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FLUO-CARBONATE APATITE AS THE MAIN CONSTITUENT OF MOST PHOSPHATE ROCKS

by

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The rock phosphates used in our industry usually contain comparatively small quantities of calcium carbonate as a secondary constituent. The question as to the form in which calcium carbonate is present is still being debated by scientists. Whilst in 1912 Schaller (1) assumed that calcium carbonate was incorporated in the apatite complex and that the phosphatic mineral francolite represented fluo-carbonate apatite, more recent works (2) have appeared where the authors endeavoured to prove that CaCO_3 represented an independent phase in the form of sub-microscopical particles of calcite. The question of the incorporation of calcium carbonate is interesting, not only from the purely scientific point of view, but also inasmuch as it is of practical value because it is obvious that the possibility of breaking down phosphates is closely linked with this question. J. H. Caro and W. L. Hill (3) also demonstrated that there was a clear connection between the content of incorporated carbonate in phosphates, their solubility in citric acid and neutral citrate solution, and their fertiliser action.

In a paper published jointly with I. Asemissen (4) the problem of the carbonate was investigated chemically and radiographically in the case of three rock phosphates with a specially high carbonate content, i.e. Constantine, Gafsa and Curacao phosphates. It was possible to show that the first two phosphates represented fluo-carbonate apatites, whilst the third consisted generally speaking of a mixture of hydroxyl-apatite and beta-tricalcium phosphate. These investigations were continued at Dänischburg and extended to other phosphates. It is proposed to report further on the results obtained.

Chemical analysis.

The result of the chemical analyses of the various rock phosphates is summarised in table No.1 (see appendix) and compared with the analysis of francolite which is extensively dealt with in the literature. As will be seen from the table, Kola apatite does not contain any calcium carbonate, being a very pure fluo-apatite. In contradistinction to this, the CaCO_3 content of Togo phosphate amounts to 4%, rising to 7.5% in the case of francolite and up to approximately 15% with Curacao phosphate. According to the formula by Schaller for fluo-carbonate apatite, $9 \text{CaO} \cdot 3 \text{P}_{25} \cdot \text{Ca}(\text{F}_2, \text{CO}_3) \cdot \text{H}_2\text{O}$, 3 mols of $\text{Ca}_3(\text{PO}_4)_2$ correspond

to 1 mol (CaF₂ + CaCO₃).

The lower row of table No.1 shows the calculated mol proportions of the analysed phosphates. As will be seen only the calcium fluoride content of Curacao phosphate lies below the value calculated for the fluo-apatite. The remaining phosphates, however, contain a considerable excess of CaF₂ attaining a maximum of 156% in the case of Constantine phosphate. If, according to the formulation of Schaller, the CO₃-ion were to be incorporated in the apatite complex in place of the F-ions, double and treble excess would be obtained in the place of the fluorine-ion in the lattice. These analytical results make it seem improbable that the CaCO₃ of the analysed phosphates is incorporated in this manner in the apatite lattice.

Leaching of the calcium carbonate.

On the basis of earlier papers (5) an endeavour was made to separate the unattached carbonate from that incorporated in the apatite complex by leaching the phosphate, using for this purpose a 2% citric acid. Whilst according to the older method leaching was carried out in one phase, the accuracy of our test was increased by treating the sample 4 to 5 times with the solution and by analysing it after each treatment.

Method: Grind sample to pass a 0.05 mm-Screen and analyse. Agitate with a 2% citric acid in the proportion of 1:10 i.e. 20 grammes to 200 filter, rinse with water, dry at 100°, weigh and analyse again for CaO, P₂O₅, F and CO₂. The residue of the sample is treated in the same way as many times as seems desirable.

Table No.2 shows the results of the leaching experiments: the CO₂ values determined in the extraction residues have been converted to the CaCO₃ determined in the original substance and the mol ratios (CaF₂ + CaCO₃) / 3 Ca₃ (PO₄)₂ have been indicated. The table reveals considerable difference in the behaviour of the normal phosphates with high fluorine content as compared with Curacao phosphate. In the latter case the CaCO₃ content decreases, as does also the sum of the mols (CaF₂ + CaCO₃), with each successive leaching. In the case of the other phosphates, however, this content decreases only in the first phase of extraction and remains constant in further extractions. From this behaviour it can be concluded that the CaCO₃ portion, which remains constant and which cannot be extracted, is incorporated in the apatite lattice, whilst the extractable portion is present in small particles in the form of calcite. According to the extraction analysis the tested phosphates contain the following quantities of apatite carbonate and calcite carbonate.

Table No.3

Phosphate	% apatite CaCO ₃	% Calcite - CaCO ₃
Togo	3.8	0.2
Pebble	6.1	1.3
Morocco	8.3	4.1
Constantine	11.7	2.3
Gafsa	10.6	3.9

It is impossible to provide such values in respect of Curacao phosphate as no constant composition could be determined during agitation. Presumably, the whole of the 14.7% of CaCO₃ exist in the form of "sub-microscopical" calcite. There is however always a possibility that with a continued agitation a certain proportion may be recognisable as being fixed.

It should be specially noted that the sum of mols ($\text{CaF}_2 + \text{CaCO}_3$) does not decrease to 1 after extraction with citric acid, but represents, for each type of phosphate, a constant value considerably above 1. This again would appear to indicate that the calcium carbonate plays a different rôle in the structure of the apatite lattice from what was hitherto assumed.

Radiographic proof of calcite existing apart from apatite.

In order to confirm the results obtained by chemical tests, various samples were thoroughly investigated by means of radiography. The main objections raised in recent times to the hypothesis of fluo-carbonate apatite are based on the fact that it is difficult to prove the existence of calcite as distinct from apatite, because the principal interference of calcite ($d = 3,038 \text{ \AA}$) coincides with a medium strength interference of apatite. For our investigations we used the counter-tube-method with automatic^{*} "Glanzwinkel" recording which enables the experimenter to make a comparatively simple and accurate evaluation of the diagram. For the diagrams of the various phosphates, attention is drawn to the publication mentioned previously. At this juncture we are concerned with showing the existence of calcite as distinct from apatite. For this purpose X-ray diagrams of mixtures of synthetic fluo-apatite with additions of 1, 2, 4, 6, and 10% of calcite were made. Figure 1 of appendix shows the range of angles of the diagrams within which the main interference of calcite falls.

As will be seen from illustration No. 1, the calcite is indicated at 2% by a widening of the apatite interference (120) (210) and is readily discernible at 4%.

The existence of calcite can be determined more accurately if, for the purpose of measurement, the proportion of the intensities of the apatite interferences (002) and (120) is chosen. In view of the fact that the main interference of calcite coincides with (120), this proportion decreases with an increase in the calcite content. In Figure 2 of the appendix these proportions are demonstrated with Constantine phosphate.

In evaluating the diagrams of the extracted samples a relative intensity at (002)/(120) of 2.0 to 2.2 is found, while this amounts to only 1.5 in the original sample. Conversely, a ratio of 1.5 is encountered with extracted samples if 2% of calcite is added. As shown by chemical tests, exactly this quantity of calcite was found in Constantine phosphate by means of extraction.

In the corresponding experiment with Curaçao phosphate the radiographic tests did not provide an unequivocal result owing to the varying intensity of the incidence of interferences of the betatricalcium phosphate which obviously is present in a relatively coarse crystalline form and hence exists apart from apatite in a non-homogeneous distribution. As a beta-tricalcium phosphate interference further coincides with the main interference of the calcium carbonate and the interference of apatite (120), the X-ray diagram could not be evaluated.

Radiographic proof of the incorporation of CaCO_3 in the apatite lattice.

It still remained to be proved that the main quantity of calcium carbonate existing in the rock phosphate in addition to this small quantity of calcite, - in the case of Constantine

* lit. "low angle scatter"

phosphate for example 11.7% - is actually incorporated in the apatite lattice. For this purpose further radiographs under particularly sensitive conditions of photography were made, calculating from the results the lattice constants of the various phosphate samples. The results are shown in the following table No. 4.

T a b l e 4.

Phosphates	a_0			c_0		
Curaçao	9.41	±	0.01 Å	6.87	±	0.01 Å
Hydroxyl apatite synth.	9.407	±	0.005 Å	6.876	±	0.005 Å
Kola	9.364	±	0.005 Å	6.886	±	0.005 Å
Fluo-apatite, synth.	9.361	±	0.005 Å	6.871	±	0.005 Å
Gafsa	9.31	±	0.01 Å	6.88	±	0.01 Å
Constantine	9.30	±	0.01 Å	6.88	±	0.01 Å

The three phosphates containing carbonate, namely Curaçao, Gafsa and Constantine, clearly show a broadening of the lines as compared with Kola and the synthetic apatites. The widening is independent of the "Glanzwinkel" and therefore cannot be attributed to a distortion of the lattice, but to the small size of the primary particles. Bredig, Franck and Fuldner (6) observed that the particle size of phosphate containing carbonate is usually smaller than that of phosphates free from carbonate.

This table shows in particular that the a_0 values of Gafsa and Constantine are smaller than those of the pure fluo-apatites. The decrease in the a_0 -value is still more pronounced than that observed by McConnell and Gruner (7) in the case of francolite ($a_0 = 9.34 \pm 0.01$). This is understandable owing to the higher content of incorporated carbonate in the rock phosphate investigated by us. According to these observations, the elementary nucleus of fluo-carbonate apatite is clearly smaller than that of the pure fluo-apatite. The possibility of the carbonate ion replacing the fluorine cannot be seriously discussed, quite apart from the fact that the fluorine content of Gafsa and Constantine phosphate is higher than that corresponding to the theoretical value of fluo-apatite. It is much more likely that the phosphorus is replaced in the crystal lattice by carbonate. This was the assumption of various American authors. (8). The pronounced excess of fluorine in phosphates containing carbonate may link up with this fact.

Synthesis of fluo-carbonate apatite.

In view of the fact that both the radiographic analysis of rock phosphates and the chemical analyses point most strongly to the hypothesis of incorporation, we endeavoured in conclusion to produce fluo-carbonate apatite synthetically. This synthesis was all the more important as in the past it had not been possible to achieve this with certainty in the case of carbonate apatite free from fluorine.

The experiments were conducted in the following manner: equivalent solutions of calcium chloride on the one hand, and mixtures of ammonium phosphate, ammonium fluoride and sodium carbonate on the other hand, were mixed together very slowly in a large volume of water, drop by drop, the mixture being agitated

all the time. The pH value of the solutions was fixed at 6.0 and 7.0 respectively. When mixing the solutions these concentrations of hydrogen ions were maintained by adding drop by drop ammonia to the reaction mixture.

The analytical results of five of the substances prepared in this manner are summarised in table No. 5 (see appendix). Details in regard to these substances are as follows:

Hydroxyl-apatite.

Precipitation of boiling solution by passage of ammonia.
Ca⁺⁺ : PO₄ ''' = 5 : 3. Precipitate dehydrated at 450°.

Fluo-apatite.

Precipitation of boiling solution at pH 6.
Ca⁺⁺ : PO₄ ''' : F' = 5 : 3 : 1.
Precipitate calcined at 1000°.

Fluo-carbonate apatite No. 4.

Precipitation agitation and passage of large volume of CO₂ at 40° at pH 6. Ca⁺⁺ : PO₄ ''' : F' = 5 : 2.4 : 2.6 Dehydration of precipitate at 450°.

Fluo-carbonate apatite No. 15.

Reaction conditions as above but Ca⁺⁺ : PO₄ ''' : F' = 5 : 2.0 : 2.1
Dehydration of precipitate at 450°.

Fluo-carbonate apatite No. 31.

Reactions conditions as above, but precipitation at pH 7.
Dehydration at 450°.

The fluo-carbonate apatite substances were tested by the extraction method in the same manner as the rock phosphates. The results of these experiments are to be seen from table No. 6. (See appendix). As will be seen from this table, the content of non-extractable CaCO₃ of these substances ranges from 10 to 13%. Whilst substance No. 4 does not contain any calcite, substance No. 15 contains 4.5% and substance No. 31, 2.6%. The similarity of behaviour of these substances during the extraction analysis as compared with North-African phosphates is surprising.

In conclusion, X-ray diagrams of these synthetic substances were made by means of a Guinier camera. In the following only four of the most important of the numerous radiographs are given: (For illustration No. 3 see appendix).

The pronounced agreement of Kola phosphate and synthetic fluo-apatite on the one hand and Gafsa phosphate and fluo-carbonate apatite on the other hand is readily discernible. When scrutinising the diagrams carefully, also the difference between fluo-apatite and fluo-carbonate apatite are noticeable; they consist of the splitting of the interference (112) and (121) in the case of fluo-apatite, which does not occur in the case of fluo-carbonate apatite, and, further, of the relative position of the interferences of groups (231) (140) (402) and (004). This is in agreement with Silvermann, Fuvat and Weiser (5) who draw attention to the fact that the difference of fluo-apatite, hydroxyl apatite and fluo-carbonate apatite is based on a change in the distances of the interferences (231) and (004).

We are still continuing the synthetic experiments briefly described above, in order to ascertain up to what limit calcium carbonate can be incorporated in the apatite lattice and what rôle the fluorine content plays in this connection. According to the present results it is possible to state that calcium carbonate of rock phosphate is not an unimportant secondary constituent, but is directly connected with the structure of the apatite complex. Hence the fluo-carbonate apatite must be regarded as the main constituent of the majority of rock phosphates.

SUMMARY.

A series of rock phosphates was analysed chemically and radiographically. It has been demonstrated that a preponderant quantity of the calcium carbonate contained in rock phosphates is incorporated in the apatite lattice and that in the majority of rock phosphates it is in the form of fluo-carbonate apatite. The observations made by means of analyses were confirmed in the laboratory by the synthesis of fluo-carbonate apatite.

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T A B L E 1

ANALYSES OF TESTED ROCK PHOSPHATES.

Phosphate	Kola	Togo	+) Fran- colit	Pebb- le	Mor- occo	Const- antine	Gafsa	Cura- çao
% P ₂ O ₅	38.40	36.20	38.21	35.00	31.46	28.92	25.70	36.61
% CaO	51.40	51.78	55.42	49.65	50.58	49.42	44.12	49.46
% MgO	n.d.	-	-	0.48	0.55	n.d.	n.d.	n.d.
% SrO	1.45	-	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
% F	3.39	4.02	4.05	3.92	4.00	4.03	3.04	0.67
% CO ₂	-	1.76	3.30	3.25	5.47	6.15	6.36	6.46
% SO ₃	-	0.26	-	0.66	1.11	3.29	3.54	1.50
% Al ₂ O ₃ +Fe ₂ O ₃	2.67	2.67	-	1.70	1.08	1.25	2.24	*1.86
% Na ₂ O + K ₂ O	0.83	n.d.	0.04	n.d.	n.d.	1.74	1.96	1.66
% SiO ₂	1.86	2.95	-	3.69	2.72	1.69	7.96	-
% loss on ignition, excluding CO ₂	0.40	1.03	0.66	2.70	3.20	4.21	5.43	1.27
Total	100.40	100.67	101.70	101.05	100.17	100.70	100.35	99.49
- % O for F	1.43	1.69	1.70	1.65	1.68	1.70	1.28	0.28
Total %	98.97	98.98	100.00	99.40	98.49	99.00	99.07	99.21
As 3 Mol Ca ₃ (PO ₄) ₂								
Mol CaF ₂	0.99	1.24	1.19	1.26	1.43	1.56	1.33	0.21
Mol CaCO ₃	-	0.47	0.84	0.91	1.68	2.06	2.40	1.71
Mol CaF ₂ +CaCO ₃	0.99	1.71	2.03	2.17	3.11	3.62	3.73	1.92

-) Extracted from papers.

n.d. = not determined.

T A B L E 2

EXTRACTION ANALYSIS OF ROCK PHOSPHATES.

Mol CaF_2 and Mol CaCO_3 corresponding to 3 Mol $\text{Ca}_3(\text{PO}_4)_2$

Type of phosphate	Orig. Subst.	E X T R A C T I O N				
		1	2	3	4	
<u>Togo</u>	% CaCO_3	4.00	3.65	3.58	4.01	3.83
	Mol CaF_2	1.24	1.32	1.30	1.30	1.32
	Mol CaCO_3	0.47	0.43	0.42	0.47	0.45
	M. $\text{CaF}_2 + \text{CaCO}_3$	1.71	1.75	1.72	1.77	1.77
<u>Pebb- le</u>	% CaCO_3	7.40	5.91	6.36	6.10	5.94
	Mol CaF_2	1.26	1.34	1.31	1.35	1.37
	Mol CaCO_3	0.91	0.72	0.77	0.74	0.72
	M. $\text{CaF}_2 + \text{CaCO}_3$	2.17	2.06	2.08	2.09	2.09
<u>Mor- occo</u>	% CaCO_3	12.45	8.25	8.52	8.30	8.16
	Mol CaF_2	1.43	1.49	1.49	1.49	1.47
	Mol CaCO_3	1.68	1.15	1.15	1.12	1.12
	M. $\text{CaF}_2 + \text{CaCO}_3$	3.11	2.64	2.64	2.61	2.59
<u>Const- stan- tine</u>	% CaCO_3	14.00	12.00	11.70	11.60	11.70
	Mol CaF_2	1.56	1.54	1.54	1.56	1.60
	Mol CaCO_3	2.06	1.77	1.72	1.71	1.72
	M. $\text{CaF}_2 + \text{CaCO}_3$	3.62	3.31	3.26	3.27	3.32
<u>Gafsa</u>	% CaCO_3	14.50	10.70	10.50	10.50	10.50
	Mol CaF_2	1.33	1.56	1.60	1.63	1.63
	Mol CaCO_3	2.40	1.77	1.74	1.73	1.73
	M. $\text{CaF}_2 + \text{CaCO}_3$	3.72	3.33	3.34	3.36	3.36
<u>Cura- çao</u>	% CaCO_3	14.70	11.90	10.60	9.50	8.50
	Mol CaF_2	0.21	0.20	0.20	0.20	0.19
	Mol CaCO_3	1.71	1.39	1.23	1.10	0.99
	M. $\text{CaF}_2 + \text{CaCO}_3$	1.92	1.59	1.43	1.30	1.18

T A B L E 5

ANALYSES OF SYNTHETIC PHOSPHATIC SUBSTANCES.

Preparation	Hydroxyl- Apatite	Fluor- Apatite	Fluorcarbonate-Apatite		
			No.4	No.15	No.31
% P ₂ O ₅	42.40	42.01	37.10	36.85	33.23
% CaO	55.78	54.76	54.75	52.60	56.70
% F	-	3.78	4.83	4.96	4.84
% CO ₂	-	-	4.34	7.73	6.84
% loss on ignition, excluding CO ₂	1.24	-	-	-	-
Total	99.42	100.55	101.02	102.14	101.61
- % O for F		1.59	2.03	2.09	2.04
Total %	99.42	98.96	98.99	100.05	99.57

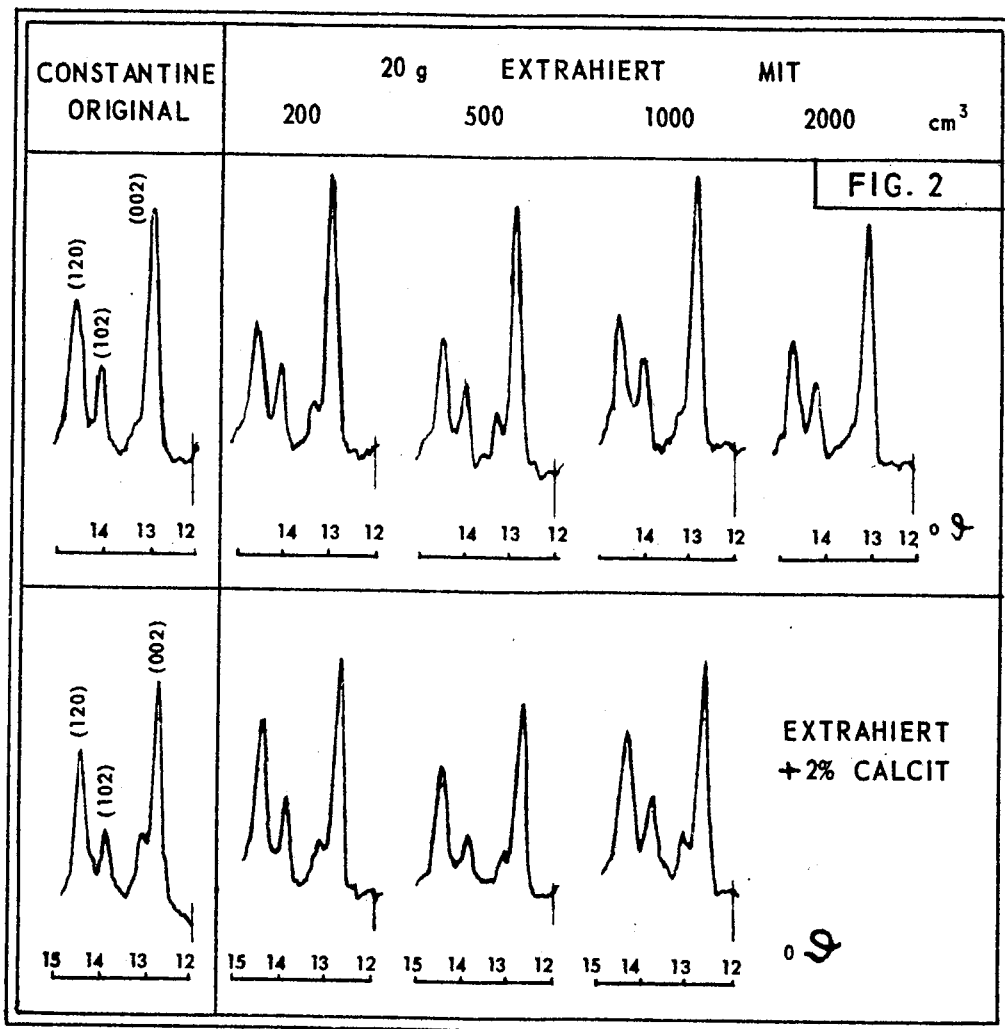
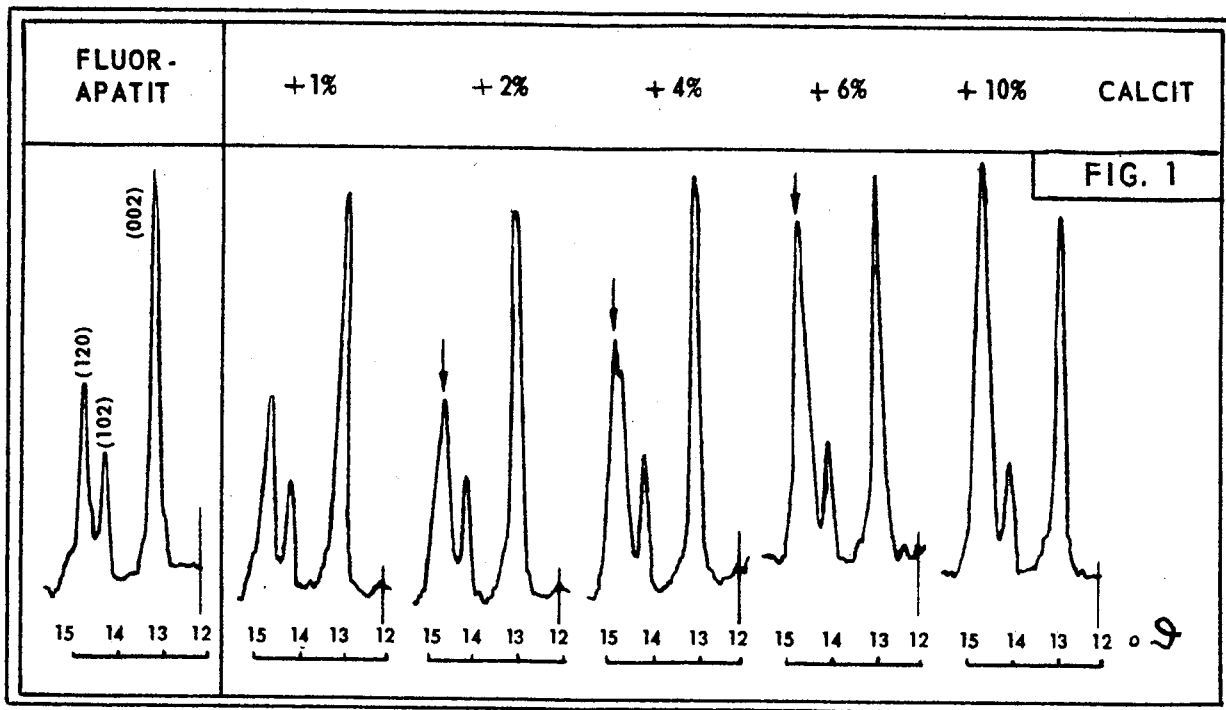
As 3 Mol Ca₃(PO₄)₂

Mol CaF ₂	-	1.01	1.46	1.51	1.63
Mol CaCO ₃	-	-	1.50	2.03	1.99
Mol CaF ₂ +CaCO ₃	-	1.01	2.96	3.54	3.62

T A B L E 6

EXTRACTION ANALYSIS OF SYNTHETIC PHOSPHATESMol CaF₂ and Mol CaCO₃ corresponding to 3 Mol Ca₃(PO₄)₂

Preparation.	Orig-Subst.	E x t r a c t i o n					
		1	2	3	4	5	
4	% CaCO ₃	9.88	10.82	9.88	8.57	9.88	
	Mol CaF ₂	1.46	1.48	1.50	1.49	1.48	
	Mol CaCO ₃	1.50	1.64	1.50	1.32	1.52	
	M. CaF ₂ + CaCO ₃	2.96	3.12	3.00	2.81	3.00	
15	% CaCO ₃	17.55	12.13	12.05	12.81	13.00	
	Mol CaF ₂	1.51	1.59	1.59	1.61	1.56	
	Mol CaCO ₃	2.03	1.40	1.39	1.48	1.50	
	M. CaF ₂ + CaCO ₃	3.54	2.99	2.98	3.09	3.06	
31	% CaCO ₃	15.53	13.88	13.30	12.83	12.50	12.93
	Mol CaF ₂	1.63	1.62	1.74	1.79	1.82	1.79
	Mol CaCO ₃	1.99	1.78	1.71	1.65	1.60	1.65
	M. CaF ₂ + CaCO ₃	3.62	3.40	3.45	3.44	3.42	3.44



(112)
(121)(211)

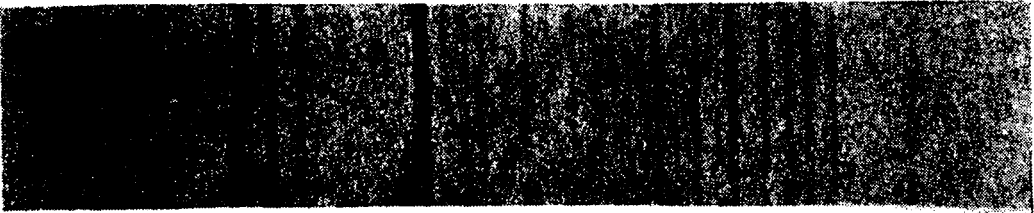
Al

Al

(231)(321)
(140)(410)
(402)
(004)

FIG.
3.

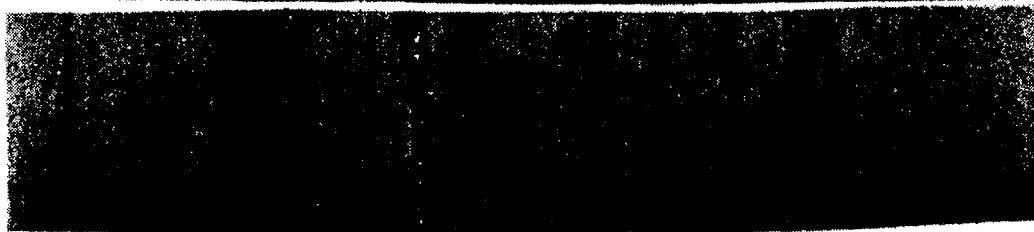
Kolaphosphat



*Fluorapatit,
synthetisch*



Gafosphosphat



*Fluorcarbonat-
apatit, synth.*

