NATIONAL BUREAU OF STANDARDS REPORT

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CRYSTALLOGRAPHIC INVESTIGATION OF TRICALCIUM PHOSPHATE HYDRATE

by

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Samuel R. Stephenson



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CHAPTER V

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CRYSTALLOGRAPHIC INVESTIGATION OF TRICALCIUM PHOSPHATE HYDRATE

Abstract

By the use of the hydrothermal bomb technique, crystals of tricalcium phosphate hydrate were grown from about 500 angstrom units to approximately 3 microns in length. By this means it was possible to obtain accurate crystallographic data which, when combined with the chemical data, suggested that this substance might be hydroxy apatite with phosphoric acid occluded in the ratio of 0.6 H_3PO_4 to one $Ca_{10}(PO_4)_6(OH)_2$.

1. INTRODUCTION

The existence of tricalcium phosphate hydrate, or α-tricalcium phosphate as it is sometimes called, is a problem which concerns workers in many fields. It has been suggested by Dallemagne and his coworkers (1), (2) that this substance, admixed with magnesium and calcium carbonate, is the main inorganic constituent of bone, dentin and cementum. However, at this writing, chemists, biologists and mineralogists, as well as scientists in other branches of research, cannot agree as to whether this substance is a real chemical entity or is merely a defective or physically modified hydroxy apatite. The main problem has been the inability of the experimentalist to make exact x-ray and optical measurements on this material because of the extremely small size of the crystals of tricalcium phosphate hydrate found in natural or laboratory samples.

There are two main structural concepts of this precipitated calcium phosphate in which the formula $Ca:PO_4$ ratio is 1.50 as opposed to 1.67 for hydroxy apatite. One viewpoint, held by Dallemagne, Brasseur and Melon (3), is that since the x-ray patterns of these substances are quite similar but their optical and chemical properties are different, tricalcium phosphate hydrate may be thought of as a calcium-deficient hydroxy apatite, $Ca_9(PO_4)_6H_2(OH)_2$, with two hydrogen ions in place of the missing calcium. On the other hand, Bale,

LeFevre and Hodge (4) maintain that the tricalcium phosphate hydrate is merely hydroxy apatite with phosphate ions adsorbed in sufficient quantities to reduce the Ca:PO_4 ratio to the 1.50 value.*

In order to characterize tricalcium phosphate hydrate conclusively, it is necessary to enlarge the crystals so that precise crystallographic measurements can be made. Then, by combining these x-ray and optical data with the chemical data, it may be possible to reach a reasonable conclusion.

2. CRYSTAL GROWTH

Commercial tricalcium phosphates were chosen as specimens for the crystal growth experiments. These substances had an original particle size of about 500 angstrom units. As cited by Hodge, LeFevre and Bale (5), the composition of commercial tertiary calcium phosphates is found to vary considerably. Therefore, precautions were taken to choose only those phosphates which had a Ca:PO_4 ratio as close as possible to 1.50, the theoretical ratio in α-tricalcium phosphate.

The material was then treated in a hydrothermal bomb according to the method of Morey and Ingerson (6). A charge of about two grams of the original, poorly crystallized material was introduced into the platinum-lined chamber of the bomb (roughly 20 ml in volume). This was then covered with about 4 ml of distilled water, the bomb was sealed, using a platinum gasket, and was inserted into a furnace held at the desired temperature for a given time. The temperatures used ranged from 250 to 450° C (482 to 842° F), resulting in hydrothermal pressures that attained approximately 2,000 psi. The experiments lasted from a few hours to a few weeks.

The results of the crystal growth were followed by x-ray diffraction and electron and optical microscopy. In Figure 1 the improvement of crystallinity is shown by the sharpening of the x-ray pattern of the sample treated in a bomb at 300° C (572° F) for two days. The same samples are shown in Figures 2 and 3, as seen under the electron microscope, the former being the untreated, the latter the treated sample. Figure 4 shows the same sample treated at 300° C for one week. It is of interest to note that the crystallite size of the original unimproved sample, as calculated by the x-ray line broadening

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*For a more complete review of the theories concerning tricalcium phosphate hydrate, see the article by Dallemagne and coworkers mentioned above (3).

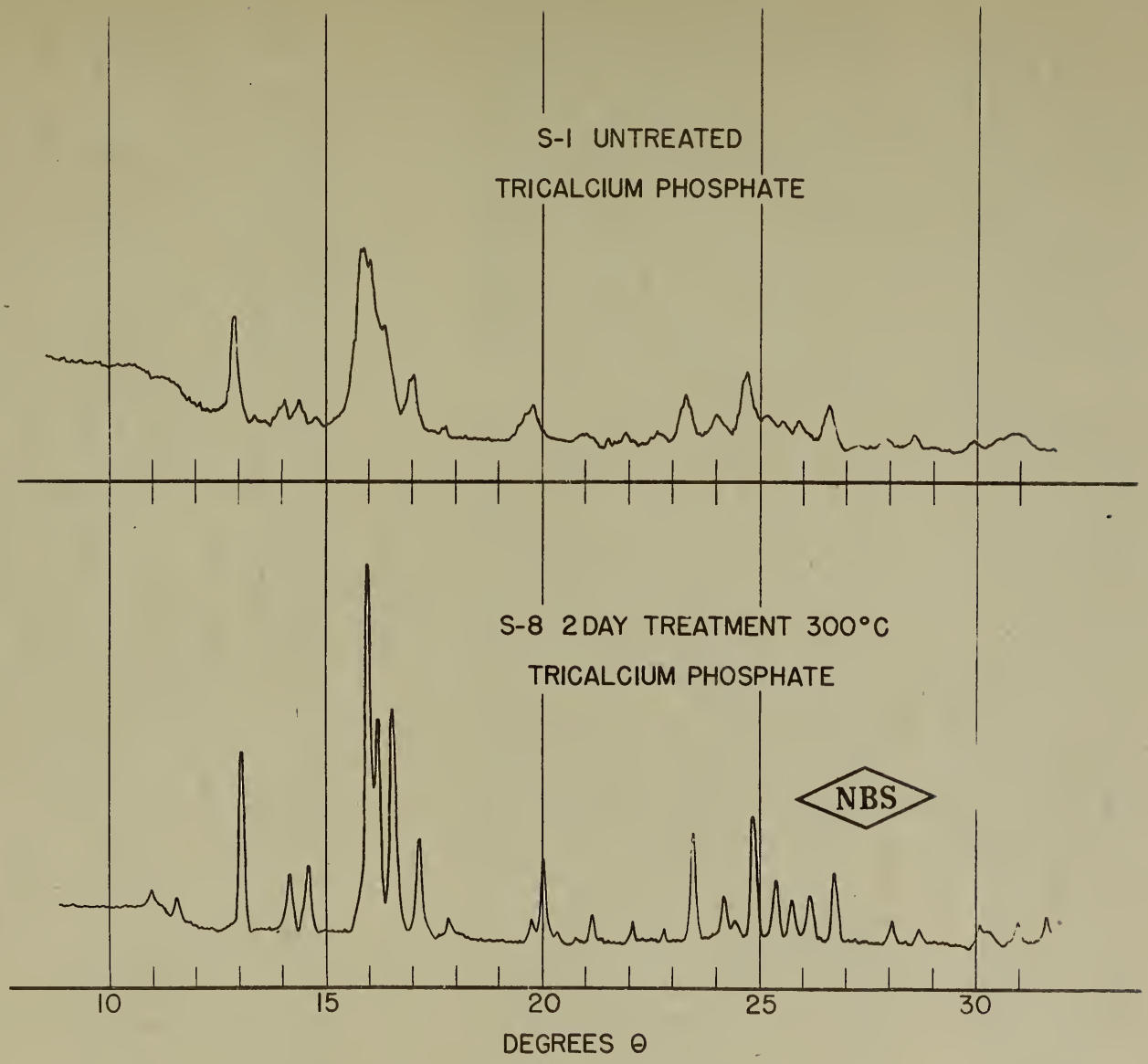


Fig. 1. X-ray powder diagrams of untreated and treated tricalcium phosphate hydrate.

(Figure 1) according to the method outlined by Warren and Biscoe (7), came to an average value of 500 angstroms. This checks very well with the finest particles seen in the electron micrograph of this substance (Figure 2). Since the particle size and the crystallite size are of about the same dimensions, this leads to the conclusion that the ultimate particles of the tricalcium phosphate hydrate observed are single crystals.

There has been no attempt in this paper to report on a systematic study of the hydrothermal growth of the tricalcium phosphate crystals. The experimental conditions mentioned herein were chosen arbitrarily since they suited the available equipment and furnished us with crystals large enough for making accurate x-ray and optical measurements.

The results of a few representative crystallization experiments can be seen in Column 5 of Table 1. This table contains data on only those samples made from Baker & Adamson C.P. tribasic calcium phosphate (Serial Number 3772). It was found that the minimum treatment necessary to sharpen the x-ray diffraction pattern (i.e., to grow the crystals larger than about 0.1 micron) was a two-hour digestion in the hydrothermal bomb at 300° C (572° F) with a resulting internal pressure of approximately 2,000 psi. As the same treatment was continued for a week, the crystals grew to a length of about two to three microns (Figure 4). This size seems to be the practical maximum that can be attained under these experimental conditions, since doubling the time of digestion produced no measurable increase in particle size.

3. ANALYSIS

The original, poorly crystallized samples and a few of the improved samples were analyzed for calcium and phosphate, and the $Ca:PO_4$ ratios were calculated. The methods used are described on pages 358 and 396 respectively of Kolthoff and Sandell (8). The calcium was precipitated as the oxalate and ignited to constant weight as CaO, while the phosphate was determined by precipitating it as magnesium ammonium phosphate and igniting to constant weight as $Mg_2P_2O_7$. The results are given as the $Ca:PO_4$ ratios in Column 3 of Table 1.

In every hydrothermal experiment the residual bomb water was analyzed by microchemical qualitative methods for the presence of calcium and/or phosphate ions. In general these methods depend upon the addition of a suitable reagent to a drop of the unknown solution which has been placed on a slide mounted on the stage of a petrographic microscope. The separation of a solid phase which possesses crystalline properties peculiar to the ion being sought is verified by microscopy.

Table 1

Typical Results of Chemical and Physical Analyses
of Samples of Tricalcium Phosphate Hydrate and Hydroxy Apatite

Sample No.	Bomb time and temperature	Ca:PO_4 ratio	Refractive index average	Crystal size	Lattice constants		Density	X-ray after 900° C
					a	c		
				microns				
S-1	Untreated alpha TCP*	1.495	1.60	.05	9.43	6.88	2.89	beta TCP
S-4	2 hrs 300°C	-----	1.60	0.1	9.42	6.88	----	beta TCP
S-8	2 days 300°C	1.492	1.60	0.5	9.42	6.87	2.89	beta TCP
S-10	7 days 300°C	1.508	1.60	1.0	9.43	6.88	----	beta TCP
S-11	2 days 300°C	-----	1.60	0.5	9.44	6.88	----	beta TCP
S-12	7 days 200°C	-----	1.60	0.1	9.42	6.88	----	beta TCP
S-15	(hydroxy apatite)	1.642	1.64	0.5	9.45	6.89	3.13$^{\mp}$	OH-Ap
S-29	(OH-Ap+H_3PO_4) 7 days 300°C	-----	1.61	0.5	9.45	6.89	2.96	beta TCP

*Tricalcium phosphate

$^{\mp}$This density calculated from x-ray data; others observed.

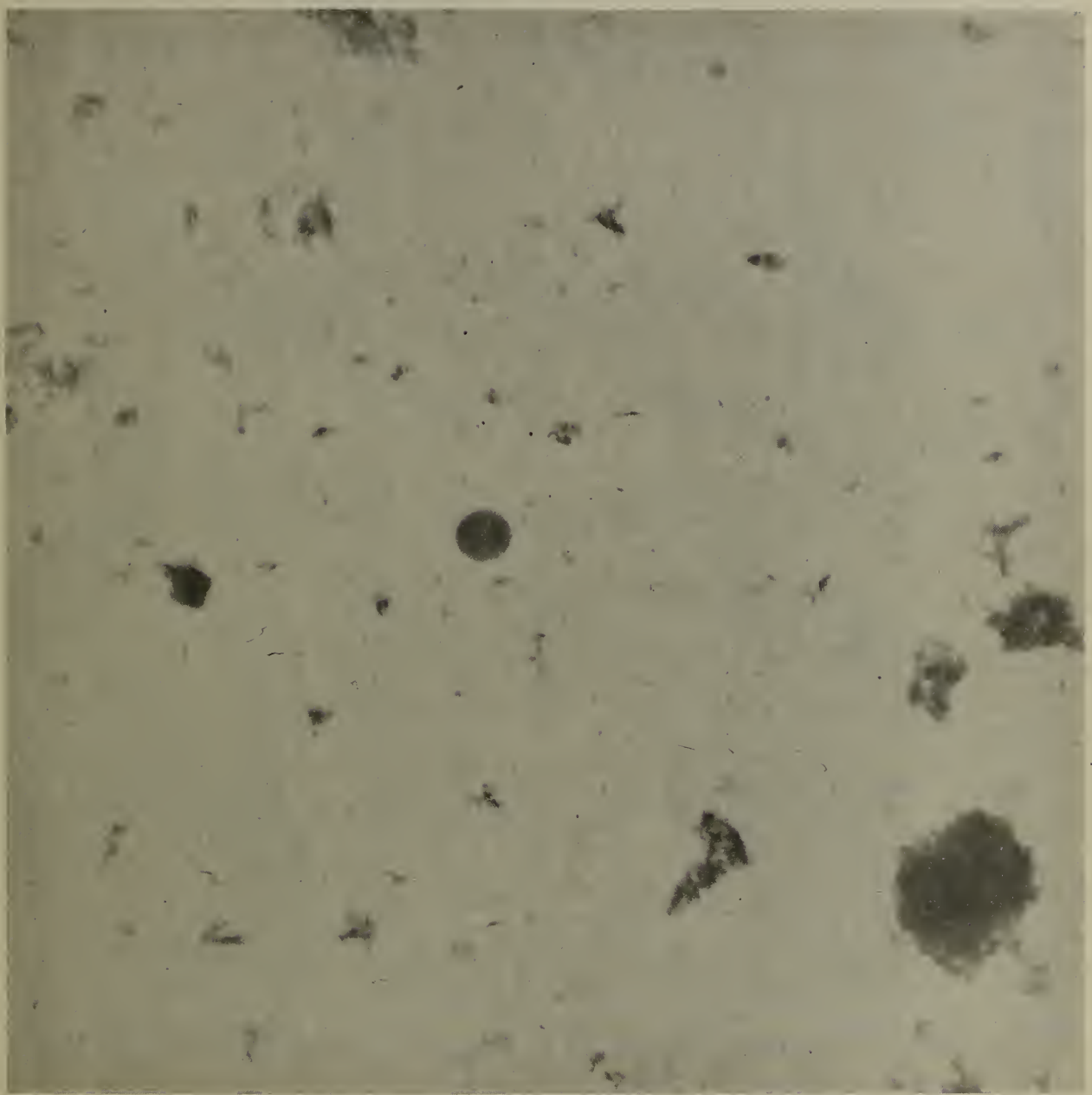


Fig. 2. Electron micrograph of untreated tricalcium phosphate hydrate. Magnification 25,000 diameters. The spherical polystyrene particle in center of picture is about 1/4 micron.

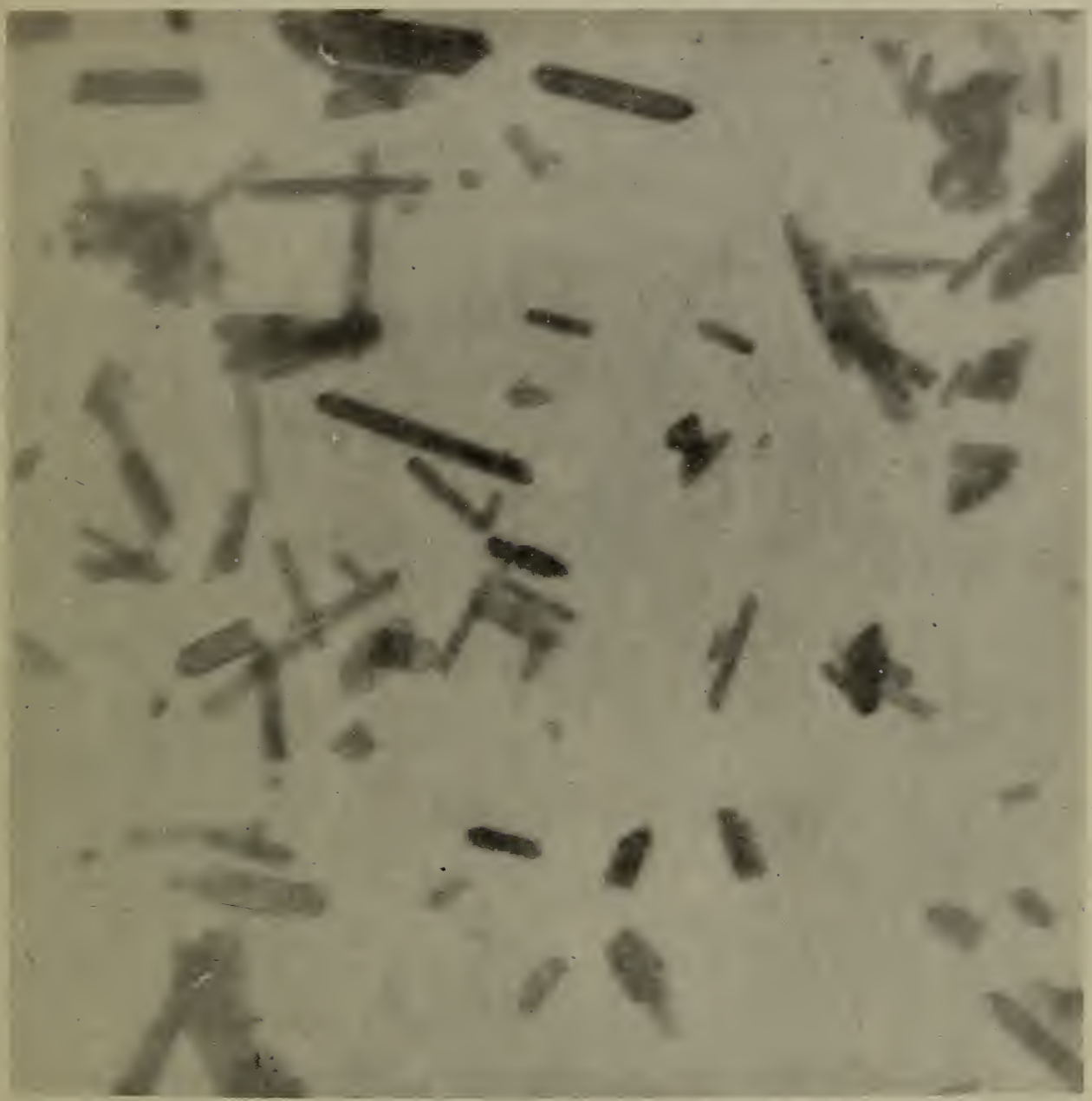


Fig. 3. Electron micrograph of tricalcium phosphate hydrate treated for two days at 300° C in a hydrothermal bomb. Magnification 25,000 diameters.

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Fig. 4. Electron micrograph of tricalcium phosphate hydrate treated for seven days at 300° C in a hydrothermal bomb. Magnification 25,000 diameters.

In the case of the calcium an attempt was made to precipitate $Ca(C_2O_4)\cdot 3HO$ and, in the case of the phosphorus, to precipitate the complex compound formed between the phosphate ion and silver nitrate.*

There was no trace of calcium or phosphate found in all of the microanalyses. It was then decided to abandon the complete chemical analyses since it could be assumed that there was no change in the original $Ca:PO_4$ ratio if there was no appearance of these ions in the water phase. In general it can be concluded from the analytical results that the original substance had a $Ca:PO_4$ ratio equivalent to the theoretical ratio of tricalcium phosphate hydrate and that no change occurred during the hydrothermal treatment of this sample.

4. IGNITION OF PHOSPHATES

It is well established that calcium phosphates which display the x-ray diffraction pattern of hydroxy apatite and have a $Ca:PO_4$ ratio of 1.50 will give an x-ray diffraction pattern of β-tricalcium phosphate when ignited at 900° C (1652° F) (5), (10). On the other hand, it is also known that a calcium phosphate giving the hydroxy apatite x-ray pattern and having a ratio of 1.67 will not change its x-ray pattern upon ignition at the same temperature (5), (10). This has been used as a method of differentiating between tricalcium phosphate hydrate and a hydroxy apatite. Some samples of tricalcium phosphate hydrate and a hydroxy apatite were subjected to such an ignition at 900° C for at least eight hours, and the resulting x-ray diffraction patterns are tabulated in Column 9 of Table 1.

5. X-RAY DIFFRACTION AND OPTICAL STUDIES

All of the calcium phosphates studied were examined as powders in a geiger counter x-ray spectrometer using $CuK\alpha$ radiation. A few of the typical results can be seen in Figures 1 and 5. The principal observation made on the patterns of tricalcium phosphate hydrate is that they are very similar to one another regardless of the conditions under which they were prepared. In fact, with the exception of very slight differences in cell dimensions (see Table 1, Columns 6 and 7), the various tricalcium phosphate patterns are identical. The x-ray powder pattern of a typical sample of "improved" tricalcium phosphate hydrate (S-8) was carefully compared with the powder

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*For details of these methods refer to pages 114 and 336 respectively of Chamot and Mason's Handbook of Chemical Microscopy, Volume II (9).

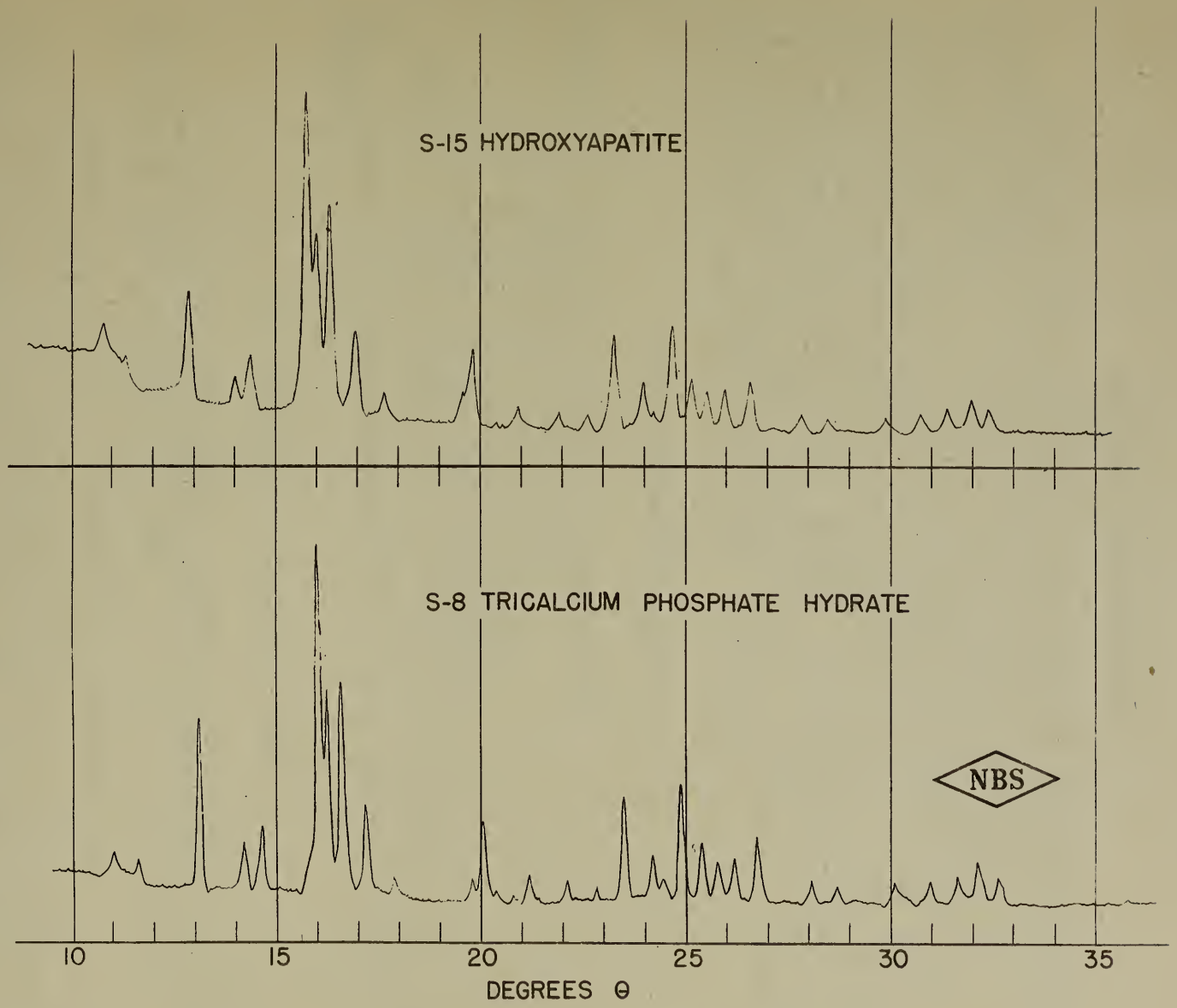


Fig. 5. Comparison of the x-ray powder diagrams of hydroxy apatite and a typical tricalcium phosphate hydrate.

pattern of hydroxy apatite* (S-15). These patterns are shown in Figure 5 and Table 2.

All samples were examined with the petrographic microscope. The average indices of refraction obtained by the Becke line method are listed in Column 4 of Table 1.

6. DENSITY MEASUREMENTS

The densities of some of the samples were determined by a modification of the ordinary picnometer method usually applied to liquids. After the picnometer was calibrated with distilled water, a quantity of the powdered sample to be studied was added to the dry weighed picnometer and the entire system was weighed again. The picnometer was then half filled with water and subjected to a vacuum treatment for five to ten minutes in order to rid the sample of any air which might lead to erroneous density measurements. The picnometer was then filled to the mark and weighed at 20° C (68° F). The density was calculated according to the method outlined by Hidnert and Peffer (11) using the following equation:

$$D = \frac{dS}{S + P + Vd - W'}$$

where V = internal volume of picnometer
D = density of the powder
d = density of water at 20° C
S = weight of the powder sample
P = weight of the dry picnometer
and W' = total weight of the picnometer, powder and water.

The results of these measurements may be seen in Column 8 of Table 1.

7. ADSORBED PHOSPHATE IONS

Bale, LeFevre and Hodge (4) write the reaction (unbalanced) in which tricalcium phosphate hydrate transforms to β-tricalcium phosphate upon ignition at 900° C (1652° F) as follows:

$$3Ca_9(PO_4)_6Ca(OH)_2 + (PO_4)_2^{-3} \longrightarrow 10Ca_3(PO_4)_2$$

This viewpoint stems from their theory that tricalcium phosphate hydrate is indeed hydroxy apatite with adsorbed phosphate ions.

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*Sample obtained from the National Institute of Dental Research. This sample is not pure hydroxy apatite, as shown by its analysis (Table 1); however, there were no spurious lines in the diffraction pattern and so it was chosen as a standard.

Table 2

Comparison of X-ray Diffraction Data of Hydroxy Apatite and Tricalcium Phosphate Hydrate

hkl	Hydroxy apatite		Tricalcium Phosphate	
	Degrees θ	Relative intensity	Degrees θ	Relative intensity
200 020	10.80	16.5	10.85	9.95
111	11.34	9.2	11.45	8.5
002	12.89	35.6	12.95	48.5
102 012	14.00	9.7	14.05	16.6
120 210	14.35	17.0	14.50	18.95
121 211	15.80	100.00	15.92	100.00
112	16.05	57.8	16.11	58.0
300 030	16.35	64.1	16.50	61.7
202 022	16.95	26.2	17.05	27.2
301 031	17.65	9.2	17.75	7.1
130 310	19.55	11.3	19.65	9.0
221	19.80	24.9	19.90	23.6
103 013	20.35	2.6	20.25	4.5
311 131	20.55	2.4	20.65	3.6
302 032	20.90	7.9	21.05	9.5
400 040	21.92	6.6	21.98	7.8
203 023	22.62	6.0	22.70	5.9
222	23.25	30.1	23.40	32.0
312 132	23.98	16.0	24.10	14.7
230 320	24.23	6.8	24.35	8.3
213 123	24.70	33.8	24.80	35.5
321 231	25.20	17.3	25.30	19.0
410 140	25.55	12.8	25.65	13.3
402 042	25.95	13.6	26.08	14.7
004	26.60	17.1	26.65	21.5
500 050	27.85	7.9	27.97	7.6
133 313	28.49	4.7	28.58	5.2

Continued in next column.

A series of experiments was performed to test the above reaction. A charge of two grams of hydroxy apatite was added to the hydrothermal bomb and covered with 4 ml of a dilute solution of ortho phosphoric acid, the concentration of which was adjusted to change the total $Ca:PO_4$ ratio of the charge (solid plus liquid) from 1.67 to 1.50. This was then sealed as usual and heated for seven days at 300° C (572° F). The resultant sample was examined by x-ray and optical methods and part of the sample was ignited for 12 hours at 900° C (1652° F). The results, as seen in Table 1 (Sample S-29) show that by adding phosphate ion to hydroxy apatite and igniting it at 900° C, a β-tricalcium phosphate structure can be achieved. It should be noted that the addition of the phosphate ion has lowered the index of refraction from 1.64 to 1.61, the latter figure resembling the index of refraction of the chemically precipitated samples of tricalcium phosphate hydrate.

8. CONCLUSIONS

From the analytical data obtained it might be concluded that tricalcium phosphate hydrate is distinctly different from hydroxy apatite. However, their x-ray diffraction patterns are very similar, as shown in Figure 5 and Table 2. The small difference in the a axis might be explained by the fact that this axis in the "hydrate" crystal was not developed beyond 0.1 to 0.2 micron and such maldeveloped axes have been known to give erroneous axial lengths (12). There are also some differences in the intensities which remain unexplained at this point.

In general a structure must appear in some periodic arrangement whose size is of the order of 100 angstroms or greater in order to be detected by x-ray diffraction. It is conceivable that some substance or substances may be present in the tricalcium phosphate hydrate in large enough amounts to alter the $Ca:PO_4$ ratio, the index of refraction, the density and the ignition properties without being in a developed, crystalline state which would appear in the x-ray data.

To correlate the analytical results with the above x-ray diffraction data one may assume some sort of phosphate ion adsorption or occlusion in the amount needed to change the $Ca:PO_4$ ratio of hydroxy apatite from 1.67 to 1.50. If this apparent excess of phosphate, six percent by weight, were present in a separate crystalline phase, it would be detected by x-ray diffraction, assuming of course the crystallites were larger than about 100 angstrom units.

The x-ray diffraction data, which show very little difference between hydroxy apatite and tricalcium phosphate hydrate, can also be interpreted to show that the Dallemagne and Brasseur (3) formulation $Ca_9(PO_4)_6H_2(OH)_2$ might be true. This configuration theoretically would give a pattern quite similar to the hydroxy apatite. However, if the density of this substance is calculated from the unit cell volume, obtained from the x-ray data, and the molecular weight suggested by the above formula, it is found to be 3.03 as opposed to an observed value of 2.89. If the average index of refraction is also calculated using the Gladstone and Dale method (13), the theoretical index is found to be 1.65, while the observed index is 1.60. If the hydrate is assumed to be a monohydrate instead of the proposed dihydrate, the theoretical index of refraction is found to be 1.64, which also does not agree with the observed value. To reconcile the density and index of refraction data with the x-ray diffraction data it may be assumed that some sort of diluent which fails to give a diffraction pattern is adsorbed or occluded in the hydroxy apatite crystals, lowering the density and index of refraction by the amounts shown.

It is well to add that the method of Gladstone and Dale is only approximate and does not always give exact results. However, it is felt that when we compare similar compounds as above, the method is sufficiently accurate for our purposes. Thus we can state that any of the suggested formulas for tricalcium phosphate hydrate would give indices of refraction almost coincident with that of hydroxy apatite.

A complete analysis of tricalcium phosphate hydrate shows that it contains anywhere from 1.15 to 7.30 percent of volatile water (5). The above evidence does not completely explain the existence of this excess water in these tricalcium phosphate hydrate crystals. It is strongly indicated that this water is not contained in the structure. One can guess that it is surface-adsorbed water. There is some evidence from preliminary work done by the authors that when enlarged tricalcium phosphate hydrate crystals are subjected to differential thermal analysis, the curves are quite dissimilar to those obtained from the fine particle material. This lends support to the hypothesis of water adsorption since the enlarged particles could not accommodate such a large excess of water on the surface.

A systematic study of the addition of phosphate to hydroxy apatite is still under way. So far our experiments have shown that by the addition of phosphoric acid to hydroxy apatite a well crystallized product can be obtained which satisfies the tricalcium phosphate hydrate formula. This product has a density and a refractive index different from those calculated on the basis of an apatite of the composition $Ca_9H_2(PO_4)_6(OH)_2$, while the x-ray diffraction pattern is clearly very similar to that of hydroxy apatite.

There has been some question raised as to whether the improved crystals of tricalcium phosphate hydrate are the same as the original material. Since they analyze the same and no phosphate or calcium was found in the residual bomb water, and since no amount of bomb treatment, ranging from two hours to one week, changed the index of refraction, the density or the x-ray pattern, it is clear that there has been no chemical or crystallographic change during this hydrothermal growth.

The exact nature and placement of the physically admixed ions, which according to this hypothesis make the hydroxy apatite appear to be tricalcium phosphate hydrate, can only be speculated upon. Surface adsorption of phosphate ions cannot be the entire effect. In the 3-micron crystals of the improved tricalcium phosphate hydrate it would be impossible for six percent by weight of the entire crystal to be phosphate ions adsorbed in any reasonable number of layers on the crystal surfaces. This lends emphasis to the explanation that the bulk of the phosphate diluent is occluded in the submicroscopic faults of the hydroxy apatite crystal. We measure a density of 2.89 on these tricalcium phosphate hydrate crystals, which differs from the theoretical value of 3.13 for hydroxy apatite. Considering the six percent occlusion as phosphate ion, we cannot completely justify this low density by this factor alone. Thus, there must be a small amount of empty space in the crystal which, coupled with the lower density of the phosphate ions as compared to that of hydroxy apatite, will combine to give the observed density. Apparently the phosphate ions (and the hydrogen ions associated with them for electrical neutrality) would deposit imperfectly in these entrapped surfaces during crystal growth so that there would be empty spaces remaining, thus accounting for the drop in density mentioned above. The results reported in this paper would not indicate whether the occluded ions were PO_4, HPO_4, or some other ion involving phosphorus, but regardless of the exact nature of the ion, the principle of occlusion would still be the same and there would still be 0.67 H_3PO_4 for every hydroxy apatite molecule to form one molecule of so-called tricalcium phosphate hydrate. Thus, to change the view of Hendricks and Hill (15) very slightly, the formula for tricalcium phosphate hydrate would be $Ca_{10}(PO_4)_6(OH)_2$ · occluded 0.67 H_3PO_4.

There are precedents for thinking in terms of imperfections in crystals. Addink (14) has shown that the density of certain crystals as calculated from very accurate x-ray data is found to be higher than the carefully measured density. It should be noted that these imperfections were of the order of magnitude of less than one percent, much lower than the above six percent. The mode of occlusion of excess phosphate ions in hydroxy apatite may be similar to the carbonate occlusion suggested by Hendricks and Hill (15) for the carbonate apatites.

In the biological field the higher content of phosphate in the apatite of bone, cementum and dentin as compared with enamel indicates that a mechanism may be active which permits the occlusion of these ions in greater amounts. Sobel, Hanok, Kirschner and Fankuchen (16) have shown that the PO_4:CO_3 ratio of blood serum bears a direct relationship to the PO_4:CO_3 ratio of enamel and dentin. This may indicate that the amounts of inclusions in the deposited apatites depend on the individual concentration of these ions in the serum.

9. SUMMARY

1. Crystals of so-called tricalcium phosphate hydrate were enlarged in a hydrothermal bomb from an average length of 500 angstrom units to about 3 microns without changing their Ca:PO_4 ratio, density, refractive index and the spacings of their x-ray pattern.

2. The x-ray diffraction powder patterns of tricalcium phosphate hydrate and hydroxy apatite were found to be quite similar.

3. The differences between hydroxy apatite and tricalcium phosphate hydrate insofar as density, index of refraction, and results of ignition at 900° C (1652° F) are concerned can possibly be explained by postulating a six percent phosphate ion inclusion in the entrapped surfaces of the hydroxy apatite crystal.

4. We suggest that a possible formula for tricalcium phosphate hydrate is $Ca_{10}(PO_4)_6(OH)_2$ · occluded 0.67 H_3PO_4.

Bibliography

1. Dallemagne, M. J., Bull. Soc. Roy. Sci. Liege 11, 488-95 (1942).

2. Dallemagne, M. J., and Brasseur, H., Bull Soc. Roy. Sci. Liege 11, 451-62 (1942).

3. Dallemagne, M. J., Brasseur, H., and Melon, J., Bull. Soc. Chem. Biologique 31, 425-31 (1949).

4. Bale, W. F., LeFevre, M., and Hodge, H. C., Naturwiss. 24, 636 (1936).

5. Hodge, H. C., LeFevre, M., and Bale, W. F., Ind. Eng. Chem. Anal. Ed. 10, 156-61 (1938).

6. Morey, G. W., and Ingerson, E., Amer. Mineral. 22, 1121-22 (1937).

7. Biscoe, J., and Warren, B. E., J. Appl. Phys. 13, 364-71 (1942).

8. Kolthoff, I. M., and Sandell, E. B., Textbook of quantitative inorganic analysis, (The Macmillan Co., New York, 1943).

9. Chamot, E. M., and Mason, C. W., Handbook of chemical microscopy, Vol. II, (John Wiley and Sons, Inc., New York 1940).

10. Sobel, A. E., Hanok, A., Kirschner, H. A., and Fankuchen, I., J. Dent. Res. 28, 61-67 (1949).

11. Hidnert, P., and Peffer, E. L., Density of solids and liquids, NBS Circular 487 (U. S. Government Printing Office, Washington, 1950).

12. Lennard-Jones, J. E., and Dent, B. M., Proc. Roy. Soc., A121, 247 (1928).

13. Larsen, E. S., and Berman, H., The microscopic determination of the nonopaque minerals, 2d Ed. (1934); U. S. Geological Survey Bull. 848, Washington, D. C.

14. Addink, N. W. H., Rec. Trav. Chem. 70, No. 2, 262-8 (1951).

15. Hendricks, S. B., and Hill, W. L., Proc. Nat. Acad. Sci. 36, No. 12, 731-37 (1950).

16. Sobel, A. E., Hanok, A., Kirschner, H. A., and Fankuchen, I. J. Biol. Chem. 179, No. 1, 205-10 (1949).

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