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# Electron microscopic studies on phosphate binding processes in the presence of iron

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**Abstract.** Phosphates are widely used as a substitute material for bones and teeth in medical sciences. It is known that phosphate and iron have a strong affinity for each other. In this study, process of formation of iron phosphate was closely monitored using scanning electron microscope equipped with backscatter electron image and energy dispersive X-ray imaging facilities. Different stages of formation of the iron-phosphate material in an environment rich in phosphate and iron were observed. Initial stage of absorbing iron on phosphate-rich substrate is the most important stage of the entire process. X-ray mapping provides strong visual evidence to track down the dispersion of major elements during this process.

## Introduction

Phosphorus (P) is the tenth most abundant element in the earth crust, and is an essential nutrient as well as a key element in mediating between living and lifeless parts of the biosphere. The hard tissues of many vertebrates contain phosphates as do the pathological calcifications [1]. Ecological cycling of phosphorus is largely controlled by the precipitation of phosphatic compounds [2]. Occasionally, the behaviour of many trace elements in biological and geochemical systems is entirely dominated by phosphates. It is a known fact that iron (Fe) has a strong affinity for phosphate.[3] Importance of the iron-phosphate bond is known and is being utilised in many applications in numerous fields such as biochemistry, pharmacology, dentistry, environmental studies and material science.

Phosphorus binding by poorly crystalline iron-oxides are known in earth science as well as in material science. Slomp et al. [4] produced good evidence for the dominant role of iron oxides in the binding of phosphorus. They suggested that Fe phases can act as both a temporary and permanent sink for phosphorus in sediments.

In addition to the iron (hydr)oxides, natural hematites also absorb phosphate. Torrent et al. [5] studied the sorption of phosphate by hematites and concluded that although the sorption capacity is similar to that of natural goethites, hematites show slower sorption and lower affinity for phosphate.

Amorphous iron (III) hydroxide as phosphate binding agent has been well known and being successfully used in dentistry. Yoda et al. [6] reported large phosphate binding capacity of amorphous iron (III) hydroxide in a wide pH range (1.5-8). On the other hand, phosphate is an impurity in iron ores and is difficult to remove due to its strong affinity to iron [7].

In material science, uses and implications of this iron – phosphate bond is numerous. For example, binding two bones, which are mainly calcium phosphate, may be initiated and accelerated by injecting an iron solution in the contact. Despite large number of applications and studies on the bonding processes of phosphate and iron, detailed microscopic level investigations on the said processes are hard to find. This study may shed light on understanding the mechanisms and steps in the processes of formation as well as degradation of the bones and other phosphate-borne material.

## Materials and methods

Natural apatite crystals exposed to meteoric weathering were used for this study, together with their associated weathering products. After a careful examination, samples showing signs of alteration and formation of secondary coatings were selected for electron microscopic studies. Some of the selected samples were cut and polished, while some were left with naturally broken surfaces. Polished samples were used for backscattered emission (BSE) and energy dispersive X-ray (EDX) studies while other samples were used for normal scanning electron microscopy (SEM) only. However, when identification of material was required, microprobe analysis (EPMA) was conducted on selected spots of both types of samples. Scanning electron microscope JEOL JX840 coupled with Oxford Instruments Link AN10000 analyser was used for this study.

## Results and Discussion

Fig. 1 shows well-formed (euhedral) calcium phosphate (apatite) crystals observed under SEM. The coating covering part of these apatite crystals are mainly amorphous iron oxide.

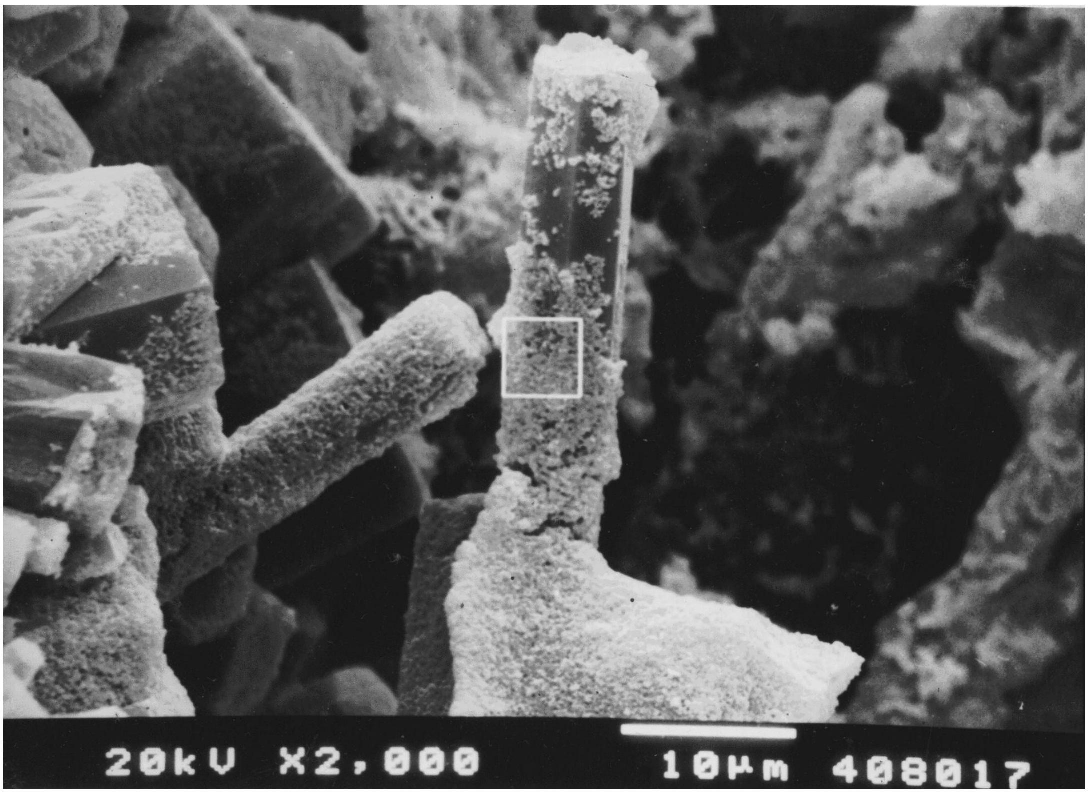

Fig. 1. Rod-shaped calcium phosphate crystals with coating of iron oxides on them.

The environment is rich in iron, in the form of iron hydroxide, released by the dissolution of iron-rich minerals. Squares marked on the photomicrographs usually indicate the area used for microprobe analysis.

During the initial stage of the process, amorphous iron oxide produces globular structures which are around 200 nm in size. Always the subsurface for these globules is a face of an apatite crystal. Once attached, they form strong and stable reaction interfaces for the subsequent action, helping accelerate the process. Fig. 2 shows some globular formation on a relatively flat surface of primary apatite.

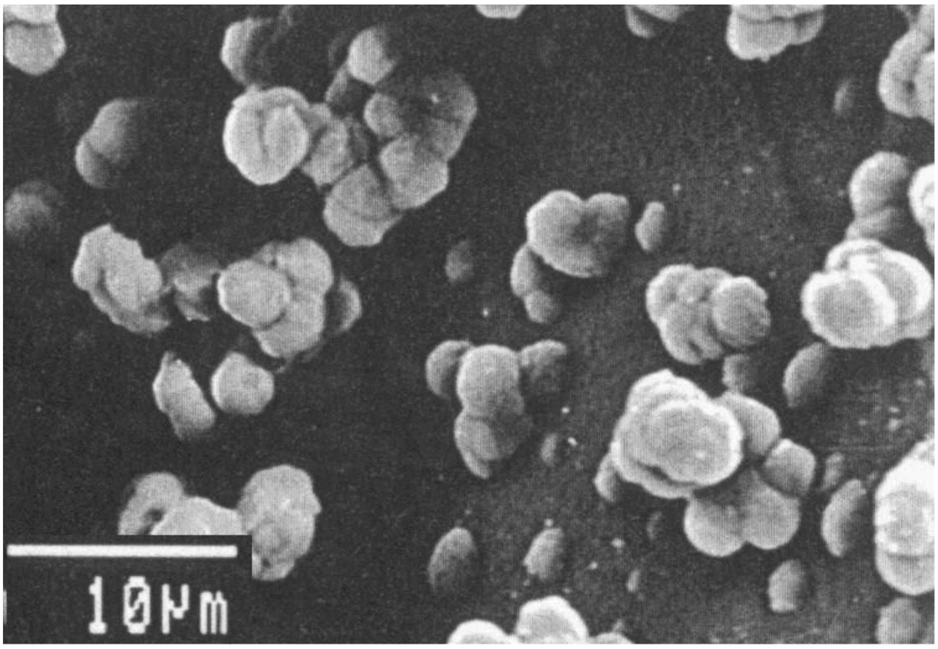

Fig. 2. Small globules of amorphous iron oxide bonded strongly on the surface of a primary apatite crystal.

Average size of a single globule is around ~2μm. Large ones are formed by adhesion of two or more globules.

With a continuous supply of iron (hydr)oxide, above process continues and sheet like structures are formed by connecting isolated globules (Fig. 3). During this process, iron and phosphate combine to form stable iron phosphate. Once the sheet-like structures are formed, they cover up the surface of apatite, thus preventing iron oxide getting in contact with the apatite. However, due to presence of phosphate in the newly formed iron-phosphate layers, any mobilised iron oxides are still getting attracted, but with a relatively lower affinity. Eventually the process stops when the phosphate or iron supply is reduced below a threshold, or when the iron phosphate layer is too rich with one of the major components (Fe or phosphate), so that it is no longer attractive to phosphate or iron.

As shown in Fig. 4, in advanced stages, iron phosphate coatings survive even after the calcium phosphate is completely gone.

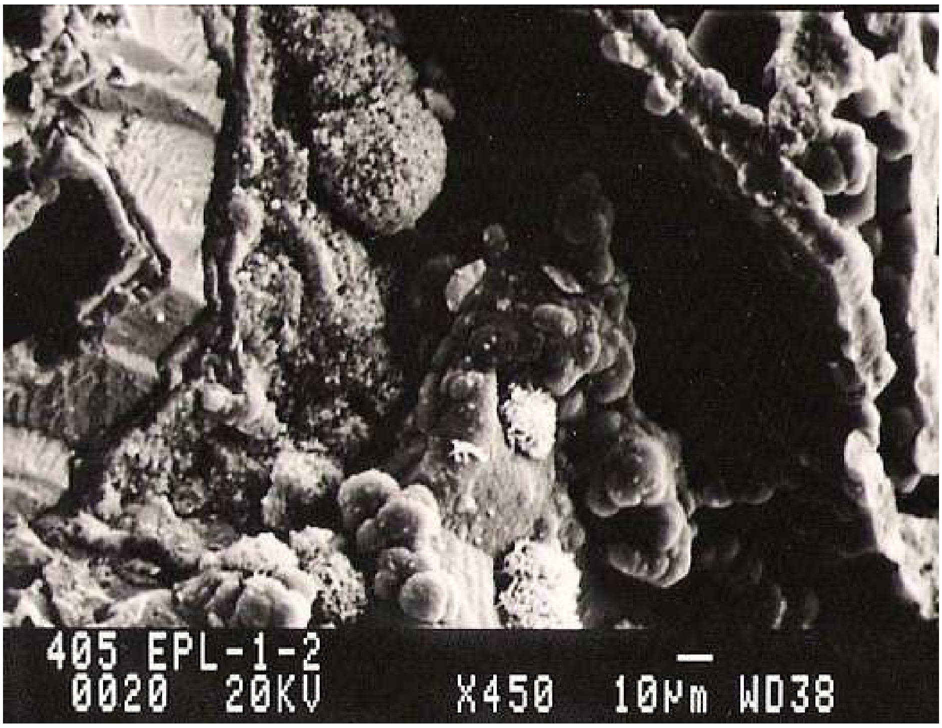

Fig. 3. Globules of iron oxide produce iron phosphates when combined with phosphate (centre).

These iron phosphate globules join together to form sheet-like structures (top left) which are stable in this environment.

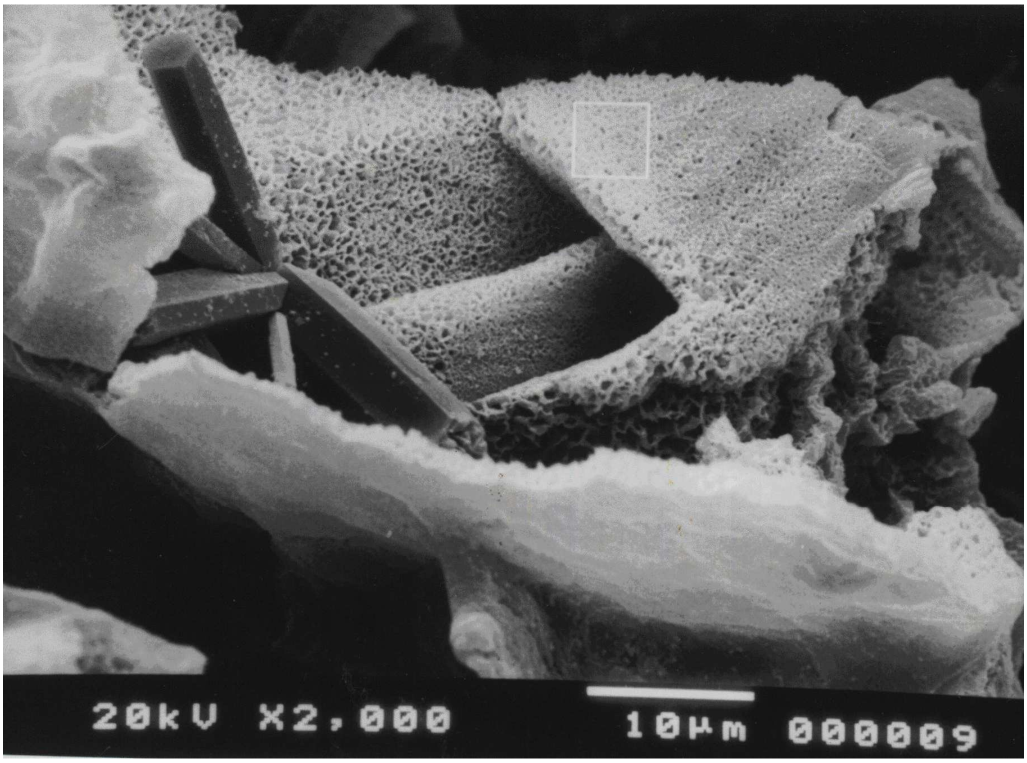

Fig. 4. Iron phosphate coating stands alone as a mat.

A few, rod-shaped apatite crystals with hexagonal cross-sections, are still seen at the left side.

Element mapping using energy dispersive X-rays provide visually striking evidence on the distribution of elements. Three major elements of our concern, P, Ca and Fe were mapped using EDX (Fig. 5).

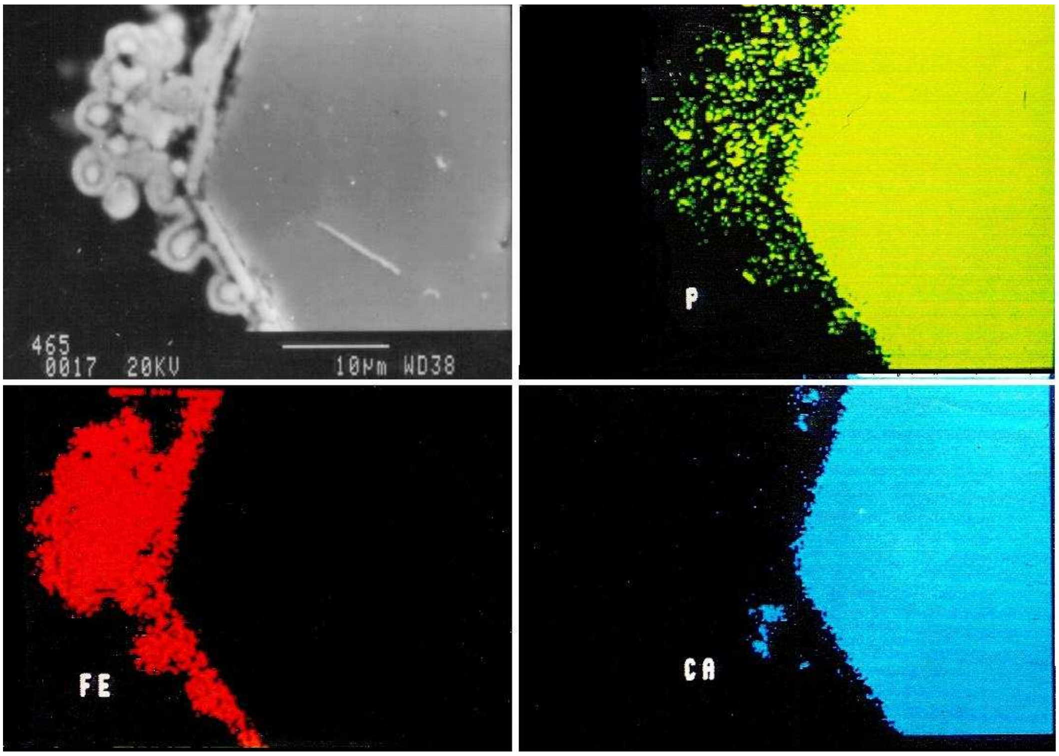

Fig. 5. X-ray maps of phosphorus (top right in greenish yellow), iron (bottom left in red) and calcium (bottom right in blue) in and around an apatite crystal undergoing dissolution.

Black colour indicates the absence of the element concerned. BSE image is shown on top left. Note the globular formation and a strong coating formed around the apatite crystal. Relatively brighter colour of the coating indicates that it is made of relatively heavier elements (i.e. iron) than those in the apatite crystal on right. X-ray images confirm that this coating is predominantly iron (bottom left) while phosphate is gradually diffused into it. Calcium is virtually absent in this coating (bottom right).

Iron phosphate is stable and resistive to dissolution in a weathering environment [8]. As a result, if an apatite grain is totally surrounded by iron phosphate coating, the grain is protected during the subsequent stages of weathering. Large number of coated apatite grains was observed in the natural environment where apatite and iron-rich minerals co-exist. Amorphous iron oxide acts as s sink for phosphate (and vice versa) forming stable product. This phenomenon may be utilised in material science, especially in biomaterial used in dentistry, artificial bones and other branches of medical sciences.

## Summary

During the dissolution of primary calcium phosphate, both Ca and P are mobilised. In the presence of iron, mobilised phosphate is immediately bound to iron forming stable iron-phosphates, while calcium is lost in the solution. Iron, when mobilised as iron (hydr)oxides, forms amorphous aggregates in the form of globules and coatings attached to the surface of the calcium phosphate. These coatings act as the precursor to form more stable and resistive iron phosphates. In subsequent stages, iron phosphate dominates the environment, if there is a continuous supply of iron and phosphate.

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