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## THE PROBLEM OF THE CARBONATE-APATITES. III. CARBONATE-APATITE FROM MAGNET COVE, ARKANSAS

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### INTRODUCTION

The problem of the carbonate-apatites is an interesting one from the standpoint of the mineralogist, to be sure, but it is also of interest to the biological chemist because of its bearing upon the composition of teeth and bones. Indeed, biological chemists have contributed considerable experimental data and have displayed such a lively interest in this problem that their viewpoint cannot be neglected even in an investigation which is purely mineralogical. Since the appearance of the first paper by the writers (1) it has become evident that doubt still exists among certain investigators as to the homogeneity of the materials investigated.

J. Thewlis, G. E. Glock and M. M. Murray (2) do not raise for the first time the question of the existence of carbonate-apatites, nor is it probable that F. Machatschki (3) raises the question for the last time. However, it is becoming increasingly more difficult to question the existence of carbonate-apatites without completely ignoring considerable evidence which indicates the existence of these rather peculiar compounds. The fact that carbonate-apatites have been described by numerous well-known mineralogists is in itself some recommendation for their existence, but nevertheless, it is well to consider the matter without prejudice and examine the evidence.

This can be done without consideration of the structural hypothesis which the writers (1) have postulated for carbonate-apatites, because the success or failure which attends the establishment of an hypothesis to account for a physical entity cannot be considered as evidence in direct proof or disproof of the entity. Certain objections to the hypothesis, which was presented to account for the occurrence of carbon in the apatite lattice, have appeared, and these will be answered in terms of the data which were presented in opposition, as well as additional data.

Thewlis, Glock and Murray (2) have objected to the evidence presented to establish the existence of carbonate-apatites, and present certain data to justify their contention that carbonate-apatites are non-existent. This was accomplished chiefly in terms of a number of analytical results. However, these results were not only unconvincing in themselves but were used in conjunction with an error in deduction which was presented as a corollary to the hypothesis presented by the writers. I. D. Borneman-Starinkevitch (4) raises a question regarding the manner of displacement of calcium and the placement of carbon in the structure, as suggested by us (1 and 5), but accepts the substitution of carbon for phosphorus (6). N. V. Belov (7) presented a modified hypothesis for the introduction of carbon which would not require the assumption of  $\text{CO}_4$  groups, but one of us (8) has shown that Belov's modified hypothesis is not in accord with the experimental data which are available to test it, although these data are quite consistent with the original hypothesis. F. Machatschki's opinion (3) is stated very briefly, but it is essentially similar to that of Thewlis, Glock and Murray, in that he believes carbonate-apatites are to be accounted for in terms of contamination—crystalline  $\text{CaCO}_3$  being contained between the fine fibers of the apatite.

It has never been demonstrated in any of these studies that such relatively pure and homogeneous substances as the carbonate-apatite from Staffel, Nassau, will produce diffraction lines of calcite or aragonite, in spite of the fact that this material yields sufficient  $\text{CO}_2$  on analysis to require more than seven per cent of  $\text{CaCO}_3$ , if the  $\text{CO}_2$  were present as simple carbonate. This is likewise true of francolite from Devon (9), and of dahllite from Mouillac, France (6), except that the  $\text{CO}_2$  obtained in the latter case would require about ten per cent of  $\text{CaCO}_3$ . However, it has been stated (2) that it is not possible to detect less than ten per cent of  $\text{CaCO}_3$  when mechanically mixed with hydroxy-apatite, and this negative evidence has been emphasized in support of the contention that carbonate-apatites are non-existent.

#### X-RAY DATA

Thewlis, Glock and Murray were cognizant of the fact that H. H. Roseberry, A. B. Hastings and J. K. Morse (10) failed to find any evidence of the presence of  $\text{CaHPO}_4$  or  $\text{CaCO}_3$  in tooth substance, but they do not mention that M. A. Bredig, H. H. Franck and H. Földner (11) claim to have prepared synthetic carbonate hydroxy-apatites and recognized small but distinct differences on comparing the patterns produced by these with diffraction patterns of hydroxy-apatite and fluor-apatite. Thewlis, Glock and Murray indicate that P. Niggli and E. Branden-

berger (2) “. . . found that less than 10 per cent of  $\text{CaCO}_3$  cannot be detected when mixed with hydroxy-apatite. . . .” The original work states: “Bei der Mischung Knochenasche: Calcit = 10:1 sind selbständige Calcitinterferenzen eben noch erkennbar neben einzelnen charakteristischen Intensitätsverschiebungen bei den Linien des Hydroxylapatits.” And further on “Kleinere Calcitgehalte dürften sich auf diesem Wege *nicht mit* der wünschbaren *Sicherheit* nachweisen lassen.”

The writers prepared a number of powder diffraction diagrams using unfiltered Fe radiation and precision cameras of 57.3 mm. radius. Diffraction diagrams which were compared with one another were obtained in the same camera and considerable care was given to preparation of samples in order to have their dimensions uniform.

It is not difficult to distinguish two lines of calcite (including the most intense line,  $d = 3.029 \text{ \AA}$ ) when five per cent of calcite is mixed with francolite [staffelite]. Aragonite also can be detected when present in quantities as little as five per cent. These statements were also found to be true when an analyzed sample of fluor-apatite was employed.

Greater difficulty is experienced in detecting the presence of calcite in non-mineral hydroxy-apatites, not on account of coincidence of the calcite and phosphate lines, but due to failure of the phosphate to produce patterns with sufficient sharpness of resolution. Were it possible to obtain a synthetic hydroxy-apatite, capable of producing lines as distinct as those obtained with minerals, it would probably not be any more difficult to detect five per cent of calcite or aragonite in hydroxy-apatite than it is in francolite or fluor-apatite. The difficulties associated with the detection of calcite or aragonite when mixed with dentine or enamel are likewise associated with the broad and diffuse lines which these substances produce.

An attempt was made to obtain hydroxy-apatite with coarser granularity by heating the phosphate in 0.5 N solution of KOH in a gold-lined bomb at  $300^\circ \text{C}$ . for ten days. (Bomb capacity 50 cc., phosphate sample 1 g., 25 cc. KOH soln.) However, this treatment failed to increase noticeably the sharpness of the diffraction diagram, and the line  $d = 3.029 \text{ \AA}$  of calcite was just visible in a sample mixed with five per cent of calcite, and even then only detectable on comparison with a pattern prepared from the phosphate alone. The slight intensity differences which arise are not sufficiently pronounced to be diagnostic.

It has been the contention of those who believe that the  $\text{CaCO}_3$  is present as contamination that the individual crystals of  $\text{CaCO}_3$  are submicroscopic—presumably so small as to produce very diffuse diffraction lines which cannot be detected among the diffraction lines of the

phosphate. However, it seems hardly probable that as much as 10 per cent of  $\text{CaCO}_3$  could be present without being capable of detection by microscopic or  $x$ -ray methods or both. This is particularly true in view of the fact that  $\text{CaCO}_3$  usually occurs as one of two distinctly crystalline forms, calcite or aragonite. It is noteworthy that no direct proof of the existence of these submicroscopic or "colloidal" particles of  $\text{CaCO}_3$  in apatite has ever been presented, and the principal arguments used in support of the existence of these particles are based upon the analytical results which are discussed below.

#### CHEMICAL DATA

If submicroscopic particles of  $\text{CaCO}_3$  were to occur in apatites, they might be expected to occur in the complex textures of teeth and bones. Even here, however, the structural and chemical similarities (13) between these complex substances of organic origin and crystalline carbonate-apatites are such as to indicate that this supposition is highly improbable. R. Klement (14) has recently discussed the chemical relations and concludes that the writers' hypothesis accounts for the analytical results in a most satisfactory manner.

Thewlis, Glock and Murray reach certain conclusions regarding the correlation of Ca/P ratios with the  $\text{CO}_2$  content, and this represents a major portion of the data which were presented. Although it is frequently true, as they have indicated, that more C replaces P than replaces Ca and this would cause an increase in Ca/P, this is not necessarily always true as the ratio (C replacing P)/(C replacing Ca) is dependent upon the ratio  $(\text{F} + \text{OH} + \text{Cl})/\text{O}$ , because electrostatic neutrality must obtain. The theoretical value of the latter ratio is 1/12 for fluorapatite but decreases in oxy-apatite (6) and increases as the sum of the atomic amount of  $(\text{F} + \text{OH} + \text{Cl})$  becomes greater than two, as it does in francolite (3). A more detailed consideration of Ca/P ratios has recently been presented by one of us (8).

Thewlis, Glock and Murray determined P by a colorimetric method involving aminonaphtholsulfonic acid, which C. H. Fiske and Y. Subbarow (15) devised for determination of very small amounts of P, and this was done apparently without any attempt to demonstrate that the colorimetric method was suitable to determinations involving large amounts of P. They have attempted to use the theoretical value  $\text{Ca}/\text{P} = 2.15^*$  (ratio of weights) [ $\text{Ca}/\text{P} = 1.667$  (atomic ratio)] but the two determinations which show 0.00% of  $\text{CO}_2$  (p. 360, table 1) yield results

\* The Ca/P ratio might be expressed better as an atomic ratio rather than a weight ratio. This is particularly true when considering analyses which indicate several ions occupying one sort of position in the lattice.

which differ by 0.14. If compared with the theoretical value the difference is 0.10 for one of these determinations, indicating an error of about five per cent, for the purpose to which these results were put. There is no way to ascertain the maximum error in terms of their determinations, but the method used for P is shown by its authors to give errors frequently as high as ten per cent of the amount present, and in the presence of certain interfering substances errors as high as 40% were obtained for single determinations.

Unfortunately about half of the determinations tabulated by Thewlis, Glock and Murray are within the limit of error. The determinations outside of the limit of error are greater than the theoretical value and these show various amounts of CO<sub>2</sub>.

On the other hand, it is noteworthy that four recent analyses (1, 6, 9, 17) by four different analysts have indicated small, but unmistakable, amounts of carbon substituting for phosphorus in the apatite lattice, supporting the hypothesis presented by the writers. Three of these analyses (1, 6, 9) also indicate the entrance of carbon into the lattice in a manner such as to displace calcium. In addition to these analyses of minerals, the analytical determinations of W. D. Armstrong (13) also indicate these same sorts of ionic substitution in dental enamel and dentine.

#### OPTICAL DATA

The birefringence ( $\Delta$ ) of apatites containing appreciable amounts of CO<sub>2</sub> shows [when these are distinctly crystalline] a significant increase above that of fluor-apatite and there is likewise a decrease in the mean refractive index ( $n_\mu$ ). A few typical determinations are as follows:  $n_\mu = 1.631$ ,  $\Delta = 0.008$  (16);  $n_\mu = 1.624$ ,  $\Delta = 0.008$  (17);  $n_\mu = 1.618$ ,  $\Delta = 0.017$  (18);  $n_\mu = 1.626$ ,  $\Delta = 0.0075$  (19);  $n_\mu = 1.631$ ,  $\Delta = 0.0067$  (20);  $n_\mu = 1.618$ ,  $\Delta = 0.012 - .019$  (21).

Table 1 indicates the effect of various sorts of ionic substitution upon the optical properties of apatite. All of the common types of substitution have been considered, whether they substitute for Ca, P, F or O. H. Hausen (22) describes the optical properties of most of the members of the apatite group, but references are given to other special sources in several instances. Whenever the data were insufficient to permit conclusions based on actual measurements, theoretical predictions have been based upon the empirical ionic refractivities calculated by J. A. Wasastjerna (28). In all cases the measured results given in Table 1 are consistent with the theoretical expectations.

It is immediately noticeable that only four sorts of ionic substitution can be expected to decrease the mean refractive index, namely, C, F, Mg, and Na. All of these elements are encountered in bone and tooth sub-

stance but only the first of these occurs in appreciable amounts (greater than one per cent). None of these constituents which decrease the refractive index, nor any of the other constituents, would be expected to increase appreciably the birefringence except carbon. As W. L. Bragg (31) has demonstrated in connection with calcite, the strong birefringence is to be accounted for in terms of the polarization caused by

TABLE 1  
EFFECT OF CERTAIN IONIC SUBSTITUTIONS UPON THE  
OPTICAL CONSTANTS OF APATITE\*

Ion	$n_{\mu}$	$\Delta = \gamma - \alpha$	References
C	decrease	large increase †	Hausen (22); others (16-21)
F	decrease	very slight	Hausen (22); Kind (23)
Cl	increase	very slight	Hausen (22)
OH	increase	very slight	Burri, Jakob, Parker and Strunz (24)
Sr	increase	very slight	Smith and Prior (25)
Mn	increase	very slight ‡	Quensel (26); Landes (27)
Na	decrease	slight	Kind (23); Wasastjerna (28)
K	increase	—	Wasastjerna (28)
Mg	decrease	—	Idem.
rare earths	increase	slight	Kind (23); Boldyrev (29)
S, Si	§	slight	McConnell (30)

\* The values for fluor-apatite are:  $n_{\mu} \geq 1.631 \leq 1.634$ ;  $\Delta \geq 0.003 \leq 0.005$ .

† Occasionally a carbonate-apatite is reported as having birefringence as low as 0.005. The variability of the birefringence probably is to be explained in terms of variation in the distribution of carbon between the calcium and phosphorus positions.

‡ H. Hausen inadvertently gives the birefringence of mangan-apatite from New Ross, Nova Scotia as 0.007. Actually this value is a maximum difference among several measurements and the birefringence is described as low by T. L. Walker and A. L. Parsons (*Univ. Toronto Studies, Geol. Series*, 17, 46, 1924).

§ Although measurements of refractive indices of ellestadite have been reported, the natural material contained an appreciable amount of chlorine. The optical properties of synthetic ellestadite prepared by R. Klement (*Naturwissenschaften*, 27, 57, 1939) have not been reported as yet.

carbon atoms forming planar  $\text{CO}_3$  groups. There is no other plausible explanation, immediately apparent, except that  $\text{CO}_3$  groups account for a considerable portion of this increase in birefringence. The effect of  $\text{CO}_4$  groups cannot be considered in the light of the rather imperfect knowledge concerning this configuration, but these tetrahedra may be distinctly asymmetric and further contribute toward the superior birefringence of these substances.\*

\* The fact that carbonate-apatites are frequently biaxial suggests that they do not exactly conform to the symmetry requirements of  $C_{63m}$ . The discrepancy in this respect, however, is so small as to escape detection by any of the usual x-ray methods.

Some of the measurements of the optical properties of carbonate-apatites have been made on finely fibrous materials which appeared slightly cloudy on microscopic examination, and it has not been possible to demonstrate in all instances that  $\text{CaCO}_3$  or carbonic acid was not present as an interstitial impurity, although none was capable of detection. Nor has a description been given of a non-fibrous carbonate-apatite which is completely homogeneous, at the same time comparing it with fluor-apatite. The carbonate-apatites that occur at Magnet Cove, Arkansas, are of special interest in this respect.

#### DESCRIPTION OF SPECIMENS FROM MAGNET COVE

One sort of apatite at Magnet Cove occurs in association with nephe-line, a light-colored mica and schorlomite. This occurrence was briefly mentioned by J. F. Williams (32) but no mention was made of the carbonate-apatite which sometimes occurs with the fluor-apatite. This material will be referred to as type *A* to distinguish it from type *B* which is associated with titanium oxide, and more or less remotely associated with coarsely crystalline calcite and feldspar. The paragenesis of type *B* cannot be clearly ascertained because the specimens came from ground which had been disturbed by mining operations.

Both types are characterized by acicular crystals which are probably not primary, but pneumatolytic or hydrothermal in origin. Carbonate-apatite is found in association with both types of fluor-apatite. The carbonate-apatite occurs as cavity fillings and replacements. It probably formed through attack of the fluor-apatite by hydrothermal solutions rich in carbonic acid, with subsequent precipitation of carbonate-apatite in the same crystallographic orientation upon the residual crystals of fluor-apatite.

#### *Type A*

When the specimens are proportionally richer in apatite, the crystals frequently show a preferred orientation and a material with porcelainous luster occurs interstitially, sometimes replacing the fluor-apatite and sometimes as overgrowths partially filling cavities (Fig. 1). The appearance of this porcelainous substance differs distinctly from that of the fluor-apatite which exhibits the usual vitreous luster. Qualitative microchemical tests indicate that the vitreous material is essentially fluor-apatite, whereas the porcelainous substance is a carbonate-apatite, which possibly contains fluorine also. Because of the difficulties which attend the determination of alkalis in these substances, potash and soda were not determined, but this is of little significance and has no bearing on the conclusion that one of these substances contains sufficient  $\text{CO}_2$  to be considered a carbonate-apatite while the other does not.

On microscopic examination the carbonate-apatite exhibits a superior birefringence. In basal sections (Fig. 1) the carbonate-apatite occurs as sectors about a core of fluor-apatite. These sectors are biaxial with small optic angle. They exhibit zonal lamination and are somewhat cloudy, but there is no evidence of the presence of calcite or aragonite. Because the material of type *A* is cloudy and not completely homogeneous, it probably cannot be concluded with certainty that calcite and aragonite

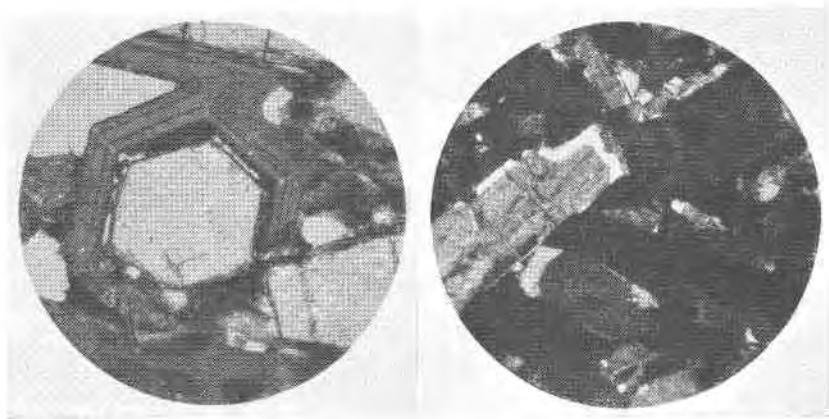


FIG. 1. Type A. Basal section of fluor-apatite with laminated incrustation of carbonate-apatite. The sectors of carbonate-apatite are biaxial with small optic angle, and the acute bisectrix is essentially parallel to *c* of the fluor-apatite. One nicol. Magnification 40 $\times$ .

FIG. 2. Type B. Section showing replacement of fluor-apatite by carbonate-apatite. The former is dark to medium gray in the photograph and the latter is light gray to white. Nicols in crossed position. Magnification 24 $\times$ .

are completely absent, although  $\text{CaCO}_3$  could not be detected in any of these specimens.

#### *Type B*

Although the material of type *B* does not contain the substance with porcelaneous luster, it liberates  $\text{CO}_2$  when small fragments are placed in warm dilute HCl. It was immediately apparent on microscopic examination that two sorts of apatite were present here also, because of the superior birefringence of certain portions of the crystals. Indeed, were it not for the differences in refractive indices of the two portions of the crystals (immediately apparent when employing both nicol prisms) one might suppose that he were dealing with homogeneous crystals of a single substance. It is significant that these crystals are not cloudy, but completely transparent, and the portions with superior birefringence are essentially homogeneous. Some small inclusions occur in the portions



with inferior birefringence but these are usually completely absent in the more highly birefringent material.

In order to ascertain that the more highly birefringent portions were surely carbonate-apatite, fragments of crushed material were examined under the microscope during their treatment with acid. The fragments were first immersed in water and covered. After selection of a prismatic cleavage fragment of uniform thickness which exhibited considerable difference in retardation in different portions, the water was displaced by HCl. Always the portion having the greater birefringence dissolved more rapidly, and frequently the bubble of CO<sub>2</sub> could be observed to form near the more highly birefringent portion of the fragment.

A thin section was likewise treated with acid after cutting away a portion of the cover glass and removing the Canada balsam with xylol. The more highly birefringent portions were again observed to liberate bubbles of CO<sub>2</sub>. To be sure, bubbles formed near portions of the section which did not exhibit a maximum retardation, but the orientation of the crystals which gave rise to the bubbles was not ascertained except in those cases where the retardation was greatest. It cannot be said with certainty, therefore, that the material with inferior birefringence does not contain CO<sub>2</sub>, but there is sufficient reason to believe that CO<sub>2</sub> is not nearly so abundant in this material.

Because of the rather intimate association of the two varieties of apatite, their identical appearance, and the small dimensions of the crystals, it was not possible to make a microchemical test on one of these substances with certainty that the other was absent. However, the tests already mentioned, together with the fact that carbonate-apatites nearly always exhibit a superior birefringence and a lower mean refractive index, are quite sufficient to demonstrate that one of these substances is a carbonate-apatite while the other is more nearly comparable to ordinary fluor-apatite.

The refractive indices were determined by the immersion method, employing a yellow filter (Wratten No. 90), with the following results:

Fluor-apatite ( <i>B</i> )	Carbonate-apatite ( <i>B</i> )
$\omega = 1.633$	$\gamma = \omega = 1.632$
$\epsilon = 1.629$	$\alpha = \epsilon = 1.625$
(both $\pm 0.001$ )	(both $\pm 0.002$ )

The fluor-apatite is uniaxial and negative. This may or may not be true also for the carbonate-apatite, because it is not possible to state that a basal section of carbonate-apatite was ever positively identified as such, because of the difficulties already mentioned.

In sections cut parallel to *c*, however, the difference in retardation between the carbonate-apatite and the fluor-apatite is about 200m $\mu$ .

This is shown in Fig. 2, which was photographed by utilizing both nicol prisms and a yellow filter. The large crystal of fluor-apatite (gray in the photograph) produced a gray interference color, while the carbonate-apatite portion (nearly white) produced a yellow interference color, the orientation being the same for both substances.

#### SUMMARY AND CONCLUSIONS

Additional evidence for the existence of carbonate-apatites is presented as a result of the microscopic examination of specimens from Magnet Cove, Arkansas. The carbonate-apatite (type *B*) is non-fibrous, completely colorless, and free from inclusions, but liberates  $\text{CO}_2$  when treated with  $\text{HCl}$ . The carbonate-apatite occurs as a replacement of fluor-apatite and is probably hydrothermal in origin.

Carbonate-apatites have optical properties distinct from those of fluor-apatite and these differences cannot be accounted for in terms of contamination by  $\text{CaCO}_3$ . The birefringence of carbonate-apatites is higher than that of fluor-apatites and the mean refractive index is lower. Carbonate-apatites may be biaxial with small optic angle.

The conclusion that carbonate-apatites are to be explained on the basis of contamination by  $\text{CaCO}_3$  is unwarranted in view of the complete absence of experimental evidence to support this contention. The occurrence of submicroscopic particles of  $\text{CaCO}_3$  in apatite has not been demonstrated, even in those cases where the carbonate-apatite appears cloudy on microscopic examination and, presumably, cannot be demonstrated when the material appears perfectly clear and transparent.

It is reasonable to consider the mineral substances of teeth and bones as hydroxy-apatite, but this view in no way interferes with the evidence indicating that they also contain carbonate-apatite. The substance of teeth and bones should properly be called a carbonate hydroxy-apatite or dahllite.

The criteria that can be used for the recognition of mineral carbonate-apatites cannot be applied directly to the substance of teeth and bones, e.g., microscopic observations are hindered by the presence of organic matter (with high birefringence). Moreover these substances are not distinctly crystalline, but cryptocrystalline. If biochemists are unwilling to accept the implications to be drawn from the mineral kingdom regarding the carbonate hydroxy-apatite composition of teeth and bones, they necessarily restrict the scope of their hypothetical considerations.

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