QUANTITATIVE DETERMINATION OF CALCITE ASSOCIATED WITH CARBONATE-BEARING APATITES*

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Abstract

The CO_2 combined as calcite in carbonate-bearing apatites has been distinguished from that combined as carbonate-apatite, or present in some form other than calcite, by use of x-ray powder patterns, differential thermal analyses, and differential solubility tests. These methods were applied to several pure apatite minerals, to one fossil bone, and to a group of phosphorites from the Phosphoria formation of Permian age from Trail Canyon and the Conda mine, Idaho, and the Laketown district, Utah. With the exceptions of pure fluorapatite, pure carbonate-fluorapatite, the fossil bone, and one phosphorite from Trail Canyon, these substances contain varying amounts of calcite, but in all the samples an appreciable part of the carbonate content is not present as calcite. The results of solubility tests, in which the particle size of sample and the length of solution time were varied, imply that the carbonate content is not due to shielded calcite entrapped along an internal network of surfaces.

Introduction

The existence of carbonate-apatite as a distinct mineral constituent of bone, teeth, and phosphorite is not universally accepted. Hendricks and Hill (1950, pp. 731–737) attribute the carbonate content of bone and of all carbonate-bearing apatites to carbonate entrapped in hydroxylapatite or in hydrated tricalcium phosphate. Other workers (Dallemagne, Brasseur, and Mélon, 1949, pp. 138–145; Dallemagne and Mélon, 1945, pp. 597–599) claim that bone is a mixture of tricalcium phosphate and calcium carbonate, but they do not question the existence of carbonate-apatite as a distinct mineral phase in dentine. McConnell and Gruner (1940, pp. 157–167) recognize carbonate-apatite as a single homogeneous mineral. The controversy has been summarized by Geiger (1950, pp. 161–181).

Staining methods (see appendix) have indicated that an appreciable part of the carbonate content of natural phosphorites is present as calcite. In order to determine quantitatively the amounts of carbonate present as calcite and as carbonate not combined as calcite, carbonate-bearing phosphorites were examined by three independent methods: x-ray analysis, differential thermal analysis, and differential solubility tests.

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X-Ray Analysis

Optically homogeneous apatites containing as much as 5.8 per cent carbon dioxide have been reported. Whether the carbon dioxide is present as calcite or as carbonate in some other form, or is integrated in the apatite structure, these substances would be expected to give x-ray patterns distinguishable from those of carbonate-free apatites. In 1933 Bredig, Franck, and Füldner (1933, pp. 959–969) reported having recognized distinct differences in the x-ray diffraction pattern of a carbonate-hydroxylapatite as compared with those of fluorapatite and hydroxylapatite. The controversy that followed is reflected in the work of Thewlis, Glock, and Murray (1939, pp. 358–363), and McConnell and Gruner (1940, pp. 157–167).

Small but measurable differences in the x-ray patterns of carbonate-fluorapatite, hydroxylapatite, and fluorapatite have been detected in the course of this investigation, and a complete account of these differences will be published later. The distinction is based on variations in spacings between the (231) and (004) lines in x-ray powder films exposed on a 57.3-mm. radius camera using nickel-filtered copper radiation.

The variations of x-ray data listed in Table 1 were obtained from two hydroxylapatites (from Holly Springs, Ga., and a synthetic product prepared by W. L. Hill of the U. S. Department of Agriculture), from two fluorapatites (from Cerro Mercado, Durango, Mexico, and Ontario, Canada), and from two carbonate-fluorapatites ("staffelite" from Staffel, Germany, and "francolite" from Cornwall, England).

TABLE 1. Comparison of X-ray Data

	Plane indices	2θ (mm.)	d-spacings (Å)	Δ[1] (mm.)
Hydroxylapatite	231	50.6	1.804	2.7
	004	53.3	1.719	
Fluorapatite	231	50.8	1.797	2.5
	004	53.3	1.719	
Carbonate-fluorapatite	231	50.9	1.794	2.3
	004	53.2	1.722	

[1] Difference between 2θ-values (in mm.) for lines (231) and (004).

The presence of calcite in artificial calcite-apatite mixtures was readily discernible. Powder films were taken of mixtures of a pure fluorapatite from Durango and chemically pure calcium carbonate, with the latter present in proportions of 2, 3, 4, 5, 7, and 10 per cent by weight. The *x*-ray pattern of the mixture containing 2 per cent calcium carbonate was indistinguishable from that of pure fluorapatite. Three characteristic calcite lines (*d*-values of 3.038 Å, 2.089 Å, and 1.914 Å) were identified in each of the remaining mixtures. The presence of calcite in amounts of 3 per cent and above is thus detectable in artificial mixtures by use of the *x*-ray method described.

DIFFERENTIAL THERMAL ANALYSIS

It is unlikely that carbonate would be held by identical bonding forces in both calcite and carbonate-apatite. Consequently the heat and temperature of decomposition of calcite should differ from those of carbonate-apatite. These properties are conveniently measured by means of a differential thermal analysis apparatus. The theoretical and operational details of this apparatus have been described by Hendricks, Goldich, and Nelson (1946, pp. 64–76).

The following investigations were performed on a portable field unit[1] that was rewired for use with platinum-platinum (90%), rhodium (10%) thermocouples.

Reference curves were prepared from the thermal data for chemically pure calcium carbonate, calcite, fluorapatite, carbonate-fluorapatite, and artificial mixtures of a pure natural fluorapatite and 2, 5, 7, and 10 per cent chemically pure calcium carbonate. The sharp and abrupt endothermic peaks resulting from the thermal decomposition of both natural calcite and chemically pure calcium carbonate are comparable to those reported in the literature (Cuthbert and Rowland, 1947, p. 113; Faust, 1950, p. 217). Fluorapatite alone gives a smooth curve when heated to 950° C. The carbonate-fluorapatite, an optically homogeneous mineral from Staffel, Germany, containing 3.1 per cent CO_2, which is equivalent to 7 per cent $CaCO_3$, did not show the distinct endothermic peak typical of calcite. Instead it gave a smooth curve, which, in relation to the fluorapatite curve, suggests a very gentle endothermic trend over the entire temperature range. These observations are in agreement with the heat-loss data reported by Geiger (1950, pp. 168, 178).

Each of the artificial mixtures of calcium carbonate and fluorapatite gave a calcite peak superimposed on the smooth fluorapatite curve. The relative heights and breadths of peaks for the different mixtures are presented in Table 2. The relative areas included under the calcite peaks,

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[1] Designed by R. A. Nelson, of the U. S. Geological Survey, and manufactured by the Eberbach & Son Co., Ann Arbor, Mich.

which were measured with a polar planimeter, are roughly proportional to the amounts of calcium carbonate present. The corresponding variations of peak temperatures with amount of calcium carbonate present are due primarily to differences in the partial pressures of the CO_2 liberated during the early stages of thermal decomposition (Rowland and Lewis, 1951, pp. 86–87).

In order to check the validity of the results, G. T. Faust was kind enough to run pure fluorapatite, carbonate-fluorapatite, and the mixture of fluorapatite and 2 per cent calcium carbonate on a more sensitive differential thermal unit (Faust, 1948, pp. 337–345). The curves obtained with our portable field unit compared favorably with those from the more precise instrument, and we ascertained that the portable unit could be depended upon to detect a minimum of 1.6 per cent calcite in natural phosphates.

TABLE 2. DIFFERENTIAL THERMAL DATA FOR ARTIFICIAL MIXTURES
OF CALCIUM CARBONATE AND FLUORAPATITE

Material	Per cent CO_2 present as calcite	Calcite peak data			
		Peak temperature (°C.)	Relative peak height	Peak breadth[1] (°C.)	Area under peak (relative)
Fluorapatite[2]	0.0	No calcite peak			
Fluorapatite[2]+2% CaCO₃	0.88	780°	1.3	55°	18
Fluorapatite[2]+5% CaCO₃	2.20	810°	2.4	50°	29
Fluorapatite[2]+7% CaCO₃	3.08	830°	3.9	55°	58
Fluorapatite[2]+10% CaCO₃	4.40	835°	4.7	110°	79
Chemically pure calcium carbonate	44.00	880°	16.6	110°	417

[1] Measured at the base of the peak in degrees centigrade.

[2] Fluorapatite from Ontario, Canada.

DIFFERENTIAL SOLUBILITY TESTS

Differential solubility methods have been applied successfully in the past to the separation of the components of a mixture. The carbonate-apatite problem is principally one of distinguishing a homogeneous from a heterogeneous mineral composition. The applicability of differential solubility tests to this problem depends on the existence of a solvent in which carbonate-apatite is relatively insoluble as compared with calcite.

A solvent that fulfills this requirement is a half-molar aqueous solution of triammonium citrate. The solubility of calcite in this solvent has been established by Rindell (1910, pp. 452–458).

The data in Table 3 indicate that calcium carbonate is approximately 50 times as soluble as either fluorapatite or carbonate-fluorapatite in this reagent.

TABLE 3. SOLUBILITIES IN 0.5 M TRIAMMONIUM CITRATE SOLUTION

Material	Solubility in grams/100 ml. solvent
Calcium carbonate, cp	0.660 g. ± 0.060
Fluorapatite, Durango, Mexico	0.014 g. ± 0.000
Carbonate-fluorapatite, Staffel, Germany	0.012 g. ± 0.003

The triammonium citrate solution was prepared by titration of chemically pure diammonium citrate with ammonium hydroxide to pH of 8.1 ± 0.1. The solubility values in Table 3 were determined by the addition of 100 ml. of solvent to 1 g. of powdered sample (ground to pass 200 mesh) in a glass-stoppered Erlenmeyer flask. The mixture was permitted to stand for 24 hours at room temperature, with intermittent shaking, after which it was filtered and the filtrate ignited to constant weight. The solubility of pure calcium carbonate was computed from the weight of the ignited product (calcium oxide).

Geiger's heat-loss data (1950, p. 168) indicate that "staffelite" loses at least 65 per cent of its CO_2 content by ignition to 900° C. The carbonate-fluorapatite solubility value given in Table 3, however, required no correction for CO_2 lost during ignition as the maximum possible loss is less than 0.0004 g., which is beyond the limiting precision of the measurements.

On the basis of solubility values obtained by 48- and 72-hour treatments, which were identical with the solubility values obtained in 24 hours (see Table 6), it was concluded that any discrepancies due to incomplete solution were not large enough to invalidate the conclusions reached by these measurements. In Rindell's original work (1910, pp. 452–458), it was assumed that equilibrium is attained in 24 hours.

The relatively high limits of error reported in Table 3 were undoubtedly due to the lack of precisely controlled conditions. The precision of these measurements can be improved by use of a controlled-temperature bath, of a constant stirring mechanism, and by very precise standardization of the solvent. The degree of precision attained, however, was sufficient for the immediate purposes of these investigations.

The calcite content of each phosphorite was determined by treating each 1 g. sample with 100 ml. of solvent in the manner described for the solubility measurements. After the mixture was filtered the insoluble residue was washed with distilled water. The dried insoluble residue and the original sample were analyzed gravimetrically for carbonate content by absorption of carbon dioxide in ascarite (Kolthoff and Sandell, 1948, pp. 385–389) after liberation of the carbon dioxide by dilute hydrochloric acid. The difference between the carbon dioxide content of the original sample and that of the leached residue was taken as a measure of carbon dioxide present as calcite. The results of the absorption method are reproducible to 1 mg.; the carbon dioxide content for 1 g. of sample is therefore reliable to 0.1 per cent

In order to establish the effectiveness of the solvent on calcite in the presence of apatite, artificial mixtures of the Durango fluorapatite containing 2, 5, 7, and 10 per cent of chemically pure calcium carbonate were treated with the solvent. In each of these check determinations the insoluble residues were found to be entirely free of calcite within the limits of error.

Analyses of Natural Phosphorites

These methods, whose reliabilities have been established for artificial mixtures and pure end members, were then applied to natural phosphorites.

Samples were selected from the phosphatic shale member of the Phosphoria formation (Idaho and Utah) on the basis of their carbonate content, as shown in Table 4.

In addition, a fossil rib bone (genus *Felsinotherium*) of probable early Pliocene age (sample 74-*M*-4) from the Boyette mine, Hillsborough County, Fla., was included in these analyses.

Table 4. Carbon Dioxide Content of Phosphorites

With visible calcite		Without visible calcite	
Sample no.	CO_2 content (per cent)	Sample no.	CO_2 content (per cent)
150 (Conda mine, Idaho)	4.7	311C (Trail Canyon, Idaho)	1.9
163 (Conda mine, Idaho)	4.5	309 (Trail Canyon, Idaho)	1.6
161 (Conda mine, Idaho)	3.1	317 (Trail Canyon, Idaho)	1.3
164B (Conda mine, Idaho)	2.5	300 (Trail Canyon, Idaho)	1.2
1007-1 (Laketown, Utah)	1.8	315B (Trail Canyon, Idaho)	1.1
164A (Conda mine, Idaho)	1.4		
1007-7 (Laketown, Utah)	1.4		

A compilation of the results obtained by the three methods appears in Table 5. The samples are arranged in the order of increasing calcite content as determined by the solubility method (column 3).

The differential thermal data in columns 4 and 5 show an orderly progression of increasing temperatures and endothermic peak heights with increasing calcite content for the samples containing more than 0.7 per cent CO_2 combined as calcite.

In addition to calcite, the phosphorites contain small but varying amounts of thermally active substances, chiefly clays, organic matter, and iron oxides. Of these materials, certain clays may undergo thermal changes in the temperature region of the calcite decomposition, thereby interfering with the endothermic peak due to calcite alone. For most of the materials examined, this interference was not great enough to cause a serious discrepancy in the calcite peak measurements. Of the group of samples in Table 5, sample 163 has the lowest phosphate content; accordingly the relative proportions of foreign materials is greater; and the contaminating substances have interfered by causing a broadening of the calcite peak at its base, which has resulted in an abnormally large area under the peak. Where the above-mentioned thermally active sub-

TABLE 5. COMPARISON OF RESULTS OBTAINED BY SOLUBILITY, DIFFERENTIAL THERMAL, AND *X*-RAY METHODS ON NATURAL PHOSPHATE MATERIALS

| Sample | Total CO_2 content (per cent) in un-leached sample | Per cent CO_2 present as calcite[1] | Differential thermal analysis Calcite peak data | | | | *X*-ray data | |
			Peak temperature (° C.)	Relative peak height	Peak breadth[2] (° C.)	Area under peak (relative)	Calcite lines	Δ[3] (mm.)
Carbonate-fluorapatite[4]	3.1	0.0	No calcite peak				Absent	2.3
315*B* (Trial Canyon, Idaho)	1.1	0.0	No calcite peak				Absent	2.3
74-*M*-4 (Boyette mine, Fla.)	2.9	0.0	No calcite peak				Absent	2.3
311*C* (Trial Canyon, Idaho)	1.9	0.1	No calcite peak				Absent	2.5
300 (Trial Canyon, Idaho)	1.2	0.2	No calcite peak				Absent	2.4
318 (Trial Canyon, Idaho)	1.3	0.2	No calcite peak				Absent	2.3
309 (Trial Canyon, Idaho)	1.6	0.2	No calcite peak				Absent	2.3
317 (Trail Canyon, Idaho)	1.3	0.2	No calcite peak				Absent	2.4
164*A* (Conda mine, Idaho)	1.4	0.4	No calcite peak				Absent	2.3
1007-7 (Laketown, Utah)	1.4	0.4	No calcite peak				Absent	2.3
1007-1 (Laketown, Utah)	1.8	0.6	No calcite peak				Absent	2.3
162 (Conda mine, Idaho)	2.3	0.7	775°	0.5	22°	5	Absent	2.3
164*B* (Conda mine, Idaho)	2.5	1.0	785°	1.2	30°	18	Absent	2.3
161 (Conda mine, Idaho)	3.1	1.4	790°	1.9	60°	34	Absent	2.3
163 (Conda mine, Idaho)	4.5	3.1	800°	4.3	95°	99	Present	2.2
150 (Conda mine, Idaho)	4.7	4.0	835°	6.7	60°	70	Present	2.3

[1] Results of triammonium citrate solubility tests.
[2] Measured at the base of the peak in degrees centigrade.
[3] Difference between 2θ-values (in mm.) for lines (231) and (004).
[4] From Staffel, Germany.

stances are comparatively negligible, as in sample 150, where they are essentially absent, the resulting thermal curves are almost identical with those obtained from the artificial calcite-apatite mixtures.

The presence or absence of the three calcite lines in x-ray powder films (Table 5, column 8) depends to a certain extent on the quality of the pattern. The artificial mixture of fluorapatite and 3 per cent calcium carbonate gave a sharp pattern in which the calcite lines could be detected. Sample 161, a phosphorite that contains 3.2 ± 0.2 per cent calcite as determined by the solubility tests, gave a less distinct pattern in which the calcite lines were not visible. The x-ray pattern obtained from sample 163, a phosphorite containing 7.0 ± 0.2 per cent calcite, showed the same poor definition and high background intensity as that obtained from sample 161, but in this case the calcite lines were detectable.

The last column lists the differences between the 2θ-values for lines (231) and (004) referred to in Table 1.

Samples from the Conda mine in southeast Idaho are unweathered, black, and dense, whereas those from the nearby outcrop at Trail Canyon are weathered, brown, and less consolidated. Both groups of samples are from equivalent parts of the Phosphoria formation. This correlation is based on the distinctive character of a single bed of brecciated nodules of phosphatized palaeoniscoid fish scales and small coprolitic masses (?) identified by D. H. Dunkle, of the U. S. National Museum. At the Conda mine (sample 150) this bed contains 4.1 per cent of free calcite, whereas at Trail Canyon (sample 300) the calcite content is negligible. The characteristically low calcite content of the Trail Canyon samples as compared to that from the Conda mine is probably due to natural leaching processes. The other samples from Trail Canyon and the Conda mine are "pelletal phosphorites" typical of the phosphatic shale member of the Phosphoria formation in southeast Idaho.

All samples contain at least 75 per cent apatite. The average organic content of the Conda mine samples is higher than that of the Trail Canyon samples by about 3 per cent. The samples from the Laketown district, Utah, are sieve fractions of one bed that contains visible calcite, detrital material, and secondary clays but is devoid of organic matter.

SPECIAL CONSIDERATIONS

Hendricks and Hill (1950, p. 737) have concluded from investigations of the mineral constituents of bone that "carbonate is present on entrapped surfaces and not as constituent within the lattice of the mineral francolite, the typical 'carbonate apatite' . . . ." If the carbonate present in these samples is present as calcite entrapped at crystallite boundaries it is possible that some part of the included calcite would not be accessible

to the solvent. The following experiments were designed to test the availability of calcite occluded along a continuous, as well as along a discontinuous, network of surfaces.

Two samples, 150 (Conda) and 162 (Conda), containing 4.7 per cent and 2.3 per cent CO_2, respectively, were treated with the solvent, a half-molar solution of triammonium citrate, for 24, 48, and 72 hours. The carbon dioxide content of the leached residues was essentially constant, as shown in Table 6.

TABLE 6. CARBON DIOXIDE CONTENT OF RESIDUES OF SAMPLES 150 AND 162 AFTER LEACHING FOR VARIOUS LENGTHS OF TIME

Sample	Carbon dioxide content (per cent) after leaching for:		
	24 hours	48 hours	72 hours
150 (Conda mine)	0.9 ± 0.0	0.9 ± 0.0	0.9 ± 0.0
162 (Conda mine)	1.6 ± 0.1	1.6 ± 0.0	1.5 ± 0.1

These results indicate that equilibrium between the solid phases, consisting mainly of apatite, and the liquid phase, containing dissolved calcium carbonate, dissolved apatite, and solvent is established after 24 hours. Preliminary solubility measurements (Table 3) show that 100 ml. of solvent, saturated with apatite, can dissolve more than 0.6 g. of calcium carbonate. One-gram samples of 150 and 162 contain sufficient carbon dioxide to account for 0.11 g. and 0.05 g. of calcium carbonate, respectively. The liquid phase in a mixture of 1 g. of either of these materials and 100 ml. of solvent, in equilibrium with the solid phase, is unsaturated with respect to $CaCO_3$. Under these conditions no solid calcium carbonate should exist in contact with the liquid.

If the carbonate is restricted to a continuous network of calcite along entrapped surfaces, the calcite would be accessible to the solvent only at the points where the network was exposed at the surface of the particle. Under these conditions the amount of calcite dissolved by the solvent should vary with the length of time. The absence of such variation (Table 6) is evidence against a continuous network of occluded calcite.

Additional evidence comes from a study of the relation of the solubility of carbonate-apatite to particle size. The carbonate-fluorapatite, an optically homogeneous mineral from Staffel, Germany, contains 3.1 per cent CO_2, which is equivalent to about 7 per cent calcium carbonate. The solubility measurements (Table 5) indicate that no calcium carbonate is present. The carbonate content is therefore present as a con-

stituent of the apatite structure, or as some other form of carbonate that is not combined as calcite. Three sieve fractions ($+60 -84$, $+165 -200$, and $+325 -400$) of this mineral were treated with the solvent for 24 hours. The relative surface areas per given weight of material have been computed for each sieve size. These computations, which take into account the columnar shape of the fragments (length of columns are approximately twice their width), give the values listed in Table 7.

TABLE 7. RELATIVE SURFACE AREAS FOR DIFFERENT PARTICLE
SIZES OF CARBONATE-FLUORAPATITE

Sieve size	Relative surface area
$+ 60 - 84$	1.00
$+165 -200$	2.86
$+325 -400$	6.44

In each size fraction no difference in the CO_2 content of the leached residue as compared with that of the unleached material was detectable within the limits of measurement.

The volume of a single particle of the smallest size group ($+325 -400$ mesh) is 1.3×10^{-7} cm.^{3}, and it represents more than a sixfold increase in surface area per unit weight of material over that of the coarsest group ($+60 -84$ mesh). Regardless of the dimensions of "entrapped" calcite, if the 3.1 per cent CO_2 content of this carbonate-fluorapatite is present as calcite, the calcite must occupy 9.2 per cent of the total volume. To the extent of the increase in surface area represented by the difference between the coarsest and finest particle sizes considered here, the experimental observations constitute an argument against occluded calcite along a discontinuous network. Furthermore, if any carbonate is present as occluded calcite, its distribution in this mineral must be random. The solubility relations of this mineral to half-molar triammonium citrate solution are generally those expected from a single, very slightly soluble, homogeneous compound.

CONCLUSIONS

The presence of calcite in carbonate-bearing phosphorites has been determined by use of x-ray methods, differential thermal analyses, and solubility tests. The minimal detectable amounts of calcite, as shown by the results in Table 5, are 7.0 per cent, 1.6 per cent, and 0.1 per cent, respectively, for the above methods.

Application of these procedures leads to the conclusion that in some samples (carbonate-fluorapatite from Staffel, Germany; 74-M-4; and

315B, Trail Canyon) no part of the CO_2 content, which ranges from 3.1 to 1.1 per cent, is present as calcite. The other phosphorites examined in this survey contain variable amounts of calcite, but in all of them an appreciable part of the carbonate is not present in the form of calcite.

The results of solubility tests, in which the particle size of sample and the length of solution time were varied, imply that the carbonate content is not due to shielded calcite entrapped along continuous or discontinuous surfaces.

APPENDIX

EXPOSURE OF CALCITE OBSCURED BY ORGANIC MATTER IN PHOSPHATE ROCK

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Small amounts of calcite in some samples of phosphate rock from southeastern Idaho are often concealed in thin sections or powder mounts by the high content of organic matter, and no clue to the presence of the calcite is offered by chemical analysis for total CO_2 because the major mineral constituent is a carbonate-bearing apatite. By the slight modification and combination of two well-known petrographic techniques, the presence and distribution of calcite and the reason for its obscurity were made clear.

Rectangular blocks $1\frac{1}{2}$ inches by 1 inch by 1 inch of black phosphatic rock were cut and placed in small porcelain crucibles so that the blocks were resting only on corners and edges. They were then placed in a Tempco Electric Furnace and heated through three temperature stages as follows: 1 hour with the temperature control set at "low" (from room temperature to 200° C.), $1\frac{1}{2}$ hours at "medium" (from 200° C. to 425° C.), and $1\frac{1}{2}$ hours at "high" (from 425° C. to 775° C.). At the end of this time the blocks turned white.

Slow and gradual heating prevented the samples from decrepitating because of sudden loss of water, and keeping the temperature below 800° C. avoided any appreciable destruction of the calcite. It is possible that calcite near the outer surfaces of the blocks calcines at this temperature, as the dissociation meets progressively less interference nearer the surface.

Uncovered thin sections were prepared from the blocks roasted in this manner and then were stained by the silver nitrate-potassium chromate method described by Krumbein and Pettijohn (1938, p. 496).

The thin sections turned a grayish orange pink (5YR 7/2), a color that can be resolved by means of the petrographic microscope into microscopic spots of reddish brown calcite fairly evenly distributed throughout the cryptocrystalline phosphate pellets.

When these factors concerning the calcite are considered, that is, its relative paucity compared with the organic matter, its small size, and even distribution, it is understandable that more than 2 per cent of this highly birefringent mineral could be rendered invisible.

The precise quantitative method for the detection of calcite in the presence of carbonate-bearing apatite, described in the main body of this report, was subsequently developed so that the chief value of this experiment now lies in exposing the distribution of calcite hitherto hidden by organic matter in phosphate rocks. It is also reassuring to observe that the silver nitrate-potassium chromate method of staining will operate on particles of very small size.

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