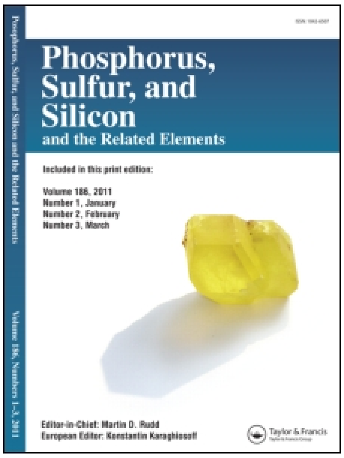

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Dykman, A. S. , Batelin, O. E. , Abramov, N. V. and Evgrashin, N. V.(1993) 'Calcium Phosphates of Hydroxylapatite Structure', Phosphorus, Sulfur, and Silicon and the Related Elements, 76: 1, 195 — 198
To link to this Article: DOI: 10.1080/10426509308032392
URL: http://dx.doi.org/10.1080/10426509308032392

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Phosphorus, Sulfur, and Silicon, 1993, Vol. 76, pp. 195–198
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CALCIUM PHOSPHATES OF HYDROXYLAPATITE STRUCTURE

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In the $CaO-P_2O_5-H_2O$ system it may be separated crystalline precipitate which gives X-ray photographs corresponding to stoichiometric calcium hydroxylapatite (SCHA) but differs from it by composition. CaO/P_2O_5 mole ratio of those compounds varies in the range from 2.66 to 3.34 whereas that of SCHA is 3.34.

Apatite-like calcium phosphates (ALCP) are subjects of many investigations. Their structures and compositions were for a long time points of discussions. For this reason, we have carried out a comparative analysis of existing ideas concerning ALCP.

Many works were dedicated to the investigation of ALCP with CaO/P_2O_5 of 3.0 which is most frequently met with and, according to classic chemistry laws, should have the composition $Ca_3(PO_4)_2$. The presence of water in composition of this compound as well as the resemblance of X-ray photographs of it and of SCHA allowed to assume that the above compound was tricalciumphosphate hydrate (TCPH), isomorphous to SCHA. Some investigators suggested to use as a criterion of TCPH distinction from SCHA different thermal stability of these compounds: it was shown that at temperatures above 700°C, TCPH turned into β-$Ca_3(PO_4)_2$ whereas SCHA did not change under this conditions and begins to destruct only at temperatures above 900°C. It was, however, impossible to explain with help of this theory the presence of a great amount of pyrophosphates, which were found in the sample of TCPH calcined at 400-600°C. For this reason, it was assumed the presence of HPO_4^{-2} groups in the above substance casting doubt on the TCPH existence as an individual compound.

A number of investigators attempted to describe ALCP with the aid of adsorption theory according to which SCHA sorbs on its surface HPO_4^{2-} ions which results in a decrease in CaO/P_2O_5. From this point of view, ALCP's with CaO/P_2O_5 above 3.34 are treated as SCHA's with surface-sorbed calcium ions. It was, however, shown that specific surface area which had ALCP was insufficient to "quarter" that amount of HPO_4^{2-} ions which was necessary to decrease CaO/P_2O_5 from 3.34 to corresponding values for each sample.

Results of the investigation carried out by us witness that ALCP's have extreme ability to absorb calcium ions. So, ALCP synthesis has been carried out by means of pouring together solutions of calcium chloride and triammonium phosphate under conditions stirring of the forming suspension. CaO/P_2O_5 in reagents was 5.0, suspension pH was 9.0-9.2. The precipitate obtained was separated from suspension, washed up to chlorine ions disappearance and dried. CaO/P_2O_5 in the ALCP was 3.03. The sample obtained had CaO/P_2O_5 only 3.04 if using the proposed synthesis procedure to add calcium chloride suspension in such amount to reach CaO/P_2O_5 ratio 40. (Table 1) Thus, alteration of CaO/P_2O_5 can be associated with adsorption of calcium or phosphate ions on the ALCP surfaces only in very narrow range of these ratios.

TABLE 1 Conditions of apatite-like calcium phosphate (ALCP) preparation process and it's physical-chemical characteristics.

ALCP preparation conditions			ALCP samples characteristics		
CaO/P_2O_5 in reagents	CaO/P_2O_5 in susp.	Susp. pH	CaO/P_2O_5 in ALCP	Specific area, m^2/g	Phase compos.
5.0	5.0	9.0-9.2	3.03	81	SCHA
5.0	40.0	9.0-9.2	3.04	84	SCHA

ALCP preparation process temperature is 20°C

To explain the existence of ALCP's with different CaO/P_2O_5, it was proposed that ALCP's are mixtures of SCHA with acidic phosphates, e.g. $Ca(H_2PO_4)_2*H_2O$, $CaHPO_4*2H_2O$ or octacalcium phosphates. However, difference in the main conditions of SCHA and acidic phosphates preparation as well as the fact that this phosphates were not found by known analytical methods as individual compounds, which called their presence in ALCP in question.

From other point of view, the model suggested by A.S.Posner is now the most reliable one. He postulated the existence of compounds having SCHA lattice in certain places of which the statistical absence of calcium ions takes place; other ions, e.g. hydrogen ones can be substituted for absent ions to preserve electrical neutrality. The calcium excess of ALCP with CaO/P_2O_5 > 3.34 may be randomly distributed throughout the structure as CaO for example. Such phosphates it was proposed to be named calcium deficient hydroxylapatites (CDHA).

According to data obtained, CDHA composition can be described by formula $Ca_{10-x}M_{2x}(PO_4)_6(OH)_2$ (I), where M is univalent cation (H^+ or Na^+).

Based on Posner's theory, one can explain alterations of CDHA during calcination. Below 600°C the formation of $P_2O_7^{4-}$ takes place in the CDHA structure (Reaction 1). At temperatures above 600°C ß-$Ca_3(PO_4)_2$ appears which is accompanied by a decrease in pyrophosphate content and the hydroxylapatite structure destruction; this is connected with interaction of structure hydroxyl groups with $P_2O_7^{4-}$ ions (reaction 2).

$$2HPO_4^{2-} \xrightarrow{T<600^\circ C} P_2O_7^{4-} + H_2O \qquad (1)$$

$$P_2O_7^{4-} + H_2O \xrightarrow{T>600^\circ C} 2PO_4^{3-} + H_2O \qquad (2)$$

The question concerning the formula describing CDHA composition was widely discussed. The starting point for the formula determination having been HPO_4^{2-} content in the sample. So, L.Winand found that only a half of the number of HPO_4^{2-} which could predict on the basis of formula (1) was in CDHA samples. Based on those results, Winand assumed that is in the case of the absence of calcium ion in the hydroxylapatite lattice one hydroxyl ion "went away" and one hydrogen ion "came" to retain the charge balance. So, L.Winand suggested that CDHA described with the formulae: $Ca_{10-x}H_x(PO_4)_6(OH)_{2-x}$ (II), where $0 \leq x \leq 2$.

In Posner's opinion, compositions of undried CDHA precipitates are described by formula (I) and a half of hydrogen ions reacts during the process of drying with structure hydroxyls yielding "x" moles of water (Reaction 3):

$$Ca_{10-x}H_{2x}(PO_4)_6(OH)_2 \xrightarrow{100-120^\circ C} Ca_{10-x}H_x(PO_4)_6(OH)_{2-x} + xH_2O \qquad (3)$$

To determine true compositions of undried CDHA's, we proposed to prepare the sample of calcium deficient chloroapatite (CDCLA) (Sample II). There can be no doubt that reaction (3) cannot proceed during CDCLA sample drying. Therefore, in the case of the trustworthiness of formula (I) for "wet precipitates", one must found in CDCLA twice as many HPO_4^{2-} groups as compared with CDHA. The analysis of calcinated samples I and II shown the same content of pyrophosphates in them which proved the trustworthiness of formula II rather than of formula I. (Table 2)

TABLE 2 Physical-chemical properties of calcium phosphates.

Sample	Sample calcination conditions	CaO/P_2O_5 molar ratio	Content of phosphorus in condenced form, % of total P	Calculated cotent of phosphorus in condenced form % of total P	Phase composition (X-ray data)	Functional groups (IR data)			
						HPO_4	P_2O_7	Poly- and meta-phosphates	Structure hydroxyl
I	Noncalcined	2.58	-	-	HA	+	-	-	+
II	Noncalcined	2.58	-	-	HA	+	-	-	+
I	530°C	2.98	16.9	17.7	HA	-	+	+	+
II	6 hrs	2.58	17.2	17.7	HA	-	+	+	+
I	800°C	3.00	0.5	-	β-$Ca_3(PO_4)_2$	-	-	-	-
II	8 hrs	2.99	15.9	-	HA*	-	+	+	-

HA - calcium hydroxylapatite
* - small amount of β-$Ca_3(PO_4)_2$

The data obtained can be used for purposeful search for highly efficient catalysts for petrochemical processes.