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Review

A detailed history of calcium orthophosphates from 1770s till 1950☆

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ABSTRACT

Due to the chemical similarity with human bones and teeth, calcium orthophosphates are the inorganic substances of a special importance for the human being: they appear to be the excellent compounds to construct artificial bone grafts. In addition, calcium orthophosphates are necessary for both animals and plants as the source of important chemical elements. Obviously, these facts have not become apparent immediately; thus, providing the detailed annals of the knowledge development on the subject is the purpose of this review. The chosen time scale started with the earliest available studies of 1770s (to the best of my findings, calcium orthophosphates had been unknown before), passed through the entire 19th century and finished in 1950, because since then the amount of publications rapidly increased and the subject became too broad. In addition, since publications of the second half of the 20th century are easily accessible, other scientists have already reviewed the substantial amount of them. Many forgotten and poorly known historical facts, names, approaches, concepts and misconceptions have been extracted from the old publications. To maximize objectivity, an extensive quotation has been used. Then the old data have been systematized, reanalyzed and reconsidered from the modern points of view. The reported historical findings clearly demonstrate that many famous scientists of the past contributed to the subject. Furthermore, the significant quantity of the modern scientific facts, ideas and experimental approaches appear to have been known for very many decades and, in fact, a good deal of the recent investigations on calcium orthophosphates is just either a further development of the earlier studies or a rediscovery of the already forgotten knowledge.

Contents

☆ Dedicated to the cherished memory of the late Prof. Racquel Z. LeGeros.

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1. Introduction

By virtue of abundance in the nature and presence in the living organisms, calcium orthophosphates (Table 1) appear to be the chemical compounds of a special interest in many fields of science, including geology, chemistry, biology and medicine [1,2]. As seen from Table 1, calcium orthophosphates with the Ca/P ratio within 1.5–1.67 are called apatites (hydroxyapatite, fluorapatite and oxyapatite). As a mineral species, apatite was first recognized in 1786 by "the father of German geology" Abraham Gottlob Werner (1750–1817) and named by him from the ancient Greek απατάω (apatao) — "to mislead" or "to deceive" because it had previously been mistaken for other minerals, such as beryl, tourmaline, chrysolite, amethyst, fluorite, *etc*. Currently, apatite is the name for a group of minerals with the same crystallographic structure and does not indicate one chemical composition. However, in this review, the term "apatite" is referred to calcium orthophosphates only and means CDHA, HA, FA and OA (Table 1).

As follows from the designation, all calcium orthophosphates contain both calcium (Ca, atomic number 20) and phosphorus (P, atomic number 15) as the major constituencies. The history of both chemical elements is long. Namely, according to Wikipedia, the free encyclopedia, calcium (from Latin *calx*, genitive *calcis*, meaning "lime") compounds were known as early as the first century, when the ancient Romans prepared lime as calcium oxide [3]. However, calcium sulfate (also known as plaster of Paris or lime plaster) had been known much earlier: three statues were discovered in a buried pit at 'Ain Ghazal in Jordan those were sculpted with lime plaster over armatures of reeds and twine. They were made in the pre-pottery Neolithic period, around 7200 BC. However, calcium in a pure state was not isolated until 1808, when the famous British chemist and inventor Sir Humphry Davy (1778–1829) electrolyzed a mixture of lime and mercuric oxide [4,5].

Phosphorus is a bit younger. The discovery of this element in a pure state (its name given from Greek mythology, Φωσφόρος meaning "light-bearer" (Latin: Lucifer), referring to the "Morning Star", the planet Venus) is credited to the German merchant and alchemist Hennig Brand (ca. 1630–ca. 1710) in 1669, although other alchemists might have discovered phosphorus around the same time. Brand experimented with urine, which contained considerable quantities of dissolved phosphates from the normal metabolism [6]. As the matter stands, the earliest research publication, containing the word "phosphorus" in the title belongs to M. Krafft from Holland and was printed in 1677 in French *Journal des Sçavans* [7], which was the earliest academic journal published in Europe. In 1680, the famous British natural philosopher, chemist, physicist and inventor Robert Boyle (1627–1691) also deposited a paper on phosphorus, but it was published only in 1693, shortly after his death [8]. However, it was the famous French chemist Antoine Laurent Lavoisier (1743–1794), who recognized phosphorus as a chemical element in 1777. It turns out that phosphorus was the first element discovered since antiquity [6].

2. General definitions, major problems and limitations

To begin with, one must define the subject and outline the problems. According to Wikipedia: "History (from Greek στορία — historia, meaning "inquiry, knowledge acquired by investigation") is the discovery, collection, organization, and presentation of information about past events. It is a field of research which uses a narrative to examine and analyse the sequence of events, and it sometimes attempts to investigate objectively the patterns of cause and effect that determine events. The task of historical discourse is to identify the sources which can most usefully contribute to the production of accurate accounts of past." [9]. Therefore, all written below should be considered as a set of the chronological narratives on various aspects of calcium orthophosphates, in which extensive quotations from old publications appear to be the historical facts and data suitable for analysis and reconsideration from the modern points of view.

Unfortunately, the requirement "to identify the sources" meets serious problems, due to the substantial difficulties with accessing to the scientific literature published in the first half of the 19th century and before. In addition, that time, both the scientific concepts and the presentation ways were rather different from the modern ones, while the chemical formulae had not been introduced yet. More to the point, scientific journals were rare and just a few of them are currently available in the electronic form. To complicate things further, numerous old journals have been discontinued, merged and/or renamed, which strongly complicates accessing to the papers published in those journals. Luckily, Google Inc. has scanned a great number of old books as a part of its project to make the world's books discoverable online. This timely

Table 1
Existing calcium orthophosphates and their major properties [1,2].

Ca/P molar ratio	Compounds and their typical abbreviations	Chemical formula	Solubility at 25 °C, $-\log(K_s)$	Solubility at 25 °C, g/L	pH stability range in aqueous solutions at 25 °C
0.5	Monocalcium phosphate monohydrate (MCPM)	$Ca(H_2PO_4)_2 \cdot H_2O$	1.14	~18	0.0–2.0
0.5	Monocalcium phosphate anhydrous (MCPA or MCP)	$Ca(H_2PO_4)_2$	1.14	~17	[a]
1.0	Dicalcium phosphate dihydrate (DCPD), mineral brushite	$CaHPO_4 \cdot 2H_2O$	6.59	~0.088	2.0–6.0
1.0	Dicalcium phosphate anhydrous (DCPA or DCP), mineral monetite	$CaHPO_4$	6.90	~0.048	[a]
1.33	Octacalcium phosphate (OCP)	$Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$	96.6	~0.0081	5.5–7.0
1.5	α-Tricalcium phosphate (α-TCP)	α-$Ca_3(PO_4)_2$	25.5	~0.0025	[b]
1.5	β-Tricalcium phosphate (β-TCP)	β-$Ca_3(PO_4)_2$	28.9	~0.0005	[b]
1.2–2.2	Amorphous calcium phosphates (ACP)	$Ca_xH_y(PO_4)_z \cdot nH_2O$, n = 3–4.5; 15–20% H_2O	[c]	[c]	~5–12 [d]
1.5–1.67	Calcium-deficient hydroxyapatite (CDHA or Ca-def HA)[e]	$Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$ $(0 < x < 1)$	~85	~0.0094	6.5–9.5
1.67	Hydroxyapatite (HA, HAp or OHAp)	$Ca_{10}(PO_4)_6(OH)_2$	116.8	~0.0003	9.5–12
1.67	Fluorapatite (FA or FAp)	$Ca_{10}(PO_4)_6F_2$	120.0	~0.0002	7–12
1.67	Oxyapatite (OA, OAp or OXA)[f]	$Ca_{10}(PO_4)_6O$	~69	~0.087	[b]
2.0	Tetracalcium phosphate (TTCP or TetCP), mineral hilgenstockite	$Ca_4(PO_4)_2O$	38–44	~0.0007	[b]

[a] Stable at temperatures above 100 °C.
[b] These compounds cannot be precipitated from aqueous solutions.
[c] Cannot be measured precisely. However, the following values were found: 25.7 ± 0.1 (pH = 7.40), 29.9 ± 0.1 (pH = 6.00), 32.7 ± 0.1 (pH = 5.28). The comparative extent of dissolution in acidic buffer is: ACP ≫ α-TCP ≫ β-TCP > CDHA ≫ HA > FA.
[d] Always metastable.
[e] Occasionally, it is called "precipitated HA (PHA)".
[f] Existence of OA remains questionable.