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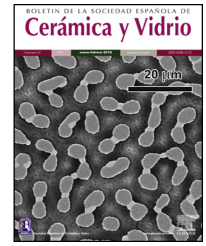

Calcium phosphates for biomedical applications

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ABSTRACT

The history of calcium phosphates in the medicine field starts in 1769 when the first evidence of its existence in the bone tissue is discovered. Since then, the interest for calcium phosphates has increased among the scientific communities. Their study has been developed in parallel with new advances in materials sciences, medicine or tissue engineering areas. Bone tissue engineering is the field where calcium phosphates have had a great importance. While the first bioceramics are selected according to bioinert, biocompatibility and mechanical properties with the aim to replace bone tissue damaged, calcium phosphates open the way to the bone tissue regeneration challenge. Nowadays, they are present in majority of commercial products directed to repair or regenerate damaged bone tissue. Finally, in the last few decades, they have been suggested and studied as drug delivering devices and as vehicles of DNA and RNA for the future generation therapies.

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Fosfatos de calcio para aplicaciones biomédicas

Palabras clave:
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RESUMEN

La historia de los fosfatos de calcio en el campo de la medicina comienza en 1769, cuando se descubre la primera evidencia de su existencia en el tejido óseo. Desde este momento los fosfatos de calcio despiertan un gran interés entre la comunidad científica. Su estudio se ha desarrollado en paralelo a nuevos avances en la ciencia de materiales, la medicina o la ingeniería de tejidos. Uno de los campos en que más repercusión ha tenido es en la reparación del tejido óseo. Si bien las primeras biocerámicas fueron seleccionadas en base a su bioinercia, biocompatibilidad y propiedades mecánicas, con el objetivo de remplazar el hueso dañado, los fosfatos de calcio abrieron las puertas al desafío de la regeneración ósea. Nuevos conceptos como biorreabsorción, bioactividad y osteoinducción aparecieron con ellos, convirtiéndoles en excelentes candidatos a resolver este reto. En la actualidad forman parte de la composición de la mayoría de productos comerciales cuyo objetivo es la reparación o la regeneración del tejido óseo. Además, en las últimas décadas se han postulado como soportes en la liberación controlada de fármacos, así como vehículos de material genético para las terapias génicas del futuro.

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Introduction

Apatite was the first calcium phosphate recognized as mineral specie. It was in 1786 when Abraham Gottlob, well-known as the father of German geology, discovered this mineral. It was named by him as apatao from the ancient Greek απατάω. Apatao means "to mislead" or "to deceive" because it had previously been confused for other minerals, namely beryl, tourmaline, chrysolite, amethyst, fluorite, *etc.* [1]. Nowadays, apatite is the name for a group of minerals with the same crystallographic structure. In the case of calcium phosphates (CaP), the term "apatite" involves CaP with Ca/P ratios within 1.5–1.67. In contrast, Nicolas Louis Vauquelin (1763–1829), discovered the existence of acidic CaP. All these CaP phases and their corresponding formulas are summarized in Table 1. CDHA, HA, FA, and OA belong to the apatite's group while MCPM, MCPA, DCPD, and DCPA belong to the acidic phases group.

CaP are interesting compounds in many fields of science, including geology, chemistry, biology and medicine due to their abundance in the nature and presence in the living organism [1]. The present review will be focused on the study CaP for biomedical applications and their progresses in the biomaterials field thanks to the advances experienced in materials engineering and new challenges in medicine.

History of calcium phosphates: from their discovering in living organisms to their applications in medicine

In 2013, Sergey V. Dorozhkin realized an excellent chronological study where he describes the history of CaP since their discovering in bones and teeth until their last applications in medicine [1]. According to this study, in the last quarter of the 17th century appeared the first studies about the structure and composition of bones, teeth and other types of calcified tissues. Must be highlighted the study published by Antonie Philips van Leeuwenhoek in 1677, where he describes the observation of small pipes in the shinbone of a calf, nowadays named Haversian canals because of the British physician Clopton Havers, and transparent globuls in cow teeth or elephants ivories, which was the first recognition of CaP single crystals in bones [1,2]. It was 1769 when the famous Swedish chemist and metallurgist Johan Gottlieb Gahn discovered the first evidence of CaP existence in bones [1]. In 1770, the presence of orthophosphates was also revealed in blood serum [1].

In the 19th century have to be underlined the studies of Fourcroy, who established the chemical composition of teeth with Vauquelin, or Sir Humphry Davy, who established in 1814 the general principles of bone and teeth formation, well-known as biomineralization [1]. He exposed that bones mainly consist on a gelatinous membrane in the earliest period of animal life, which is destined to gradually acquire calcium phosphate giving their subsequent hardness and durability to the bones. Other studies realized during this century conclude interesting observations. For example, CaP found is not found in infants [1], or in lower amounts in pregnant women [3] compared to normal adults. There was realized compositional studies in different bones of human body [4] or bones from young and old individuals [5].

CaP have been widely studied from a biological, structural and morphological points of view [1]. Nowadays, it is considered that CaP are of a special importance since they are the most important inorganic constituents of hard tissues in vertebrates [6]. In the form of a poor crystalline, non-stoichiometric, ion-substituted CDHA (commonly referred to as "biological apatite"), CaP are present in bones, teeth, deer antlers and tendons of mammals to give these organs stability, hardness and function [7].

During last few centuries, CaP have been proposed to treat various diseases such as rachitis scrofula, diarrhea, ulcerations, inflammations, caries or fractures of the bones [1]. Nowadays, they are commonly applied in orthopedic and maxillofacial application as well as in dentistry. Moreover, apart from these applications, they have been recently suggested as vehicles of drugs [8], peptides or ADN molecules [9]. However, the field has been the bone tissue engineering, in which they are mainly studied to get the ideal implant to regenerate bone tissue while it is resorpted.

Bone tissue engineering

One of the most impressive challenges for the scientific community, especially during the last few years, has been the artificial generation of tissues, organs or even entire living organisms. Sergey V. Dorozhkin explains in his review about the History of CaP, how this compositions are introduced in the bone tissue engineering field. There are numerous archeological findings, which prove the attempts from ancient civilizations to repair the human body [10]. The earliest successful implants were in the skeletal system [1].

The first chirurgical intervention to repair a bone defect was realized by Ambroise Paré in the 16th century and the first bone autograft was realized by Philipp Franz von Walther in the 18th century [1]. CaP are not introduced until 1870s when Dr. Junius E. Cravens used a CaP powder mixed with lactic acid as dentin-like material for pulp capping. By the end of the 19th century, the plaster of Paris was started to be used as a bone-filling substitute [1].

First *in vivo* assays performed with CaP as an artificial material to repair surgically created defects were realized in 1920 by the surgeon Fred Houdlette Albee [11], who invented bone grafting. A radiographic analysis was carried out to demonstrate bone growth and material degradation.

Simultaneously, the term "Bioceramics" is introduced [1]. It can be noted that ceramics in a strict sense not only means, crystalline or polycrystalline inorganic nonmetallic compound, but also refers to cements and glass or glass–ceramics.

The interest for ceramics as potential bone grafts powerfully has grown in 1960s owing to their biomechanical properties. The first generation of bioceramics just pretended to substitute damaged bone. However, new concepts such as biodegradation, resorption or osteoinduction appear in this field. From this point, the challenge consisted on the developing of a porous CaP which must be colonized by cells and resorpted to be replaced by new bone. Moreover, the advantage of CaP, compared to other bioceramics, is their chemical similarity to mammalian bones and teeth, which contributes to a bone bonding ability and enhances new bone formation [12].

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