAP-CaF ₂ _SrHAP | HAP/FAP | HAP/FAP | FAP (CaF ₂) | (Ca-deficient) HAP/FAP or (brushite/ β -TCP) | HAP (CaF ₂) | FAP |
| FAP_SrCO ₃ | HAP/FAP | HAP/FAP | FAP (CaF ₂) | (Ca-deficient) HAP/FAP or (brushite/ β -TCP) | HAP (CaF ₂) | FAP SrCO ₃ |
| FAP-HAP_SrCO ₃ | HAP/FAP | HAP/FAP | HAP/FAP | (Ca-deficient) HAP/FAP or (brushite/ β -TCP) | FAP | FAP SrCO ₃ |
| FAP-CaF ₂ _SrCO ₃ | HAP/FAP | HAP/FAP | FAP (CaF ₂) | (Ca-deficient) HAP/FAP or (brushite/ β -TCP) | HAP (CaF ₂) | FAP SrCO ₃ , CaF ₂ |

(a) based on estimated saturation index after 3d reaction time; “/”: phase distinction was not possible; “()”: indications for this phase are provided; (-) saturation index for FAP was impossible to calculate due to concentrations below detection limit.

The observed indications of potential co-existence of brushite or β -TCP in solids obtained from F-free suspensions might be related to the reaction time (3d) which achieved meta-stable rather than equilibrium conditions. Therefore, these phases could be intermediates as suggested by others.^{2, 3, 11, 43}

Precipitated Ca/P ratios, which were the basis of data interpretation in many previous studies require careful evaluation, in particular since PO_4 -containing seeds like apatite can release PO_4 to solution, changing the solution stoichiometry and thus affecting phase formation. The assumption that HAP/FAP precipitation is facilitated by the use of an apatitic seed rather than on non-apatitic surfaces^{2, 8, 13} is not supported by outcomes from this study, since HAP/FAP formed in both systems of SrHAP and SrCO_3 . Moreover, this study shows that the precipitation of HAP/FAP can be performed on seeds of Ca-free apatite (and on carbonate), which facilitates solid characterizations and thus, could have some potential in future research.

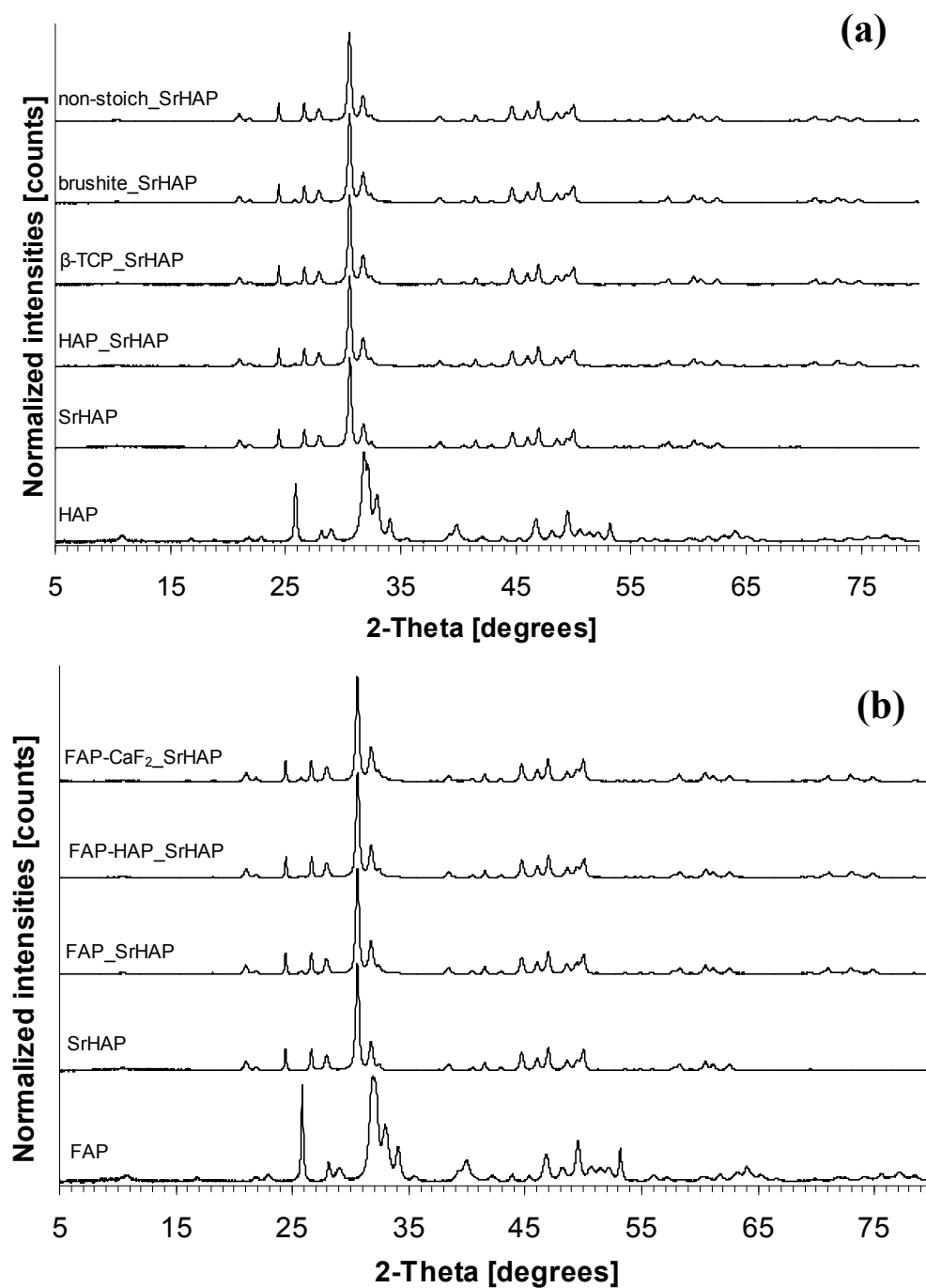
The observation that solution stoichiometry does not control the solid phase (3d) is essential for the optimization of F removal from drinking water by the method of heterogeneous surface precipitation.^{4, 9} This filter method is used in practice to increase F removal by the addition of soluble calcium-phosphate pellets to HAP-based filter systems. The pellets dissolve over time, releasing Ca and PO_4 to solution, but in non-stoichiometric ratios (Table 3.1). The released ions subsequently precipitate and as has been shown here, can form the thermodynamically most stable phases HAP (calcium-phosphate systems) or FAP (calcium-phosphate-fluoride systems). Since the contact time of water with the filter media can be significantly shorter than 3d, the formation of intermediate phases such as CaF_2 or OCP is possible and could affect F uptake in these filters significantly. Uptake could be enhanced if CaF_2 precipitates in addition to FAP or could be retarded if F-free intermediates form rather than FAP. It would therefore be of

interest to perform a comprehensive solid characterization of the HAP-pellet filter media after it has been in contact with F-containing water.

3.4 Acknowledgements

Highly appreciated are the supports for the XPS analysis by Erik Lewin and valuable discussions on FTIR and XRD analysis by Stephan Hug and Gwenn Lesaout. Special thanks go to Songhak Yoon for the possibility of uncountable XRD measurements. We are grateful to Hermann Moench for the assistance and advice in various laboratory works. The XAFS experiments were performed on the X07MB beamline. Acknowledged is the funding from the Swiss National Science Foundation (200021-117992).

3.5 Supporting Information for Chapter 3



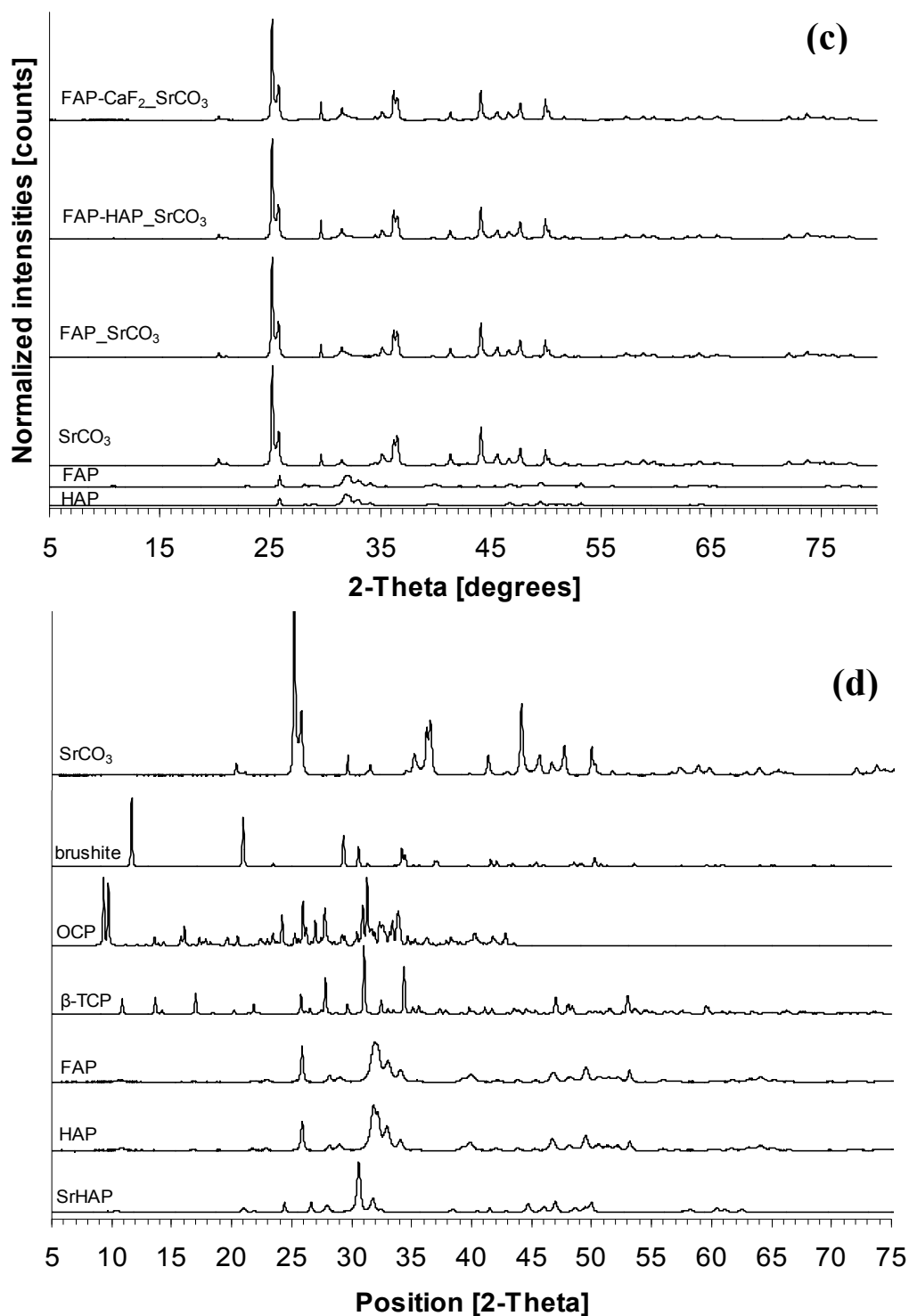
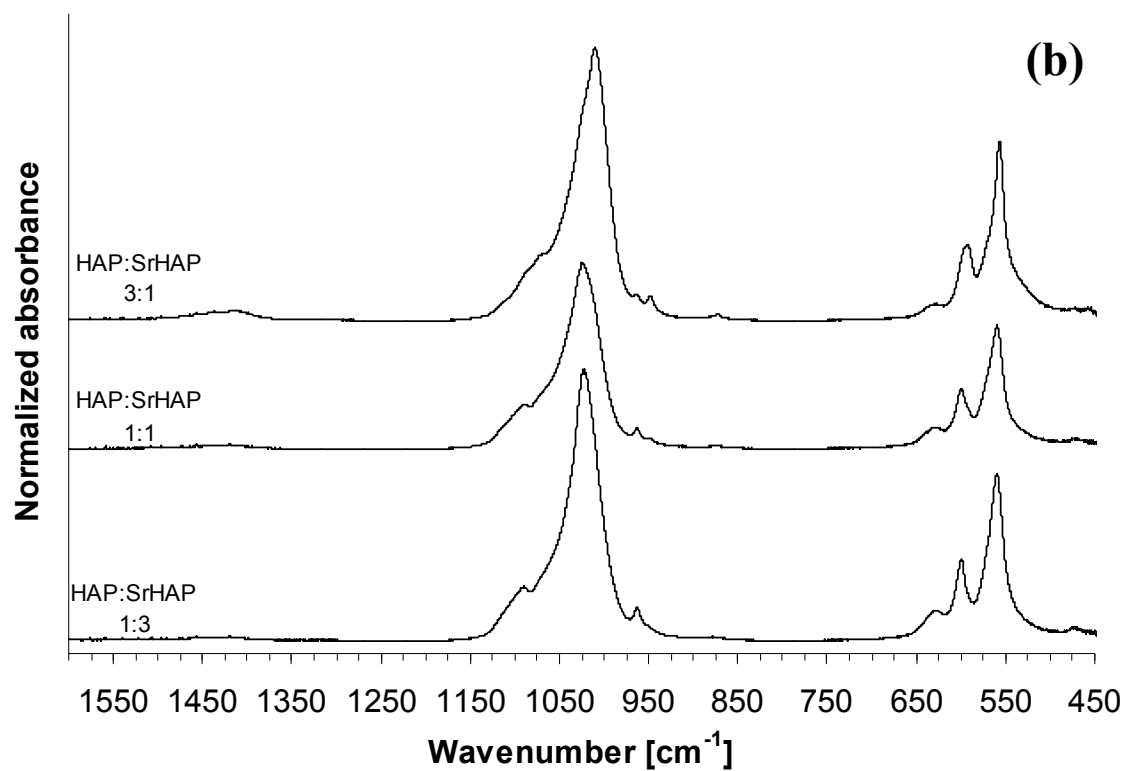
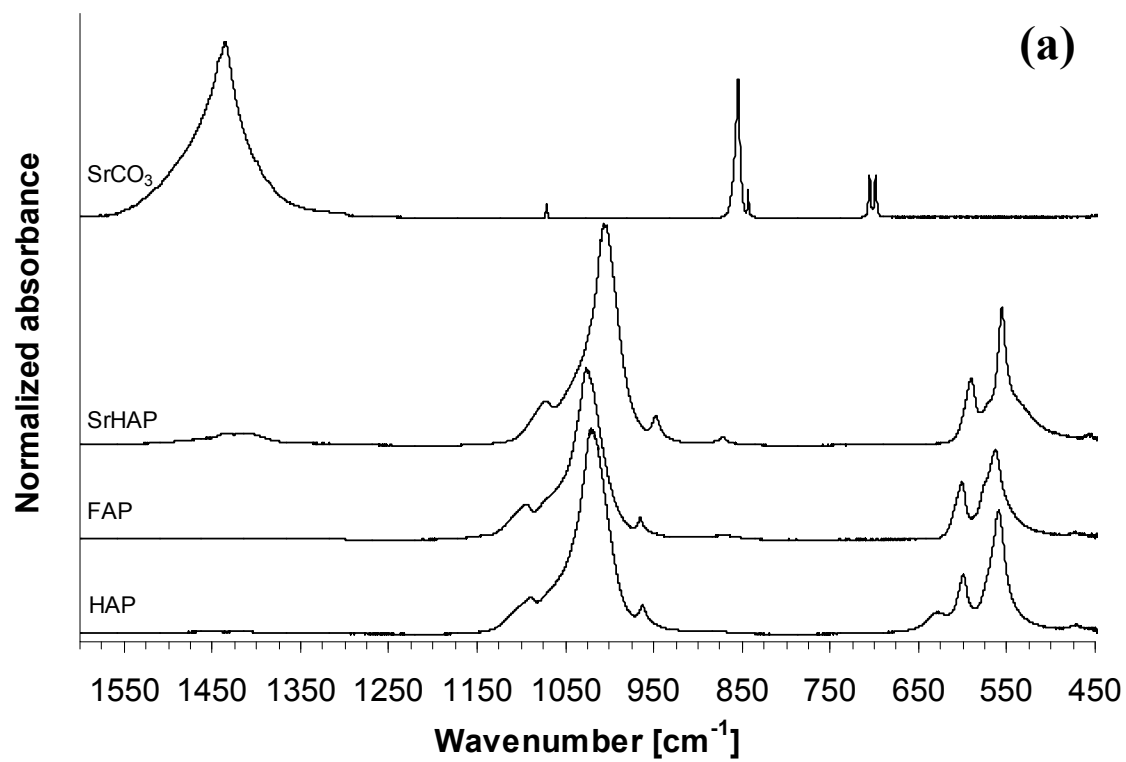
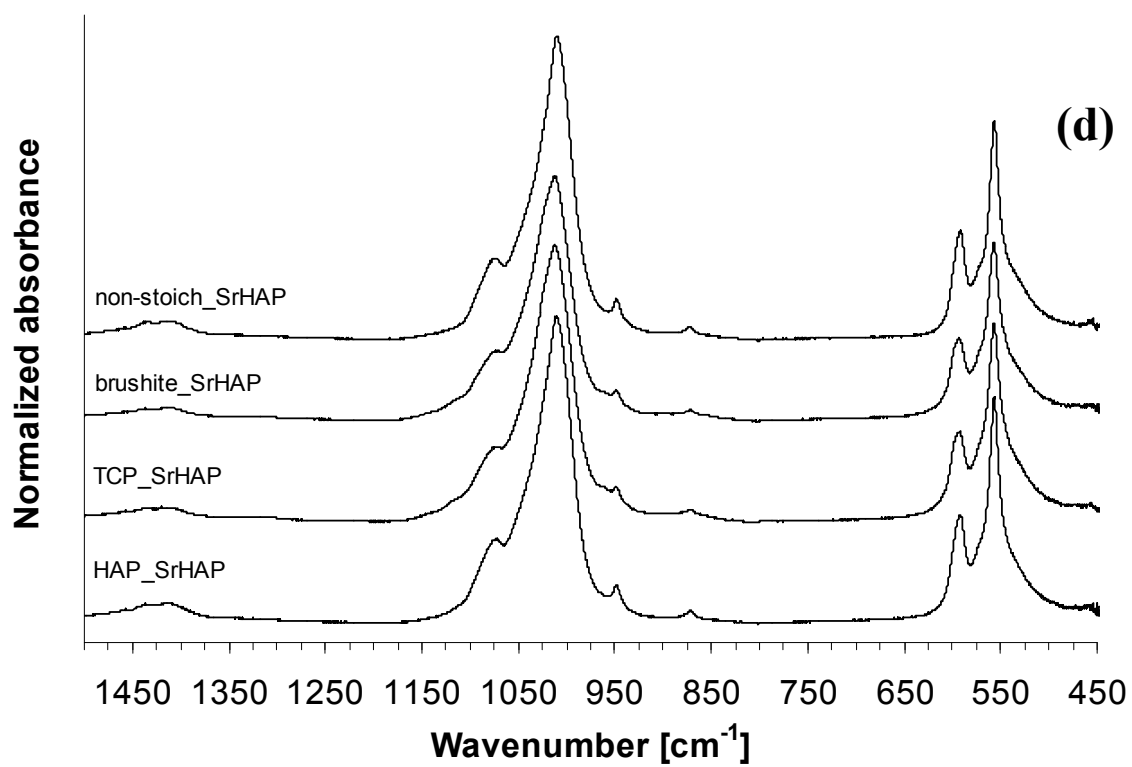
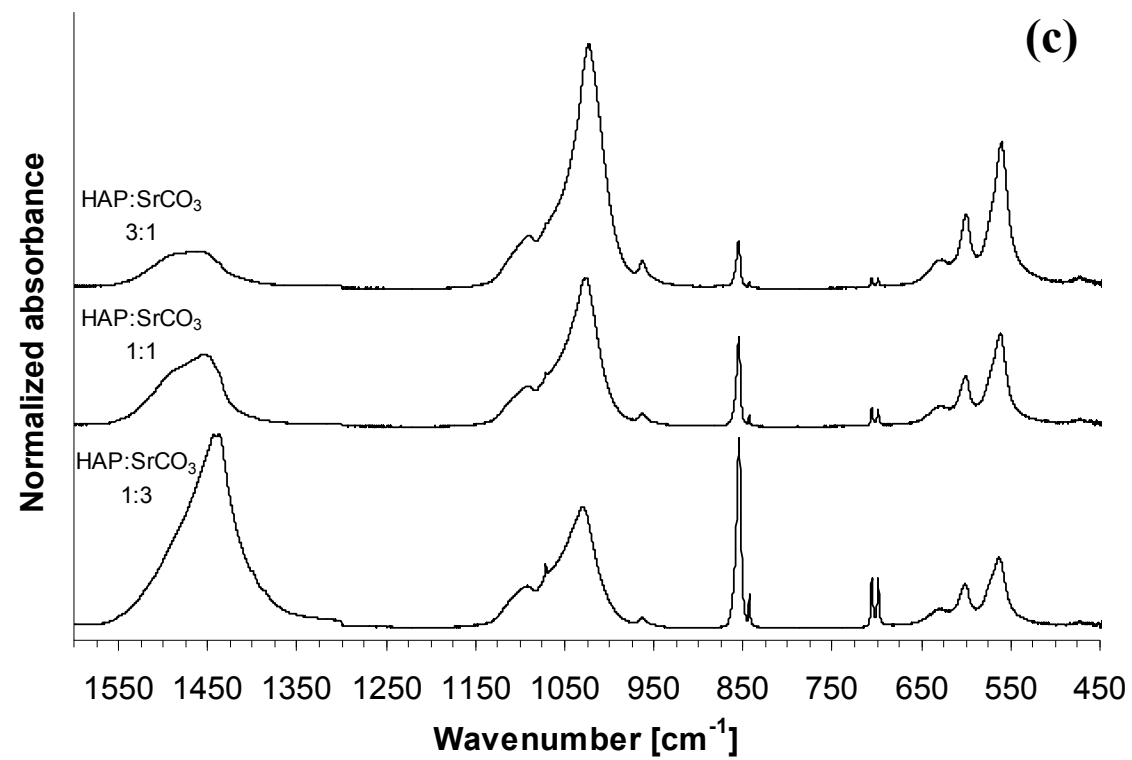


Figure 3S1 Complete x-ray diffractograms of (a) HAP, SrHAP and F-free SrHAP-based precipitates; (b) FAP, SrHAP and F-containing SrHAP-based precipitates; (c) HAP, FAP, SrCO₃ and all SrCO₃-based precipitates. The diffractions of all SrHAP-based samples and the reference SrHAP were normalized to (1 1 2) reflection of SrHAP at 30.6° 2θ; all SrCO₃-based samples and the reference SrCO₃ were normalized to (1 1 1) reflection at 25.1° 2θ; HAP and FAP were normalized to the (2 1 1) reflection at 31.8° 2θ. (d) Comparison of SrHAP, HAP, FAP and SrCO₃ with diffractograms of β-TCP⁵¹, OCP²⁷ and brushite.²⁸





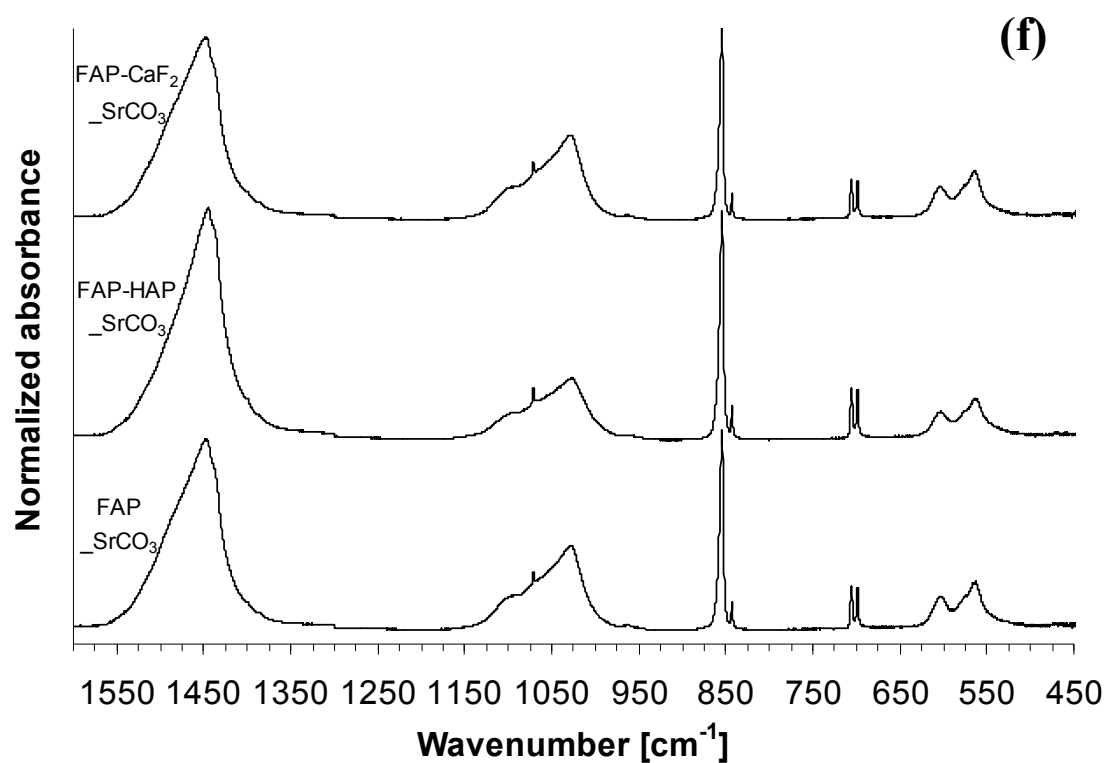
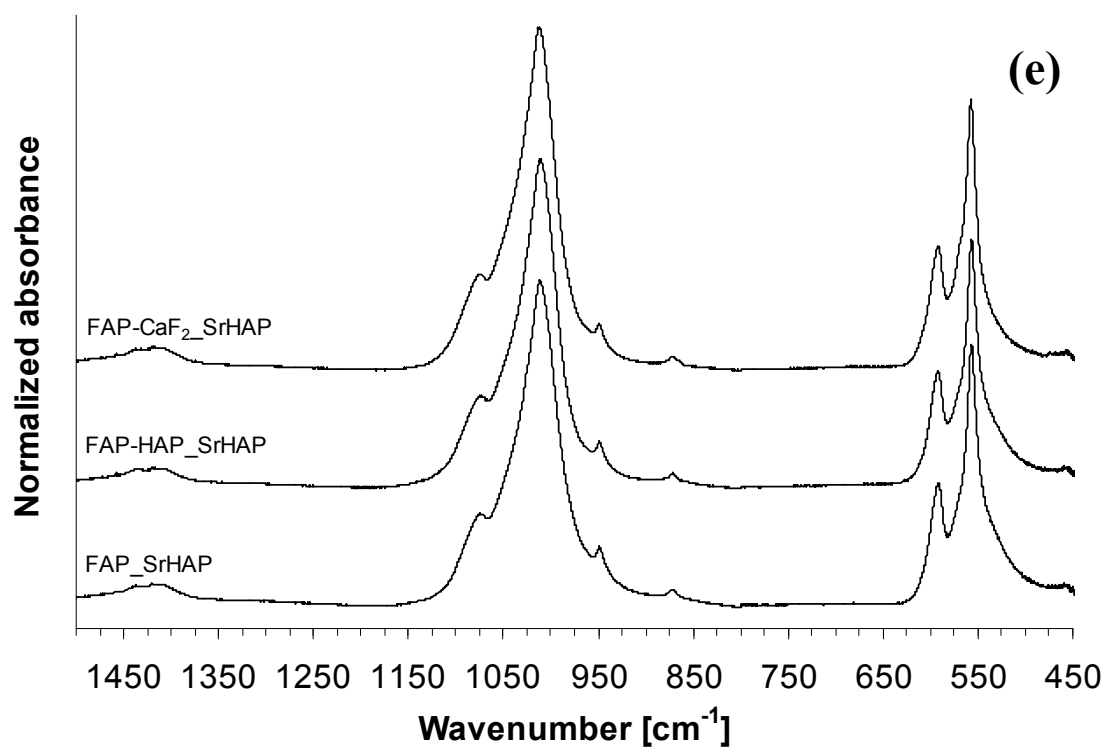


Figure 3S2 FTIR absorbance spectra of (a) references HAP, FAP, SrHAP and SrCO₃; (b) physical mixtures of the references HAP and SrHAP, (c) mixtures of HAP and SrCO₃; (d) F-free SrHAP-based precipitates; (e) F-containing SrHAP-based precipitates; (f) F-containing SrCO₃-based precipitates. All spectra were normalized to the baseline.

Table 3S1 FTIR absorbances of references SrHAP, HAP, FAP, SrCO₃, physical mixtures of HAP with SrHAP (1:1), HAP with SrCO₃ (1:1), absorbances observed in all precipitates and literature values for brushite, OCP and β -TCP

| SrHAP | HAP | FAP | SrCO ₃ | HAP/SrHAP 1:1 | HAP/SrCO ₃ 1:1 | F-free SrHAP- based | F-containing SrHAP-based | F- containing SrCO ₃ - based | brushite ^a | OCP ^a | β -TCP ^a |
|----------|------|----------|-------------------|---------------|---------------------------|---------------------------|-----------------------------|--|-----------------------|------------------|---------------------------|
| | | | | | | | | | | | 432vw |
| | | | | | | | | | | 447vw | |
| 457w | | | | | | | | | | | |
| | | | | | | | | | | 464vw | |
| | | | | | | | | | 525s | 525w,sh | |
| 530vw,sh | | | | | | | | | | | |
| | | | | | | | | | | | 541m |
| | | | | | | | | | | | 550m |
| 555s | 559s | 564s | | 561m | 562m | 557s | 557s | 565m | | 559m | |
| | | 577vw,sh | | | | | 570vw, sh (B1, B3) | | 575 m | 575w,sh | |
| | | | | | | | | | | | 589w |
| 591s | 600s | 601s | | 600m | 602m | 593s | 592s | 604m | | 599m | 602m |
| | 630m | | | | 631w, sh | | | | | 630w, sh | |
| | | | | | | | | | 658w | | |
| | | | 698m | | 699w | | | 699m | | | |
| | | | 705m | | 706w | | | 706m | | | |
| | | | | | | | | | 788m | | |
| | | | 843m | | 843w | | | 843m | | | |
| | | | 854vs | | 855m | | | 854vs | | | |
| | | | | | | | | | | 865w | |
| 872vw | | | | | | 872vw | 872vw | | 872m | | |

| | | | | | | | | | | | |
|---------------|---------------|---------------|---------------|--------------------|-------------------------|--------------------|---------------|-------------------|-----------------|--------------|-----------------|
| | | | | | | | | | | 910w | |
| | | | | | | | | | | | 945m |
| <i>948m</i> | <i>963m</i> | <i>966m</i> | | <i>949vw, 965w</i> | <i>963w</i> | <i>950m</i> | <i>950m</i> | | | 962w | |
| | | | | | | | | | | | 972s |
| | | | | | | | | | 984s | | |
| | | | | | | | | | 1000w,sh | | |
| <i>1006vs</i> | <i>1022vs</i> | <i>1027vs</i> | | <i>1025s</i> | <i>1028m</i> | <i>1011-1013vs</i> | <i>1012vs</i> | <i>1030m</i> | | 1025s | 1010w,sh |
| | | | | | | | | | | 1035s | |
| | | | | | | | | | | | 1041vs |
| | | | | | | | | | | 1055s | |
| | | | | | | | | | 1060s | | |
| <i>1075m</i> | <i>1091m</i> | <i>1096m</i> | <i>1071w</i> | <i>1092w,sh</i> | <i>1072vw, 1094w,sh</i> | <i>1077m</i> | <i>1077m</i> | <i>1071vw</i> | 1070s | 1075s | 1080w,sh |
| | | | | | | | | <i>1104vw,sh</i> | | 1105s | 1094w,sh |
| | | | | | | | | | | | 1119s |
| | | | | | | | | | 1132s | | |
| | | | | | | | | | | 1190w | |
| | | | | | | | | | 1215m | | |
| | | | | | | | | | | 1280w | |
| | | | | | | | | | | | |
| | | | <i>1435vs</i> | | <i>1455m+1492w,sh</i> | | | <i>1448-1451s</i> | | | |

(a) Fowler et al. (1966)³²; bold: absorbances could be obscured with observed absorbances of all SrHAP-based precipitates, framed: absorbances could be obscured with observed absorbances of SrCO₃-based precipitates; italic: intensity of absorbance was visually estimated; intensities of absorbances are described as *m*: medium, *s*: strong, *w*: weak, *v*: very, *sh*: shoulder.

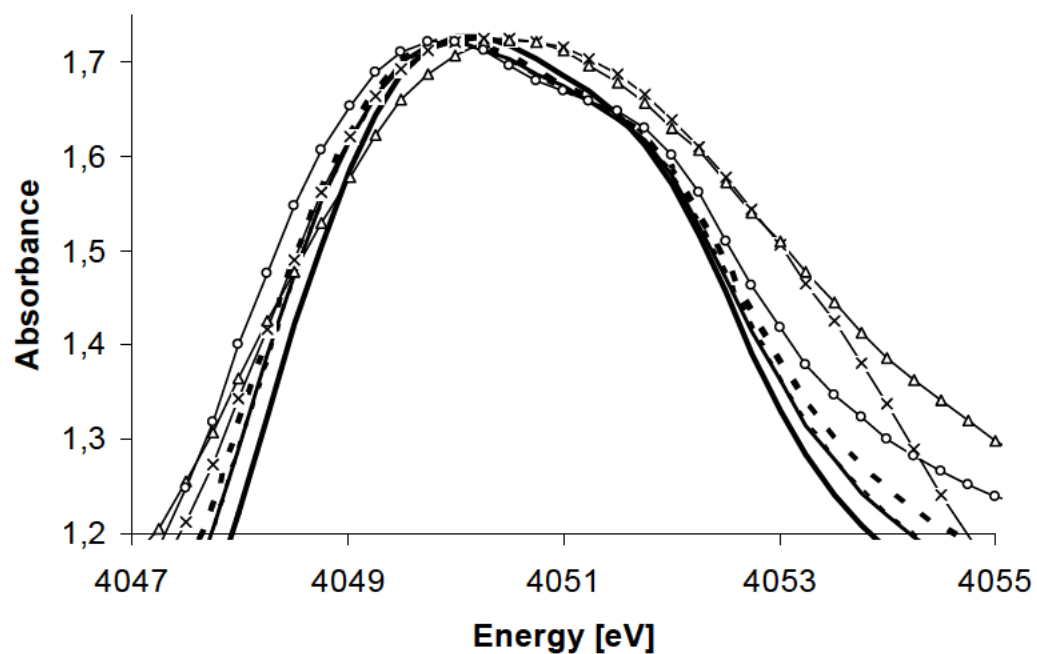


Figure 3S 3 White line peak of HAP (—○—), brushite (—x—), β -TCP (—△—), HAP_SrHAP (thick dotted), β -TCP_SrHAP (thin dotted), brushite_SrHAP (thin solid), non-stoich_SrHAP (thick solid) obtained by XANES.

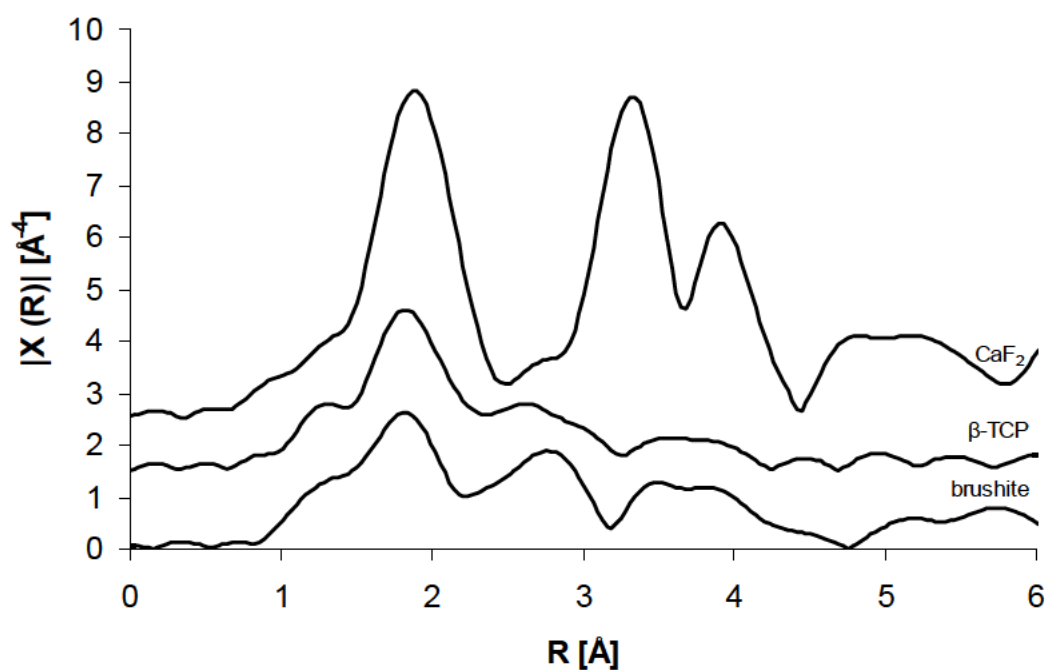


Figure 3S4 Spectra of brushite, β -TCP and CaF_2 obtained by EXAFS analysis.

Table 3S2 Total dissolved Sr, Ca, PO₄ (and F) concentrations, pH and saturation indices as function of sampling times for all precipitation experiments. The first row gives potential saturations with respect to added elemental concentrations; (-): concentration below detection limit.

| HAP_SrHAP | | | | | | |
|--------------|-------------|------------------|------------------------------|-------------------------|-------------------------|--------------------------------------|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | Sr _{tot} mM | Ca _{tot} mM | PO ₄ _{tot} mM |
| | | | | 0.11 ± 0.04 | | 0.09 ± 0.02 |
| | 7.30 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.11 ± 0.04 | 4.96 ± 0.16 | 3.09 ± 0.12 |
| 0.02 ± 0.00 | 6.76 ± 0.04 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.27 ± 0.02 | 3.36 ± 0.12 | 2.62 ± 0.15 |
| 0.08 ± 0.00 | 6.92 ± 0.22 | 8.65 ± 10.39 | 0.00 ± 0.00 | 0.28 ± 0.03 | 3.01 ± 0.16 | 2.32 ± 0.23 |
| 0.17 ± 0.00 | 7.07 ± 0.29 | 13.67 ± 12.26 | 0.00 ± 0.00 | 0.26 ± 0.06 | 2.40 ± 0.40 | 1.68 ± 0.42 |
| 0.25 ± 0.00 | 7.18 ± 0.17 | 18.73 ± 7.40 | 0.00 ± 0.00 | 0.25 ± 0.04 | 2.14 ± 0.22 | 1.41 ± 0.24 |
| 0.50 ± 0.00 | 7.28 ± 0.00 | 23.61 ± 2.27 | 0.00 ± 0.00 | 0.26 ± 0.03 | 1.97 ± 0.18 | 1.28 ± 0.18 |
| 1.00 ± 0.00 | 7.43 ± 0.20 | 32.38 ± 2.53 | 0.62 ± 0.87 | 0.21 ± 0.01 | 1.26 ± 0.25 | 0.64 ± 0.24 |
| 2.01 ± 0.01 | 7.57 ± 0.30 | 37.06 ± 0.81 | 0.64 ± 0.91 | 0.19 ± 0.03 | 0.81 ± 0.07 | 0.27 ± 0.02 |
| 4.17 ± 0.24 | 7.48 ± 0.40 | 38.62 ± 2.29 | 0.64 ± 0.91 | 0.20 ± 0.04 | 0.69 ± 0.19 | 0.22 ± 0.07 |
| 6.96 ± 1.47 | 7.51 ± 0.38 | 40.28 ± 3.89 | 1.41 ± 0.18 | 0.20 ± 0.05 | 0.62 ± 0.23 | 0.20 ± 0.08 |
| 23.88 ± 0.13 | 7.58 ± 0.33 | 45.63 ± 4.94 | 10.62 ± 12.05 | 0.18 ± 0.07 | 0.39 ± 0.17 | 0.13 ± 0.05 |
| 48.36 ± 0.20 | 7.58 ± 0.42 | 47.14 ± 5.09 | 10.93 ± 12.43 | 0.18 ± 0.05 | 0.32 ± 0.13 | 0.10 ± 0.01 |
| 71.96 ± 3.19 | 7.58 ± 0.44 | 47.77 ± 5.98 | 13.23 ± 15.69 | 0.18 ± 0.06 | 0.28 ± 0.13 | 0.09 ± 0.02 |

| HAP_SrHAP | | | | | |
|---------------|----------------------|----------------------|---------------|---------------|---------------|
| SI HAP | SI CaCO ₃ | SI SrCO ₃ | SI brushite | SI OCP | SI β-TCP |
| 8.01 ± 7.65 | -1.69 ± -2.89 | -1.70 ± -2.08 | 0.29 ± -0.62 | 4.40 ± 3.99 | 3.95 ± 3.40 |
| 4.20 ± 3.70 | -2.43 ± -4.25 | -1.91 ± -3.12 | -0.15 ± -0.90 | 1.80 ± 1.42 | 1.82 ± 1.22 |
| 5.05 ± 5.14 | -2.26 ± -2.61 | -1.67 ± -2.10 | -0.14 ± -2.13 | 2.19 ± 2.10 | 2.19 ± 2.10 |
| 5.07 ± 5.14 | -2.15 ± -2.45 | -1.51 ± -1.85 | -0.26 ± -0.96 | 2.00 ± 1.75 | 2.13 ± 1.97 |
| 5.10 ± 4.82 | -2.08 ± -2.71 | -1.39 ± -2.09 | -0.29 ± -0.90 | 2.04 ± 0.86 | 2.18 ± 1.37 |
| 5.50 ± 5.53 | -2.00 ± -2.75 | -1.26 ± -1.99 | -0.31 ± -0.73 | 2.29 ± 2.30 | 2.38 ± 2.27 |
| 5.56 ± 5.71 | -1.95 ± -2.10 | -1.12 ± -1.36 | -0.64 ± -0.74 | 1.95 ± 2.09 | 2.21 ± 2.35 |
| 4.11 ± 4.26 | -1.96 ± -2.10 | -0.98 ± -1.14 | -1.16 ± -1.50 | 0.38 ± 0.51 | 1.20 ± 1.32 |
| 2.68 ± 2.82 | -2.12 ± -2.24 | -1.03 ± -1.11 | -1.39 ± -4.59 | -0.84 ± -0.77 | 0.33 ± 0.39 |
| 2.16 ± 2.27 | -2.16 ± -2.33 | -1.02 ± -1.15 | -1.47 ± -2.13 | -1.25 ± -1.38 | 0.04 ± -0.03 |
| 0.51 ± 0.40 | -2.33 ± -2.67 | -1.03 ± -1.30 | -1.85 ± -2.22 | -2.58 ± -3.39 | -0.92 ± -1.58 |
| 0.32 ± 0.46 | -2.39 ± -2.56 | -0.99 ± -1.11 | -2.07 ± -3.52 | -3.01 ± -2.96 | -1.18 ± -1.14 |
| -0.17 ± -0.04 | -2.45 ± -2.63 | -1.00 ± -1.14 | -2.15 ± -2.88 | -3.42 ± -3.46 | -1.47 ± -1.48 |

| β -TCP_SrHAP | | | | | | |
|--------------------|-------------|------------------|------------------------------|-------------------------|-------------------------|--------------------------------------|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | Sr _{tot} mM | Ca _{tot} mM | PO ₄ _{tot} mM |
| | | | | 0.11 ± 0.05 | | 0.07 ± 0.04 |
| | 7.30 ± 0.00 | | | 0.11 ± 0.05 | 5.05 ± 0.00 | 3.51 ± 0.04 |
| 0.01 ± 0.01 | 6.63 ± 0.10 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.23 ± 0.02 | 3.82 ± 0.48 | 2.96 ± 0.05 |
| 0.09 ± 0.01 | 6.67 ± 0.03 | 1.76 ± 1.66 | 0.00 ± 0.00 | 0.27 ± 0.03 | 3.66 ± 0.15 | 2.93 ± 0.22 |
| 0.18 ± 0.01 | 6.82 ± 0.12 | 7.86 ± 5.13 | 0.00 ± 0.00 | 0.30 ± 0.03 | 3.19 ± 0.003 | 2.50 ± 0.37 |
| 0.26 ± 0.01 | 6.86 ± 0.13 | 10.40 ± 5.52 | 0.00 ± 0.00 | 0.30 ± 0.03 | 3.05 ± 0.04 | 2.41 ± 0.47 |
| 0.55 ± 0.00 | 6.91 ± 0.08 | 20.90 ± 4.95 | 0.00 ± 0.00 | 0.27 ± 0.02 | 2.28 ± 0.41 | 1.69 ± 0.72 |
| 1.03 ± 0.04 | 7.16 ± 0.15 | 31.02 ± 4.98 | 0.00 ± 0.00 | 0.25 ± 0.02 | 1.58 ± 0.33 | 1.00 ± 0.66 |
| 2.05 ± 0.05 | 7.16 ± 0.16 | 35.96 ± 0.86 | 0.00 ± 0.00 | 0.27 ± 0.04 | 1.26 ± 0.08 | 0.77 ± 0.45 |
| 4.01 ± 0.01 | 7.16 ± 0.20 | 37.63 ± 1.27 | 0.00 ± 0.00 | 0.23 ± 0.002 | 1.05 ± 0.12 | 0.65 ± 0.37 |
| 6.01 ± 0.01 | 7.27 ± 0.01 | 39.98 ± 0.56 | 0.00 ± 0.00 | 0.23 ± 0.01 | 0.97 ± 0.09 | 0.60 ± 0.35 |
| 24.03 ± 0.05 | 7.29 ± 0.00 | 42.86 ± 2.06 | 0.00 ± 0.00 | 0.23 ± 0.02 | 0.77 ± 0.10 | 0.52 ± 0.21 |
| 48.05 ± 0.05 | 7.29 ± 0.01 | 44.90 ± 2.52 | 0.00 ± 0.00 | 0.22 ± 0.04 | 0.65 ± 0.16 | 0.47 ± 0.15 |
| 78.01 ± 8.47 | 7.28 ± 0.04 | 46.15 ± 2.63 | 0.00 ± 0.00 | 0.22 ± 0.04 | 0.55 ± 0.17 | 0.42 ± 0.14 |

| β -TCP_SrHAP | | | | | | |
|--------------------|----------------------|----------------------|---------------|---------------|-----------------|--|
| SI HAP | SI CaCO ₃ | SI SrCO ₃ | SI brushite | SI OCP | SI β -TCP | |
| 8.05 ± 6.07 | -1.70 ± -4.13 | -1.74 ± -2.06 | 0.31 ± -2.08 | 4.44 ± 2.47 | 3.98 ± 1.84 | |
| 3.90 ± 3.99 | -2.57 ± -2.97 | -2.19 ± -2.92 | -0.21 ± -0.79 | 1.56 ± 1.58 | 1.60 ± 1.57 | |
| 3.76 ± 3.40 | -2.54 ± -3.86 | -2.05 ± -2.79 | -0.20 ± -1.25 | 1.49 ± 1.04 | 1.57 ± 1.00 | |
| 4.33 ± 4.32 | -2.40 ± -2.87 | -1.82 ± -2.42 | -0.21 ± -1.58 | 1.74 ± 1.56 | 1.82 ± 1.60 | |
| 4.43 ± 4.43 | -2.36 ± -2.80 | -1.76 ± -2.33 | -0.22 ± -2.34 | 1.79 ± 1.57 | 1.87 ± 1.64 | |
| 4.19 ± 4.33 | -2.41 ± -2.87 | -1.73 ± -2.31 | -0.40 ± -0.61 | 1.52 ± 1.65 | 1.65 ± 1.74 | |
| 3.64 ± 3.60 | -2.26 ± -2.94 | -1.43 ± -1.90 | -0.64 ± -0.83 | 0.91 ± 0.96 | 1.30 ± 1.20 | |
| 2.84 ± 1.40 | -2.34 ± -2.78 | -1.40 ± -1.98 | -0.84 ± -1.20 | 0.14 ± -0.08 | 0.80 ± 0.18 | |
| 2.28 ± 1.72 | -2.40 ± -2.79 | -1.44 ± -1.74 | -0.98 ± -1.34 | -0.37 ± -0.71 | 0.44 ± -0.65 | |
| 2.95 ± 3.05 | -2.33 ± -3.83 | -1.33 ± -2.40 | -0.96 ± -1.17 | 0.09 ± 0.19 | 0.77 ± 0.79 | |
| 2.12 ± 1.82 | -2.40 ± -3.26 | -1.31 ± -2.39 | -1.13 ± -1.71 | -0.64 ± -0.86 | 0.29 ± -0.12 | |
| 1.64 ± 1.25 | -2.47 ± -3.04 | -1.32 ± -2.04 | -1.24 ± -2.45 | -1.07 ± -1.95 | -0.01 ± -0.75 | |
| 1.15 ± 1.12 | -2.55 ± -2.93 | -1.33 ± -1.89 | -1.37 ± -3.03 | -1.53 ± -1.77 | -0.34 ± -0.61 | |

| Brushite_SrHAP | | | | | | |
|----------------|-------------|------------------|------------------------------|-------------------------|--------------|-------------|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | Sr _{tot} mM | | |
| | | | | 0.10 | ± | 0.03 |
| | | | | | | 0.07 ± 0.02 |
| | 7.30 ± 0.00 | | | 0.10 ± 0.03 | 5.07 ± 0.00 | 5.18 ± 0.02 |
| 0.01 ± 0.01 | 6.63 ± 0.10 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.20 ± 0.03 | 3.31 ± 0.46 | 4.58 ± 0.02 |
| 0.09 ± 0.01 | 6.62 ± 0.15 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.23 ± 0.01 | 2.93 ± 0.56 | 4.46 ± 0.11 |
| 0.22 ± 0.02 | 6.45 ± 0.25 | 1.40 ± 1.98 | 0.00 ± 0.00 | 0.26 ± 0.002 | 2.77 ± 0.20 | 4.12 ± 0.17 |
| 0.28 ± 0.01 | 6.52 ± 0.06 | 4.85 ± 6.01 | 0.00 ± 0.00 | 0.26 ± 0.003 | 2.48 ± 0.11 | 3.92 ± 0.27 |
| 0.53 ± 0.05 | 7.16 ± 0.15 | 27.46 ± 15.76 | 0.00 ± 0.00 | 0.19 ± 0.04 | 1.48 ± 0.60 | 2.89 ± 0.86 |
| 1.03 ± 0.04 | 7.27 ± 0.01 | 35.72 ± 9.94 | 0.00 ± 0.00 | 0.14 ± 0.01 | 0.68 ± 0.13 | 2.23 ± 0.43 |
| 2.01 ± 0.01 | 7.22 ± 0.16 | 37.50 ± 12.46 | 1.13 ± 1.60 | 0.12 ± 0.01 | 0.47 ± 0.11 | 2.05 ± 0.42 |
| 4.01 ± 0.01 | 7.31 ± 0.01 | 40.82 ± 10.16 | 2.01 ± 1.01 | 0.11 ± 0.01 | 0.34 ± 0.04 | 1.94 ± 0.39 |
| 6.01 ± 0.01 | 7.30 ± 0.04 | 47.49 ± 19.02 | 8.91 ± 10.78 | 0.11 ± 0.02 | 0.31 ± 0.04 | 1.90 ± 0.43 |
| 24.01 ± 0.01 | 7.26 ± 0.01 | 48.57 ± 19.34 | 8.93 ± 10.81 | 0.10 ± 0.005 | 0.26 ± 0.01 | 1.94 ± 0.39 |
| 48.02 ± 0.02 | 7.28 ± 0.00 | 51.72 ± 19.14 | 8.94 ± 10.83 | 0.09 ± 0.01 | 0.18 ± 0.03 | 1.89 ± 0.41 |
| 78.02 ± 8.46 | 7.34 ± 0.03 | 52.17 ± 19.77 | 9.00 ± 10.91 | 0.08 ± 0.0003 | 0.13 ± 0.001 | 1.88 ± 0.41 |

| Brushite_SrHAP | | | | | | |
|----------------|----------------------|----------------------|---------------|---------------|---------------|--|
| SI HAP | SI CaCO ₃ | SI SrCO ₃ | SI brushite | SI OCP | SI β-TCP | |
| 8.40 ± 5.30 | -1.72 ± -4.54 | -1.80 ± -2.40 | 0.43 ± -2.93 | 4.78 ± 1.75 | 4.21 ± 1.00 | |
| 3.83 ± 3.70 | -2.65 ± -3.39 | -2.23 ± -2.56 | -0.11 ± -1.30 | 1.64 ± 1.34 | 1.64 ± 1.28 | |
| 3.59 ± 3.62 | -2.72 ± -3.26 | -2.20 ± -2.58 | -0.17 ± -1.04 | 1.43 ± 1.34 | 1.47 ± 1.32 | |
| 2.97 ± 3.12 | -2.91 ± -3.06 | -2.30 ± -2.42 | -0.33 ± -0.68 | 0.93 ± 1.06 | 1.05 ± 1.15 | |
| 2.44 ± 2.37 | -2.91 ± -3.68 | -2.27 ± -2.97 | -0.35 ± -1.15 | 0.60 ± 0.43 | 0.83 ± 0.56 | |
| 4.70 ± 4.59 | -2.35 ± -4.48 | -1.60 ± -2.27 | -0.26 ± -0.60 | 1.94 ± 1.92 | 2.01 ± 1.81 | |
| 3.67 ± 3.73 | -2.52 ± -3.21 | -1.59 ± -2.57 | -0.60 ± -1.03 | 0.92 ± 0.95 | 1.31 ± 1.24 | |
| 2.31 ± 1.67 | -2.73 ± -3.47 | -1.69 ± -2.24 | -0.81 ± -1.39 | -0.13 ± -0.73 | 0.54 ± -1.22 | |
| 2.15 ± 2.09 | -2.76 ± -3.88 | -1.65 ± -2.93 | -0.93 ± -1.45 | -0.34 ± -0.42 | 0.40 ± 0.19 | |
| 1.80 ± 1.77 | -2.83 ± -3.95 | -1.65 ± -2.63 | -1.00 ± -1.41 | -0.60 ± -0.63 | 0.19 ± 0.03 | |
| 1.27 ± 1.25 | -2.95 ± -3.90 | -1.74 ± -2.65 | -1.09 ± -1.58 | -1.01 ± -1.06 | -0.13 ± -0.29 | |
| 0.69 ± 0.76 | -3.08 ± -3.75 | -1.77 ± -2.53 | -1.23 ± -1.59 | -1.50 ± -1.45 | -0.50 ± -0.54 | |
| 0.19 ± 0.19 | -3.15 ± -4.07 | -1.76 ± -2.69 | -1.36 ± -1.86 | -1.96 ± -1.99 | -0.81 ± -0.95 | |

| Non-stoich_SrHAP | | | | | | |
|------------------|--------------|------------------|------------------------------|-------------------------|-------------------------|--------------------------------------|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | Sr _{tot} mM | Ca _{tot} mM | PO ₄ _{tot} mM |
| | | | | 0.09 ± 0.01 | | 0.06 ± 0.004 |
| | 7.30 ± 0.00 | | | 0.09 ± 0.01 | 2.01 ± 0.0002 | 4.15 ± 0.004 |
| 0.05 ± 0.00 | 6.71 ± 0.29 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.16 ± 0.03 | 1.31 ± 0.26 | 3.45 ± 0.73 |
| 0.13 ± 0.00 | 6.84 ± 0.10 | 0.15 ± 0.21 | 0.00 ± 0.00 | 0.18 ± 0.05 | 1.18 ± 0.28 | 3.28 ± 0.97 |
| 0.22 ± 0.00 | 6.81 ± 0.12 | 0.34 ± 0.48 | 0.00 ± 0.00 | 0.20 ± 0.03 | 1.29 ± 0.003 | 3.19 ± 0.98 |
| 0.30 ± 0.00 | 6.90 ± 0.001 | 3.38 ± 3.34 | 0.00 ± 0.00 | 0.20 ± 0.03 | 0.99 ± 0.20 | 3.06 ± 0.86 |
| 0.55 ± 0.00 | 6.99 ± 0.41 | 8.40 ± 8.74 | 0.00 ± 0.00 | 0.21 ± 0.005 | 0.76 ± 0.09 | 2.90 ± 0.74 |
| 2.05 ± 0.00 | 7.19 ± 0.14 | 14.95 ± 5.72 | 0.00 ± 0.00 | 0.18 ± 0.04 | 0.40 ± 0.05 | 2.47 ± 0.60 |
| 4.05 ± 0.00 | 7.26 ± 0.00 | 17.93 ± 2.28 | 0.00 ± 0.00 | 0.17 ± 0.03 | 0.27 ± 0.02 | 2.36 ± 0.65 |
| 6.05 ± 0.00 | 7.28 ± 0.02 | 18.67 ± 1.88 | 0.00 ± 0.00 | 0.17 ± 0.03 | 0.24 ± 0.02 | 2.39 ± 0.60 |
| 24.05 ± 0.00 | 7.28 ± 0.02 | 20.00 ± 1.05 | 0.00 ± 0.00 | 0.16 ± 0.01 | 0.18 ± 0.01 | 2.37 ± 0.75 |
| 47.94 ± 0.18 | 7.28 ± 0.03 | 20.39 ± 0.49 | 0.00 ± 0.00 | 0.15 ± 0.01 | 0.16 ± 0.03 | 2.38 ± 0.76 |
| 72.08 ± 0.04 | 7.28 ± 0.02 | 20.48 ± 0.37 | 0.00 ± 0.00 | 0.15 ± 0.0004 | 0.16 ± 0.02 | 2.40 ± 0.74 |

| Non-stoich_SrHAP | | | | | |
|------------------|----------------------|----------------------|---------------|---------------|---------------|
| SI HAP | SI CaCO ₃ | SI SrCO ₃ | SI brushite | SI OCP | SI β-TCP |
| 6.72 ± 3.76 | 0.72 ± 0.87 | 1.01 ± 1.16 | 0.12 ± -3.43 | 3.48 ± 0.48 | 3.22 ± 0.06 |
| 2.89 ± 3.02 | 0.44 ± 0.59 | 1.15 ± 1.30 | -0.42 ± -1.31 | 0.68 ± 0.74 | 0.95 ± 0.98 |
| 2.92 ± 2.53 | 0.49 ± 0.64 | 1.29 ± 1.44 | -0.38 ± -0.92 | 0.83 ± 0.59 | 1.07 ± 0.61 |
| 2.96 ± 2.84 | 0.45 ± 0.60 | 1.29 ± 1.44 | -0.38 ± -1.50 | 0.80 ± 0.32 | 1.07 ± 0.64 |
| 3.04 ± 3.09 | 0.44 ± 0.59 | 1.34 ± 1.49 | -0.43 ± -0.86 | 0.84 ± 0.85 | 1.08 ± 1.00 |
| 4.33 ± 4.48 | 0.35 ± 0.50 | 1.36 ± 1.51 | -0.48 ± -0.62 | 1.51 ± 1.66 | 1.67 ± 1.81 |
| 2.52 ± 2.57 | 0.02 ± 0.17 | 1.26 ± 1.41 | -0.74 ± -1.47 | 0.09 ± 0.04 | 0.66 ± 0.54 |
| 1.85 ± 1.16 | -0.13 ± 0.02 | 1.27 ± 1.42 | -0.88 ± -1.77 | -0.45 ± -1.00 | 0.28 ± -0.50 |
| 1.65 ± 0.05 | -0.19 ± -0.04 | 1.25 ± 1.40 | -0.93 ± -1.92 | -0.62 ± -1.52 | 0.16 ± -1.26 |
| 1.07 ± 0.91 | -0.27 ± -0.12 | 1.25 ± 1.40 | -1.05 ± -1.61 | -1.08 ± -1.23 | -0.20 ± -0.51 |
| 0.98 ± 0.99 | -0.28 ± -0.13 | 1.23 ± 1.38 | -1.09 ± -1.50 | -1.15 ± -1.16 | -0.27 ± -0.39 |
| 0.88 ± 0.86 | -0.30 ± -0.15 | 1.26 ± 1.41 | -1.10 ± -1.55 | -1.23 ± -1.26 | -0.33 ± -0.48 |

| FAP_SrHAP | | | | | | | | | | | | | | | | | | | | | |
|--------------|------|---|------|------------------|---|-------|------------------------------|---|-------|-------------------------|---|-------|-------------------------|---|------|--------------------------------------|---|-------|------------------------|---|--------|
| Time hrs | pH | | | 0.1mM NaOH mL | | | 0.1mM HNO ₃ mL | | | Sr _{tot} mM | | | Ca _{tot} mM | | | PO ₄ _{tot} mM | | | F _{tot} mM | | |
| | | | | | | | | | | 0.09 | ± | 0.003 | | | | 0.06 | ± | 0.004 | | | |
| | 7.30 | ± | 0.00 | | | | | | | 0.09 | ± | 0.003 | 5.12 | ± | 0.01 | 3.15 | ± | 0.02 | 1.03 | ± | 0.01 |
| 0.01 ± 0.01 | 6.67 | ± | 0.09 | 0.00 | ± | 0.00 | 0.00 | ± | 0.00 | 0.20 | ± | 0.03 | 3.37 | ± | 0.36 | 2.62 | ± | 0.36 | 0.67 | ± | 0.24 |
| 0.08 ± 0.00 | 6.46 | ± | 0.21 | 1.75 | ± | 0.00 | 0.00 | ± | 0.21 | 0.23 | ± | 0.05 | 2.81 | ± | 0.14 | 2.21 | ± | 0.19 | 0.50 | ± | 0.06 |
| 0.18 ± 0.01 | 6.27 | ± | 0.64 | 6.45 | ± | 0.00 | 0.00 | ± | 1.63 | 0.26 | ± | 0.09 | 2.37 | ± | 0.05 | 1.85 | ± | 0.10 | 0.38 | ± | 0.02 |
| 0.25 ± 0.00 | 6.58 | ± | 0.81 | 13.60 | ± | 0.00 | 0.00 | ± | 4.38 | 0.23 | ± | 0.08 | 1.98 | ± | 0.11 | 1.55 | ± | 0.12 | 0.28 | ± | 0.04 |
| 0.43 ± 0.11 | 6.92 | ± | 1.18 | 21.25 | ± | 0.00 | 0.00 | ± | 9.82 | 0.22 | ± | 0.11 | 1.45 | ± | 0.38 | 1.14 | ± | 0.34 | 0.29 | ± | 0.10 |
| 1.28 ± 0.39 | 7.52 | ± | 0.40 | 30.40 | ± | 0.03 | 0.02 | ± | 2.97 | 0.16 | ± | 0.10 | 0.70 | ± | 0.14 | 0.50 | ± | 0.02 | 0.16 | ± | 0.12 |
| 2.25 ± 0.35 | 7.55 | ± | 0.40 | 34.06 | ± | 0.91 | 0.64 | ± | 3.76 | 0.12 | ± | 0.11 | 0.31 | ± | 0.23 | 0.27 | ± | 0.09 | 0.10 | ± | 0.10 |
| 4.02 ± 0.02 | 7.55 | ± | 0.33 | 35.35 | ± | 1.19 | 0.84 | ± | 3.41 | 0.17 | ± | 0.05 | 0.19 | ± | 0.17 | 0.19 | ± | 0.05 | 0.07 | ± | 0.08 |
| 6.00 ± 0.00 | 7.53 | ± | 0.37 | 35.68 | ± | 1.33 | 0.94 | ± | 3.23 | 0.11 | ± | 0.07 | 0.20 | ± | 0.09 | 0.20 | ± | 0.02 | 0.06 | ± | 0.08 |
| 24.10 ± 0.09 | 7.57 | ± | 0.35 | 45.85 | ± | 19.81 | 14.01 | ± | 17.19 | 0.16 | ± | 0.05 | 0.20 | ± | 0.06 | 0.16 | ± | 0.01 | 0.0040 | ± | 0.0037 |
| 48.07 ± 0.02 | 7.60 | ± | 0.40 | 45.85 | ± | 32.88 | 23.27 | ± | 17.19 | 0.13 | ± | 0.06 | 0.19 | ± | 0.06 | 0.17 | ± | 0.03 | | - | |
| 72.04 ± 0.06 | 7.60 | ± | 0.41 | 45.85 | ± | 32.88 | 23.27 | ± | 17.19 | 0.14 | ± | 0.08 | 0.18 | ± | 0.05 | 0.17 | ± | 0.02 | | - | |

| FAP_SrHAP | | | | | | | | | | | |
|---------------|----------------------|----------------------|---------------|---------------|---------------|------------------|---------------|------------------|--|--|--|
| SI HAP | SI CaCO ₃ | SI SrCO ₃ | SI brushite | SI OCP | SI β-TCP | CaF ₂ | FAP | SrF ₂ | | | |
| 7.91 ± 5.91 | -1.70 ± -4.49 | -1.83 ± -3.29 | 0.26 ± -2.13 | 4.29 ± 2.33 | 3.89 ± 1.73 | 1.38 ± -0.47 | 14.47 ± 12.72 | -2.25 ± -3.97 | | | |
| 3.43 ± 3.16 | -2.58 ± -3.27 | -2.20 ± -2.94 | -0.29 ± -1.82 | 1.19 ± 0.59 | 1.36 ± 0.78 | 0.91 ± 0.77 | 10.38 ± 8.47 | -2.21 ± -2.34 | | | |
| 2.14 ± 2.27 | -2.88 ± -3.09 | -2.38 ± -2.71 | -0.56 ± -1.10 | 0.14 ± 0.23 | 0.52 ± 0.57 | 0.56 ± 0.04 | 9.04 ± 9.14 | -2.41 ± -2.75 | | | |
| 2.34 ± 2.49 | -2.92 ± -2.80 | -2.37 ± -2.28 | -0.74 ± -0.75 | 0.18 ± 0.33 | 0.57 ± 0.72 | 0.25 ± -0.56 | 9.02 ± 9.17 | -2.60 ± -2.92 | | | |
| 4.23 ± 4.38 | -2.49 ± -2.36 | -1.90 ± -1.78 | -0.64 ± -0.62 | 1.31 ± 1.46 | 1.56 ± 1.71 | -0.08 ± -0.57 | 10.32 ± 10.47 | -2.88 ± -3.11 | | | |
| 5.70 ± 5.85 | -2.04 ± -1.90 | -1.35 ± -1.21 | -0.79 ± -0.82 | 1.84 ± 1.99 | 2.22 ± 2.37 | -0.19 ± -0.55 | 11.35 ± 11.50 | -2.94 ± -3.67 | | | |
| 3.90 ± 4.05 | -2.13 ± -2.29 | -1.23 ± -1.68 | -1.09 ± -1.95 | 0.26 ± 0.37 | 1.10 ± 1.19 | -0.96 ± -0.92 | 9.32 ± 9.46 | -3.61 ± -3.65 | | | |
| 0.40 ± 0.06 | -2.57 ± -3.31 | -1.41 ± -2.80 | -1.68 ± -1.80 | -2.24 ± -2.21 | -0.84 ± -1.05 | -1.85 ± -1.79 | 5.53 ± 4.79 | -4.26 ± -4.23 | | | |
| -0.86 ± -0.75 | -2.80 ± -3.47 | -1.39 ± -1.91 | -2.02 ± -2.07 | -3.30 ± -3.17 | -1.65 ± -1.59 | -2.45 ± -2.33 | 3.73 ± 3.71 | -5.88 ± -6.41 | | | |
| -0.43 ± -0.32 | -2.72 ± -3.09 | -1.41 ± -2.14 | -2.02 ± -3.07 | -3.33 ± -3.39 | -1.51 ± -1.56 | -2.28 ± -2.13 | 4.67 ± 4.81 | -4.54 ± -4.39 | | | |
| -2.11 ± -2.63 | -2.94 ± -3.46 | -1.40 ± -1.92 | -2.19 ± -2.71 | -4.34 ± -4.86 | -2.35 ± -2.87 | -4.30 ± -4.82 | 2.23 ± 1.71 | -6.26 ± -6.79 | | | |
| -2.28 ± -2.81 | -2.97 ± -3.50 | -1.26 ± -1.69 | -2.22 ± -2.74 | -4.47 ± -4.99 | -2.45 ± -2.97 | - | - | -7.52 ± -3.16 | | | |
| -2.36 ± -2.89 | -3.00 ± -3.52 | -1.25 ± -1.80 | -2.23 ± -2.75 | -4.53 ± -5.05 | -2.50 ± -3.02 | - | - | -8.53 ± -3.65 | | | |

| FAP-HAP_SrHAP | | | | | | | |
|---------------|-------------|------------------|------------------------------|-------------------------|-------------------------|--------------------------------------|------------------------|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | Sr _{tot} mM | Ca _{tot} mM | PO ₄ _{tot} mM | F _{tot} mM |
| | | | | 0.16 ± 0.02 | | 0.09 ± 0.01 | |
| | 7.30 ± 0.00 | | | 0.16 ± 0.02 | 5.11 ± 0.003 | 3.15 ± 0.01 | 0.51 ± 0.0003 |
| 0.01 ± 0.01 | 6.49 ± 0.27 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.25 ± 0.02 | 3.34 ± 0.41 | 2.36 ± 0.86 | 0.24 ± 0.12 |
| 0.08 ± 0.00 | 6.75 ± 0.07 | 5.35 ± 2.33 | 0.00 ± 0.00 | 0.31 ± 0.18 | 2.79 ± 0.03 | 1.92 ± 0.61 | 0.15 ± 0.11 |
| 0.17 ± 0.00 | 7.23 ± 0.06 | 16.33 ± 8.31 | 0.00 ± 0.00 | 0.24 ± 0.05 | 2.25 ± 0.12 | 1.14 ± 0.05 | 0.13 ± 0.12 |
| 0.25 ± 0.00 | 7.27 ± 0.01 | 20.03 ± 6.74 | 0.00 ± 0.00 | 0.23 ± 0.06 | 2.12 ± 0.34 | 1.07 ± 0.09 | 0.04 ± 0.02 |
| 0.50 ± 0.00 | 7.28 ± 0.03 | 22.78 ± 4.00 | 0.00 ± 0.00 | 0.22 ± 0.05 | 1.62 ± 0.01 | 0.74 ± 0.19 | 0.06 ± 0.06 |
| 1.00 ± 0.00 | 7.27 ± 0.03 | 27.81 ± 4.01 | 0.00 ± 0.00 | 0.18 ± 0.03 | 1.17 ± 0.06 | 0.40 ± 0.25 | 0.03 ± 0.03 |
| 2.00 ± 0.00 | 7.29 ± 0.03 | 31.64 ± 3.86 | 3.05 ± 4.00 | 0.17 ± 0.002 | 0.87 ± 0.06 | 0.27 ± 0.24 | 0.01 ± 0.004 |
| 4.00 ± 0.00 | 7.27 ± 0.01 | 33.96 ± 4.60 | 6.65 ± 9.09 | 0.17 ± 0.03 | 0.68 ± 0.15 | 0.17 ± 0.14 | 0.01 ± 0.002 |
| 6.06 ± 0.01 | 7.32 ± 0.05 | 35.83 ± 5.69 | 9.03 ± 10.78 | 0.16 ± 0.04 | 0.60 ± 0.20 | 0.12 ± 0.11 | 0.01 ± 0.001 |
| 24.01 ± 0.01 | 7.37 ± 0.14 | 39.35 ± 8.66 | 15.63 ± 15.65 | 0.18 ± 0.05 | 0.50 ± 0.24 | 0.09 ± 0.06 | - |
| 48.00 ± 0.00 | 7.25 ± 0.03 | 39.55 ± 8.52 | 18.13 ± 18.57 | 0.20 ± 0.05 | 0.49 ± 0.23 | 0.10 ± 0.07 | - |
| 72.38 ± 0.53 | 7.33 ± 0.08 | 39.80 ± 8.18 | 18.14 ± 18.59 | 0.21 ± 0.05 | 0.47 ± 0.22 | 0.09 ± 0.07 | - |

| FAP-HAP_SrHAP | | | | | | | | | | | |
|---------------|----------------------|----------------------|---------------|---------------|---------------|------------------|---------------|------------------|--|--|--|
| SI HAP | SI CaCO ₃ | SI SrCO ₃ | SI brushite | SI OCP | SI β-TCP | CaF ₂ | FAP | SrF ₂ | | | |
| 7.94 ± 5.32 | -1.70 ± -4.47 | -1.60 ± -2.49 | 0.27 ± -2.61 | 4.32 ± 1.80 | 3.90 ± 1.17 | 0.78 ± -1.84 | 14.19 ± 11.46 | -2.63 ± -3.52 | | | |
| 2.61 ± 2.73 | -2.76 ± -2.90 | -2.25 ± -2.37 | -0.47 ± -1.57 | 0.45 ± 0.48 | 0.79 ± 0.80 | 0.02 ± -0.08 | 9.28 ± 9.40 | -2.98 ± -3.06 | | | |
| 3.22 ± 2.44 | -2.53 ± -3.17 | -1.89 ± -2.33 | -0.41 ± -1.20 | 0.92 ± 0.05 | 1.20 ± -1.25 | -0.41 ± -0.35 | 9.47 ± 9.34 | -3.42 ± -3.47 | | | |
| 5.07 ± 4.97 | -2.04 ± -2.72 | -1.41 ± -2.62 | -0.40 ± -1.44 | 1.89 ± 1.64 | 2.12 ± 1.80 | -0.54 ± -0.42 | 10.89 ± 10.98 | -3.49 ± -3.38 | | | |
| 5.12 ± 5.10 | -2.02 ± -2.75 | -1.36 ± -2.02 | -0.43 ± -1.05 | 1.90 ± 1.81 | 2.13 ± 1.94 | -1.59 ± -1.59 | 10.42 ± 10.49 | -4.52 ± -4.65 | | | |
| 4.09 ± 3.57 | -2.10 ± -3.14 | -1.36 ± -2.20 | -0.67 ± -1.40 | 1.01 ± 0.63 | 1.51 ± 0.90 | -1.33 ± -1.19 | 9.32 ± 9.27 | -4.16 ± -4.03 | | | |
| 2.78 ± 2.86 | -2.24 ± -3.55 | -1.43 ± -2.67 | -1.05 ± -1.27 | -0.12 ± -0.03 | 0.65 ± 0.64 | -2.12 ± -1.99 | 7.35 ± 6.98 | -4.85 ± -4.72 | | | |
| 1.95 ± 2.08 | -2.34 ± -4.40 | -1.42 ± -2.59 | -1.34 ± -1.42 | -0.90 ± -0.77 | 0.07 ± 0.17 | -3.44 ± -3.46 | 6.17 ± 6.29 | -6.05 ± -6.08 | | | |
| 0.42 ± 0.53 | -2.47 ± -3.21 | -1.46 ± -2.34 | -1.69 ± -1.82 | -2.21 ± -2.10 | -0.86 ± -0.81 | -3.92 ± -4.04 | 4.60 ± 4.69 | -6.43 ± -6.58 | | | |
| -0.37 ± -0.50 | -2.46 ± -2.82 | -1.41 ± -1.83 | -1.89 ± -2.11 | -2.95 ± -2.93 | -1.33 ± -1.50 | -4.01 ± -4.24 | 3.87 ± 3.73 | -6.46 ± -6.75 | | | |
| -0.70 ± -0.62 | -2.46 ± -2.59 | -1.30 ± -1.55 | -2.12 ± -2.90 | -3.61 ± -3.80 | -1.68 ± -1.82 | - | - | - | | | |
| -1.57 ± -1.93 | -2.66 ± -3.06 | -1.43 ± -2.22 | -2.15 ± -2.57 | -3.97 ± -4.12 | -2.06 ± -2.45 | - | - | - | | | |
| -1.39 ± -1.58 | -2.57 ± -2.78 | -1.31 ± -1.70 | -2.19 ± -2.69 | -4.01 ± -5.05 | -2.02 ± -2.75 | - | - | - | | | |

| FAP-CaF ₂ -SrHAP | | | | | | | | | |
|-----------------------------|-------------|------------------|------------------------------|-------------------|-------------|-------------------------|--------------------------------|--|------------------------|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | Sr _{tot} | | Ca _{tot} mM | PO ₄ _{tot} | | F _{tot} mM |
| | | | | mM | | | mM | | |
| | 0.10 ± 0.03 | | | | 0.06 ± 0.02 | | | | |
| | 8.05 ± 0.22 | | | 0.08 ± 0.04 | 6.19 ± 1.86 | 1.60 ± 2.20 | 1.55 ± 2.19 | | |
| 0.005 ± 0.01 | 7.30 ± 2.19 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.17 ± 0.17 | 4.70 ± 2.10 | 2.36 ± 1.09 | 2.12 ± 1.37 | | |
| 0.01 ± 0.01 | 6.45 ± 0.07 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.20 ± 0.12 | 3.20 ± 0.62 | 1.68 ± 0.50 | 0.81 ± 0.34 | | |
| 0.08 ± 0.00 | 6.40 ± 0.13 | 2.97 ± 0.00 | 0.00 ± 3.44 | 0.22 ± 0.12 | 2.78 ± 1.11 | 1.43 ± 0.68 | 0.82 ± 0.01 | | |
| 0.17 ± 0.00 | 6.37 ± 0.37 | 9.29 ± 0.00 | 0.00 ± 5.40 | 0.20 ± 0.09 | 2.33 ± 1.00 | 1.22 ± 0.70 | 0.70 ± 0.03 | | |
| 0.25 ± 0.00 | 6.69 ± 0.26 | 16.64 ± 0.00 | 0.00 ± 6.17 | 0.17 ± 0.05 | 1.96 ± 1.33 | 0.96 ± 0.66 | 0.74 ± 0.26 | | |
| 0.50 ± 0.00 | 7.28 ± 0.04 | 27.33 ± 0.55 | 0.39 ± 4.18 | 0.15 ± 0.04 | 1.47 ± 1.21 | 0.62 ± 0.56 | 1.00 ± 0.62 | | |
| 1.00 ± 0.00 | 6.95 ± 0.50 | 29.79 ± 0.58 | 0.41 ± 6.67 | 0.12 ± 0.01 | 1.05 ± 1.08 | 0.35 ± 0.43 | 0.77 ± 0.22 | | |
| 2.04 ± 0.06 | 7.48 ± 0.31 | 38.96 ± 2.14 | 1.51 ± 5.20 | 0.11 ± 0.004 | 0.45 ± 0.25 | 0.02 ± 0.008 | 0.90 ± 0.40 | | |
| 3.99 ± 0.01 | 7.27 ± 0.07 | 40.19 ± 0.29 | 3.05 ± 4.62 | 0.11 ± 0.003 | 0.37 ± 0.18 | 0.01 ± 0.003 | 0.86 ± 0.34 | | |
| 6.00 ± 0.00 | 7.40 ± 0.14 | 40.82 ± 1.41 | 4.65 ± 4.72 | 0.12 ± 0.002 | 0.36 ± 0.18 | 0.01 ± 0.002 | 0.86 ± 0.29 | | |
| 24.13 ± 0.18 | 7.38 ± 0.14 | 41.59 ± 8.35 | 9.58 ± 4.28 | 0.15 ± 0.02 | 0.29 ± 0.11 | 0.01 ± 0.002 | 0.43 ± 0.38 | | |
| 48.00 ± 0.00 | 7.30 ± 0.04 | 41.72 ± 7.97 | 10.46 ± 4.46 | 0.17 ± 0.03 | 0.28 ± 0.12 | 0.04 ± 0.05 | 0.46 ± 0.29 | | |
| 72.00 ± 0.00 | 7.32 ± 0.02 | 41.72 ± 7.97 | 10.46 ± 4.46 | 0.19 ± 0.06 | 0.25 ± 0.07 | 0.01 ± 0.002 | 0.21 ± 0.06 | | |

| FAP-CaF ₂ -SrHAP | | | | | | | | | |
|-----------------------------|----------------------|----------------------|---------------|---------------|---------------|------------------|---------------|------------------|--|
| SI HAP | SI CaCO ₃ | SI SrCO ₃ | SI brushite | SI OCP | SI β-TCP | CaF ₂ | FAP | SrF ₂ | |
| 8.07 ± 7.54 | -1.67 ± -2.19 | -1.83 ± -2.35 | 0.26 ± -0.26 | 4.37 ± 3.85 | 3.96 ± 3.44 | 2.39 ± 1.86 | 15.10 ± 14.57 | -1.28 ± -1.80 | |
| 7.76 ± 7.91 | -1.94 ± -1.85 | -2.20 ± -2.95 | 0.01 ± 0.06 | 4.07 ± 4.22 | 3.66 ± 3.81 | 2.12 ± 2.20 | 14.79 ± 14.94 | -1.61 ± -3.80 | |
| 1.16 ± 1.29 | -3.04 ± -3.44 | -2.66 ± -3.04 | -0.75 ± -1.00 | -0.55 ± -0.44 | -0.04 ± 0.03 | 1.02 ± 0.83 | 8.36 ± 8.48 | -1.95 ± -1.89 | |
| 1.61 ± 1.76 | -3.05 ± -3.04 | -2.71 ± -3.21 | -0.80 ± -0.78 | -0.27 ± -0.12 | 0.18 ± 0.32 | 0.96 ± 0.50 | 8.87 ± 9.02 | -2.02 ± -2.24 | |
| 2.08 ± 2.23 | -2.84 ± -3.04 | -2.33 ± -3.02 | -0.77 ± -0.80 | -0.01 ± 0.14 | 0.42 ± 0.56 | 0.75 ± 0.23 | 9.12 ± 9.27 | -2.18 ± -2.44 | |
| 3.25 ± 3.35 | -2.37 ± -3.63 | -1.65 ± -1.69 | -0.68 ± -0.75 | 0.70 ± 0.82 | 1.07 ± 1.12 | 0.84 ± 0.87 | 10.17 ± 10.30 | -2.23 ± -2.65 | |
| 4.77 ± 4.92 | -2.27 ± -2.15 | -1.85 ± -1.90 | -0.76 ± -0.63 | 1.50 ± 1.65 | 1.80 ± 1.95 | 1.10 ± 1.21 | 11.47 ± 11.62 | -1.99 ± -2.05 | |
| 3.83 ± 3.98 | -2.20 ± -2.48 | -1.35 ± -1.54 | -1.01 ± -0.88 | 0.66 ± 0.81 | 1.20 ± 1.35 | 0.63 ± 0.71 | 10.33 ± 10.48 | -2.30 ± -2.56 | |
| -3.86 ± -3.77 | -2.69 ± -2.90 | -1.70 ± -3.19 | -2.97 ± -3.46 | -6.37 ± -6.68 | -3.66 ± -3.99 | 0.44 ± 0.49 | 2.78 ± 2.54 | -2.16 ± -2.27 | |
| -4.43 ± -4.95 | -2.63 ± -3.36 | -1.51 ± -2.04 | -3.26 ± -3.78 | -7.04 ± -7.57 | -4.04 ± -4.57 | 0.29 ± 0.30 | 1.71 ± 1.18 | -2.20 ± -2.33 | |
| -6.28 ± -6.80 | -2.75 ± -3.03 | -1.61 ± -2.90 | -3.57 ± -4.09 | -8.44 ± -8.96 | -5.12 ± -5.65 | 0.24 ± 0.23 | 0.10 ± -0.42 | -2.18 ± -2.37 | |
| -6.13 ± -6.65 | -2.69 ± -2.90 | -1.37 ± -1.77 | -3.55 ± -4.07 | -8.33 ± -8.86 | -5.04 ± -5.56 | -0.52 ± -0.45 | 0.23 ± -0.30 | -3.53 ± -4.05 | |
| -2.47 ± -2.32 | -2.86 ± -3.34 | -1.46 ± -2.69 | -2.60 ± -2.49 | -4.85 ± -4.70 | -2.75 ± -2.60 | -0.53 ± -0.62 | 3.50 ± 3.28 | -3.07 ± -3.59 | |
| -5.73 ± -6.25 | -2.90 ± -3.42 | -1.39 ± -1.92 | -3.43 ± -3.95 | -7.96 ± -8.49 | -4.78 ± -5.31 | -1.22 ± -1.75 | 0.13 ± -0.39 | -3.22 ± -3.75 | |

| FAP_SrCO ₃ | | | | | | | |
|-----------------------|-------------|------------------|------------------------------|-------------------------|-------------------------|--------------------------------------|------------------------|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | Sr _{tot} mM | Ca _{tot} mM | PO ₄ _{tot} mM | F _{tot} mM |
| | | | | 0.05 ± 0.003 | | | |
| | 7.30 ± 0.00 | | | 0.05 ± 0.003 | 5.11 ± 0.001 | 3.07 ± 0.001 | 1.02 ± 0.0002 |
| 0.01 ± 0.01 | 6.78 ± 0.04 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.10 ± 0.02 | 3.62 ± 0.03 | 2.43 ± 0.61 | 0.34 ± 0.11 |
| 0.08 ± 0.00 | 6.83 ± 0.00 | 1.00 ± 1.41 | 0.00 ± 0.00 | 0.11 ± 0.01 | 3.56 ± 0.34 | 2.42 ± 0.79 | 0.27 ± 0.01 |
| 0.17 ± 0.00 | 6.85 ± 0.01 | 2.53 ± 2.93 | 0.00 ± 0.00 | 0.09 ± 0.003 | 3.58 ± 0.42 | 2.49 ± 0.99 | 0.32 ± 0.07 |
| 0.25 ± 0.00 | 6.89 ± 0.05 | 5.21 ± 3.80 | 0.00 ± 0.00 | 0.09 ± 0.01 | 3.46 ± 0.87 | 2.42 ± 1.22 | 0.28 ± 0.05 |
| 0.50 ± 0.00 | 6.82 ± 0.30 | 14.64 ± 3.34 | 0.00 ± 0.00 | 0.34 ± 0.39 | 1.76 ± 0.80 | 1.08 ± 0.84 | 0.17 ± 0.09 |
| 1.00 ± 0.00 | 7.26 ± 0.02 | 27.94 ± 2.06 | 0.00 ± 0.00 | 0.48 ± 0.07 | 0.65 ± 0.04 | 0.16 ± 0.04 | 0.08 ± 0.002 |
| 2.00 ± 0.00 | 7.30 ± 0.00 | 29.48 ± 3.36 | 3.17 ± 4.48 | 0.49 ± 0.08 | 0.52 ± 0.02 | 0.07 ± 0.01 | 0.09 ± 0.04 |
| 4.00 ± 0.00 | 7.34 ± 0.00 | 29.48 ± 3.37 | 8.83 ± 10.36 | 0.69 ± 0.05 | 0.58 ± 0.08 | 0.10 ± 0.10 | 0.09 ± 0.06 |
| 6.07 ± 0.09 | 7.37 ± 0.04 | 29.48 ± 3.37 | 10.55 ± 10.04 | 0.75 ± 0.09 | 0.56 ± 0.06 | 0.09 ± 0.09 | 0.09 ± 0.04 |
| 25.01 ± 0.72 | 7.49 ± 0.00 | 29.48 ± 3.37 | 28.57 ± 20.41 | 0.93 ± 0.45 | 0.48 ± 0.09 | 0.02 ± 0.01 | 0.11 ± 0.03 |
| 48.00 ± 0.00 | 7.33 ± 0.02 | 29.69 ± 3.67 | 49.14 ± 34.14 | 1.44 ± 0.41 | 0.59 ± 0.05 | 0.03 ± 0.02 | 0.10 ± 0.03 |
| 72.33 ± 0.47 | 7.28 ± 0.07 | 29.69 ± 3.67 | 53.68 ± 28.15 | 1.58 ± 0.66 | 0.59 ± 0.14 | 0.04 ± 0.03 | 0.09 ± 0.03 |

| FAP_SrCO ₃ | | | | | | | | | | |
|-----------------------|----------------------|----------------------|---------------|---------------|---------------|------------------|---------------|------------------|--|--|
| SI HAP | SI CaCO ₃ | SI SrCO ₃ | SI brushite | SI OCP | SI β-TCP | CaF ₂ | FAP | SrF ₂ | | |
| 7.73 ± 4.21 | -0.93 ± -5.67 | -1.31 ± -2.61 | 0.20 ± -4.66 | 4.12 ± 0.33 | 3.77 ± -0.04 | 1.36 ± -2.05 | 14.28 ± 10.96 | -2.53 ± -3.83 | | |
| 4.07 ± 4.07 | -1.64 ± -2.66 | -1.58 ± -2.53 | -0.26 ± -0.80 | 1.59 ± 1.54 | 1.69 ± 1.53 | 0.31 ± 0.08 | 10.58 ± 10.45 | -3.11 ± -3.23 | | |
| 4.37 ± 4.37 | -1.58 ± -2.79 | -1.45 ± -2.33 | -0.23 ± -0.67 | 1.80 ± 1.78 | 1.85 ± 1.72 | 0.09 ± -2.21 | 10.81 ± 10.81 | -3.28 ± -3.99 | | |
| 4.52 ± 4.56 | -1.56 ± -2.80 | -1.53 ± -3.14 | -0.21 ± -0.58 | 1.92 ± 1.94 | 1.93 ± 1.86 | 0.23 ± -0.21 | 10.96 ± 10.97 | -3.24 ± -3.59 | | |
| 5.05 ± 5.19 | -1.52 ± -2.02 | -1.49 ± -2.28 | -0.19 ± -0.36 | 2.27 ± 2.40 | 2.19 ± 2.28 | 0.10 ± -0.63 | 11.37 ± 11.50 | -3.35 ± -3.83 | | |
| 3.89 ± 4.04 | -1.73 ± -1.72 | -1.14 ± -1.30 | -0.66 ± -0.59 | 1.14 ± 1.29 | 1.40 ± 1.55 | -0.44 ± -0.39 | 10.08 ± 10.23 | -3.44 ± -3.78 | | |
| -0.04 ± -0.14 | -1.75 ± -3.60 | -0.26 ± -0.94 | -1.76 ± -2.27 | -2.64 ± -2.74 | -1.11 ± -1.35 | -1.65 ± -2.60 | 5.47 ± 5.39 | -3.67 ± -4.63 | | |
| -1.49 ± -2.26 | -1.80 ± -3.17 | -0.20 ± -0.99 | -2.23 ± -3.31 | -4.07 ± -4.76 | -2.06 ± -2.95 | -1.65 ± -1.75 | 3.97 ± 3.37 | -3.54 ± -3.60 | | |
| -0.04 ± 0.11 | -1.72 ± -2.66 | -0.03 ± -1.03 | -1.99 ± -1.98 | -2.80 ± -2.65 | -1.24 ± -1.11 | -1.56 ± -1.57 | 5.18 ± 5.33 | -3.32 ± -3.29 | | |
| 0.03 ± 0.18 | -1.70 ± -2.41 | 0.04 ± -1.40 | -2.04 ± -2.01 | -2.82 ± -2.67 | -1.23 ± -1.09 | -1.62 ± -1.70 | 5.22 ± 5.37 | -3.34 ± -3.36 | | |
| -2.54 ± -2.67 | -1.66 ± -2.37 | 0.25 ± -0.07 | -2.80 ± -3.21 | -5.39 ± -5.46 | -2.88 ± -3.12 | -1.51 ± -1.66 | 2.79 ± 2.50 | -3.08 ± -3.12 | | |
| -2.59 ± -2.61 | -1.78 ± -2.55 | 0.23 ± -0.22 | -2.66 ± -2.98 | -5.20 ± -5.19 | -2.83 ± -2.96 | -1.50 ± -1.65 | 2.87 ± 2.75 | -2.98 ± -3.05 | | |
| -1.58 ± -1.44 | -1.83 ± -2.22 | 0.22 ± -0.02 | -2.47 ± -2.55 | -4.33 ± -4.18 | -2.27 ± -2.14 | -1.57 ± -1.65 | 3.99 ± 4.14 | -3.01 ± -3.04 | | |

| FAP-HAP_SrCO ₃ | | | | | | | | |
|---------------------------|-------------|------------------|------------------------------|-------------------------|-------------------------|--------------------------------------|------------------------|--|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | Sr _{tot} mM | Ca _{tot} mM | PO ₄ _{tot} mM | F _{tot} mM | |
| | | | | 0.05 ± 0.0005 | | | | |
| | 7.30 ± 0.00 | | | 0.05 ± 0.0005 | 5.11 ± 0.0003 | 3.07 ± 0.0002 | 0.51 ± 0.0003 | |
| 0.01 ± 0.01 | 6.68 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.08 ± 0.01 | 3.53 ± 0.13 | 2.39 ± 0.63 | 0.30 ± 0.18 | |
| 0.08 ± 0.00 | 6.75 ± 0.08 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.09 ± 0.002 | 3.63 ± 0.29 | 2.50 ± 0.68 | 0.29 ± 0.17 | |
| 0.17 ± 0.00 | 7.09 ± 0.26 | 8.55 ± 5.59 | 0.00 ± 0.00 | 0.08 ± 0.004 | 2.88 ± 0.24 | 1.88 ± 0.57 | 0.27 ± 0.17 | |
| 0.24 ± 0.01 | 7.09 ± 0.27 | 18.70 ± 7.50 | 0.00 ± 0.00 | 0.06 ± 0.01 | 2.19 ± 0.58 | 1.30 ± 0.61 | 0.23 ± 0.05 | |
| 0.53 ± 0.04 | 7.28 ± 0.02 | 25.13 ± 6.24 | 0.00 ± 0.00 | 0.06 ± 0.01 | 1.32 ± 0.44 | 0.69 ± 0.32 | 0.11 ± 0.01 | |
| 1.00 ± 0.00 | 7.28 ± 0.01 | 31.88 ± 0.10 | 0.10 ± 0.15 | 0.27 ± 0.06 | 0.62 ± 0.12 | 0.16 ± 0.01 | 0.06 ± 0.003 | |
| 2.00 ± 0.00 | 7.30 ± 0.05 | 31.88 ± 0.10 | 0.30 ± 0.14 | 0.39 ± 0.003 | 0.54 ± 0.11 | 0.08 ± 0.001 | 0.04 ± 0.001 | |
| 4.08 ± 0.12 | 7.29 ± 0.04 | 31.88 ± 0.10 | 4.80 ± 3.67 | 0.56 ± 0.11 | 0.62 ± 0.21 | 0.12 ± 0.08 | 0.02 ± 0.0002 | |
| 6.17 ± 0.24 | 7.34 ± 0.02 | 31.88 ± 0.10 | 5.99 ± 3.74 | 0.60 ± 0.11 | 0.58 ± 0.19 | 0.10 ± 0.06 | 0.02 ± 0.0002 | |
| 24.63 ± 0.90 | 7.45 ± 0.02 | 31.88 ± 0.10 | 12.55 ± 2.40 | 0.79 ± 0.11 | 0.54 ± 0.09 | 0.04 ± 0.002 | 0.01 ± 0.003 | |
| 48.00 ± 0.00 | 7.29 ± 0.08 | 40.55 ± 10.81 | 31.96 ± 17.94 | 1.01 ± 0.19 | 0.57 ± 0.04 | 0.04 ± 0.01 | 0.01 ± 0.001 | |
| 72.00 ± 0.00 | 7.34 ± 0.06 | 40.55 ± 10.81 | 35.09 ± 13.95 | 1.20 ± 0.30 | 0.59 ± 0.03 | 0.04 ± 0.01 | 0.01 ± 0.01 | |

| FAP-HAP_SrCO ₃ | | | | | | | | | |
|---------------------------|----------------------|----------------------|---------------|---------------|---------------|------------------|---------------|------------------|--|
| SI HAP | SI CaCO ₃ | SI SrCO ₃ | SI brushite | SI OCP | SI β-TCP | CaF ₂ | FAP | SrF ₂ | |
| 7.75 ± 4.38 | -0.92 ± -5.22 | -1.31 ± -3.35 | 0.21 ± -3.77 | 4.14 ± 0.70 | 3.78 ± 0.20 | 0.76 ± -3.02 | 14.00 ± 10.68 | -3.13 ± -5.18 | |
| 3.38 ± 3.28 | -1.77 ± -3.51 | -1.77 ± -2.76 | -0.34 ± -0.91 | 1.12 ± 1.00 | 1.31 ± 1.05 | 0.24 ± 0.24 | 9.90 ± 9.28 | -3.25 ± -3.22 | |
| 4.18 ± 4.29 | -1.67 ± -2.23 | -1.67 ± -2.42 | -0.26 ± -0.63 | 1.67 ± 1.74 | 1.72 ± 1.73 | 0.22 ± 0.20 | 10.50 ± 10.52 | -3.26 ± -3.26 | |
| 6.10 ± 6.25 | -1.30 ± -1.46 | -1.27 ± -1.44 | -0.22 ± -0.42 | 2.76 ± 2.90 | 2.68 ± 2.81 | 0.06 ± 0.07 | 11.84 ± 11.98 | -3.41 ± -3.39 | |
| 5.52 ± 5.67 | -1.37 ± -1.46 | -1.31 ± -1.41 | -0.43 ± -0.49 | 2.24 ± 2.39 | 2.30 ± 2.45 | -0.25 ± -1.01 | 11.38 ± 11.53 | -3.69 ± -4.37 | |
| 3.97 ± 4.11 | -1.42 ± -1.87 | -1.14 ± -1.97 | -0.81 ± -0.96 | 0.86 ± 0.99 | 1.34 ± 1.44 | -1.08 ± -1.84 | 9.54 ± 9.67 | -4.29 ± -4.77 | |
| 0.06 ± 0.06 | -1.74 ± -2.40 | -0.48 ± -1.23 | -1.77 ± -2.37 | -2.61 ± -2.68 | -1.08 ± -1.24 | -1.94 ± -2.47 | 5.40 ± 5.41 | -4.19 ± -5.19 | |
| -1.04 ± -1.42 | -1.77 ± -2.91 | -0.29 ± -1.15 | -2.10 ± -2.88 | -3.65 ± -4.01 | -1.77 ± -2.30 | -2.43 ± -3.28 | 4.06 ± 3.75 | -4.46 ± -5.62 | |
| 0.04 ± 0.18 | -1.74 ± -2.41 | -0.17 ± -1.33 | -1.88 ± -1.96 | -2.65 ± -2.51 | -1.15 ± -1.05 | -2.72 ± -3.23 | 5.00 ± 5.14 | -4.65 ± -5.44 | |
| 0.03 ± 0.18 | -1.71 ± -2.16 | -0.08 ± -0.73 | -1.98 ± -2.06 | -2.80 ± -2.66 | -1.21 ± -1.09 | -2.94 ± -3.47 | 4.81 ± 4.95 | -4.81 ± -5.62 | |
| -1.25 ± -1.26 | -1.63 ± -2.29 | 0.15 ± -0.92 | -2.40 ± -3.03 | -4.18 ± -4.26 | -2.04 ± -2.22 | -3.60 ± -3.77 | 3.15 ± 3.18 | -5.36 ± -5.74 | |
| -2.36 ± -2.85 | -1.82 ± -2.65 | 0.06 ± -0.34 | -2.52 ± -3.60 | -4.94 ± -6.17 | -2.64 ± -3.55 | -3.92 ± -4.47 | 2.00 ± 0.55 | -5.57 ± -7.19 | |
| -1.85 ± -1.86 | -1.75 ± -2.53 | 0.16 ± -0.75 | -2.47 ± -3.18 | -4.60 ± -4.70 | -2.38 ± -2.57 | -3.37 ± -3.29 | 2.79 ± 2.88 | -5.03 ± -5.00 | |

| FAP-CaF ₂ -SrCO ₃ | | | | | | | |
|---|-------------|------------------|------------------------------|-------------------------|-------------------------|--------------------------------------|------------------------|
| Time hrs | pH | 0.1mM NaOH mL | 0.1mM HNO ₃ mL | Sr _{tot} mM | Ca _{tot} mM | PO ₄ _{tot} mM | F _{tot} mM |
| | | | | 0.06 ± 0.01 | | | |
| | 7.30 ± 0.00 | | | 0.06 ± 0.01 | 6.17 ± 0.02 | 3.08 ± 0.01 | 3.08 ± 0.01 |
| 0.01 ± 0.01 | 6.90 ± 0.42 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.09 ± 0.002 | 3.85 ± 0.01 | 2.28 ± 0.55 | 1.08 ± 0.94 |
| 0.09 ± 0.01 | 7.00 ± 0.33 | 11.85 ± 16.76 | 0.00 ± 0.00 | 0.09 ± 0.001 | 3.82 ± 0.02 | 2.25 ± 0.60 | 1.02 ± 0.83 |
| 0.18 ± 0.01 | 7.01 ± 0.36 | 11.85 ± 16.76 | 0.00 ± 0.00 | 0.08 ± 0.02 | 3.05 ± 1.12 | 1.72 ± 1.25 | 0.90 ± 0.67 |
| 0.25 ± 0.00 | 7.07 ± 0.28 | 15.61 ± 12.60 | 0.00 ± 0.00 | 0.08 ± 0.02 | 2.90 ± 0.99 | 1.58 ± 1.09 | 0.74 ± 0.81 |
| 0.47 ± 0.05 | 7.29 ± 0.01 | 23.52 ± 2.58 | 0.00 ± 0.00 | 0.07 ± 0.01 | 2.21 ± 0.26 | 0.96 ± 0.34 | 0.74 ± 0.69 |
| 0.98 ± 0.02 | 7.34 ± 0.02 | 33.66 ± 2.88 | 1.32 ± 1.87 | 0.38 ± 0.09 | 0.87 ± 0.24 | 0.06 ± 0.05 | 0.53 ± 0.62 |
| 1.97 ± 0.05 | 7.42 ± 0.11 | 33.66 ± 2.88 | 4.25 ± 2.62 | 0.86 ± 0.05 | 0.89 ± 0.25 | 0.06 ± 0.08 | 0.56 ± 0.56 |
| 4.17 ± 0.33 | 7.33 ± 0.01 | 33.66 ± 2.88 | 27.07 ± 27.49 | 0.83 ± 0.14 | 0.79 ± 0.12 | 0.02 ± 0.02 | 0.56 ± 0.65 |
| 5.97 ± 0.05 | 7.41 ± 0.11 | 33.66 ± 2.88 | 27.80 ± 26.91 | 0.87 ± 0.17 | 0.77 ± 0.09 | 0.01 ± 0.005 | 0.52 ± 0.61 |
| 24.51 ± 0.72 | 7.36 ± 0.14 | 33.66 ± 2.88 | 32.86 ± 20.74 | 1.21 ± 0.20 | 0.81 ± 0.12 | 0.01 ± 0.01 | 0.61 ± 0.70 |
| 48.00 ± 0.00 | 7.33 ± 0.02 | 33.66 ± 2.88 | 39.50 ± 12.20 | 1.56 ± 0.38 | 0.86 ± 0.08 | 0.01 ± 0.01 | 0.60 ± 0.68 |
| 71.87 ± 0.19 | 7.31 ± 0.04 | 33.86 ± 2.60 | 44.78 ± 6.43 | 1.99 ± 0.24 | 0.90 ± 0.05 | 0.01 ± 0.004 | 0.58 ± 0.67 |

| FAP-CaF ₂ -SrCO ₃ | | | | | | | | | |
|---|----------------------|----------------------|---------------|---------------|---------------|------------------|---------------|------------------|--|
| SI HAP | SI CaCO ₃ | SI SrCO ₃ | SI brushite | SI OCP | SI β-TCP | CaF ₂ | FAP | SrF ₂ | |
| 7.96 ± 7.31 | -0.88 ± -2.26 | -1.30 ± -2.17 | 0.23 ± -0.92 | 4.27 ± 3.61 | 3.89 ± 3.07 | 2.37 ± 0.74 | 14.98 ± 14.34 | -1.55 ± -2.37 | |
| 6.35 ± 6.50 | -1.35 ± -1.35 | -1.36 ± -1.37 | -0.15 ± -0.23 | 3.05 ± 3.20 | 2.85 ± 3.00 | 1.44 ± 1.54 | 12.61 ± 12.76 | -2.07 ± -1.97 | |
| 5.77 ± 5.92 | -1.31 ± -1.44 | -1.30 ± -1.43 | -0.19 ± -1.48 | 2.47 ± 2.54 | 2.49 ± 2.55 | 1.36 ± 1.44 | 12.59 ± 12.73 | -2.14 ± -2.05 | |
| 4.27 ± 3.99 | -1.41 ± -1.65 | -1.35 ± -1.55 | -0.38 ± -0.57 | 1.48 ± 1.28 | 1.71 ± 0.57 | 1.06 ± 1.07 | 10.98 ± 10.69 | -2.38 ± -2.36 | |
| 4.44 ± 3.96 | -1.38 ± -1.79 | -1.33 ± -1.66 | -0.37 ± -0.53 | 1.66 ± 1.66 | 1.83 ± 1.54 | 0.96 ± 1.09 | 10.88 ± 10.56 | -2.48 ± -2.35 | |
| 5.04 ± 5.15 | -1.23 ± -1.96 | -1.11 ± -1.68 | -0.52 ± -0.79 | 1.78 ± 1.86 | 2.03 ± 2.04 | 0.88 ± 0.99 | 11.08 ± 10.99 | -2.53 ± -2.43 | |
| 0.33 ± 0.48 | -1.55 ± -2.07 | -0.29 ± -0.98 | -2.00 ± -1.96 | -2.60 ± -2.45 | -1.05 ± -0.91 | 0.21 ± 0.35 | 5.83 ± 5.97 | -1.87 ± -1.73 | |
| 1.46 ± 1.61 | -1.44 ± -1.68 | 0.14 ± -0.28 | -1.89 ± -1.77 | -1.81 ± -1.66 | -0.42 ± -0.27 | 0.21 ± 0.32 | 7.02 ± 7.17 | -1.62 ± -1.50 | |
| -1.59 ± -1.44 | -1.63 ± -2.27 | 0.01 ± -1.01 | -2.59 ± -2.59 | -4.46 ± -4.31 | -2.32 ± -2.18 | 0.25 ± 0.39 | 3.90 ± 4.02 | -1.52 ± -1.38 | |
| -2.44 ± -2.29 | -1.54 ± -1.93 | 0.11 ± -0.85 | -3.01 ± -3.10 | -5.53 ± -5.39 | -2.97 ± -2.84 | 0.19 ± 0.33 | 2.89 ± 3.00 | -1.56 ± -1.41 | |
| -2.66 ± -2.86 | -1.60 ± -2.41 | 0.21 ± -0.14 | -2.80 ± -3.07 | -5.43 ± -5.45 | -2.93 ± -3.16 | 0.31 ± 0.45 | 3.36 ± 3.09 | -1.31 ± -1.17 | |
| -2.61 ± -2.46 | -1.63 ± -2.56 | 0.24 ± -0.40 | -2.93 ± -2.87 | -5.42 ± -5.27 | -2.99 ± -2.85 | 0.32 ± 0.46 | 2.99 ± 3.13 | -1.21 ± -1.07 | |
| -3.86 ± -3.73 | -1.65 ± -3.00 | 0.32 ± -0.56 | -3.26 ± -3.32 | -6.61 ± -6.47 | -3.78 ± -3.69 | 0.32 ± 0.46 | 1.78 ± 1.80 | -1.17 ± -1.03 | |

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Chapter

4

Synthesis and Characterization of Strontium Hydroxyapatite – $\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$

Abstract

Strontium hydroxyapatite ($\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$, SrHAP) has provoked some interest since it is a suitable seeding template for the precipitation of calcium-phosphates, where the use of a calcium-free nucleation surface facilitates phase distinction. Since SrHAP is not a commercial product it has been synthesized by different research groups, but mainly resulted in impure products.

Strontium hydroxyapatite was synthesized by the addition of phosphoric acid to dissolved strontium nitrate. The aim was the production of pure, crystalline SrHAP. The final precipitate was intensively investigated by FTIR, Thermogravimetry Analysis (TGA), TEM, XRD and XPS. Further the specific surface area, specific density and thermal stability up to 1500°C were determined. The results were consistent for the formation of SrHAP, though impurities of SrCO_3 and $\text{Sr}(\text{OH})_2$ were detected.

4.1 Introduction

Strontium hydroxyapatite has received moderate interest in the past years because of its potential use to immobilise radioactive strontium,^{1, 2} its potential application in nanoelectronics³ or as a catalyst for the oxidation of methane.⁴ Because of its use in medical and dental treatment, it was synthesized in solid solutions with HAP.⁵ Recently, it has been used as a seeding template for the heterogeneous precipitation of calcium phosphates (chapter 3).

To date, SrHAP is not a commercial product and different methods have been applied for its synthesis.

Neutralisation. Analogous to HAP production,⁶⁻⁹ SrHAP can be synthesized by neutralizing a boiling strontium hydroxide ($\text{Sr}(\text{OH})_2$) solution with phosphoric acid. This method is suitable for the production of large quantities of SrHAP, though its

crystallinity can be rather poor and the final precipitate has been observed to contain some quantities of other strontium phases, such as strontium hydrogen phosphate (SrHPO_4) or tristrontium phosphate ($\text{Sr}_3(\text{PO}_4)_2$).¹⁰

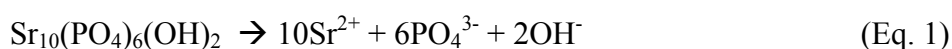
Solid-solid reaction. For this method, SrHPO_4 is heated up to 900°C with numerous grindings over many hours (analogous to Kikuchi et al. (1994)¹¹). The main disadvantage of this method is the difficulty of obtaining pure SrHAP, since i) a homogeneous substrate mixing during heating has to be guaranteed, and ii) loss of crystal water at high temperatures could lead to a decomposition of the SrHAP crystal structure to $\text{Sr}_3(\text{PO}_4)_2$, which was observed by Kikuchi et al. (1994).¹¹

Double-composition. Collin (1959)¹² synthesized SrHAP by adding dissolved ammonium phosphate ($(\text{NH}_4)_2\text{HPO}_4$) to a boiling aqueous strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) solution, while the addition of concentrated NH_3 maintained the solution pH at approximately 11. The suspension was then heated to 95°C , stirred for 6h and the precipitate was then washed repeatedly and was finally dried at 110°C . The strontium-to-phosphate (Sr/P) ratio of the final precipitate was stoichiometric for SrHAP (1.67). Li et al. (2001)¹³ and Kim and Park (2005)³ also used this method, but heated the suspension to 180°C prior to filtering the precipitate. Sugiyama et al. (1996)⁴ calcined the product at 500°C . According to Leroux and Lacout (2001)¹⁰ the double-composition method results in homogeneous and well-crystallized SrHAP, but this method is only applicable to the preparation of small quantities.

Solids obtained by the double-composition method were characterized mainly by XRD,^{3, 10, 4} sometimes in combination with FTIR^{10, 13} and/or TEM.^{3, 13} An extended solid characterization was provided by Li et al. 2011,¹³ but inconsistency in data

analysis indicated impure SrHAP. Sugiyama et al. (1996)⁴ determined the specific surface area and performed XPS.

The solubility of SrHAP was determined by Dedhiya et al. (1972)¹⁴ for the formation of a calcium-strontium hydroxyapatite surface layer in an acidic medium (pH 4.0-5.0) by dissolving HAP in the presence of strontium ions. The obtained solubility product of SrHAP ranged between approximately -75.0 and -89.8 (log K_s) according to the reaction:



In the present study SrHAP was synthesized using a modified version of the double-composition method. A comprehensive solid characterization of surface and bulk composition by XPS, TEM/EDX, FTIR and TGA was performed. The crystallinity and purity of the product prior and after thermal treatment was verified by XRD. Further, the specific surface area, specific density and the dissolution at 25°C of the synthesized SrHAP were determined.

4.2 Experimental Section

Chemicals and Materials

Chemicals used were of at least “pro analysis” grade (p.a., from Merck): nitric acid (65% supra pure), phosphoric acid (85%), ammonia (25%), strontium nitrate. Nanopure water (Barnstead NANOpure Diamond UV, resistivity > 18MΩ-cm) was used for rinsing and solution preparations and all vessels used were acid-washed (0.65% HNO₃ followed by ≥3 rinses with nanopure water).

Synthesis of SrHAP

The synthesis of SrHAP was performed as described previously^{12, 15, 3, 13} though it was slightly modified with regards to reactants, reaction times and synthesis

temperature. In order to obtain 100g SrHAP, a stoichiometric amount of $\text{Sr}(\text{NO}_3)_2$ was dissolved in 1L nanopure water by motor-driven stirring with 800 rpm. The solution pH was increased from 5.6 to 12.3 by the addition of 0.25L ammonia (25%) (instead of concentrated NH_3)¹². Argon gas (instead of NH_3 -gas)¹² was directly bubbled into the suspension to eliminate CO_2 . After 30 min the solution was clear and the temperature was slowly increased to 55°C within 8h. Phosphoric acid (44%) (instead of dissolved $(\text{NH}_4)_2\text{HPO}_4$)^{15, 3, 13} was added with approximately 0.2 mL sec^{-1} . The pH was controlled to be above 7.5 by the addition of extra ammonia (ca. 3.6L, 25%). After 24h (3h¹⁵) all solutions had been added and the stirring speed was reduced to 300 rpm, while the temperature was increased to 80°C. Once the 80°C was achieved (of 95°C,¹² 70°C,^{15, 13} 180°C^{3, 13}), the stirring speed was further reduced to 100 rpm. After 6h (of 12h,¹⁵ 0.5h,¹³ 10 min³) the system was cooled to room temperature by stirring at 50 rpm overnight (instead of heating the substrate to 180°C for 8h¹³ or 10h³). Finally, the material was washed 10 times with nanopure water, filtered (0.45- μm cellulose acetate), dried at 100°C for 24h (of 80°C, 12h,¹³ 80°C, 5h³) and ground to a fine white powder for further analysis.

Equilibration

A total of 32 suspensions, each containing 0.25g powdered SrHAP were equilibrated in 50 mL nanopure water on a rotary shaker (IKA KS 260 basic, 200 rpm). The batches were closed to the atmosphere. Twenty-four samples (Batch 1) were equilibrated at 25°C in parallel with 8 samples (Batch 2) at 40°C. In order to determine the required equilibration time, samples (15 mL, filtered 0.20- μm nylon, PALL, acidified to 0.65% HNO_3) were taken from Batch 1 once a week (with more intensive sampling in the first week). The samples were analysed for solution pH and elemental composition (measured by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)).

The total dissolved concentrations of strontium (Sr) and phosphate (PO₄) did not differ by more than 10% in the last three weeks. After 6 weeks the temperature of the Batch 2 samples was reduced to 25°C and the samples were re-equilibrated for a further 48d. After 91d, the 8 samples of Batch 2 and the remaining 10 samples of Batch 1 were taken to determine equilibrium concentrations. From each batch 5 samples were analysed for total Dissolved Inorganic Carbon (DIC).

The pH (Metrohm 713) was measured after an electrode (Metrohm 6.0259.100) two-point calibration was performed by using Titrisol buffers (pH 4 and 9) and checked by measuring buffer of pH 7 (Titrisol; ionic strength I = 0.11 M).

Saturation indices were calculated according to $(\log (IAP/K_{s0})^{1/\eta})$, for SrCO₃ and Sr(OH)₂. Please note that the log K_s values for SrCO₃ of -9.15 reported by Motimer¹⁶ and of -9.96 reported by Euler¹⁷ (reaction equations and conditions of value determination are not provided) were lower than that for CaCO₃ of -8.35 reported by Martell and Smith.¹⁸

Elemental, Total Organic Carbon (TOC) and Dissolved Inorganic Carbon (DIC) analyses

Elemental analyses by ICP-OES, ICP-MS and TOC and DIC analyses were performed as described in Sternitzke et al. 2012.¹⁹

Acid digestion

Approximately 0.1g powdered SrHAP was digested in 10 mL 33% HNO₃ overnight before the volume was adjusted to 100 mL with nanopure water. Dilutions of 1:100 and 1:1000 were analyzed for Sr and PO₄ by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) measurements. The experiment was performed in triplicate.

Specific density

The specific density of SrHAP was determined by pycnometry at 20°C. Approximately 0.1g of solid material was added to 50 mL cyclo hexane (Sigma-Aldrich, p.a.) and put under vacuum for about 5 min to eliminate air from pore spaces before the actual determination took place. The experiment was performed in triplicate.

BET

The specific surface area of SrHAP was determined by the nitrogen adsorption-desorption method for meso-porous material of Brunauer, Emmett and Teller (BET) using a Carlo Erba Sorptomatic 1900 instrument. Prior the analysis the powdered SrHAP (0.5g) was dried and degassed under vacuum at 110°C for 48h. The experiment was performed in triplicate.

XPS

A surface survey of powdered SrHAP was performed by X-ray Photoelectron Spectroscopy (XPS) according to Sternitzke et al. 2012.¹⁹ For each sample a single analysis was conducted.

TEM/EDX

Transmission Electron Microscopy (TEM) including Energy Dispersive X-ray (EDX) analysis was performed as described in Sternitzke et al. 2012.¹⁹ The EDX data were collected for single crystals of four different micrographs obtained from three analogously prepared samples.

FTIR

Fourier Transform Infrared Spectroscopy (FTIR, FTS 575C, Portman Instruments AG, Software BIO-RAD Win-IR, version 4.14) measurement was conducted as a single analysis according to Sternitzke et al. 2012,¹⁹ though slightly different instrument set-

ups were used. The velocity of recording the spectra was 10 kHz, with a filter of 1.2 kHz, UDR 2, a resolution of 2, an aperture of 0.25 cm^{-1} , and a sensitivity of 16; the signal was approximately -3.77 counts. A background scan was taken before and after measurements, which was subtracted from the sample scan. The data were normalized to the baseline.

TGA

Thermogravimetric analysis (TGA, NETZSCH STA 409 C/CD, Blazers MID) was performed on 100mg powdered SrHAP. The sample, filled in a Differential Thermal Analysis/Thermogravimetric (DTA/TG) crucible of Al_2O_3 , was heated in an atmosphere of synthetic air for a temperature range of 40 - 1500°C at a rate of $10^\circ\text{C min}^{-1}$. The observed elemental mass alterations in relation to the change in temperature per time were applied for the determination of mass losses attributed to oxygen, dioxygen, water, carbon monoxide, carbon dioxide, hydrogen phosphate, dihydrogen phosphate and phosphoric acid. After analysis the solid was collected and examined by XRD.

XRD

Powder X-ray Diffraction (XRD; X'Pert PRO) with Cu $K\alpha$ radiation (45 kV and 40 mA) was conducted on compacted SrHAP powder. A second run was conducted for the solid obtained at the endpoint of TGA. Since its amount was relatively small (less than 100 mg) the material was stuck on a disc. The obtained XRD patterns were compared to reference cards of the International Centre for Diffraction Data (ICDD). The program HighScorePlus 2.2 provided by PANalytical was used for data evaluation.

4.3 Results and Discussion

The double-composition method was used to synthesize SrHAP. After a complete reaction a surface and bulk Sr/P stoichiometry of 1.67 would be expected. If the product were to be impure, the stoichiometry could be different and phases such as SrHPO_4 , $\text{Sr}_3(\text{PO}_4)_2$, collin salt ($\text{Sr}_6\text{H}_3(\text{PO}_4)_5 \cdot 2\text{H}_2\text{O}$), SrCO_3 or strontium hydroxide ($\text{Sr}(\text{OH})_2$) should be detectable. In the case of incomplete reaction, reactant residues of $\text{Sr}(\text{NO}_3)_2$ and H_3PO_4 should be distinguishable.

Density, surface area, molar ratios and carbon content

From acid digestion the molar Sr/P ratio of the synthesized SrHAP was 1.95 ± 0.78 , indicating an excess of Sr relative to stoichiometric SrHAP ($\text{Sr/P} = 1.67$). The TOC of the solid SrHAP was approximately 0.03 ± 0.02 wt%, the TIC around 0.24 ± 0.005 wt%. The specific density of 2.99 ± 0.23 g cm⁻³ was lower than that reported by Sudarsanan and Young (1972)²⁰ (3.80 g cm⁻³) and the specific surface area of 42.1 ± 1.7 m² g⁻¹ was also lower than that obtained by Sugiyama et al. (1996)⁴ (60.3 m² g⁻¹).

TEM/EDX

The SrHAP crystals in the present study were needle-shaped (Figure 4.1a) with an average length of 100 to 200 nm and diameters ranging from 20 to 40 nm. Their morphology was similar to those from literature.^{3, 13} An EDX analysis resulted in an atomic Sr/P ratio of 2.20 ± 0.36 atm% ($n = 4$), which was higher than the expected stoichiometric Sr/P ratio of 1.67. The finding supports results from acid digestion that the synthesized SrHAP was enriched in Sr.

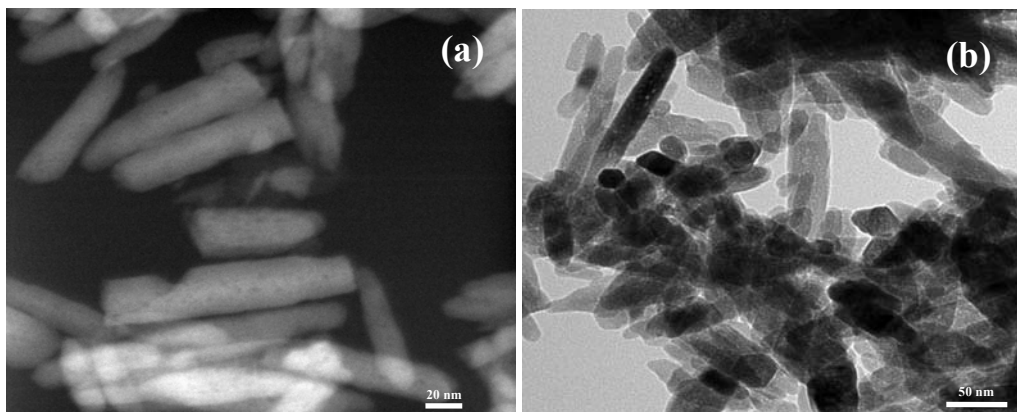


Figure 4.1 Transmission micrographs of (a) SrHAP crystals and (b) in presence of rhombohedral structures.

In the present study, several TEM images have been taken and indications of neither plate- or flake-like crystals for SrHPO_4 nor for $\text{Sr}_3(\text{PO}_4)_2$ (plates),³ nor for SrCO_3 (flakes)²¹ were found. However rhombohedral structures with dimensions of 30 x 40 nm were detected (Figure 4.1b). Although these structures could be the results of i) surface effects of the sample or ii) unready crystallized SrHAP particles, it is also possible that iii) these phases were collin salt ($\text{Sr}_6\text{H}_3(\text{PO}_4)_5 \cdot 2\text{H}_2\text{O}$ (rhombohedral))³ or $\text{Sr}(\text{OH})_2$ (globular to rhombohedral).²² Since these structures were only observed attached to needle-shaped particles their PO_4 content could not be detected specifically for phase distinction.

XPS

The surface composition of SrHAP was determined by XPS and resulted in assignments for Sr, oxygen (O), and phosphate (P) (Table 4.1).⁴ In comparison to nominal values the SrHAP surface was clearly enriched in Sr by approximately 3 atm%, but slightly deficient in O and P. This resulted in an atomic Sr/P ratio of 1.99.

The SrHAP surface was also slightly enriched in adventitious carbon (C), which was surface bound carbon (C-C) and oxygen bound carbon (C-O) which was either incorporated in SrHAP or existed as a co-precipitate in form of SrCO_3 .

Table 4.1 Peak identification for SrHAP obtained by XPS including total contents of Sr, P, O and C of the sample in comparison to nominal values.

| Peak identification | C (KLL) | O (KLL) | O (1s) | Sr (3s) | C (s1) | Sr (3p1) | Sr (3p3) | P (2s) | Sr (3d) | P (2p) | Sr (4s) | O (2s) | Sr (4p) |
|---------------------|---------|---------|--------|---------|--------|----------|----------|--------|---------|--------|---------|--------|---------|
| Binding energy [eV] | 1220 | 977 | 531 | 357 | 301 | 279 | 268 | 190 | 133 | 133 | 49 | 37 | 19 |

| | Sr (3p1) | P (2s) | O (1s) | C (1s) | | O/P | Sr/P |
|-----------------|----------|--------|--------|--------|--|------|------|
| SrHAP nominally | 23.80 | 14.30 | 61.90 | - | | 4.37 | 1.67 |
| SrHAP | 26.91 | 13.56 | 59.11 | 0.36 | | 4.37 | 1.99 |

FTIR

The FTIR spectrum of SrHAP (Figure 4.2a) agrees with that for SrHAP with strong absorbances at 1006, 591, and 555 cm^{-1} , medium absorbances at 1075 and 948 cm^{-1} , two weak absorbances at 457 and 872 cm^{-1} and a weak shoulder was observed at 530 cm^{-1} .²³ The peaks at 1073, 1006, and 948 cm^{-1} are assigned to P-O stretching modes, while the peaks at 591, 555, and 457 cm^{-1} are assigned to O-P-O bending modes.²³ The weak shoulder observed at 530 cm^{-1} (Figure 4.2b) can most likely be assigned to the OH libration mode in SrHAP.²³ The weakness of this absorbance could be caused by i) strong absorbances of nearby PO-modes, which partly overlap with the OH mode, or ii) it indicates non-stoichiometric SrHAP with incomplete OH incorporation.

In contrast, Li et al. (2011)¹³ assumed an OH libration mode for SrHAP at 1636 cm^{-1} . This seems unlikely as this position is too far from the OH libration mode for HAP at 630 cm^{-1} (Figure 4.2b). The interatomic distances within the SrHAP crystal structure are

greater than in HAP due to the greater atom radius of Sr, leading to lower distortion of the crystal structure and thus lower stability relative to the structure of HAP. The effect of Sr incorporation can be observed by shifts of the PO-modes of SrHAP to lower wavenumbers relative to those of HAP. However, the PO-modes of SrHAP and HAP are close and thus it could be expected that the OH libration of SrHAP would be located close to the same PO modes (600 and 560 cm^{-1}) as for HAP. The observed absorbance reported by Li et al. (2011)¹³ at 1636 cm^{-1} can most probably be assigned to residual nitrate from synthesis.²⁴

The simultaneous presence of SrHPO_4 is unlikely, since the characteristic²⁵ broad absorbances above 1500 cm^{-1} were not observed in the present study. The other absorbances for SrHPO_4 (e.g. 521 , 547 , 572 , 601 , 892 , 934 , 1010 , 1105 , 1134 , and 1188 cm^{-1})²⁵ or those for $\text{Sr}_3(\text{PO}_4)_2$ (e.g. 449 , 564 , 950 , 999 , 1019 and 1090 cm^{-1})²⁶ could have been obscured by the relatively broad features of SrHAP. Thus, the presence of $\text{Sr}_3(\text{PO}_4)_2$ cannot be entirely excluded from FTIR. Sharp absorbances²⁷ for $\text{Sr}(\text{OH})_2$ at 3590 cm^{-1} were not identified in the present study. In the present study, absorbances for carbonate¹³ were observed at 1420 and 1445 cm^{-1} , while it is reported that SrCO_3 exhibits an absorbance at 1435 cm^{-1} .¹⁹ Other possible SrCO_3 -assigned absorbances at 698 , 705 , 843 and 854 cm^{-1} were not seen, but could not have been obscured.

In the present study another absorbance was observed at 872 cm^{-1} , which was also noticed by Li et al. (2011),¹³ who assigned this absorbance to a HPO_4 group. This group could be i) a surface-bound residue from synthesis, or ii) be incorporated into the SrHAP crystal structure, which would result in a non-stoichiometric SrHAP as suggested by others.¹⁰ A reference FTIR spectrum for collin salt ($\text{Sr}_6\text{H}_3(\text{PO}_4)_5 \cdot 2\text{H}_2\text{O}$) was not found in literature so it was not possible to evaluate whether or not this phase was present in the synthesized SrHAP.

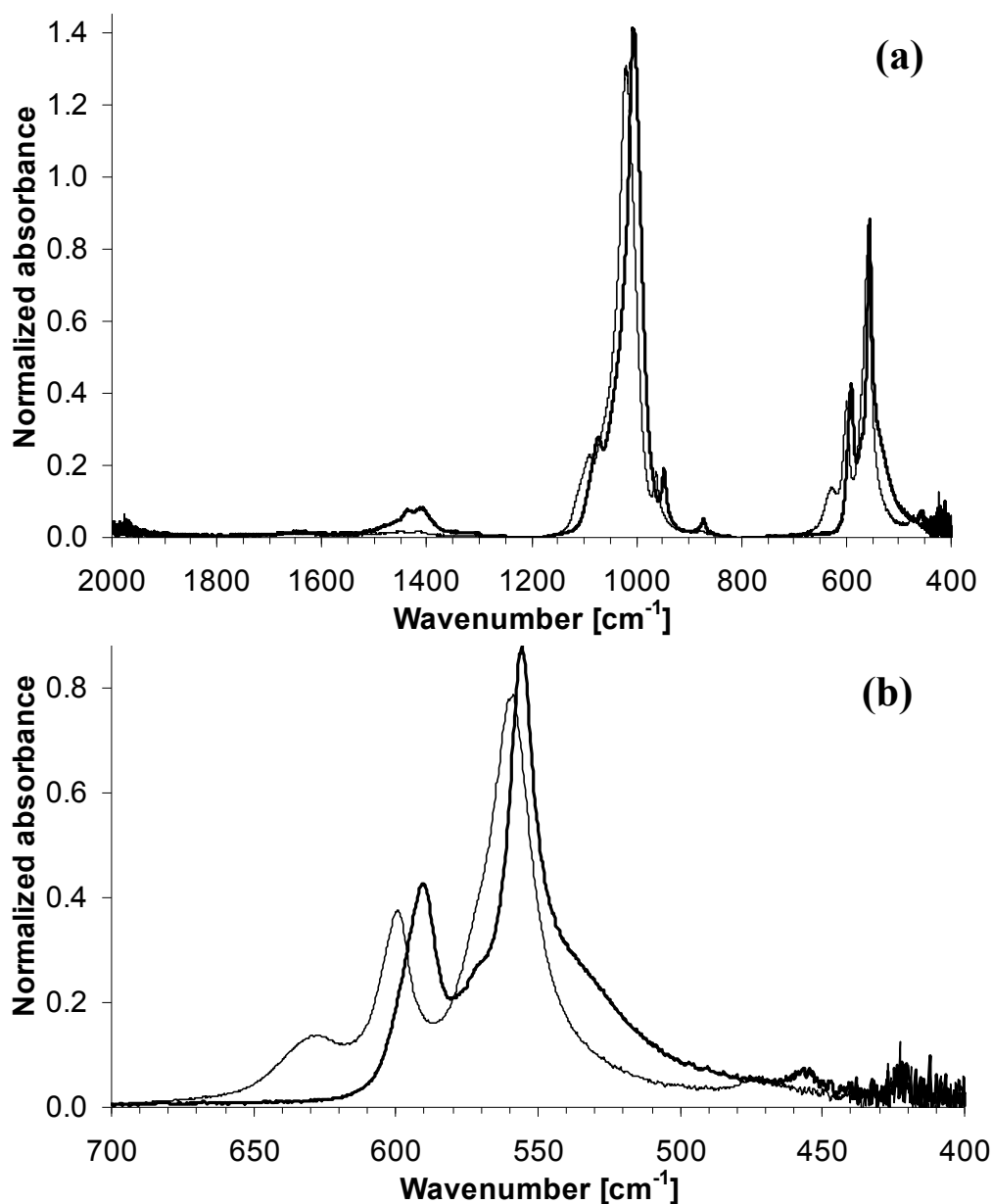


Figure 4.2 FTIR absorbance spectra of SrHAP (thick) and HAP (thin) (a) for the region 400-2000 cm^{-1} , and (b) 400-700 cm^{-1} .

TGA

The co-presence of other phases next to SrHAP with different thermal stabilities should be observable by TGA. Once these phases decompose mass changes of the samples will be noticed, while the evaporated compounds can be detected according to their elemental mass weight.

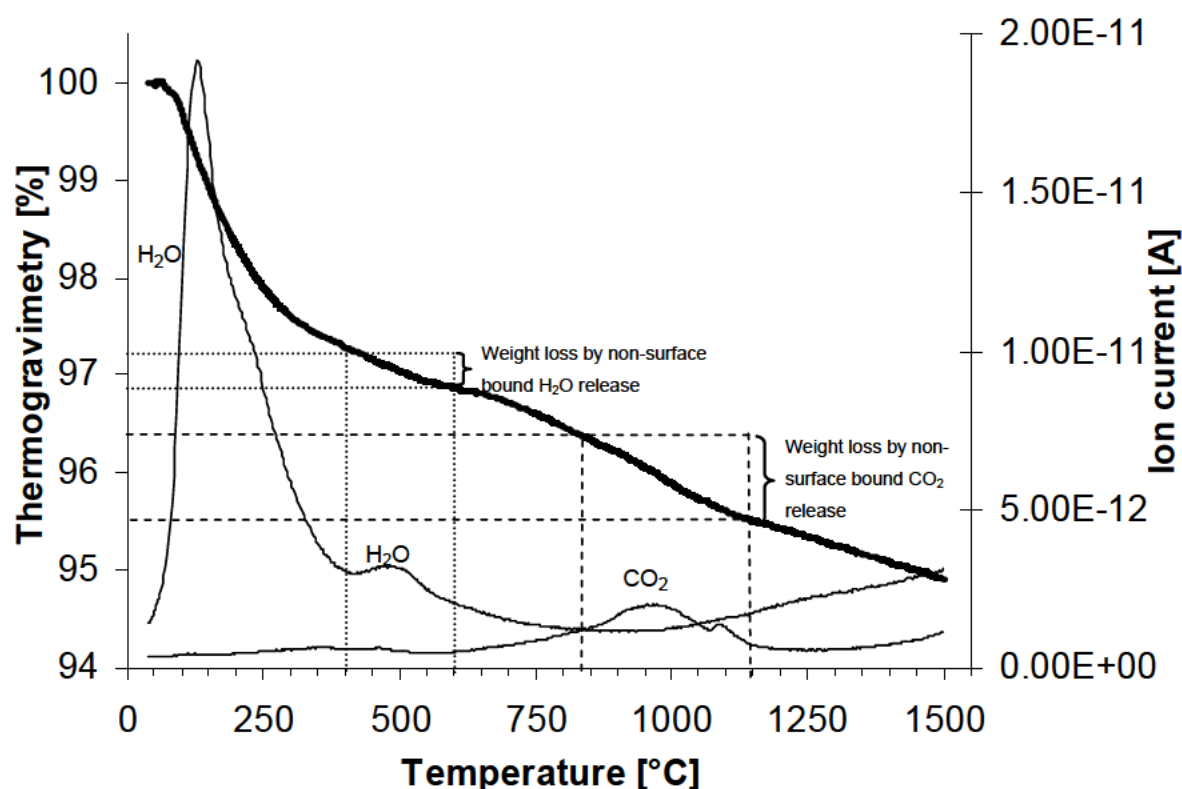


Figure 4.3 Thermogravimetric sample loss (thick, scale left y-axis) of 100 mg SrHAP during TGA measurement as function of temperature. Highest mass loss of about 2.5 wt% was observed up to 300°C. Compounds were detected according to their elemental mass weight. Most significant compounds determined as function of time are H₂O and CO₂. The dotted lines provide visual help for the mass loss attributed to H₂O between 400-600°C and of dashed lines for CO₂ loss between 840-1150°C.

The complete decomposition of a stoichiometric SrHAP (100 mg) heated up to 1500°C would release about 2.3 mg (2.3 wt%) OH. From TGA a release of H₂O was observed in two stages, between 110 and 200°C and between 400 and 600°C (Figure 4.3). The first is expected to be the result of the release of surface water. The water release of roughly 0.5 wt% between 400 and 600°C would be too small for OH release from SrHAP decomposition. Therefore, the low water loss could be an indication for i) a (partial) decomposition of non-stoichiometric SrHAP, which would agree with hypothesis of non-stoichiometric SrHAP from OH-assigned absorbances in FTIR, or ii) decomposition of Sr(OH)₂.²⁸ The presence of Sr(OH)₂ in very small quantities (0.5 mg

H₂O equals 3.33 wt% Sr(OH)₂) would be in agreement with rhombohedral Sr(OH)₂ crystals observed in TEM and reasonable for SrHAP synthesis under alkaline conditions.

Apart from surface water, the initial weight loss of the sample (up to 400°C) also was attributed to surface bound CO (Figure 4S1a), which is consistent with findings from XPS, FTIR and TIC/TOC analyses. Above 840°C two CO₂ releases were observed. Between 840°C and 1050°C about 0.70 wt% CO₂ evolved and at 1100°C roughly 0.05 wt% CO₂ was released. The CO₂ evolution above 840°C might be attributed to decomposition of SrCO₃,²⁹ which could have been co-present in small amounts and/or as an amorphous phase in SrHAP. The CO₂ release at 1100°C could be attributed to either i) a release of CO₃ incorporated in very low amounts within the SrHAP crystal structure under assumption of complete decomposition of SrHAP above 1100°C or ii) decomposition of another CO₂-containing phase that was not detected before. The TOC analysis of solid SrHAP resulted in 0.03 wt% (triplicate analysis), the estimated amount of carbonatic CO₂ was higher from TGA (single analysis) of 0.75 wt% (0.75 mg CO₂ equals 1.49 wt% SrCO₃), but still below the detection limits for any of the applied techniques of XPS, FTIR or XRD.

An identification of hydrogen phosphates (HPO₄²⁻, H₂PO₄³⁻, H₃PO₄) was not possible since their detection was too close to the background signal. This suggests that no phosphate residuals from synthesis remained on the SrHAP surface.

XRD

The x-ray diffractogram of synthesized untreated SrHAP (Figure 4.4) agreed with that calculated by Sudarsanan and Young (1972).²⁰ The diffractogram indicated the mineral crystal structure to be hexagonal (P6₃/m) as supported by the morphology of

the SrHAP crystals observed in TEM. Reflections of highest intensity were noticed for (1 1 2), (2 1 1), and (3 0 0) at 36.7° , 30.6° , and 31.8° 2θ , respectively.

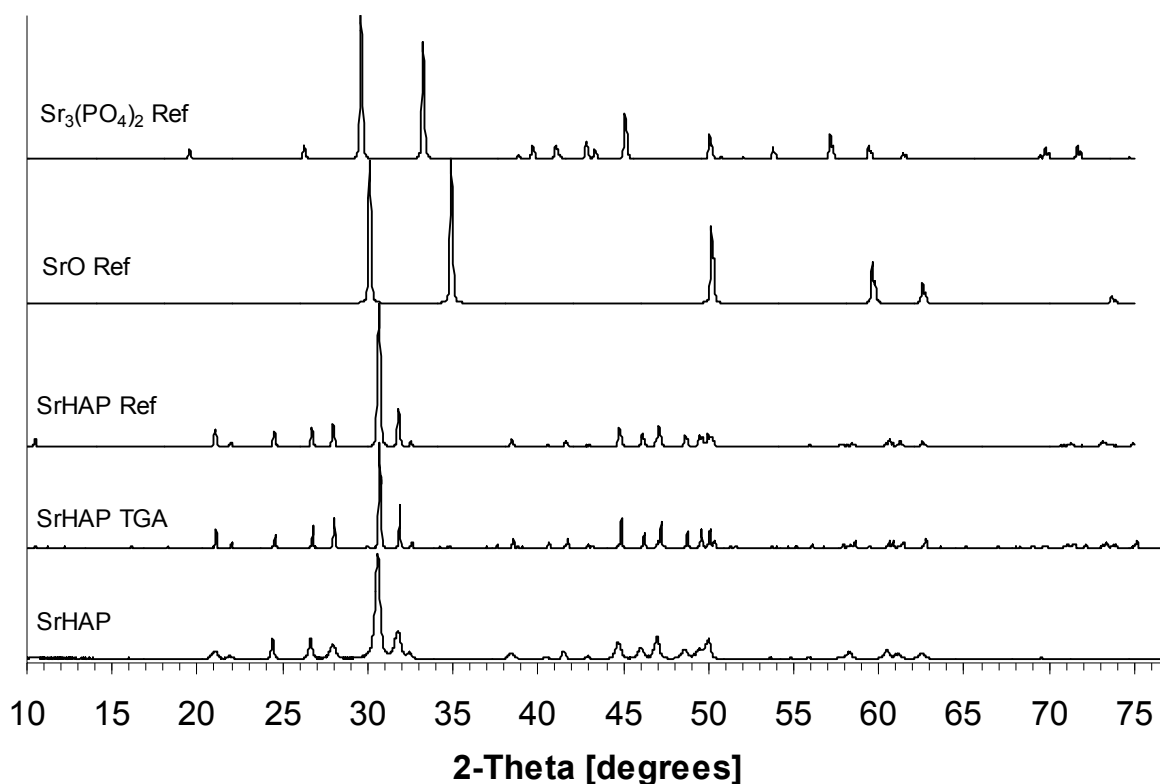


Figure 4.4 X-ray diffraction patterns of synthesized SrHAP and SrHAP after TGA measurement in comparison to references of SrHAP,²⁰ SrO³⁰ and $\text{Sr}_3(\text{PO}_4)_2$ ³¹ The SrHAP samples before and after TGA treatment were normalized to the intensity of the reflection (1 1 2) at 30.7° 2θ .

Also the diffractogram of the solid obtained from TGA after heating up to 1500°C agreed with that of SrHAP, but traces of SrO were detected at 30.09° (1 1 1), 34.89° (2 0 0) and 50.16° (2 2 0) 2θ .³⁰ A semi-quantitative analysis of the two phases resulted in approximately 98% SrHAP and 2% SrO. The detection of SrO support the hypotheses of a decompositions of $\text{Sr}(\text{OH})_2$ by release of H_2O and/or SrCO_3 by release of CO_2 . Moreover, heating up to 1500°C could have made the residual compound SrO more crystalline and thus detectable in XRD.

Since SrHAP was still the predominant phase after heating to 1500°C, a decomposition of SrHAP was not observed, which is inconsistent with other studies. Li et al. (2011)¹³ observed the decomposition of SrHAP into $\text{Sr}_3(\text{PO}_4)_2$ during heating to 900°C. It has to be noted that their SrHAP contained some quantities of SrHPO_4 and possibly also nitrate as a residual from incomplete synthesis. Also the formation of $\text{Sr}_2\text{P}_2\text{O}_7$, analogous to $\text{Ca}_2\text{P}_2\text{O}_7$ which was observed as a final product in TGA for calcium-deficient HAP,³² was not observed.

Moreover, the fact that SrHAP is still the main phase after heating up to 1500°C indicates that i) the reaction time in TGA of less than 3h (heating up from 40°C to 1500°C) was insufficient for SrHAP decomposition at given conditions and/or ii) that the produced SrHAP is thermally stable.

Evaluation of the Sr/P ratio in synthesized SrHAP

Bulk analyses of unreacted SrHAP using both acid digestion and EDX and surface-specific analysis using XPS showed that the Sr/P ratio ranged between 1.95 and 2.20, which is significantly higher than the expected stoichiometric ratio of 1.67. The high ratio cannot be explained by the presence of PO_4 -free Sr salts. Correction of the ratio for the $\text{Sr}(\text{OH})_2$ content, estimated by TGA analysis to be 3.3 wt%, and the SrCO_3 content estimated by TGA of 1.5 wt%, would result in a final Sr/P of 1.73. Although the TGA data evaluation is based on single analysis and by-eye estimate for weight loss, a content of 13 wt% $\text{Sr}(\text{OH})_2$ would be needed to account for the measured Sr/P ratio of 2.0 and it is unlikely that the errors would be so large.

In contrast to unreacted SrHAP, reacted SrHAP from 46d equilibration in nanopure water showed an average molar Sr/P of 1.17 at pH 7.7 with dissolved Sr and PO_4 concentrations of 0.27 and 0.23 mM, respectively (Table 4.2). The concentrations were

independent of equilibration temperature (25°C vs. 40°C). The significantly lower Sr/P ratio relative to the one observed in unreacted SrHAP of around 2.0 suggests the formation of a surface layer that is of different composition (PO₄-deficient, Sr-enriched) than of the unreacted SrHAP and makes data difficult to evaluate. In contrast, surface layers of HAP were often found to be calcium-deficient,³³⁻³⁵ which means the Ca/P ratio in solution was greater than 1.67. This elevated Ca/P ratio was postulated to result from the formation of a surface layer on HAP bulk with a composition of a different calcium-phosphate, such as brushite (CaHPO₄*2H₂O) or β -tricalcium phosphate (β -Ca₃(PO₄)₂).

Due to the presence of SrCO₃ and Sr(OH)₂, which both have a higher solubility than SrHAP, it would be expected that these phases dissolve, resulting in an increased Sr/P ratio in solution. Moreover, the lower dissolved Sr concentration cannot be explained by SrCO₃ precipitation, since the saturation index for SrCO₃ was estimated to be around -0.3 ($\log(IAP/K_{s0})^{1/n}$), with DIC concentrations ranging between 0.21 to 0.30 mM. The suspensions were also undersaturated with respect to Sr(OH)₂ ($\log K_s = -0.6$).

One hypothesis for a lower Sr content in suspension is an adsorption of Sr onto the SrHAP surface. The adsorption of Ca onto HAP was observed in preliminary studies,³⁶ if Ca only was added to the HAP suspensions. The surface site concentration would be sufficient for some Sr adsorption. The number of unit cells for PO₄ sites on the SrHAP surface, where Sr could sorb to, were estimated to range between 0.0018 mmol m⁻² and 0.0141 mmol m⁻² (unit cell dimensions of a=b: 0.9745 nm, c: 0.7265 nm).²⁰ This is equivalent to 0.37 to 2.96 mmol L⁻¹ PO₄ sites for each batch system (5g L⁻¹, specific surface area of 42 m² g⁻¹) and would be sufficient for Sr adsorption resulting in the observed dissolved Sr concentration.

Since the observations were not consistent for stoichiometric SrHAP and the solution data was inconsistent with solid data, a determination of a solubility product for the synthetic SrHAP was impossible. Using a solubility constant reported by Dedhiya et al. (1972)¹⁴ for stoichiometric SrHAP of -37.50, the value was adjusted for the observed pH and ionic strength in the present study to be -36.47. This K_s value would result in a total dissolved Sr concentration of 0.15 mM (considering the actual observed 0.22 mM $\text{PO}_{4\text{tot}}$), which is half the concentration as was observed (0.26 mM). If considering the observed Sr concentration, a total dissolved PO_4 concentration of 0.02 mM would be expected, while the observed value is more than ten times higher (0.22 mM).

Table 4.2 Results from SrHAP equilibration (5g L⁻¹) over 91d. Samples have been equilibrated at 40°C for 43d prior they were set to 25°C over 46d.

| Sample No | amount [mg] | total equilibration time [d] | pH | Ionic strength [mM] | Sr _{tot} [mM] | PO _{4tot} [mM] | Sr/P |
|-------------------------------------|-------------|------------------------------|------------------|---------------------|------------------------|-------------------------|------------------|
| 1 | 250.3 | 0.05 | 7.82 | 0.66 | 0.18 | 0.17 | 1.05 |
| 2 | 247.9 | 0.11 | 7.89 | 0.70 | 0.19 | 0.18 | 1.05 |
| 3 | 250.8 | 0.17 | 7.99 | 0.72 | 0.19 | 0.18 | 1.05 |
| 4 | 248.1 | 0.34 | 8.00 | 0.70 | 0.19 | 0.18 | 1.06 |
| 5 | 250.5 | 1.03 | 7.98 | 0.72 | 0.19 | 0.18 | 1.06 |
| 6 | 249.4 | 3.03 | 8.00 | 0.79 | 0.21 | 0.20 | 1.05 |
| 7 | 251.9 | 8.03 | 7.88 | - | - | - | - |
| 8 | 250.6 | 14.99 | 7.87 | 0.77 | 0.21 | 0.20 | 1.10 |
| 9 | 252.4 | 21.02 | 7.83 | 0.74 | 0.21 | 0.19 | 1.10 |
| 10 | 249.1 | 27.00 | 7.86 | 0.80 | 0.22 | 0.20 | 1.10 |
| 11 | 250.1 | 43.12 | 7.82 | 0.90 | 0.24 | 0.24 | 1.00 |
| 12 | 251.9 | 50.07 | 7.77 | 0.78 | 0.23 | 0.20 | 1.15 |
| 13 | 250.4 | 56.00 | 7.70 | 0.84 | 0.25 | 0.21 | 1.17 |
| 14 | 249.3 | 71.09 | 7.71 | 0.86 | 0.26 | 0.21 | 1.24 |
| 15 | 249.8 | 91.00 | 7.65 | 0.93 | 0.27 | 0.23 | 1.17 |
| 16 | 247.6 | 91.00 | 7.64 | 0.91 | 0.27 | 0.23 | 1.17 |
| 17 | 248.0 | 91.00 | 7.60 | 0.92 | 0.28 | 0.23 | 1.18 |
| 18 | 248.1 | 91.00 | 7.64 | 0.95 | 0.29 | 0.24 | 1.20 |
| 19 | 252.8 | 91.00 | 7.65 | 0.95 | 0.28 | 0.24 | 1.18 |
| 20 | 250.9 | 91.00 | 7.65 | 0.96 | 0.29 | 0.24 | 1.19 |
| 21 | 247.4 | 91.00 | 7.65 | 0.94 | 0.28 | 0.24 | 1.19 |
| 22 | 250.0 | 91.00 | 7.65 | 0.94 | 0.28 | 0.24 | 1.18 |
| 23 | 249.6 | 91.00 | 7.69 | 0.94 | 0.28 | 0.24 | 1.17 |
| 24 | 252.5 | 91.00 | 7.66 | 0.94 | 0.28 | 0.23 | 1.20 |
| average±standard deviation (n = 10) | | | 7.65±0.02 | 0.94±0.02 | 0.28±0.01 | 0.24±0.004 | 1.18±0.01 |
| 25 | 250.5 | 91.00 | 7.72 | 0.90 | 0.26 | 0.23 | 1.14 |
| 26 | 251.5 | 91.00 | 7.73 | 0.86 | 0.26 | 0.21 | 1.21 |
| 27 | 250.3 | 91.00 | 7.72 | 0.85 | 0.25 | 0.21 | 1.23 |
| 28 | 248.7 | 91.00 | 7.74 | 0.84 | 0.25 | 0.20 | 1.24 |
| 29 | 251.5 | 91.00 | 7.73 | 0.92 | 0.27 | 0.23 | 1.15 |
| 30 | 249.9 | 91.00 | 7.73 | 0.94 | 0.27 | 0.24 | 1.15 |
| 31 | 251.9 | 91.00 | 7.73 | 0.92 | 0.27 | 0.23 | 1.15 |
| 32 | 248.6 | 91.00 | 7.74 | 0.93 | 0.27 | 0.24 | 1.14 |
| average±standard deviation (n = 8) | | | 7.73±0.01 | 0.89±0.04 | 0.26±0.01 | 0.22±0.01 | 1.17±0.04 |

4.4 Conclusions

In previous studies the double composition method was described as an appropriate method for the synthesis of pure, crystalline SrHAP. Surface and bulk compositions found in this study showed Sr-rich SrHAP with a Sr/P of about 2.0, while solution data was inconsistent with a Sr/P of 1.2. While other studies mainly observed impurities such as SrHPO_4 , results within the present study provided evidence for the co-presence of Sr(OH)_2 and SrCO_3 .

4.5 Acknowledgements

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4.6 Supporting Information for Chapter 4

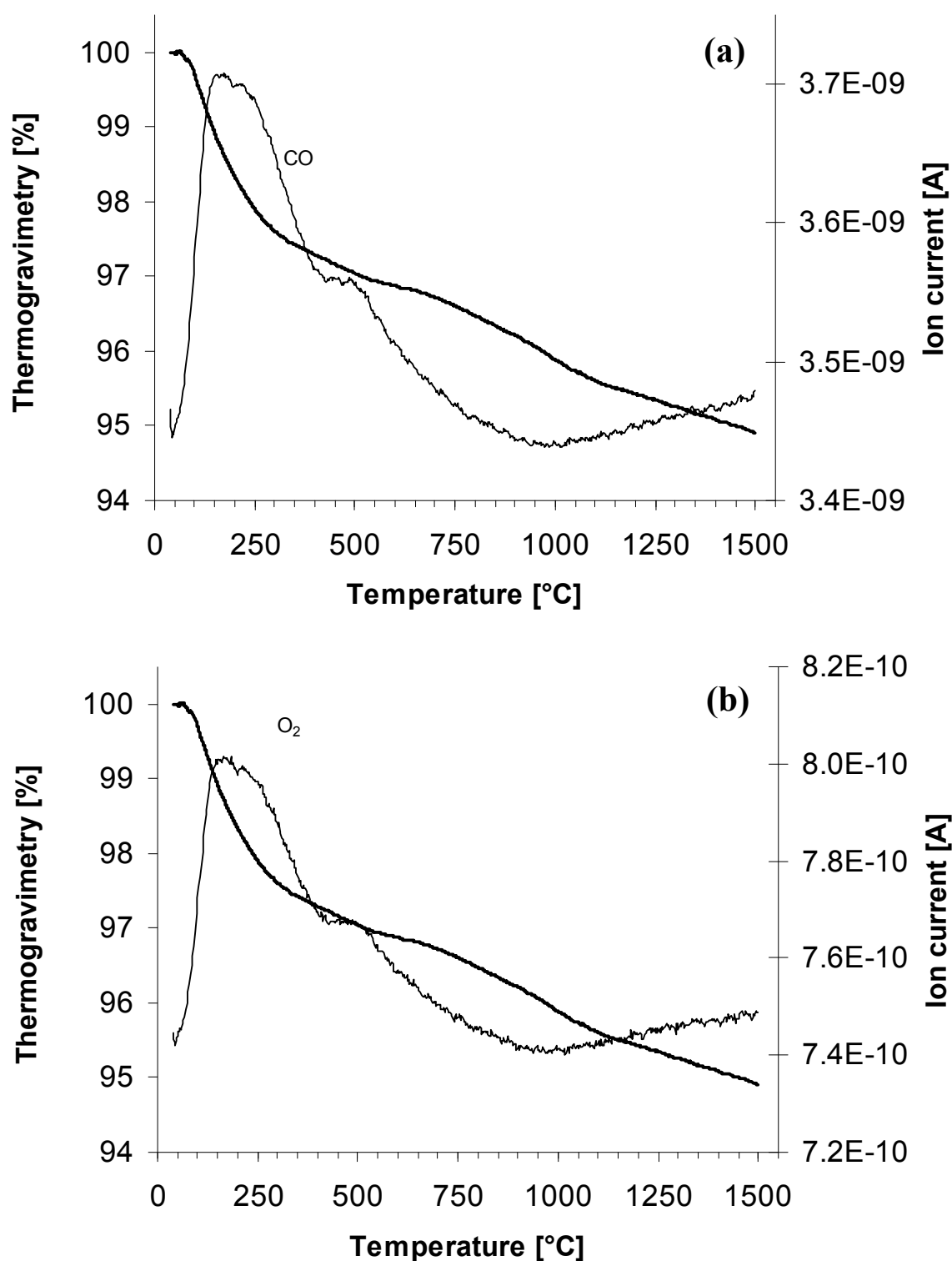


Figure 4S1 Thermogravimetry obtained for SrHAP attributed to the loss of CO (a) and O₂ (b).

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Chapter 5

Conclusions

5.1 Summary

This project has addressed fundamental processes involved in F uptake in apatitic systems under ambient conditions with a view to the optimization of fluoride removal filters. While numerous studies exist and processes are broadly understood, prior work focused on medical research and the characterization of processes that could provide insight to the mechanisms involved in F uptake has been incomplete. Here, the focus has been on investigating F uptake on HAP and removal from solution through surface precipitation processes.

In the current project, the uptake of F on HAP was investigated as function of environmentally relevant solution pH, initial F concentration, and the presence of potentially-competing anions like sulfate, bicarbonate and chloride. Heterogeneous calcium-phosphate precipitates were investigated on Ca-free seeding templates and solids were comprehensively examined by various techniques. The seeding template SrHAP used for heterogeneous calcium-phosphate precipitations was synthesized by a method that was previously described for the synthesis of pure crystalline SrHAP. The research questions posed in Chapter 1 will be discussed in terms of the main outcomes from work presented in Chapters 2 to 4 in the following paragraphs.

5.2 Uptake of fluoride on synthetic HAP

The research questions guiding the work on F uptake on HAP were the following:

- What is the predominant process responsible for F-uptake on HAP under controlled environmentally-relevant conditions?
- Is it possible to quantify the F uptake on HAP by solid characterization techniques?
- To what depth is F incorporated into the HAP crystal?

Fluoride uptake experiments (Chapter 2) showed that adsorption of F to the HAP surface was the predominant process. Fluoride uptake was pH-dependent, increasing with decreasing pH, which indicates a competition with OH ions on the HAP surface sites. A maximum uptake of 0.01 mmol m^{-2} was observed at pH 6.5 within the timescale (28d) of the experiments. Fluoride uptake was not affected by the presence of the anions bicarbonate, sulfate or chloride in concentrations up to 50 mM. Together with solid characterization, the results indicate that adsorption to the surface is an important step, followed by substitution of F for OH within the HAP crystal structure. While adsorption of F on HAP is known to be a relatively fast process, the long equilibration times that were required indicated that F substitution is slow and that the F uptake capacity significantly depends on reaction time.

The F uptake on bulk of HAP was quantified using the OH libration mode at 630 cm^{-1} in FTIR analysis. The decrease of the mode intensity was proportional to F uptake from solution and was further consistent with findings from XPS data. The outcome shows that FTIR is a promising method to quantify the transformation of HAP to FAP.

The thickness of the F layer formed on synthetic HAP was investigated using NanoSIMS and found to be approximately 4.5-6.5 nm. In XPS, which analysed a relatively larger sample area, this profiling was not fully supported, but the solid composition was found to be FAP-like. The F-enrichment on the reacted HAP surface suggests that F exchange for OH ions is limited to the unit cells at the crystal surface within the timeframe of the experiments (28d).

5.3 Precipitation of calcium-phosphate phases on SrHAP and SrCO_3

The research on precipitation of calcium-phosphate phases on SrHAP and SrCO_3 were framed by the following research questions:

- What kind of calcium-phosphate phases precipitate in presence of an apatitic seeding template as function of different Ca/P and Ca/P/F ratios?
- Is it possible to distinguish clearly between new Ca-containing precipitates and a Ca-free seed surface by use of surface and bulk sensitive techniques?
- Do the same calcium-phosphate phases precipitate if a carbonated seed is used instead of an apatitic template?

Although some studies were previously performed on calcium-phosphate precipitates, this present work used SrHAP as a seeding template for the first time to simulate an apatitic, but Ca-free surface, which facilitates solid characterization of surface precipitates. In Chapter 3, phase formation was found to be independent of the initially added Ca/P ratios and surface composition of the precipitates determined by XPS agreed for HAP or FAP. Shifts of Ca and F binding energies towards energy levels of CaF_2 were observed for samples where FAP formation was PO_4 -limited and Ca/F was stoichiometric for FAP and CaF_2 .

Findings from XRD and FTIR could not fully rule out the presence of other calcium-phosphates. Results from XANES and a feature in EXAFS indicated the precipitates to be Ca-deficient HAP, or to be mixtures of HAP with brushite and/or β -TCP, possibly as intermediates in the formation of HAP formation. Such intermediates have been reported previously based on the observations of the first few minutes of the reaction; some intermediates may have persisted for the 3d reaction time in the present study. These intermediates are expected to dissolve over longer reaction times allowing the precipitation of the thermodynamically most stable phase, HAP.

The results obtained by solid characterization provided evidence that the Ca/P ratios in the precipitate (estimated by elemental loss from solution) were insufficiently reliable. This needs to be taken into account in the evaluation of previous studies, which mainly used Ca/P ratios for phase identification.

The calcium-phosphate phases precipitated on SrHAP or SrCO₃ in this study constituted only about 10% of the total solid phase (i.e., approximately 0.2g precipitate and 2g of seed). This complicated phase distinction by solid characterization techniques. Nonetheless, Ca and PO₄ could be detected by XPS in samples where a Ca- and PO₄-free seed was used, clearly demonstrating the presence of phase mixtures. The incorporation of F could also be demonstrated and the presence of CaF₂ in some samples was indicated by shifts of Ca and F atomic binding energies towards energy levels characteristic for CaF₂. Although the crystal structure of HAP/FAP and SrHAP are different, only one peak was observed in XRD that could not be attributed to SrHAP and thus indicated the presence of HAP/FAP. For SrCO₃-based solids, the SrCO₃-assigned peaks were broader and of relatively higher intensity. Thus identification of HAP/FAP was based only on a peak shoulder in the diffractogram. The FTIR spectra of SrHAP and HAP/FAP are generally different, but physical mixtures of both phases exhibited overlaps of their absorbances. For the SrCO₃ seeding templates, FTIR is a more promising technique for phase distinction since the absorbances of SrCO₃ and HAP/FAP are clearly dissimilar. From all applied bulk characterization techniques, XAFS detects also amorphous phases, while its selectivity is similar to that of XPS.

Phases formed in SrCO₃-based systems were found to agree with phases precipitated in SrHAP systems, although some indications occurred in EXAFS analysis that the solids precipitated in presence of SrCO₃ were rather HAP than FAP-like. Therefore, the

necessity of an apatitic seeding template for the precipitation of apatites as mentioned in previous studies cannot be fully supported by outcomes from the present study.

5.4 Synthesis and characterization of SrHAP

The synthesis of SrHAP, which was used as a Ca-free apatitic seeding template to promote calcium-phosphate precipitation, was explored in Chapter 4. The double composition method, which was previously described as a suitable procedure for the synthesis of pure, crystalline SrHAP, was used. In the present study, the final product was fully characterized and was found to be crystalline but enriched in Sr. A possible explanation for the Sr-enrichment is the presence of $\text{Sr}(\text{OH})_2$ and SrCO_3 as by-products of the synthesis; this explanation is supported by TGA analysis.

5.5 Implications for F removal using bone char filters (including contact precipitation)

Bone char is composed to over 90% of HAP. The surface area is also comparable with that of nanosized HAP, since the bone granules are relatively porous even though larger in size. The F uptake studies carried out on synthetic HAP (Chapter 2) may therefore be used to assess the utilisation of bone char as a filter material to remove F. However, it should be pointed out that, depending on the bone char production, the quality of the bone granules can be quite low (i.e., characterized by a high content of organic and inorganic carbon). White and grey coloured bone char are known to have a low F uptake capacity, while black bone char is more effective for F uptake (Albertus, 2000).¹ It must also be noted that the contact time between the water and filter media during filtration is significantly shorter (a few hours) than applied in the batch studies. Nevertheless, similar processes are expected:

- The predominant F uptake mechanism might be adsorption onto the surface and into the pores of bone granules. If contact time is greater than a few hours (e.g. in pores of the bone granules) substitution reactions can be expected.
- The release of OH ions as a consequence of F uptake will cause the filtered water to become alkaline. This is not only undesirable for drinking water quality it will also significantly lower F uptake capacity. Preconditioning of filter material with an acidic solution could increase filter capacity to some extent.
- Fluoride uptake capacity does not seem to be affected by anions that are commonly present in F-containing water.
- The F uptake experiments with HAP have shown that F exchange for OH ions within the top unit cells at the surface of the HAP crystals. This could explain why regeneration of F-reacted bone char with NaOH is only partially successful as has been shown in laboratory experiments at Eawag and in field studies in Kenya. A maximum recovery of 60% of sorption and substitution sites on bone char has been observed after 24h (0.1-0.25 M NaOH). Much longer regeneration times could be necessary and this would certainly be commercially unfeasible.

The use of the contact precipitation method developed by the Catholic Diocese of Nakuru Water Quality group increases the F uptake capacity and avoids the need for bone char regeneration. However, the pellets that they employ release Ca and PO₄ at a Ca/P ratio below 1.0. The reason for this is that the soluble calcium phosphate that they employ is brushite and through the precipitation of less soluble salts (β-TCP, OCP, HAP/FAP) at the surface of the pellets, a greater proportion of Ca relative to PO₄ is removed from solution.

- Precipitation experiments have shown that phase formation for HAP/FAP is independent of Ca/P ratios, but solutions require elemental concentrations to achieve saturation degrees for the desired phases. Even though saturation concentrations with respect to HAP/FAP may be achieved in the effluent of the filter systems (as has been monitored), there is no guarantee that saturation levels also occur locally at the bone char granules. Therefore, formation of intermediates in the filter systems, such as brushite or OCP, is very likely. The formation of intermediates is also favored by the relatively short contact time of the treated water in the filter beds as compared with the 3d equilibration times studied here.
- The pellets themselves (in addition to the bone char granules) probably act as a seeding surface for new precipitates. For instance, if the pellets contain some brushite, it could be dissolved and re-precipitated as FAP directly at the water-pellet interface. The formation of an FAP surface layer covering the pellets could hinder further dissolution of the pellets and consequently cause a shorter filter lifetime.
- If concentrations achieve levels of supersaturation with respect to HAP/FAP, these phases could also freely precipitate without the aid of a seeding surface.
- Once HAP is formed as a new phase, it can act like bone char - its surface sites can adsorb F and subsequently F can substitute for OH within the HAP crystal structure.

5.6 Outlook

As F uptake capacity on synthetic HAP was found to be higher than on bone char, synthetic HAP would be a suitable material for the replacement of bone char. In particular HAP could be an alternative substrate to remove elevated F concentrations from drinking water in regions where bone char is ethically not accepted. However, the implementation of synthetic HAP for this purpose may be limited by production or import costs. Further, the powdered HAP needs to be pressed to pellets, which then could be crushed to granules for use as packing of the filters (e.g. a hand press was used in lab for granules production). In preliminary studies the granules showed similar F uptake than on powdered HAP. However the granules production may increase implementation costs.

5.6.1 Remaining open questions and further research needed in model systems

1) Formation of intermediates during heterogeneous calcium-phosphate precipitation.

The use of Ca-free seeding templates to distinguish calcium-phosphate precipitates allows the further investigation of the possible formation of intermediate phases during HAP/FAP precipitation. In previous studies, intermediates were observed within the first minutes of reaction; thus, samples should be taken at appropriate times. If phase formation is compared for different types of seeding templates used, the results should demonstrate whether or not apatitic seeds facilitate HAP/FAP precipitation.

2) Phase formation for cases non-stoichiometric for FAP. In the present study only Ca/P/F ratios stoichiometric for FAP were investigated for precipitation of F-containing phases. Thus, it would be interesting to know what phases are formed under non-stoichiometric conditions for FAP precipitation.

3) Optimizing the SrHAP synthesis. The synthesis of SrHAP was previously described as a suitable method for the production of pure, crystalline SrHAP. As some impurities

were observed in the present study and in the studies before, the method still could be optimised for purity. Also the use of relatively high amounts of ammonia can be unfeasible for large-scale SrHAP production.

5.6.2 Further research needed related to F removal using bone char filters (including contact precipitation)

Although a comprehensive solid characterization of contact precipitation filter media that was in contact with F-containing water is still lacking, the outcomes of the present study allows a number of suggestions for optimization of the contact precipitation technology to achieve maximum F uptake. Significantly increased F uptake capacity might be achieved by a combination of the following modifications, which certainly need to be evaluated prior to implementation.

1) Contact time of treated water with filter media. The longer the treated water is in contact with the filter media the more F is removed. This is based on adsorption and substitution reactions on bone char and pellets in addition to pellet dissolution generating precipitation conditions. This would suggest that filling the filters overnight would increase their effectiveness.

Two different kinds of household bucket filter systems are used: i) simple bone-char-only filters with space for about 12 L water and ii) contact precipitation filters with a 30 L treatment bucket and space for only 6 L of water. The daily water consumption per person in East Africa is about 2.5 - 4 L (mainly for drinking and cooking) (Thompson et al., 2001)² and the number of family members within one household varies. Community filters with large reservoir tanks that allow continuous but slow flow through the filter material may be a more practical option.

2) pH conditions of water to be treated. A decrease of the pH value of the water to be treated (inlet) might result in higher F uptake. This is based on a faster release of OH⁻ (and CO₃²⁻) from the apatitic surface sites in addition to a faster dissolution of the pellets, releasing dissolved Ca and PO₄³⁻ to solution for precipitation reactions. Options for decreasing pH in solution are i) the inlet of CO₂ gas into the water prior filtering, ii) pretreatment with sulphuric acid or iii) the addition of ascorbic acid as a relatively non-toxic salt.

3) Dissolution of calcium-phosphate pellets. Since it has been found that HAP/FAP formation is independent of the available Ca/P ratio, an optimization of the pellet composition would need to focus on their dissolution to increase the dissolved Ca and PO₄³⁻ concentrations and thus the degree of saturation for HAP/FAP precipitation. This could be achieved with a decreased solution pH as mentioned above and by the use of pellets that are smaller in size as those which are currently employed.

4) Pre-filter step. In order to provide higher Ca and PO₄³⁻ concentrations and to minimize local effects of partial dissolution around one pellet, a pre-filter step could be implemented by the addition of a thin layer of pellets before the water passes through the actual contact precipitation media. Though, it has to be considered that FAP could be formed as a surface layer on the pellets, which could hinder their further dissolution.

5) Post-filter step. Up to now, a relatively high PO₄³⁻ content in the outlet of the filters has been observed. Enhanced PO₄³⁻ concentration can cause bacterial growth, which is a disadvantage for water quality. In order to remove PO₄³⁻ from the treated water iron phases could be used to eliminate elevated PO₄³⁻ concentrations.

The proposed modifications for filter optimization might result in increased filter costs and thus in a decreased attractiveness of the bone char and contact precipitation filters. Thus, alternatives might be discussed. Although column studies with synthetic HAP under environmentally relevant conditions for the investigation of F uptake are still pending, it is expected that the replacement of bone char by synthetic HAP in the contact precipitation filters achieve at least similar, most probably higher F uptake as currently observed. This uptake might be even higher than it could be achieved by any of the modifications for bone char-based filter optimizations. Thus, future studies may focus on local HAP production, its implementation and cost reduction.

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Curriculum Vitae

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