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The precursor of apatite: Octacalcium phosphate (OCP) in the earth and environmental sciences - A review

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ABSTRACT

Octacalcium phosphate (OCP) is a solid phase that is well known in the biomedical field because it is widely used and tested as a precursor to bioapatite to treat various diseases affecting bones and teeth. In contrast, the knowledge of OCP in the earth sciences and its actual and possible applications in the environmental field are much less well known. With this review, we aim to fill this gap by showing that OCP is a much more widespread phase than is thought in various geological systems, and its properties allow its effective use in the environmental field, especially when it is used in the removal of various contaminants from wastewater and drinking water. This review not only lists the occurrences of OCP in nature or its uses in the environmental field but also proposes a critical analysis of the literature. In particular, a thorough examination of the failure to recognize OCP in numerous studies has highlighted the importance of performing low-angle XRD measurements in order to achieve proper identification of calcium phosphate minerals. A useful analytical protocol for recognizing and distinguishing OCP from similar phases such as those in the apatite group is suggested. Finally, we propose that OCP be recognized as a natural mineral species by the International Mineralogical Association-Commission on New Minerals Nomenclature and Classification (IMA-CNMNC). Such recognition, in our opinion, would provide a renewed and stimulating impetus to studies on the geochemical and mineralogical cycle of phosphorus.

1. Introduction

The aim of this review is to present and discuss the natural occurrence of octacalcium phosphate (OCP), its role in the earth sciences and its use for environmental remediation purposes.

OCP is a mineral with the ideal formula $Ca_8(HPO_4)_2(PO_4)_4 \bullet 5H_2O$ that plays a key role in calcium (Ca) and phosphorus (P) mobility in a wide range of geological and environmental contexts (Oxmann and Schwendenmann, 2014, 2015). Although it is not recognized by the International Mineralogical Association (IMA) as a valid species, OCP has been found as an authigenic phase in sedimentary rocks, and its occurrence is crucial for the genesis of phosphorite sedimentary deposits (Yang et al., 2022). OCP belongs to the family of calcium orthophosphate compounds, a group of minerals whose synthetic equivalents have been extensively studied as biocompatible materials (Dorozhkin, 2016). The orthophosphate minerals with Ca^{2+} as a cation with phosphate (PO_4^{3-}) and its conjugate acids from the IMA database are listed in Table 1 (Lafuente et al., 2016).

Among these phases, the natural occurrence of calcium orthophosphate is largely represented by apatite, a mineral series composed of three isomorphic endmembers: hydroxylapatite (HAP, $Ca_5(PO_4)_3OH$); chlorapatite (ClAP, $Ca_5(PO_4)_3Cl$); and fluorapatite (FAP, $Ca_5(PO_4)_3F$). In the geological record, apatite is commonly represented by FAP, with a minor molar percentage of HAP and ClAP (Nash, 1984). Brushite ($CaPO_3OH \bullet 2H_2O$), also known as dicalcium phosphate dihydrate (DCPD), is a common cave mineral that forms in acidic environments in the presence of guano and calcium carbonate minerals (Marincea et al., 2004). Brushite itself could be a precursor of OCP and HAP both in natural environments (Sala et al., 2023) and in laboratory experiments (Idini et al., 2019a). Monetite, which is the anhydrous equivalent of brushite, can form at the expense of brushite under drying conditions or after thermal decomposition even at low temperature (Dosen and Giese, 2011). With respect to the tricalcium phosphate named tuite (TCP, $Ca_3(PO_4)_2$), a clarification is necessary: it is common to find in biomedical and material science literature the erroneous sentence that TCP is the synthetic equivalent of mineral whitlockite, but the stoichiometry of this mineral includes magnesium and hydrogen in the structural formula $Ca_9Mg(PO_3OH)(PO_4)_6$. Therefore, the sole

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mineral that contains only Ca, P and O in its formula is tuite, and its occurrence is strictly related to uncommon ultrahigh-pressure geological conditions (Skelton and Walker, 2017). Among the calcium orthophosphate minerals that naturally could be precursors of apatite under supergenic conditions (thus excluding tuite, which, according to Dorozhkin (2012), cannot precipitate from aqueous solutions), OCP is the least soluble phase, and the Ca/P molar ratio is closer to that of apatite (Table 1). In fact, the role of OCP as a crystalline precursor of apatite has been ascertained in numerous geological and biological contexts (Suzuki, 2013; Yang et al., 2022). Due to the research on OCP as biomaterial, the literature on the mineralogical properties of OCP is very vast (Suzuki, 2013), highlighting that the most important feature of OCP lies in its ability to aggregate Ca and P under circumneutral conditions and then possibly convert them into apatite. The transformation OCP → apatite also occurs in natural environments, such as alkaline waters (Borkiewicz et al., 2010; Idini et al., 2020) and soils (von Wandruszka, 2006). The transformation of OCP into apatite is favored by the layered structure of OCP (Fig. 1), which is composed of a hydrated layer, where 9 out of 10 water molecules are bound to the $Ca_6(HPO_4)_4^{4+}$ complex sandwiched between two apatitic layers [2 • $Ca_5(PO_4)_4^{2-}$] (Mathew and Tagaki, 2001).

The atomic arrangement in the apatitic layer is the cornerstone of the epitaxial growth of apatite starting from the OCP structure, and the reaction takes place without involving a dissolution-precipitation mechanism (Xia et al., 2011). Another important feature of OCP is that within the hydrated layer, the anion HPO_4^{2-} can be replaced/exchanged with a wide variety of ions (Yokoi et al., 2023).

After this necessary framing of the main characteristics of OCP, the next sections of this review address the occurrence of OCP in different earth systems, and a particular focus will be placed on the environmental aspects. Finally, the powder X-ray diffraction (PXRD) pattern of OCP and its diagnostic reflections in comparison with those of apatite are discussed.

2. Marine geology and hydrogeochemistry

The apatite minerals are ubiquitous in igneous (Webster and Piccoli, 2015), metamorphic (Harlov, 2015) and extraterrestrial rocks (McCubbin and Jones, 2015). However, during the process of compiling bibliography regarding the natural occurrence of OCP and its role as precursor of apatite, we found clues only in the field of sedimentary geology, especially with regard to the mineral francolite.

Francolite, a variety of fluorapatite also known as authigenic carbonate apatite, is the main constituent of phosphorite deposits originating from marine sediments (Mcarthur, 1985). The elemental composition of francolite reflects the composition of the water solution from which it precipitates: commonly CO_3^{2-} and SO_4^{2-} partially replace PO_4^{3-} up to 6 wt%, and also Na > Mg > Sr can partially replace Ca (Mcarthur, 1985; Jarvis, 1994). Phosphorites are ubiquitous geographically and on a broad geologic time scale (Cook, 1984); currently, phosphorite deposits represent the most important exploitable source of P worldwide (Chernoff and Orris, 2002). The genesis of phosphorites is currently debated in different parts of the world (Ruttenberg and Berner, 1993; Chen et al., 2023). The pathway of francolite precipitation from seawater has been debated for several years due to the complexity of the P cycle (Cappellen and Berner, 1988; Föllmi, 1996; Delaney, 1998). The P cycle (Fig. 2) can be summarized into four main steps: 1) weathering of phosphate rock, which can be of igneous or sedimentary origin (Cook, 1984); 2) eluvial and fluvial transport; 3) sedimentation and burial in marine basins; 4a) tectonic uplift and consequent increase in continental erosion; and 4b) sediment subduction in an active tectonic margin and subsequent anatexis during the formation of a volcanic arc (Ma et al., 2022).

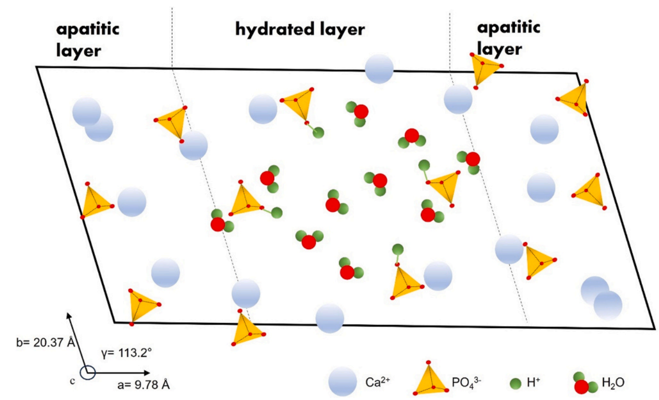

Fig. 1. Sketch drawing of the atomic positions in the OCP lattice. The view was parallel to the (001) plane. Crystallographic data from Idini and Frau (2021).

In this cycle, the mineralogical pathway of P involves chemical and biochemical degradation of apatite, the transport of both inorganic P as orthophosphate and organic P from plants and animals, and the subsequent precipitation of francolite in sedimentary basins. However, direct observation of francolite formation in seawater was ambiguous until the research of Oxmann and Schwendenmann (2014), who reported that OCP precedes the crystallization of francolite (see the P cycle in Fig. 2 between step 2 and step 3). In long-term incubation experiments in brackish water, OCP was shown to form, whereas francolite failed to

Table 1
List of phosphate minerals with Ca^{2+} as a cation and their synthetic equivalents (Lafuente et al., 2016; [a]Dorozhkin, 2012; [b]Song et al., 2015). The SI values were calculated for PO_4^{3-} = 0.645 mM, Ca/P = 1.67, and CO_3^{2-} = 5.0 mM. n.a. = not available.

Abbreviation	Mineral name	Synthetic equivalent name	Chemical formula	Ca/P molar ratio
HAP	Hydroxylapatite	calcium hydroxyphosphate	$Ca_5(PO_4)_3OH$	1.67
FAP	Fluorapatite	calcium fluoride phosphate	$Ca_5(PO_4)_3F$	1.67
ClAP	Chlorapatite	calcium chloride phosphate	$Ca_5(PO_4)_3Cl$	1.67
OCP	*Unnamed*	octacalcium phosphate	$Ca_8(HPO_4)_2(PO_4)_4 \bullet 5H_2O$	1.33
DCPA	Monetite	dicalcium phosphate anhydrous	$Ca(PO_3OH)$	1
DCPD	Brushite	dicalcium phosphate dihydrate	$Ca(PO_3OH) \bullet 2H_2O$	1
TCP	Tuite	tricalcium phosphate	$Ca_3(PO_4)_2$	1.5

Abbreviation	-log(K_s) at 25 °C[a]	Solubility[a] (mg/L)	Saturation Index (SI) calculated at different pH values (25 °C)[b]			
			pH 6	pH 7	pH 8	pH 9
HAP	116.8	0.3	2.741	8.357	12.757	15.941
FAP	120	0.2				
ClAP	n.a.	n.a.				
OCP	96.6	8.1	−2.9084	0.7614	3.2764	4.6366
DCPA	6.90	48				
DCPD	6.59	88	−0.9412	−0.3682	−0.1590	−0.3136
TCP	25.5	2.5	−1.9036	1.1910	3.4958	5.0108

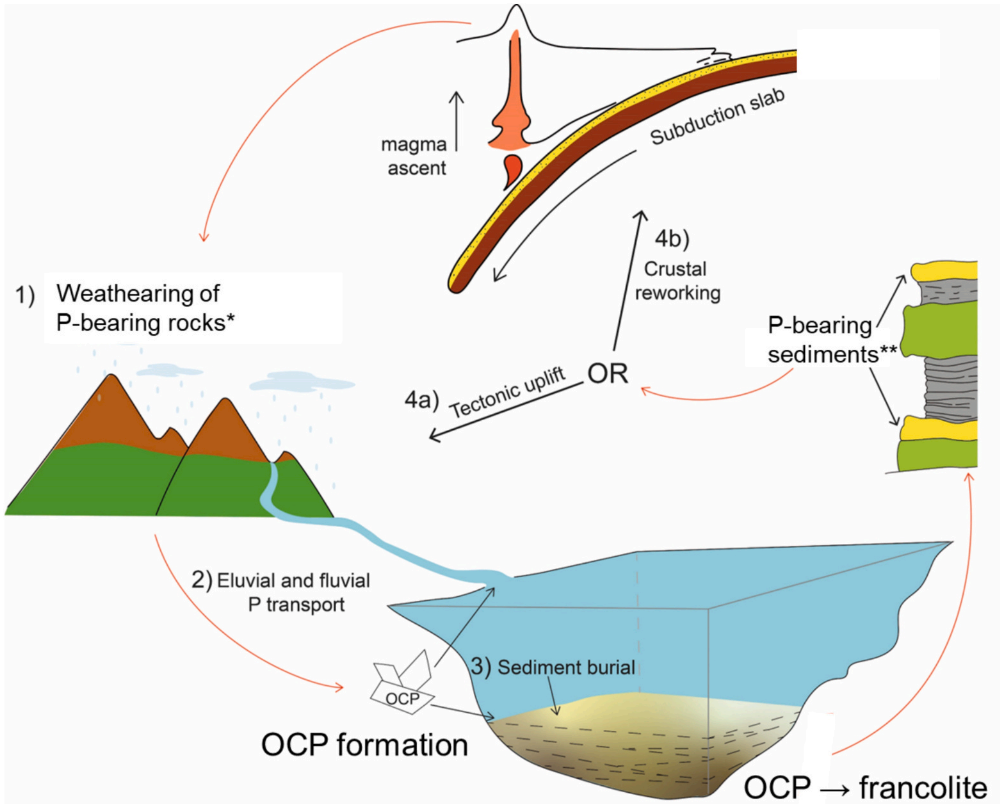

Fig. 2. Sketch drawing of the OCP occurrences in the inorganic phosphorus cycle. The weathering of phosphate rock (1) produces P sediment transported (2) into marine basins. In this stage the OCP starts to form. The sediment burial (3) and diagenesis form the P-bearing sedimentary sequences. The OCP transforms into francolite during the diagenesis process after the sediment burial (3).
The sedimentary sequences could be tectonically uplifted (4a) or recycled during the subduction and reworked during anatexis (4b).
*P-minerals in igneous and metamorphic rocks are mainly represented by apatite supergroup minerals, monazite supergroup minerals and alunite supergroup minerals.
**P-minerals in the sedimentary sequences are represented mainly by fluorapatite var. francolite, vivianite, struvite and P-bearing Fe(III)-oxy-hydroxides.

precipitate even under supersaturation conditions (Gunnars et al., 2004). The failure of francolite to precipitate from brackish waters is assumed to be caused by the inhibitory effect of magnesium, which is present in seawater at a concentration of ~1.28 g/kg (Millero et al., 2008). Summarizing the literature, it appears that natural OCP forms in environments where P and Ca are supersaturated relative to apatite, but where apatite is kinetically inhibited from forming. These environments are necessarily aqueous (e.g., marine, but not limited to the ocean). Given its instability, we do not actually know whether OCP can form (although very unlikely) through solid-state metamorphic reactions or by direct crystallization from a magmatic melt, where apatite can form instead. OCP formation is also unlikely in environments where phosphates are common but an aqueous medium is absent, such as on asteroids or meteorites.

The biological uptake of P is an important temporary sink of the global P budget in terms of geological time (Föllmi, 1996). In fact, biological activity can strongly affect orthophosphate precipitation, which cannot be explained by macroenvironmental mineral-equilibria alone, as in the case of the common association of francolite and vivianite $Fe_3^{2+}(PO_4)_2 \cdot 8H_2O$ (Rothe et al., 2016; Rodriguez et al., 2021). Of great interest is the case reported by Liu et al. (2016): OCP has been identified on the leaf surface of *Potamogeton crispus,* an aquatic plant spread worldwide. The mechanism of OCP formation is related to the Ca released by *P. crispus* and the P taken from the water. Research has indicated that *P. crispus* can effectively reduce the P concentration in water through the formation of OCP (Wang et al., 2022). The biological role in precipitation of OCP has also been found in low-P aquatic environments (Büttner et al., 2021); in fact, due to bacterial activity, current phosphatic stromatolites have been discovered in freshwater with a P concentration of only 0.28 μg/L where OCP precipitates together with amorphous Ca-PO_4 and apatite. It should be noted that the fossil phosphatic stromatolites composed by francolite have been used as proxy for the P concentration in seawater during past geological eras. For example, the work of Shiraishi et al. (2019) calculates a P concentration $>$ 5 μM as the minimum threshold for francolite precipitation, whereas the work of Büttner et al. (2021) notes that the phosphatic stromatolites require a 17-fold lower P concentration.

These scientific findings raise two cutting-edge considerations: i) OCP and, in general, Ca-PO_4 phases can precipitate under chemical conditions very far from saturation because of the influence of biological activity; ii) the fossil record of phosphatic stromatolites cannot be used as a proxy for high P concentrations in former marine environments (Büttner et al., 2021).

The biological role of OCP as a precursor to bioapatite is well known (Carino et al., 2018). Considering the “evolutive radiation” of inorganic phosphatic parts of living organisms since the Lower Cambrian (Knoll, 2003), OCP formation may have played an important role in the history of “mineral evolution” (Hazen et al., 2008). Therefore, we believe that crystallographic clues to the presence of OCP should also be investigated in the paleontological records.

3. Water pollution remediation

3.1. Drinking water

The increasing demand for safe water is a global concern, as evidenced by the United Nations 2030 agenda (https://sdgs.un.org/2030agenda), especially in Sustainable Development Goal n.6 "Ensure availability and sustainable management of water and sanitation for all". Therefore, research on water treatment against anthropogenic and geogenic sources of contamination has made great progress. Among the different pollutants, fluorine (F) is recognized as one of the most harmful inorganic pollutants in groundwater (WHO, 2022). It is estimated that more than 300 million people are exposed to fluorosis disease, and the most important source of fluoride (F^-) intake for populations is groundwater containing more than 1.5 F^- mg/L (Fawell et al., 2006). Experimentally, OCP has been shown to be effective for removing F^- from aqueous solutions (Idini et al., 2019a, 2019b, 2020). The application of the OCP method in northern Tanzania, which is one of the most fluorotic areas worldwide where fluorosis disease has a major socio-economic impact (Gutierrez et al., 2021; Nocella et al., 2022), has allowed the successful treatment of groundwater with F^- concentrations up to 20.9 mg/L (Idini et al., 2020). The F^- removal mechanism is based on the OCP transformation into fluorapatite according to the following reaction (Idini and Frau, 2021):

$$Ca_8(HPO_4)_2(PO_4)_4 \bullet 5H_2O_{(OCP)} + 1.6\ F^- \rightarrow 1.6\ Ca_5(PO_4)_3F_{(FAP)} + 1.2\ HPO_4^{2-} + 5\ H_2O + 0.8\ \ H^+ \quad (1)$$

This method is particularly ingenious because it is based on the same mineralogical principle as F^- accumulation in the hard tissues of the human body that causes fluorosis. In fact, the inorganic part of animal and human bones and teeth consists of the nonstoichiometric Ca-deficient carbonate hydroxylapatite, also called bioapatite, the crystallization of which occurs subsequent to the formation of its natural precursor OCP. Upon long-term exposure to high levels of F, fluoride ions may accumulate in hard tissue through the formation of FAP instead of bioapatite (Idini et al., 2019a, 2019b).

OCP has also been used to remove dissolved metals from water, such as lead (Pb) and cadmium (Cd) (Mirković et al., 2024), which, due to their high toxicity, have very low permissible limits in drinking water (WHO, 2022; Table 2). A common source of Pb in drinking water is the corrosion of domestic pipes in buildings (Chan et al., 2020). A possible solution against the presence of Pb in tap water is the addition of orthophosphate salt to inhibit the corrosion of pipes (WHO, 2022). Ferraa et al. (2023) indicated that OCP was very effective at creating a protective layer due to its ability to sink metals and react with them to form insoluble salts. In fact, in the work of Pham Minh et al. (2012), OCP was successfully tested for Pb removal from aqueous solution, and the proposed reaction highlights the affinity of Pb for Ca replacement in the apatitic structure according to the following reaction:

$$Ca_8(HPO_4)_2(PO_4)_4 \bullet 5H_2O_{(OCP)} + 10\ Pb^{2+} \rightarrow 2\ Pb_5(PO_4)_3(OH) + 8\ Ca^{2+} + 4\ \ H^+ + 3\ H_2O \quad (2)$$

The solid product of reaction (2) is the hydroxylpyromorphite mineral (a member of the apatite group). A very similar removal mechanism was reported by Zhu et al. (2020) according to the following reaction derived from XRD and chemical data:

$$Ca_8(HPO_4)_2(PO_4)_4 \bullet 5H_2O_{(OCP)} + 7.5\ Pb^{2+} \rightarrow Ca_{2.5}Pb_{7.5}(PO_4)_6(OH)_2 + 4\ \ H^+ + 5.5\ Ca^{2+} + 3\ H_2O \quad (3)$$

Cadmium and Cd compounds are classified as "Class 1 human carcinogens" by the International Agency for Research on Cancer (Joseph, 2009). One of the most important sources of Cd contamination is the use of raw phosphate rock as fertilizer (Cabrera et al., 1998). Phosphate rocks, which are composed mainly of apatite of sedimentary origin, are usually enriched in Cd at concentrations up to several hundred mg/kg (Mar and Okazaki, 2012). The Cd enrichment phenomenon during phosphate rock diagenesis is explained by the similarities in terms of charge, ionic radius and coordination between Ca^{2+} and Cd^{2+} in the apatite crystal structure. A similar Cd uptake mechanism was used in the experiments of Guo et al. (2023), where the Cd-bearing calcite ($Ca_{1-x}Cd_x)CO_3$ reacts with orthophosphate in aqueous solution, and OCP acts as a sink for Cd. In particular, the experiments showed that although the presence of Cd^{2+} in calcite inhibited its replacement by Ca-phosphate phases, more than 98 % of the Cd was incorporated in DCPD (brushite), and even the low amounts of Cd^{2+} released into the solution were recaptured when DCPD was naturally converted to OCP or when the Cd-bearing calcite was completely replaced by HAP (hydroxylapatite). These results indicate that a very mobile toxic metal such as Cd^{2+} can be effectively immobilized by Ca-phosphate minerals such as OCP. Comprehensive research on the role of metals in the calcium-orthophosphate hydrolysis reaction (Lundager Madsen, 2008) has shown that OCP can effectively accommodate a wide range of cations (e.g., Mg^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, and Zn^{2+}) more favorably than HAP can. However, as noted by Boanini et al. (2010), the adsorption mechanism should also be considered, as well as ion exchange. Unfortunately, these studies are oriented to the production of ion-substituted OCP for medical purposes, but these results could inspire water treatment experiments with the aim of better defining whether and how OCP could be effective in the removal and immobilization of several polluting metals.

Interesting results have also been obtained with regard to emerging water contaminants, which are often related to the increasing concentration of chemical residues such as antibiotics (Wilkinson et al., 2022) and pesticides (WHO, 2022) in surface water and groundwater. According to the research of Zhu et al. (2020), the antibiotic tetracycline (TC) is effectively removed by OCP through a sorption process in the hydrated layer. Admittedly, this result is consistent with the fact that during the OCP synthesis, a broad range of organic macromolecules can be inserted into the crystal structure with the aim of using OCP for drug delivery both in vitro and in vivo experiments (Bigi and Boanini, 2019). The mechanism of uptake of organic macromolecules by OCP is related to the loss of HPO_4^{2-} and water molecules from the hydrated layer (Tsai et al., 2010). Therefore, it is conceivable that the same process used in the synthesis of doped OCP could also occur during water treatment for the removal of organic pollutants such as TC.

Table 2 summarizes the removal capacities of OCP for the different contaminants discussed above.

Table 2
Octacalcium phosphate removal capacity for different water pollutants. u.d. = under development.

Pollutant	Removal Capacity (mg/g)	WHO limit (mg/L)	Ref.
Fluoride (F^-)	25.7	1.5	Idini et al., 2019a
Lead (Pb^{2+})	1715.3	0.01	Zhu et al., 2020
Cadmium (Cd^{2+})	114.94	0.003	Zhu et al., 2020
Tetracycline (TC)	39.84	u.d.	Zhu et al., 2020

3.2. Wastewater

The need to reduce the input of P and nitrogen (N) from anthropogenic sources to aquatic ecosystems is widely recognized because these elements are directly responsible for the eutrophication of fresh water (Conley et al., 2009). Concerns related to the eutrophication of fresh water have been addressed since the 1970s, indicating that for several decades coastal regions throughout the world have experienced an increase in the incidence of toxic or otherwise harmful algal blooms (Anderson et al., 2002). The lack of proper management of wastewater in rural areas is one of the primary sources of P input into aquatic systems (Renman and Renman, 2010). In the seminal work of Vohla et al. (2011), where 89 materials were reviewed for their P removal capacity, a positive correlation with CaO and pH indicated that the precipitation of Ca-PO_4 compounds was the main process of P retention in constructed wetlands. Among several small-scale methods, the simple use of a column filter loaded with Polonite® (also named "heated opoka") has resulted in very high P removal performance and long-term applicability (Vohla et al., 2011; Hamisi et al., 2022). Polonite is the trade name for a calcined sedimentary rock called "opoka", which is mainly composed of calcite ($CaCO_3$), quartz (SiO_2) and opal ($SiO_2 \cdot nH_2O$) (Jurkowska and Świerczewska-Gładysz, 2022). The calcination process of the opoka stone causes the decomposition of $CaCO_3$ into more soluble CaO, strongly increasing the availability of Ca^{2+} to react with phosphate in solution (Zapater-Pereyra et al., 2014). OCP has been found to be the main P sink in filters loaded with Polonite (Eveborn et al., 2009). Interestingly, the presence of OCP in the Polonite filter is also effective at removing Pb from water in a very similar way as previously described (Table 2; Butkus et al., 2016).

Another important source of P in wastewater is urine, so research on the separation of urine from wastewater and its treatment with the aim of recovering nutrients is becoming imperative (Sohn et al., 2023). OCP was found to naturally precipitate together with struvite $(NH_4)Mg(PO_4) \cdot 6H_2O$ in pipes and urine collection tanks. This phenomenon is quite intriguing because it shows that OCP can also precipitate in very complex systems with high concentrations of several ions (e.g., K, Na, Mg, Cl, SO_4, and NH_4). The degradation of urine, so-called ureolysis, produces ammonia (NH_3) and ammonium ion (NH_4^+) among the final products and is accompanied by a sharp increase in pH (Mobley and Hausinger, 1989). When the pH increases above 7, decreases in Ca and P are observed, indicating the precipitation of OCP (Udert et al., 2003). In fact, although thermodynamic simulations have shown that HAP should be the only calcium phosphate mineral formed in urine solutions, OCP is observed as a precursor phase that slowly transforms into HAP (Udert et al., 2003). Similarly, OCP has been found in the solid portion of dairy manure after anaerobic digestion or after hydrothermal processing (Güngör and Karthikeyan, 2008; Sibrell et al., 2015; Deng et al., 2020). The recovery of P from wastewater through OCP precipitation has two positive effects: 1) reducing the P load in wastewater and 2) allowing the recovered P to be recycled as a soil amendment and fertilizer (Güngör and Karthikeyan, 2008; Sohn et al., 2023). The importance of P recovery is crucial: P is geographically and geologically concentrated in specific areas worldwide, and the global demand for P is increasing due to its multiple uses (e.g., as fertilizer and for battery manufacture). Therefore, phosphorus and phosphate rocks are included in the list of Critical Raw Materials (CRM) compiled by the European Commission (Grohol and Veeh, 2023).

4. Soil

The presence of OCP in soils has been extensively discussed since 1970 (Webber and Mattingly, 1970). It was observed that when a common phosphate fertilizer (i.e., monocalcium phosphate, $Ca(H_2PO_4)_2$) was added to a calcareous soil, the P concentration was controlled by the solubility of OCP rather than HAP. Similar experiments confirmed that the addition of KH_2PO_4 to calcareous soil leads to the formation of OCP and HAP as the most stable Ca-PO_4 phases; therefore, both OCP and HAP act as sinks for inorganic P (Abedi and Talibudeen, 1974). These observations indicate that the formation of poorly soluble Ca-PO_4 compounds stabilizes P in soils through two main effects: i) less labile P is less ready for plant uptake, and ii) more labile P is more susceptible to runoff from rain or irrigation (Mattingly, 1975). Since the use of phosphate fertilizers is a common practice worldwide, leaching losses of labile P through surface runoff can contribute greatly to the increase of P in water bodies, thereby increasing eutrophication (Bhattacharya, 2019). To prevent P losses, fertilizer should be applied at rates not exceeding crop uptake or at the soil P retention capacity (Pole et al., 1996). To increase soil P retention, the use of gypsum ($CaSO_4 \bullet 2H_2O$) as a source of Ca in siliceous soil has been shown to reduce water-extractable P through the formation of OCP (Chen et al., 2016). On the other hand, when soluble phosphate is applied in calcareous soils, the retention of P is naturally high (Sakin and Yanardağ, 2024) thanks to the affinity of Ca and orthophosphate for the formation of stable phases. This mineralogical pathway is the same as that of heated opoka rock (Polonite), as discussed in the previous section. Hence, a less soluble Ca-PO_4 compound, such as OCP, limits the leaching of P from soils compared to $Ca(H_2PO_4)_2$ or KH_2PO_4, reducing its input to water bodies (Attanayake et al., 2022). Another positive effect of OCP in soil is that the Olsen-P parameter, an indicator of the phytoavailable P fraction from the soil (Olsen et al., 1954), proves that OCP is effectively an inorganic P reservoir for plants (Shen et al., 2019).

Hałabuza et al. (2022) demonstrated that both limestone and ammonium phosphate fertilizers have a strong capacity to immobilize Cd, Pb and Zn in soil. Unfortunately, in this research, there was no clear evidence of which mechanism controls metal immobilization. Considering the versatility of OCP for removing foreign metal ions in aqueous solution (Lundager Madsen, 2008), its role in metal immobilization in soil should be investigated. Another clue in this direction resides in the fact that OCP is the natural precursor of apatite, and synthetic apatite is already extensively used as an amendment for metal-contaminated soils (Li et al., 2023). Highlighting the conditions for which a contaminant metal may be more or less retained in the presence of OCP and/or any reaction leading to apatite formation could be a step forward for soil science.

5. OCP identification

Correct mineralogical identification is crucial for properly recognizing a single phase in a multiphase compound. In particular, in natural contexts Ca and P can be present simultaneously in different mineralogical forms, e.g., brushite, OCP and/or apatite. The correct identification could also be tricky when a Ca-PO_4 phase is the product or the reagent of another phase and when the reaction is incomplete. In that case, the overlap of the possible identifications requires further elaboration to provide a correct interpretation. For example, using X-ray absorption near edge structure (XANES) analysis, the problem of multiphase identification of Ca-PO_4 minerals was addressed by compiling a new normalization method that accounts for 81 different spectra (Oxmann, 2014). A very common technique for identifying crystalline phases is powder X-ray diffraction (PXRD). The PXRD patterns of pure OCP (Brown et al., 1962) and natural FAP (Brophy and Nash, 1968) (Fig. 3 and Table 3) are quite different at low diffraction angles: the main reflection of OCP is located at 4.7 $2\theta^{\circ}$ (100 % relative intensity, RI), and the characteristic doublets are located at 9.441 and 9.765 $2\theta^{\circ}$ (15 and 13 RI, respectively), close to the first reflection of FAP at 10.874 $2\theta^{\circ}$ (18 RI). Above 20 $2\theta^{\circ}$, the OCP pattern overlaps the main reflections of FAP, especially in the range of 30-40 $2\theta^{\circ}$ (Fig. 3 and Table 3). There are many software programs available for processing PXRD data; in our case, we used X'Pert Highscore software (Degen et al., 2014) and asked the following question: If a low-angle scan is omitted, how does the PXRD scoring scheme for a Ca-PO_4 compound change?

The scoring scheme algorithm calculated by X'Pert Highscore software produces a relative number (i.e., the score) that indicates the similarity of an unknown phase with respect to the powder diffraction files (PDF) listed in the international database, in our case, the PDF-2 from the International Centre for Diffraction Data (ICDD) (Gates-Rector and Blanton, 2019). The score (0–100 %) is a combination of several parameters, among which the most important are i) the peak position of the unknown phase matching the reflection position of the reference pattern, ii) the number of matching reflections divided by the total number of peaks in the reference pattern, and iii) the match between the experimental intensities of the peaks of the unknown phase and the reflection intensities of the reference pattern. A higher score indicates a better match between the reference pattern and the pattern of the unknown phase. Fig. 3a shows the PXRD pattern of a sample

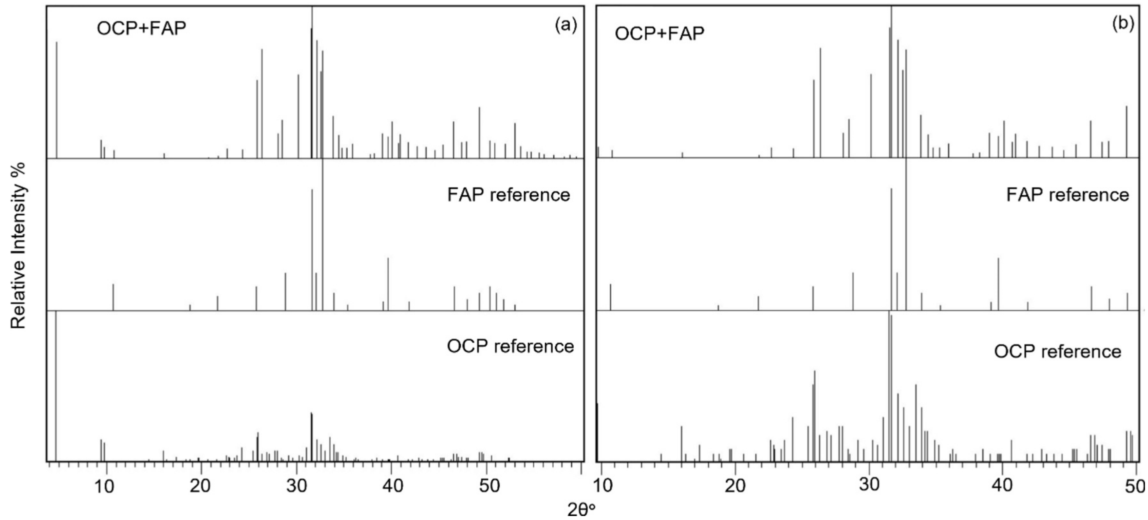

Fig. 3. PXRD reflections of a sample composed of 68 wt% OCP and 32 wt% FAP. On the left (a), the scan range was 3–60 2θ°, where low-angle OCP reflections were detectable (see the OCP reference pattern on the left). On the right (b), the PXRD pattern of the same sample was collected in the range of 10–50 2θ°, highlighting that the most intense reflections can be attributed to both OCP and FAP. Note that the relative intensity scale of the reference pattern OCP (PDF n. 00–026-1056, Brown et al., 1962) shown below OCP + FAP (a) on the left is different from that of the same reference pattern shown below OCP + FAP (b) on the right. See also Table 3.

Table 3
XRD patterns of a sample composed of 68 wt% OCP and 32 wt% FAP. The phase identification scores of OCP and FAP depend on the scan range: when excluding the range 3–10 2θ°, the OCP score decreases from 58 to 26 because the most intense reflections above 10 2θ° could be attributed to both OCP and FAP. Reference pattern of OCP: PDF n. 00–026-1056 (Brown et al., 1962), reference pattern of FAP: PDF n. 00–021-0145 (Brophy and Nash, 1968).

Scan range 3–50 2θ°			Scan range 10–50 2θ°		Reference patterns			
Score: 58 OCP, 24 FAP			Score: 44 FAP, 26 OCP		PDF 00–026-1056		PDF 00–021-0145	
Pos. 2θ°	RI [%]	Matched by	Pos. 2θ°	RI [%]	OCP	RI [%]	FAP	RI [%]
4.70	76.6	OCP			4.72	100		
9.39	12.5	OCP			9.44	15		
9.75	7.5	OCP			9.77	13		
10.81	5.6	FAP	10.81	6.0			10.87	18
16.04	3.5	OCP	16.04	4.0	16.04	8		
21.79	2.0	FAP; OCP	21.79	1.7	21.60	2		
22.73	6.7	OCP	22.73	7.5	22.67	5	21.87	10
24.33	6.4	OCP	24.33	6.9	24.30	10		
25.87	51.5	FAP; OCP	25.87	51.5	25.87	17		
26.37	72.0	OCP	26.37	72.0	26.00	20	25.96	16
28.06	16.5	OCP	28.06	15.8	26.36	6		
28.52	25.5	FAP; OCP	28.52	25.4	28.04	8		
30.16	55.2	OCP	30.16	55.1	28.62	2	28.97	25
31.53	85.7	FAP; OCP	31.53	85.7	30.32	5		
31.69	100.0	FAP; OCP	31.69	100.0	31.56	33	31.46	18
32.16	77.6	FAP; OCP	32.16	77.6	31.70	32	31.81	80
32.54	57.5	OCP	32.54	57.5	32.19	15	32.24	25
32.78	71.1	FAP; OCP	32.78	71.1	32.59	12		
33.89	28.3	FAP; OCP	33.89	28.2	33.52	17	32.94	100
34.43	15.7	OCP	34.43	15.6	33.97	12	34.10	12
34.81	7.0	OCP	34.81	6.9	34.24	7		
35.29	7.0	FAP; OCP	35.29	6.3	34.93	5		
35.94	9.6	OCP	35.94	9.5	35.25	4	35.51	4
37.80	3.0	OCP	37.80	2.9	38.02	2		
38.23	3.6	OCP	38.23	3.5	38.53	3		
39.02	16.4	OCP	39.02	16.4	39.06	2		
39.65	14.5	FAP; OCP	39.65	14.4	39.66	2	39.26	6
40.06	24.5	FAP; OCP	40.06	24.5	39.77	2	39.84	35
40.73	10.5	OCP	40.73	10.5	40.70	5		
41.80	11.1	FAP; OCP	41.80	11.0	41.83	2	42.01	6
42.72	8.0	OCP	42.72	5.6	42.28	2		
43.69	7.5	OCP	43.69	7.2	43.85	2		
45.47	9.1	OCP	45.47	9.0	45.55	3		
46.57	24.7	FAP; OCP	46.57	24.6	46.89	6	46.76	16
47.44	10.7	OCP	47.44	10.6	47.46	4		
47.92	11.4	OCP	47.92	11.2	47.92	3		
49.23	34.0	FAP; OCP	49.23	33.8	49.08	3	49.13	8

composed of 68 wt% OCP and 32 wt% FAP obtained by reacting 80 g OCP for 2 h in 20 L of natural water with 37.2 mg/L F^- ions (Idini et al., 2020). For comparison, the reference patterns of FAP and OCP are shown in Fig. 3a and b (see also Table 3).

The OCP and FAP scores calculated in the 2θ° range of 3–60 (Fig. 3a) were 58 and 24, respectively. As shown in Fig. 3a and reported in Table 3, the three most intense reflections of the OCP + FAP sample occurred at 31.7 2θ° (100 RI), 31.5 2θ° (85.72 RI) and 32.15 2θ° (77.57 RI). All three of these reflections could be attributed to both OCP and FAP, but OCP is unequivocally recognizable because of its most intense reflection at 4.7 2θ° (76.64 RI) and the doublet at 9.4 2θ° (12.5 RI) and 9.7 2θ° (7.46 RI). In Fig. 3b, the same sample was analyzed in the range of 10–50 2θ°. In this case, the OCP characteristic reflections at scan angles less than 10 2θ° were not determined, and the overlap between the OCP and FAP patterns seems to be much more difficult to resolve (Table 3). In fact, the score was reversed: 44 for FAP and 26 for OCP. In addition to these two phases, DCPA and HAP also increased in the scoring scheme up to 42 and 40, respectively. The exclusion of the 3–10 2θ° interval is more than sufficient to severely lower the reliability of the analysis, leading to misattribution to other Ca-PO_4 phases rather than OCP, although OCP is by far the most abundant phase in the analyzed sample. This discussion on how to perform PXRD analysis of Ca-PO_4 phases stems from the observation that a consistent number of research papers about apatite in different environmental contexts identify phases by scanning the sample above 10 2θ°, excluding possible XRD features of OCP (Chen and Arai, 2019). Some examples of this incorrect analytical procedure can be found in two recent papers on the innovative and effective use of brushite for removing uranium (Jiménez-Arroyo et al., 2023) or cadmium (Guo et al., 2021) from water. All these valuable studies share the removal mechanism: brushite reacts to form an apatitic phase. However, the low XRD angle 3–10 2θ° was not acquired; thus, the resulting Ca-PO_4 phase may not be correctly identified. Since OCP and apatite have different stoichiometries and chemical stabilities and may incorporate different ions in their lattice, correct identification of the phase formed could be crucial for designing and applying the most effective and efficient method of environmental remediation. Finally, the ICDD PDF database lists OCP only in the "inorganic" and "ceramic" subsets. Thus, if only the "mineral" subset is selected for the identification of minerals in a given sample, then OCP is automatically excluded from the list of possible candidates.

6. Summary and future perspectives

The purpose of this review was to provide as broad a picture as possible of the importance of octacalcium phosphate (OCP) in the fields of earth and environmental sciences.

OCP is a mineral phase belonging to the calcium-orthophosphate group. In the biomedical and material sciences, OCP plays a very important role as a graft for bone repair, taking advantage of its metastability, which leads OCP to naturally transform into hydroxylapatite (HAP) or, more precisely, into bioapatite (a nonstoichiometric Ca-deficient carbonate hydroxylapatite), an essential component of bones and teeth. Due to the extensive biomedical literature about OCP, its mineralogical features are therefore well known, while its role in the geological-environmental field is poorly understood and considered.

OCP has also been recognized to be the precursor of apatite in natural environments, whether phosphorus (P) and calcium (Ca) are naturally present in the system or OCP is used directly as a reagent to remove pollutants from water. The use of the OCP → apatite transformation has yielded excellent results in terms of the removal capacity of fluoride, lead, cadmium, pesticides and antibiotics.

Combining the literature data throughout this review, it appears that OCP nucleates in place of apatite under circumneutral pH conditions and in the natural temperature range of fresh waters and seawater. The mineralogical transformation of OCP into apatite occurs at the crystal-fluid interface or by the loss of HPO_4^{2-} and H_2O from the hydrated layer (see Fig. 1) according to the following reaction when HAP is taken as the final product:

$$0.625\ Ca_8(HPO_4)_2(PO_4)_4 \bullet 5H_2O_{(OCP)} \rightarrow Ca_5(PO_4)_3OH_{(HAP)} + 0.75\ HPO_4{}^{2-} + 1.5\ H^+ + 2.125\ H_2O \quad (4)$$

The transformation into apatite proceeds faster if fluoride or a higher pH is present in the solution. Several elements and ion complexes can be hosted in the OCP lattice, even before the transformation into apatite, an ionic substitution involving both the Ca^{2+} and HPO_4^{2-} crystallographic sites. During the transformation OCP → apatite, if fluoride and carbonate ions are present in solution, they are captured, leading to the formation of fluorapatite var. francolite. Francolite, or carbonate-rich fluorapatite, is the main constituent of phosphorite deposits, the most important exploitable source of P worldwide. During the diagenesis of phosphorite deposits, OCP plays a key role as a precursor of francolite. Understanding the mineralogical and geochemical pathways of P is of primary importance for i) preventing eutrophication of aquatic systems and ii) recovering P from sludge and wastewater. In fact, P and phosphate are included in the list of Critical Raw Materials (CRM). OCP also plays an important role in agricultural soils, where OCP tends to immobilize the P of soluble fertilizers in a less soluble form and, at the same time, makes P more bioavailable than P in apatite.

Finally, we strongly recommend that the PXRD analysis of Ca-PO_4 samples always includes scans in the low-angle range of 3–10 2θ° to unequivocally discriminate between OCP and apatite. The failure to scan this angular range in several scientific articles suggests that the presence and importance of OCP have often been misrecognized and/or unrecognized.

A better identification of OCP can be achieved by using the new OCP reference pattern (00–074-1083) that has been approved very recently with the highest quality mark by the ICDD (Kabekkodu et al., 2024) on the basis of XRD data published in Idini and Frau (2021) and supplemented by the same authors.

Based on the evidence reported in this review, the natural samples of OCP should be proposed for validation as a mineral species by the International Mineralogical Association-Commission on New Minerals Nomenclature and Classification (IMA-CNMNC). The validation of OCP as a natural mineral, not only as a synthetic phase, could greatly implement its importance in the earth and environmental sciences, while promoting a better understanding of the geochemical-mineralogical cycle of P.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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