

## OCCURRENCE OF BETA TRICALCIUM PHOSPHATE IN NORTHERN MEXICO

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### ABSTRACT

Beta tricalcium phosphate occurs as white to slightly greenish, hard, brittle masses with occasional chalkiness in veins up to one yard in thickness running through an earthy material, consisting of fine-grained beta tricalcium phosphate and quartz, lying in cavities in calcareous sedimentary rocks (chiefly limestone), and as pale yellow crystals, 1-2 mm. in length lining cavities in a white to yellowish brittle rock. The rhombohedra from both sources show the same indices of refraction;  $\omega=1.623$  and  $\epsilon=1.620$  with Na light.

A number of samples of phosphate from the Mercedes Mine, † Sabinas Hidalgo, Nuevo Leon, Mexico, were brought to the Bureau of Plant Industry, Soils and Agricultural Engineering laboratory in May 1950 for identification and analysis. The beta form of tricalcium phosphate was found to be the principal phosphate mineral in the specimens.

The natural mineral forms of tricalcium phosphate have been named martinite (3, 4) and whitlockite (2). Both have the  $x$ -ray diffraction patterns of  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$ . Martinite, found in island phosphates has indices of refraction  $\omega=1.607$ ,  $\epsilon=1.604$ , and contains water and  $\text{CO}_2$ . Whitlockite, a hydrothermal product associated with granite pegmatites, has indices of refraction  $\omega=1.629$ ,  $\epsilon=1.626$  and contains little water and no  $\text{CO}_2$ .

The Mexican  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  occurs in cavities in calcareous sedimentary rocks, chiefly limestone; some of the limestone is thought to be phosphatic. The major part of the deposit now being mined is a brownish-red earthy material. White veins of  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$ , some of large size, occur in, and at the edges of the soft earthy phosphate. The deposit has the appearance of a filled cave or solution cavity. Just above the deposit is a miniature syncline, which could have resulted from slumping after solution of the limestone, or could have antedated the phosphate and been a potential collector of solute-carrying ground water. No evidence of any high-temperature activity in the vicinity has been reported.

### DESCRIPTION OF THE SPECIMENS

1. White to yellowish, hard brittle rock, flecked with black; has cavities lined with pale-yellow crystals. Powder  $x$ -ray diffraction pat-

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† The samples were collected with the cooperation of Sr. Ignacio Pesqueira, President, and the assistance of Sr. Miguel de los Santos, Mine Manager, Fertilizantes de Mexico.

terns of bulk-ground samples contain interference maxima of  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$ , quartz and a trace of apatite. Microscopically the  $\text{Ca}_3(\text{PO}_4)_2$  is in the form of rhombohedra, the apatite in banded, oriented, radial aggregates, and quartz is in both prismatic crystals and chalcedony. The  $\text{Ca}_3(\text{PO}_4)_2$  crystals lining cavities are 1–2 mm. long but those in the mass of the rock are 0.01–0.05 mm. long. Indices of refraction of the  $\text{Ca}_3(\text{PO}_4)_2$  for Na light are  $\omega = 1.623$ ,  $\epsilon = 1.620$ .

2. White to slightly greenish, hard, brittle masses that are chalky in spots. The veins of this rock are said to range up to one yard in thickness. Powder  $x$ -ray diffraction patterns are almost identical with those made on a specimen of whitlockite from the type locality and with synthetic  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$ . The mineral occurs as rhombohedra, which appear to be cemented together with an unidentifiable amorphous substance. Traces of quartz, apatite and a carbonate are present. The indices of refraction are as described above. Thin sections showed great uniformity in the rock, the only structure being a weak rhythmic banding due to slight differences in crystal size, orientation and proportion of the cementing substance. The crystals are uniform in size, ranging mainly between 0.01 and 0.04 mm. The chemical analysis is given in Table 1.

3. Red earthy material, resembling a red clay soil, is the chief mine product. It has a weak  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$  powder  $x$ -ray pattern, plus 15–20 per cent of quartz. It is too fine-grained and stained to be studied microscopically.

4. Hydroxyl-apatite, as white to yellow crusts over essentially amorphous gray black and brown material, is present near the  $\text{Ca}_3(\text{PO}_4)_2$ . The crusts consist of oriented aggregates of fibrous crystals. Its chemical analysis is given in Table 1.

The chemical composition of the tricalcium phosphate in its major constituents is close to that of both the New Hampshire whitlockite and the Curacao martinite. The high zinc content is noteworthy; zinc and magnesium substituting for calcium would bring the  $\text{P}_2\text{O}_5$ :base ratio fairly close to that of synthetic  $\text{Ca}_3(\text{PO}_4)_2$ . The water and  $\text{CO}_2$  contents, particularly the latter, are low in comparison with martinite and most other  $\text{Ca}_3(\text{PO}_4)_2$  reported in island phosphates. Geiger-counter  $x$ -ray spectrometer patterns of the Mexican phosphate mineral, New Hampshire whitlockite and synthetic beta  $\text{Ca}_3(\text{PO}_4)_2$  were nearly identical. The indices of refraction are very close to the indices of the synthetic material, thus slightly lower than the New Hampshire specimen and considerably higher than martinite. The rhombohedral habit described (2, 3) is common to the natural materials but seldom seen in the synthetic preparations. It has been suggested (1) that the name whit-

TABLE 1. COMPOSITION OF BETA TRICALCIUM PHOSPHATE AND HYDROXYL-APATITE FROM MEXICO

Constituent	Beta $\text{Ca}_3(\text{PO}_4)_2^a$	Hydroxyl-apatite
$\text{P}_2\text{O}_5$	44.28	38.61
CaO	46.35	53.36
MgO	2.17	<0.05
ZnO <sup>b</sup>	1.99	—
$\left. \begin{array}{l} \text{Al}_2\text{O}_3 \\ \text{Fe}_2\text{O}_3 \end{array} \right\}$	0.11	0.09
$\text{Na}_2\text{O}$ ( $\text{K}_2\text{O}$ )	0.05	—
MnO	<0.01	<0.01
$\text{SiO}_2^c$	2.80	—
F	0.02	0.35
$\text{CO}_2$	0.02	—
$\text{SO}_3$	0.73	0.00
$\text{H}_2\text{O}+105^\circ\text{d}$	1.61 <sup>e</sup>	2.51 <sup>f</sup>
Apatite $\text{H}_2\text{O}$	—	1.63
$\text{H}_2\text{O}-105^\circ$	0.10	3.26
Qualitative Spectro- graphic analysis <sup>g</sup>		
5%	Ca, P	Ca, P
1-5%	Mg, Zn	—
0-X%	Mn	Si, F, Zn
0-0X%	Al, Si, Fe	Mg
0.00X%	Cu, V, Sr	Mn, Cu, Sr, Ba, Fe
0.000X%	Ni, Ba	Al

<sup>a</sup> Composition required by formula; 45.78%  $\text{P}_2\text{O}_5$ , 54.21% CaO.

<sup>b</sup> Glenn Edington, *analyst*.

<sup>c</sup> Material insoluble in 1:1 HCl+ $\text{SiO}_2$  thrown out by dehydration.

<sup>d</sup> Exclusive of water lost at 105° C.

<sup>e</sup> Ignited at 1200° C.

<sup>f</sup> Ignited at 1100° C.

<sup>g</sup> Spectrographic analysis by courtesy of Geochemistry and Petrology Branch, Geological Survey, U.S.D.I., Mrs. E. L. Hufschmidt, *Analyst*.

lockite be used for  $\beta\text{-Ca}_3(\text{PO}_4)_2$  and martinite for the corresponding mineral containing  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The Mexican specimen is nearly  $\text{CO}_2$  free and contains much less  $\text{H}_2\text{O}$  than martinite and has high refractive indices but in its low-temperature origin it resembles martinite. The zinc content perhaps also may be considered in deciding upon its name. If a series of minerals exists containing assorted substituted ions in various proportions and having gradations in properties it may become difficult to decide upon names for intermediates. In strictest interpretation based on composition and origin the Mexican mineral probably should be called martinite.

The large size of this deposit, with its relatively high purity, in a locale of sedimentary rocks is of considerable mineralogical interest. The Grafton County, New Hampshire, whitlockite is a high-temperature product and all synthetic  $\text{Ca}_3(\text{PO}_4)_2$  thus far prepared has been from high-temperature systems such as processes for thermal defluorination of phosphate rock. Martinite and related minerals are generally minor constituents in apatite or phosphorite rocks that contain rather large amounts of impurities. Beta tricalcium phosphate has been found as a constituent of urinary calculi (5)—a further indication that under the proper conditions it is a stable compound in solutions and probably can precipitate quite rapidly.

For  $\text{Ca}_3(\text{PO}_4)_2$  to form from solution the required conditions include a solution having a high  $\text{PO}_4:\text{Ca}$  ratio plus some mechanism for preventing the formation of apatite. Slow precipitation in a slightly acid medium might provide the right environment. Organic or mineral colloids or nitrogen compounds may play a role in many cases such as in the island guano occurrences and the urinary calculi. The amorphous interstitial substance among the crystals in the Mexican specimen suggests an association of a colloidal system with the deposit. The presence of apatite mixed with the  $\beta\text{-Ca}_3(\text{PO}_4)_2$  and the pure minerals in nearby parts of the same deposit indicates that precipitation conditions were delicately balanced and shifted from one mineral to the other at different times and places. The Mexican deposit appears to have accumulated as a product of the leaching action of ground water upon phosphatic limestone. Weathering of bat guano may have contributed, but the shape and nature of the deposit does not indicate this very strongly. Further field work and petrologic study are needed to establish definitely the history of the deposit.

## REFERENCES

1. FLEISCHER, M., Discussion of discredited species: *Am. Mineral.*, **29**, 326 (1944).
2. FRONDEL, C., Whitlockite: a new calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ : *Am. Mineral.*, **26**, 145 (1941).
3. FRONDEL, C., Mineralogy of the calcium phosphates in insular phosphate rock: *Am. Mineral.*, **28**, 215 (1943).
4. HENDRICKS, S. B., HILL, W. L., JACOB, K. D. AND JEFFERSON, M. E., Structural characteristics of apatite-like substances and composition of phosphate rock and bone as determined from microscopical and x-ray diffraction examinations: *Indus. and Engin. Chem.*, **23**, 1413 (1931).
5. JENSEN, A. T., On concrements from the urinary tract III: *Acta Chirurgica Scandinavica*, **85**, 473 (1941).

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