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MINERALOGY OF THE CALCIUM PHOSPHATES IN INSULAR PHOSPHATE ROCK

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ABSTRACT

The principal constituent of insular phosphate rock is a member of the apatite series, usually a carbonate-hydroxyl-fluorine-apatite. Collophane of Sandberger (1870) and Rogers (1917, 1922) is not an amorphous species distinct from apatite. X-ray study of insular and continental phosphate rock, fossil bone and teeth, urinary calculi, and other materials corresponding to collophane, as defined, proves that this substance is a submicro-crystalline variety of apatite, usually carbonate-hydroxyl-apatite, or carbonate-hydroxyl-fluorine-apatite. The name collophane may conveniently be retained as a varietal designation for fine-grained, isotropic, hydrous (and often metacolloidal) types of apatite.

The original specimens of a number of ill-defined, supposed calcium-phosphate species, described by Shepard, Julien, and others, were re-examined by x-ray and optical methods. Ornithite of Julien (1865) is an oriented pseudomorph of carbonate-hydroxyl-apatite after crystals of brushite. Nauruite of Elschner (1913) is identical with carbonate-hydroxyl-fluorine-apatite. The names pyroguanite of Shepard (1856) and sombrierite of Phipson (1862) were applied loosely to ordinary phosphate rock and entirely lack species validity. Type specimens of pyroclasite of Shepard (1856) and of monite of Shepard (1882) were not available, but these materials are doubtless identical with apatite; non-type but probably authentic specimens of both minerals were identical with carbonate-hydroxyl-fluorine-apatite. Metabrushite of Julien (1865) and stoffertite of Klein (1901) are identical with brushite. The vague material called epiglaubite by Shepard (1856) is not entitled to further record and probably is identical with brushite. Glaubapatite of Shepard (1856) is a mixture of monetite and apatite.

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Zeugite of Julien (1865), pyrophosphorite of Shepard, Jr. (1878), martinite of Kloos (1888), and whitlockite of Frondel (1941), all are identical with artificial $\beta\text{-Ca}_3(\text{PO}_4)_2$. The name whitlockite is reserved for the species. Five localities are now known for this mineral, four in insular phosphate deposits and one in granite pegmatite. The material from three of the insular occurrences is a carbonate-whitlockite, analogous to carbonate-apatite, and has relatively low indices of refraction. $\beta\text{-Ca}_3(\text{PO}_4)_2$ definitely forms in nature from water solutions at low temperatures, although all attempts to form the substance artificially have yielded only hydroxyl-apatite. The so-called martinite of Richards (1928) from Ascension Island, South Atlantic, is monetite, and the fourth known occurrence of monetite is noted from Los Monges Islands, West Indies.

INTRODUCTION

The insular phosphate rock deposits owe their origin to the replacement of coral limestone and dolomite by phosphatic solutions derived from the leaching of superficial deposits of guano. The word guano is the Spanish rendering of the Peruvian word *huano*, or excrement, and the material represents the accumulation in favorable places of the droppings of marine birds. The mineralogy of guano itself is complex and but little known. The principal constituents are calcium phosphates, ammonium phosphate and ammonium acid phosphate, together with uric acid, sodium acid urate, ammonium and calcium oxalates, ammonium and alkali sulfates and sulfate-oxalates, guanine, xanthine, and other organic substances. Mineralogically, the underlying, derived deposits of phosphate rock are simple, and consist in bulk of members of the apatite-series.

The principal concern of this investigation has been the true identity of a number of ill-defined calcium phosphates found in insular phosphate rocks and described years ago by A. A. Julien (1840-1919), C. U. Shepard (1804-1886) and his son C. U. Shepard, Jr., and others. The speculative nature of most of these substances long has been apparent, but the descriptions still remain to burden and, in some instances, confuse later workers. In addition, an *x*-ray and optical study was made of phosphate rock proper and of the rather loosely defined substance termed collophane. Every effort was made to obtain the original analyzed specimens of the minerals concerned.

The writer wishes to express his appreciation to Mr. E. P. Henderson of the U. S. National Museum for making available type material contained in that part of the Shepard collection there preserved, and for loaning other specimens from the Canfield and Roebbling collections. Professor Paul F. Kerr kindly permitted the examination of type specimens of minerals described by A. A. Julien and now contained in the collection of Columbia University. Further authentic study material was obtained from the Brush collection of Yale University through the courtesy of Dr. George Switzer, and from the collections of Harvard University.

APATITE

X-ray studies by Hendricks *et al.* (1931), Bredig *et al.* (1932, 1933), Royer (1939), and others, in conjunction with chemical analyses, have shown that the principal constituent of both insular and continental phosphate rock deposits is a material which falls into a rather definite range of the apatite series. The precise mineralogical definition of the material depends on the ratio of $\text{CO}_2:\text{OH}:\text{F}:\text{Cl}$, found by chemical analysis. No general usage has been reached, however, for the arbitrary varietal designations to be given to particular ranges of isomorphous substitution between OH-F-Cl, and C-Ca-P. The bulk of the insular apatite is a carbonate-hydroxyl-fluorine-apatite which falls approximately in the varietal range loosely assigned to francolite. Other material appears to have little or no fluorine and is properly classed as a carbonate-hydroxyl-apatite (dahllite). CO_2 is almost always present in considerable amounts as an essential constituent, but sometimes appears to be lacking. Cl always appears to be absent or present only in insignificant amounts, and a straight hydroxyl-apatite has not yet been reported from insular deposits. A hydrated tricalcium phosphate or hydrato-apatite, $\text{Ca}_9(\text{H}_2\text{O})_2(\text{PO}_4)_6$, was considered by Hendricks *et al.* (1931) to be an important constituent of the phosphate rock from Curaçao, Dutch West Indies. The substance was thought to be distinguished among the apatite-like compounds by giving the x-ray pattern of $\beta\text{-Ca}_3(\text{PO}_4)_2$ on heating to 900° , but this behavior has since been found to be shown by ordinary hydroxyl-apatite if all of the water is driven off by heating. Bulk analyses of the Curaçao rock show several per cent of CO_2 , and specimens of the substance itself give a test for CO_2 , so that the material is to be properly classed as a carbonate-hydroxyl-apatite. The mineral barrandite, $(\text{Al}, \text{Fe})\text{PO}_4 \cdot 2\text{H}_2\text{O}$, has been shown by McConnell (1940) to be an important constituent of phosphate deposits on the Island of Gran Roque, Venezuela. Barrandite and the possibly distinct mineral redondite, probably are widespread in small amounts in insular phosphate deposits, especially those in which aluminous rocks are replaced. The only other calcium phosphates now known definitely to occur in phosphate rock are brushite, monetite, and whitlockite, and these are very rare.

The apatite of the insular deposits ordinarily appears in the hand specimen as layered or banded masses of a white, yellowish or brown color. Oolitic structures and dense, compact or pulverulent varieties are less common. Pseudomorphous structures after coral or other organic remains are not infrequent. Internally banded, stalactitic or stalagmatic masses also occur. The mineral is translucent to opaque *en masse* and is transparent in thin grains. The luster is subresinous to horn-like. The

color, luster and transparency may vary widely in successive bands. Under the microscope the material usually is quite isotropic. Weak anomalous birefringence is sometimes observed, and this may vary in degree from layer to layer in a single specimen. The extinction may be undulose or parallel and perpendicular to the direction of layering. Spherulitic structures also occur. The index of refraction is, on the whole, considerably less than the mean index of macro-crystalline apatite, and varies widely. The over-all range of the writer's measurements is from about 1.565 to 1.635, or somewhat greater; the ordinary range is from 1.590 to 1.625. These values are very similar to those found by Rogers (1924) for the isotropic carbonate-hydroxyl-fluorine-apatite, which comprises fossil bone. Rogers observed an over-all range of 1.573 to 1.623 with about half of 250 measurements falling between 1.600 and 1.610. The isotropic carbonate-hydroxyl-apatite which occurs in urinary calculi (Fron del and Prien (1942)) has a somewhat lower range of index, from 1.520 to 1.605, and the average index is only about 1.575. This material, however, differs from the apatite of phosphate rock and fossil bone in lacking fluorine and in containing a relatively large amount of non-essential water. The isotropic character is due to aggregate polarization in a mass composed of submicroscopic crystallites. The low and variable index reflects the large and variable content of non-essential water. Variations in index accompanying isomorphous chemical changes apparently are completely obscured by the extraneous water.

BRUSHITE

The well-established species brushite, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, was first described by Moore (1865), who found the mineral in druses in phosphate rock from Aves Island in the Gulf of Maracaibo in the Caribbean Sea. The structure was analyzed by Hill and Hendricks (1936), who pointed out its isostructural relation to gypsum and who also determined optical and x-ray powder diffraction data. More recently, Terpstra (1937) has reviewed the morphology in the light of the structural relation to gypsum. Brushite is rather widespread in very small amounts in both insular and continental phosphate rock deposits. It typically occurs as drusy crystals in crevices in massive apatite and is a late-formed, low-temperature product. The compound CaHPO_4 , monetite, forms at higher temperatures. The mineral has been observed altered to carbonate-hydroxyl-apatite (see ornithite), to quercylite (= carbonate-apatite; dahllite) and to whitlockite, $\beta\text{-Ca}_3(\text{PO}_4)_2$ (see zeugite). Brushite frequently occurs as an incrustation upon ancient human and animal bones and has been observed in human urinary calculi.

COLLOPHANE

The name collophane (kollophan) was originally given by Sandberger in 1870 to a layered, opal-like, "amorphous" material found in the phosphate deposits on the Island of Sombrero in the West Indies. Sombrero is located at N 18°35', W 63°28', about 60 miles from St. Thomas in the Virgin Islands. The original analysis is cited below.

CaO	MgO	P ₂ O ₅	CO ₂	H ₂ O at 100°	H ₂ O at ign.	Total
50.70	0.80	39.10	3.96	3.36	1.66	99.58

Sandberger deducted the CO₂ in the belief that calcite was present as an impurity and derived the formula Ca₃(PO₄)₂·H₂O. Lacroix (1910) and Rogers (1922) later rightly maintained that the CO₂ was an essential constituent. A number of specimens from Sombrero, variously labeled as collophane, sombreroite, or phosphate rock, which answered perfectly both to the original description of collophane and to the later use of the term as applied by Rogers, were available for study. These specimens without exception gave the x-ray powder pattern of hydroxyl-fluor-apatite. The original collophane thus appears to have been a member of the apatite series. If Sandberger's analysis is accepted at its face value, the mineral is a carbonate-hydroxyl-apatite (dahllite). Fluorine may have been overlooked in this analysis.

More recently, Rogers (1922, 1924) has expressed the belief that Sandberger's mineral, together with a similar material which constitutes the bulk of so-called fossil bone and phosphate rock, could not be properly classed as apatite, as had sometimes been done, but constituted a separate mineral with properties sufficiently characteristic to entitle it to recognition as a distinct species. The name collophane was proposed for the species. The criteria offered in support of the species rank of collophane, and for its distinction from apatite, may be summarized as follows. First, the substance was thought to be amorphous and not crystalline. Second, the specific gravity and the index of refraction were too low for apatite. Finally, the material always contained an appreciable amount of water, which was lacking in apatite. At that time Rogers (1914) did not consider that (OH) ever was an essential constituent of members of the apatite group, a view now known to be in error. Chemically, collophane was regarded as an amorphous "solid solution" of calcium carbonate, calcium fluoride, calcium sulfate and calcium oxide in tricalcium phosphate.

The idea is implicit in this and in later writings of Rogers, that the so-regarded amorphous minerals which approach in composition coarsely crystalline equivalents—the "homoisochemites" of Cornu, from whom

the idea stemmed—should be made distinct species. Collophane thus was viewed as the amorphous equivalent of dahllite (or, better, francolite). This belief, and the designation of collophane itself as a distinct species, probably would not have been entertained if x -ray diffraction methods had been available at the time. It is now known through x -ray studies, in every instance with which the writer is familiar, that the so-regarded amorphous species in Cornu's homoisochemic pairs is merely a fine-grained crystalline aggregate of its macrocrystalline analogue. In some instances the "amorphous" species is definitely crystalline, but different from its macrocrystalline analogue; for example, chrysocola and diop-tase.

The writer in connection with this and other studies has had occasion to examine by x -ray and optical methods a large number of substances which fall into Rogers' definition of collophane. Included here were 30 urinary calculi composed of an isotropic hydrous and carbonated calcium phosphate (Fron-del and Prien (1942)), samples of recent and fossil bone and teeth, phosphatized fossil wood, powdery "leached guano," and many samples of insular and continental phosphate rock. All of these substances gave distinct x -ray powder patterns of apatite and, when chemical analyses were available, could be identified as specific members of the apatite series. This also has been the experience of investigators concerned with living teeth and bone. The substance nauruite (which see), which Rogers stated to be the best and most typical form of collophane which it was his privilege to see, gives an excellent x -ray powder pattern of apatite and is identified as a carbonate-hydroxyl-fluor member of the apatite series (francolite). Collophane consists of a submicroscopic aggregate of crystallites of apatite, to which the isotropic character is due, and contains essential (OH) together with an indefinite amount of adsorbed and capillary water. The low and variable index and the low specific gravity are due to the content of non-essential water. Collophane is not a distinct species but is structurally identical with apatite. The name can conveniently be used as a varietal designation for fine-grained metacolloidal apatite.

EPIGLAUBITE

The name epiglaubite was given by Shepard (1856) to an unanalyzed mineral found in phosphate rock from Mong's Island (Los Monges) in the Caribbean Sea. The mineral was stated to occur as aggregates, or interleaved masses of minute semi-transparent crystals of a shining vitreous luster implanted upon druses of "glaubapatite." The substance was stated to consist largely of hydrous calcium phosphate, possibly also with magnesia and soda. Dana (1892) suggested with reason that the substance might be metabrushite (=brushite). Authentic specimens of

epiglaubite do not appear to be extant. A non-type specimen reputedly of epiglaubite from Mong's Island was available for examination and proved to consist entirely of fine-grained dolomite. The complete inadequacy of the original description is sufficient reason for discrediting this supposed species. For purposes of record, the name may be entered questionably as a synonym of brushite.

GLAUBAPATITE

The name glaubapatite was given by Shepard (1856) to a supposed sulfate-phosphate of sodium and calcium from a locality given as Mong's Island in the Caribbean Sea. The proper locality designation is Los Monges [The Monks, *Port.*], a collection of keys at the entrance to the Gulf of Maracaibo, Venezuela. In a later note, Shepard (1882) admitted analytical errors in the first description and withdrew the name. The mineral itself was then ascribed to pyroclaspite, a substance (which see) thought by Shepard to be possibly a mixture of monetite and monite (= apatite). A non-type specimen labeled glaubapatite and answering the original description was available from the Canfield collection of the National Museum. The specimen consisted of botryoidal monetite with white, earthy whitlockite overlying massive banded apatite and limestone. The name glaubapatite is best disposed of by placing it questionably in the synonymy of both monetite and apatite.

MARTINITE

Martinite was described by Kloos in 1888 as a new calcium phosphate from phosphate rock deposits at St. Barbara on Table Mt., on the south coast of the Island of Curaçao, Dutch West Indies. Under the microscope the mineral is described as sharp rhombohedrons [the crystals appear as flattened rhomboids], about 0.05–0.06 mm. in size, with plane angles of 75° and 105°. The extinction is parallel to the diagonals of the rhomboids, and it is stated that there is a distinct cleavage parallel to the edges of the plates. The writer's observations on these crystals and on similar crystals from Sombrero (zeugite), however, show that the supposed cleavage is only a closely repeated zonal growth. Two chemical analyses by Kloos are cited in numbers 1 and 2, below. F was shown to be absent. A part of the water was stated to be driven off only at an elevated temperature. A recent analysis cited in Hendricks, Hill, Jacob and Jefferson (1931) is given in number 3.

	CaO	MgO	P ₂ O ₅	H ₂ O	Organic	ign.	insol.	Rem.	Total
1.	46.78		47.67	4.52	0.75		0.20		99.92
2.	47.63		47.87	5.46					100.96
3.	44.58	3.28	38.42			5.43		5.74	97.45

Rem. in anal. 3 is CO₂ 1.54, SO₃ 0.98, Na₂O 1.86, K₂O 0.62, SiO₂ 0.47, Fe₂O₃ 0.27.

Two non-type specimens of martinite from Curaçao which answered the original description in every particular were available for study. One of these specimens has been analyzed and examined by *x*-rays by Hendricks, *et al.* (1931); the other specimen comprised the material studied optically by Larsen (1921). The *x*-ray powder pattern of the material from Curaçao is identical in all regards with that of whitlockite, β - $\text{Ca}_3(\text{PO}_4)_2$. Hendricks, *et al.* (1931) stated that martinite gives an *x*-ray powder pattern like that of $\text{Ca}_3(\text{PO}_4)_2$, but did not consider the identity of the two substances to be definitely proven. Under the microscope the mineral appears as flattened rhomboidal plates (rhombohedral) with plane angles of 75° and 105° , and otherwise is as described by Kloos. These angles would belong to a rhombohedron with a ρ angle of $63^\circ 42'$, and this corresponds to the ρ angle $63^\circ 58'$ of the rhombohedron $\{011\bar{2}\}$, which determines the principal habit of the whitlockite from granite pegmatite.

Several significant differences exist between martinite and whitlockite. Martinite has $\omega = 1.607$, $\epsilon = 1.604$, which compares to the values $\omega = 1.629$, $\epsilon = 1.626$ of type whitlockite. Larsen's (1921) interpretation of martinite, as probably monoclinic, is in error; he gives $Y = 1.605$, but the value 0.02 given for the birefringence probably is a misprint for 0.002. The indices of martinite vary slightly in successive zones in the crystal, and in the outermost zone are above the values given. Anomalous birefringence effects of both an hourglass and a zonal type are sometimes observed. Spherulitic growths of a more highly birefringent mineral with an index above 1.61, are present. Chemically, martinite differs principally in containing about 4.5 per cent water. It is a question as to how much of this water is essential, especially in view of the reported presence of 0.75 per cent organic matter. Pure grains of the mineral effervesce in warm HCl. Martinite is similar to zeugite (= whitlockite) in its low indices, in its seeming water content, and in the presence of CO_2 , but differs from pyrophosphorite (= whitlockite) which is identical with type whitlockite in all respects. The problem of the constitution of these minerals is discussed further under whitlockite.

The so-called martinite from Ascension Island in the South Atlantic, described by Richards (1928), proved on *x*-ray and optical study of the analyzed sample to be a mixture of monetite with small amounts of apatite and newberyite. The confusion with martinite arose both from the misprint for the birefringence of that species and from the fact that the optical data given for monetite at that time by Larsen (1921) are in error, and refer instead to gypsum.

METABRUSHITE

Metabrushite was described by Julien (1865) from the island of Sombrero in the West Indies. An analysis by Julien led to the formula $\text{CaHPO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, which differs only slightly from that of brushite, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. The crystallographic, physical, and pyrognostic properties also are very similar to those of brushite. Crystal measurements with a contact goniometer by J. D. Dana, quoted by Julien in the original paper, showed the mineral to be monoclinic with a perfect cleavage $\{010\}$. Dana pointed out similarities in interfacial angles and cleavage with brushite. Lacroix (1897) and others have maintained that the two species were identical. A type specimen of Julien's was available for study. The poor quality of the crystals precluded morphological measurements, but the optical properties and the x -ray powder pattern were the same as those of brushite and the identity of the two species must be accepted.

It may be noted that Hill and Hendricks (1936) found that fine-grained brushite spontaneously loses H_2O on standing, although not when coarsely crystallized, and the writer found that a powdered commercial "C. P." preparation of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ had almost entirely dehydrated in the stock bottle to monetite, CaHPO_4 . A number of different hydrates of CaHPO_4 have been reported, but these are said to be variable mixtures of CaHPO_4 and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. The observations of Bassett (1907, 1917) indicate that a compound with the supposed composition of metabrushite, $\text{CaHPO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, does not exist. Julien thus appears to have analyzed a partly dehydrated sample of brushite.

MONETITE

Monetite, CaHPO_4 , was first described by C. U. Shepard in 1882, who found the mineral in phosphate rock deposits on the islands of Moneta and Mona in the West Indies. The chemical and morphological descriptions (the latter by E. S. Dana, quoted in Shepard) leave no doubt of the species validity of the mineral. The crystallography of the natural mineral has since been shown to be identical with that of artificial crystals of CaHPO_4 . The optical data of Larsen (1921) apparently refer to gypsum, but the later data of Barth and Berman (1934) are close to the data of Hill and Hendricks (1936) for artificial CaHPO_4 . A type specimen of monetite from Moneta was obtained from the collection of C. U. Shepard, Sr., in the custody of the National Museum. X -ray powder and optical study of this material proved its complete identity with artificial CaHPO_4 , as described by Hill and Hendricks (1936). During the course of the present studies two new localities of monetite were found. The min-

eral occurs in phosphate crusts on Ascension Island, in the South Atlantic, where it is associated with apatite and newberyite; this occurrence was described by Richards (1928) as martinite (which see). Monetite also occurs as botryoidal crusts, associated with whitlockite, deposited upon massive phosphate rock on Los Monges Islands in the Caribbean Sea off the coast of Venezuela.

MONITE

Monite was named by Shepard (1882) from its occurrence on the Island of Mona, located in the Caribbean Sea about 40 miles from the port of Mayaguez, Puerto Rico. Found with monetite and gypsum as snow-white, slightly coherent and impalpable masses with an earthy fracture and a dull luster. The analysis by Shepard is cited below after deducting 4.64 per cent gypsum, and recalculating to 100 per cent.

CaO	P ₂ O ₅	H ₂ O	Total
51.15	41.92	6.93	100.00

A search for type specimens of this mineral was unsuccessful. Several non-type specimens were, however, available for study. These all proved on optical and x-ray study to be identical with carbonate-hydroxyl-apatite. Strunz (1939) also has found that the so-called monite from the Island of Mona, is apatite, but his specimens, too, doubtlessly were not of type material. The material examined by the writer comprised hard brownish crusts with a subresinous luster and did not answer the physical description of the original monite. The statement that monite melts on heating cannot be reconciled with the behavior of either whitlockite or apatite, but this effect may have been due to fluxing by admixed gypsum or monetite. The mineral may be considered to be probably identical with carbonate-hydroxyl-apatite. Dana placed monite under collophane in the sixth edition of the *System*.

NAURUITE

The name nauruite was given by Elschner (1913) to an oolitic or banded, agate-like, phosphate rock from the Island of Nauru in the Marshall Islands, Pacific Ocean. The material is brown in color, is often translucent in quite large fragments and has a resinous luster. A specimen presented by Elschner, through R. A. Daly to Harvard University, was available for study. The material gives a good x-ray pattern of apatite. An analysis of the Nauru phosphate, cited by Elschner, is given below.

CaO	MgO	(Fe, Al) ₂ O ₃	P ₂ O ₅	CO ₂	F	SO ₃	H ₂ O	ign. loss	Less O=F	Total
52.47	0.21	0.53	38.75	1.88	1.60	0.22	1.70	3.30	0.67	99.65

The material effervesces weakly in dilute HCl. Rogers (1922) states that material from Elschner examined by him contained about 5 per cent CO₂. Nauruite is strictly identified by the *x*-ray and the chemical data as a carbonate-hydroxyl-fluor-apatite (francolite), and is entitled neither to the name nauruite nor to the name collophane (which see), as applied by Rogers.

ORNITHITE

Ornithite is a name given by Julien (1865) to small monoclinic crystals found lining cavities in coral limestone and phosphate rock on the Island of Sombbrero in the West Indies. The crystals themselves are rough and not measurable but resemble brushite. Many of the crystals have ragged terminations and other characteristics which give them much the appearance of pseudomorphs. There is a good cleavage {010}, with traces of two other cleavages. An analysis by Julien gave:

CaO	MgO	(Fe, Al) ₂ O ₃	P ₂ O ₅	H ₂ O+organ.	Total
45.768	tr.	4.623	40.139	9.449	99.979

Of the total water, 3.918 per cent is lost below 250° C. and 5.154 per cent is lost on strong ignition.

One of Julien's type specimens was available for study. Optical examination, together with study by *x*-ray powder and rotation methods, proved this substance to be a pseudomorph consisting of carbonate-hydroxyl-apatite. The cleavage of the mineral is a parting inherited from the perfect {010} cleavage of brushite. *X*-ray rotation photographs taken about lath-like parting fragments gave the powder pattern of apatite, but with an additional definite semblance of layer lines due to local variations in intensity along individual powder reflections. The calculated period is 6.8 ± 0.1 Å, which corresponds to the value 6.88 Å for [0001] of apatite. The crystals are interpreted as composed of crystallites of apatite, which have a tendency for preferential orientation of their [0001] axes parallel to the direction of elongation of the original brushite crystals. Pseudomorphs of hydroxyl-apatite after brushite have been formed artificially by Bassett (1917) and others. Crushed fragments appear under the microscope as optically homogeneous laths with parallel extinction. $\omega = 1.625$, $\epsilon = 1.623$. The indices and the birefringence may be low due to the presence of adsorbed and capillary water in a mass composed of subparallel crystallites. The substance gives a weak test for CO₂ and probably is correctly classed as a carbonate-hydroxyl-apatite, although determinations of F and Cl are lacking.

PYROCLASITE

Pyroclaseite was originally described by Shepard (1856) from Mong's

Island (Los Monges) in the Caribbean Sea. Shepard stated the substance to consist of not far from 80 per cent of phosphate of lime and ten per cent of water, with the remainder made up of carbonate of lime, sulfate of soda, a little insoluble matter and traces of sodium and fluorine. The material did not give a CO_2 test but definitely contained F. In a later note, Shepard (1882) described a second occurrence of pyroclaspate from the Islands of Mona and Moneta. The mean of two analyses cited by Shepard is given below.

CaO	Fe, Al phosph.	SO_3	P_2O_5	H_2O , ign. loss	insol.	Total
40.125	2.900	6.825	39.080	10.335	0.885	100.120

Shepard deducted 20.847 per cent of extraneous matter, mostly gypsum, from this analysis and derived the formula $6\text{CaHPO}_4 \cdot \text{Ca}_3\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$. Shepard entertained some doubt as to the species validity of the mineral, however, and thought that the substance might be only a mechanical mixture of monetite and monite—a very probable explanation (see glaubapatite). Specimens of pyroclaspate from neither Mong's Island, nor Mona and Moneta could be found in the Shepard collection. A specimen labeled pyroclaspate from Jarvis Island, West Indies, was, however, available for study. The specimen consisted of massive red oolitic apatite with small open cavities lined with a crust of a creamy white, small botryoidal mineral with a greasy luster. The latter material gave the x -ray pattern of apatite and effervesced in dilute HCl. The physical properties and chemical composition of the original pyroclaspate from Los Monges leave little doubt but that this mineral is a member of the apatite series, perhaps a hydroxyl-fluorine-apatite.

PYROGUANITE

Pyroguanite is a name given by Shepard (1856) to the ordinary phosphate rock from Mong's Island (Los Monges) in the Caribbean Sea off the Gulf of Maracaibo. The substance was thought to have been guano thoroughly fused by the action of trap rock, and to consist of two species, pyroclaspate and glaubapatite (which see). Shepard's notion of the origin of the material was gained from Captain A. F. Winslow of the sailing ship *Jane Dolen*. Winslow's ship had been forced by storm into the port of Charleston, South Carolina, in 1856, where Shepard examined its cargo of rock phosphate.

PYROPHOSPHORITE

The name pyrophosphorite was given by C. U. Shepard, Jr., in 1878, to a supposed anhydrous calcium pyrophosphate found in phosphate rock from an unnamed locality in the West Indies. Two closely agreeing chem-

ical analyses were given, and their mean is cited below.

CaO	MgO	(Fe, Al) ₂ O ₃	P ₂ O ₅	SO ₃	SiO ₂	ign. loss	Total
44.462	3.090	0.437	50.799	0.628	0.367	0.390	100.173

Specimens of snow-white, earthy pyrophosphorite from the collection of C. U. Shepard, Sr., were available for study. X-ray powder photographs of the mineral were identical in every respect with those of whitlockite, β -Ca₃(PO₄)₂. The mean index was 1.625 ± 0.003 , and the birefringence was estimated at about 0.003. These data agree closely with those for whitlockite ($\omega = 1.629$, $\epsilon = 1.626$). The substance was not entirely homogeneous but contained several per cent, at least, of an unidentified mineral with indices below 1.62. Samples of the material effervesced in spots when treated with acid, but this appears to be due only to admixture. The question of the variation in the apparent water content and in the indices of refraction of pyrophosphorite, zeugite, and martinite, all of which are identical with whitlockite, is discussed further under whitlockite.

SOMBRERITE

The name sombreroite was proposed by Phipson (1862) for a substance composed largely of tricalcium phosphate found as rock masses on the Island of Sombrero in the West Indies. Phipson's account of the material and later remarks by Julien (1863) leave no doubt that the description refers not to a specific mineral species but to the ordinary phosphate rock, *en masse*, mined at the locality. Specimens labeled sombreroite from Sombrero were found in several collections. These proved on optical and x-ray study to be apatite.

STOFFERTITE

Stoffertite is a name given provisionally by Klein (1901) to a mineral from the phosphate rock deposits on the Island of Mona in the West Indies. The morphological and optical properties agree exactly with those of brushite, but stoffertite was thought to differ from this species in having a slightly higher water content. This is very scant evidence for proposing a new species. It may be noted that hydrates other than CaHPO₄·2H₂O have not been found (cf. Bassett (1907, 1917) and de Schulten (1903)) in the system CaHPO₄-H₂O. Specimens of stoffertite were not available for examination. The mineral, however, is probably identical with brushite.

WHITLOCKITE

Whitlockite, β -Ca₃(PO₄)₂, was originally described by the writer in 1941. The mineral was found as large rhombohedral crystals as a hydro-

thermal product in a granite pegmatite at the Palermo quarry, North Groton, New Hampshire. Whitlockite is identical with the low temperature polymorph of artificial anhydrous tricalcium phosphate, β - $\text{Ca}_3(\text{PO}_4)_2$, described by Trömel (1932) and others. The optical data for β - $\text{Ca}_3(\text{PO}_4)_2$ given by Schneiderhöhn (Trömel (1932)) are cited in Table 2. Photographs of the x -ray powder pattern are given by Trömel (1932), and Trömel and Möller (1932), and the spacing data by Bredig, Franck and Fuldner (1932). The x -ray spacing data for analyzed crystals of the natural mineral are given in Table 1. The x -ray pattern and optical properties of the high temperature modification, α - $\text{Ca}_3(\text{PO}_4)_2$, differ con-

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR WHITLOCKITE
Analyzed crystals from North Groton, N.H. Cu radiation

d	I	d	I	d	I
8.03	2	2.25	2	1.60	1
6.55	5	2.19	2	1.55	5
5.24	8	2.16	2	1.46	1
4.07	4	2.07	1	1.43	1
3.45	7	2.04	2	1.40	1
3.35	1	2.00	1	1.38	1
3.21	9	1.93	6	1.25	2
3.02	1	1.88	5	1.24	2
2.88	10	1.82	1	1.18	1
2.75	3	1.77	3	1.15	1
2.68	1	1.72	7	1.11	3
2.60	9	1.70	1	1.09	1
2.52	2	1.67	2	1.05	1
2.41	2	1.63	1	1.03	1

siderably from those of the beta form. The inversion temperature is about 1180° according to Bredig, *et al.* (1932). A complete survey of the work on the basic calcium phosphates, and related systems, is given by Eisenberger, Lehrman and Turner (1940).

In the course of the present study, zeugite of Julien (1865) from Sombrero, pyrophosphorite of Shepard (1878) from an unknown locality in the West Indies, and martinite of Kloos (1888) from Curaçao, were found to be identical with whitlockite. A fourth new occurrence of whitlockite was found in phosphate rock from Los Monges Island in the Caribbean Sea. The mineral formed soft, earthy, white to gray masses under a botryoidal crust of monetite. In these occurrences, whitlockite has formed from water solutions under essentially atmospheric conditions of temperature and pressure; in two instances the mineral occurred as pseudomorphs after hydrated minerals, brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) and gypsum

($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The natural occurrences of whitlockite are unusual in that all attempts to synthesize $\text{Ca}_3(\text{PO}_4)_2$ from water solutions have resulted in the formation of hydroxyl-apatite. Both the alpha and beta modifications of $\text{Ca}_3(\text{PO}_4)_2$ hitherto have been known only as high temperature products from dry systems.

The material from some of the occurrences in insular phosphate deposits is of special interest in that it differs from type whitlockite and artificial $\beta\text{-Ca}_3(\text{PO}_4)_2$ in having relatively low indices of refraction and a relatively high (Ca, Mg)O:P₂O₅ ratio, and in the presence of carbon dioxide and a considerable amount of possibly essential water. The data are summarized in Table 2.

TABLE 2. OPTICS AND COMPOSITION OF WHITLOCKITE

	$\beta\text{-Ca}_3(\text{PO}_4)_2$, Artificial	Whitlockite, North Groton	"Pyrophosphorite," West Indies	"Zeugite," Sombbrero		"Martinite," Curaçao	Whitlockite, Los Monges
$\omega(\text{Na})$	1.622	1.629	} 1.625	1.608		1.607	} 1.600
ϵ	1.620	1.626		1.605		1.604	
CaO	54.22	46.90	44.462	44.18	44.24	46.78	present
MgO	—	2.53	3.090	3.25	3.92	—	
P ₂ O ₅	45.78	45.68	50.799	47.07	46.03	47.67	
H ₂ O	—	0.48	0.39	2.99 ²	2.97 ²	4.52	
CO ₂	—	none	none	present		present	
(Ca,Mg):P:O S.G.	3:2:8 3.19 (calc.)	2.97:2.01:8 ¹ 3.12	2.62:2.15:8 —	2.75:2.10:8 2.83:2.07:8 2.971		2.65:2.14:8 2.896	

¹ 1.91 per cent FeO and 1.73 per cent Fe₂O₃ as FeO have been added to the sum of the XO as given in calculating the ratio (Ca,Mg):P:O.

² Includes organic matter.

The divergence of the analyses from the requirements of $\text{Ca}_3(\text{PO}_4)_2$ can be ascribed to analytical error and, especially in the case of pyrophosphorite, to admixture. The role of the water reported in the analyses of the material from Sombbrero and Curaçao, is quite uncertain. Part of the water, at least, is non-essential. The material from both of the localities when heated gently in a closed tube loses water, gives off an organic odor and turns a deeper shade of color. Zeugite when heated in air at 925° for one hour turned dead-white in color and lost 3.69 per cent in weight. The x-ray powder pattern of the heated material is still identical with that of whitlockite. The x-ray pattern and indices of whitlockite did not change when the mineral was heated at 930° for two hours.*

* Whitlockite exhibits a peculiar color change when cooled. The material assumes an orange-yellow color when the temperature drops below red heat, and this color gradually changes to yellow on further cooling. The material becomes pure white again when the temperature drops below ca. 200°. A similar behavior was found by Bassett (1917) for ig-

The whitlockite from Curaçao, Sombrero, and Los Monges gives a definite CO_2 test, as previously noted, but "pyrophosphorite" and type whitlockite from granite pegmatite does not contain CO_2 . The carbonated and seemingly hydrous material is distinguished from the other material by relatively low indices of refraction (see Table 2). It has been established with some certainty, through the work of McConnell and Gruner (1937, 1940), that carbon can substitute isomorphously for Ca, P, or both, in the apatite series, with a concomitant decrease in the indices of refraction. The existence of this substitution in whitlockite must now be considered very probable. The zoning in the crystals presumably reflects variations in the Ca, P/C ratio. Zoned carbonate-apatite crystals have been described by McConnell and Gruner (1940). It is questionable whether the low indices also are connected with the presence of water, either essential or non-essential, in the crystals. Possibly (OH) substitutes for O in the PO_4 groups, but there is no increase in birefringence, nor is there reason to expect the indices to be markedly lowered thereby unless there was also an increase in cell dimensions. The x-ray photographs do not indicate any change in the dimensions of the cell. If (OH) does not enter the constitution of carbonate-whitlockite, it appears necessary for C to substitute equally for both Ca and P, in order to maintain electrical neutrality. The indices of the whitlockite from North Groton are probably slightly high as compared with pure $\text{Ca}_3(\text{PO}_4)_2$, due to the presence of iron in isomorphous substitution.

The question of the priority of the names of natural $\beta\text{-Ca}_3(\text{PO}_4)_2$, also arises. The name zeugite of Julien (1865) was first published, but the original description is so incomplete and, insofar as the chemical interpretation is concerned, erroneous, that the mineral could not again be recognized without a complete re-examination of the original material. None of the three later workers, who unwittingly described the same substance, was led to suspect the true nature of zeugite. As a matter of fact, Julien himself did not view the substance as a very definite species, and considered it to be an amorphous, accidental product, composed of variable proportions of a hypothetical compound, $8\text{CaO} \cdot 3\text{P}_2\text{O}_5$, for which the name was intended. The mere proposal of a name and a few non-definitive observations are not sufficient to establish and maintain a mineral species. Similar remarks apply to martinite of Kloos (1888), and especially to pyrophosphorite of Shepard (1878). The characterization of martinite was further complicated by two erroneous later descriptions.

nited hydroxyl-apatite, who showed that it was due to the presence of traces of copper oxide and not to rare-earths. The writer also observed that ignited hydrated tricalcium phosphate (hydroxyl-apatite) prepared according to the method of Hendricks *et al.* (1931) took on a very faint lilac tint when cooled.

Often a more or less vague early name can be retained if there is any definite reason for believing that a later found substance corresponds to the original material, in order to avoid further burdening the synonymy of the science. In the present case, however, it appears proper to retain the name whitlockite for the species.

ZEUGITE

The name zeugite was given by Julien (1865) to the substance of certain porous pseudomorphs after metabrushite (= brushite) from the Island of Sombrero in the West Indies. The two analyses given by Julien are cited below. Julien considered the principal constituent of the mineral to have the composition $8\text{CaO} \cdot 3\text{P}_2\text{O}_5$ and the remainder to be due to admixture.

	CaO	MgO (Fe,Al) ₂ O ₃	P ₂ O ₅	CO ₂	SO ₃	F	NaCl	H ₂ O+ org.	Total	
1.	44.18	3.25	0.54	47.07	tr.	0.39	tr.	n.d.	3.07	98.50
2.	44.24	3.92	0.78	46.03	0.48	tr.	tr.	1.08	2.97	99.50

One of Julien's original specimens and several non-type specimens were available. X-ray powder photographs of the mineral were identical in every respect with that of whitlockite, $\beta\text{-Ca}_3(\text{PO}_4)_2$. Under the microscope the mineral corresponds in every particular to crystals of martinite. The indices are: $\omega = 1.608$, $\epsilon = 1.605$. Julien's two analyses are in rather poor agreement with the requirements for $(\text{Ca}, \text{Mg})_3(\text{PO}_4)_2$. The phosphorus was determined by a relatively inaccurate method and may be somewhat in error. The role of the water reported in the analyses is quite uncertain; part of it without doubt is non-essential. Pure grains of the mineral give a CO₂ test with warm HCl. Zeugite is identical with martinite in its low indices, apparent water content, and in the presence of CO₂. Both substances differ from pyrophosphorite (= whitlockite) and type whitlockite in these respects. The problem of the constitution of these substances is discussed further under whitlockite. Strunz (1939) found a supposed specimen of zeugite to be identical with apatite, but his material could not have been authentic.

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