THE DUFRENITE PROBLEM*

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Abstract

It is shown that several different basic iron phosphates have been confused since earliest times under the name dufrenite. The history and nomenclature of the subject is reviewed in detail. The specific name dufrenite is here re-defined to apply to a particular mineral of the dufrenite-complex, and the new name rockbridgeite is proposed for the other common member of this complex.

Both dufrenite proper and rockbridgeite are shown to be basic phosphates of ferrous and ferric iron that ordinarily are found in a more or less oxidized condition, analogous to vivianite. Dufrenite has the probable formula $Fe''Fe'''_4(PO_4)_3(OH)_5 \cdot 2H_2O$ and while crystals are seemingly orthorhombic the substance is probably monoclinic. Hirschberg, Thuringia, may be taken as the type locality and seven other localities are described. Rockbridgeite has the probable formula $Fe''Fe'''_6(PO_4)_4(OH)_8$ and is monoclinic or triclinic. Midvale, Rockbridge County, Virginia, may be taken as the type locality and eight other localities are described. *X*-ray diffraction patterns, optical and physical properties and other characterizing data are given for both dufrenite and rockbridgeite. Dufrenite may be dimorphous with beraunite. Rockbridgeite may be isostructural with chenevixite but not with chalcosiderite. The earliest stage of alteration of dufrenite and rockbridgeite is marked by conversion of Fe'' to Fe''' with accompanying slight leaching of P_2O_5 but without any marked change in the *x*-ray diffraction pattern; this stage is followed by a more or

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less complete removal of P_2O_5 with the formation of hydrous iron oxide and the destruction of the crystal structure.

Laubmannite, a second new but rare species separated from the drufrenite-complex, has the formula $Fe''_3Fe'''_6(PO_4)_4(OH)_{12}$ and is isostructural with andrewsite, the copper analogue. Laubmannite occurs at Shady, Polk Co., Arkansas, and probably at the Nitzelbuch mine, Amberg district, Bavaria. Characterizing *x*-ray, optical and other data are given for this species and also for two other probably new but unnamed dufrenite-like minerals. Beraunite is shown to be, like dufrenite and rockbridgeite, a more or less oxidized basic ferrous-ferric phosphate and not a straight ferric phosphate as hitherto considered. A new occurrence of beraunite at Middletown, New Jersey, is described. Five new chemical analyses are reported, including one each of beraunite, laubmannite, and dufrenite and two of rockbridgeite. The reported analyses of other minerals in the dufrenite-complex that cannot definitely be shown to belong to either dufrenite or rockbridgeite are discussed.

An iron phosphate from Wheal Phoenix, Cornwall, described by Kinch and Butler to which the name sjögrenite was later applied by Krenner in the belief that it differed from other dufrenite-like minerals, is shown to be identical with ordinary dufrenite. Krenner almost certainly mistook chalcosiderite for Kinch and Butler's mineral, and the name sjögrenite should not be adopted in his meaning as urged by Quensel but be retained for the carbonate-hydroxide to which it is presently applied.

INTRODUCTION

Dufrenite is widespread in nature, but our knowledge of the mineral has been very unsatisfactory in all respects, particularly with regard to its crystallography and chemical composition. A survey of numerous Museum specimens labelled dufrenite and representing 17 different localities, many of them already described in the literature, has now revealed that several different basic iron phosphates have been confused under the name from earliest times. Two of these substances are almost equally common, and these together comprise the source material of most of the already published data relating to the supposedly single species dufrenite. It has not yet proven possible to achieve a complete description of any of these substances, however, and the purpose of the present paper is to draw attention to the problem and to record the data already at hand. A characterizing description of dufrenite proper, as here defined, and of the several dufrenite-like substances recognized during the course of the work is given on the following pages.

HISTORICAL SURVEY

The basic iron phosphate called dufrenite was first recognized as a distinct entity by Werner and other mineralogists of his time under the name *grüneisenerde*. Ullmann, writing in 1814, referred to the mineral as *grüneisenstein*, including both *strahlicher* and *ochrichter* varieties, and cited the Offhäuser and Mittelberg iron mines in the Hollerter Zug, Siegen, Westphalia, as the only localities known to him. *Fasrige*, *dichte*, *zerreibliche* and other physical varieties also were distinguished by other early writers, and there is little doubt but that several different minerals of similar appearance or constitution were confused with the true dufrenite. Chalcosiderite was separated from *grüneisenstein* by Ullmann in 1814. The mineral was thought at that time to be an iron oxide, and Haüy as late as 1822 referred to it as *fer oxidé, terreaux, jaune verdâtre.* The chemical composition of the mineral was first established by the analyses of Vauquelin in 1825 and of Karsten in 1827.

Vauquelin's mineral, not referred to by a specific name, came from a pegmatite at an unstated locality in Haute-Vienne, France. His analysis, cited beyond in Table 3, showed a very high content of MnO. A significant content of manganese is characteristic of dufrenite from pegmatites, where it ordinarily forms as an alteration of triphylite or other iron-manganese phosphates, but manganese is nearly or entirely lacking in dufrenite from iron-ore deposits, gossans or sedimentary formations. Our present knowledge of dufrenite is largely based on material from the latter types of occurrence and the mineral has been long accepted as essentially a phosphate of iron rather than of manganese. Vauquelin's material, in light of the new findings reported here, apparently corresponds to a manganese analogue of dufrenite. It seems advisable to retain the modern use of the name and apply it to an iron phosphate, or the iron-rich portion of an isomorphous series with a corresponding manganese-iron phosphate rather than to revise the established nomenclature. As will be seen, there are additional complications in the nomenclature of dufrenite, so-called, and this preliminary simplification of the problem is very desirable. An added justification for this suggestion is that there is some uncertainty as to the true identity of Vauquelin's mineral.

Karsten, who was unaware of the work of Vauquelin, gave in 1827 what can be considered to be the first definitive description of the substance later known as dufrenite. His material, referred to as *grüneisenstein*, came from an unstated locality in the Hollerter Zug at Siegen. Karsten's analysis, cited in Table 3, established the mineral as a hydrated phosphate of iron which approximated the formula $2Fe_2O_3 \cdot P_2O_5 \cdot 2\frac{1}{2}H_2O$, but it was remarked that this formula was uncertain because a significant although unknown amount of ferrous iron was present in the mineral. Nevertheless, most later workers have regarded the substance as a straight ferric compound, and the formulas $2Fe_2O_3 \cdot P_2O_5 \cdot 3H_2O$ and $5Fe_2O_3 \cdot 3P_2O_5 \cdot 8H_2O$, among others, have been proposed to represent the mineral.

A specific name, dufrénite, was first applied to the mineral in 1833 by Brongniart. According to P. A. Dufrénoy, after whom the mineral was named, Brongniart's specimens came from Hirschberg, Westphalia, and Anglar, Haute-Vienne, France. The Hirschberg locality, actually in

Thuringia, is on the Saale river about ten miles from Hof; and the locality Anglar, itself a mistake for Angelard, was confused by Dufrénoy with the occurrence of another mineral, angelardite (=vivianite), the true locality of Brongniart's mineral being Huréaux en Saint-Sylvestre in Haute-Vienne as shown by Lacroix. This probably is the locality of the specimens analyzed by Vauquelin. Some years later, in 1841, the name kraurite was proposed for the species by Breithaupt for lack of knowledge of Brongniart's name. This name is still used in preference to dufrenite in some German literature, although it clearly lacks priority.

DUFRENITE

It is here proposed, as a means of procedure, to select the earliest described occurrence of grüneisenstein that can be recognized as dufrenite, in the broad sense, and to arbitrarily establish it as dufrenite proper. Vauquelin's mineral is unsatisfactory for the purpose for reasons already indicated, aside from being unavailable, and the minerals of Karsten and of Brongniart must next be considered. Karsten's material would be ideal for the purpose if his original specimens were available. In lack of this material, recourse might be made to a specimen from exactly the same locality that his came from. Unfortunately, Karsten gave the locality only as the Hollerter Zug,[1] near Siegen, Westphalia, which includes at least several known localities for dufrenite. Two specimens of dufrenite from the Siegen area, one labelled simply Siegen, Westphalia, and the other as near Herdorf, Westphalia, were available to the writer. These specimens proved to be different. The former specimen, however, was identical with two specimens from the Hirschberg, Thuringia, locality named by Dufrénoy. It is here proposed to restrict the name dufrenite to this particular mineral. Specimens from the Huréaux locality of Dufrénoy were not available for study.

X-ray powder diffraction patterns afford the only certain means of distinguishing between the various dufrenite-like minerals. The *x*-ray powder pattern of dufrenite as here defined is given in Table 16. Identical patterns were afforded by material from seven other localities as listed in Table 1. These are at present the only proven localities for the mineral but doubtless others will be established from among the numerous localities for so-called dufrenite described in the literature.

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[1] A name given to a linear group of siderite veins extending for some miles near Siegen, and representing one of a number of named vein-systems in the central iron-ore district of Westphalia between Siegen and Altenkirchen. The Hollerter Zug is part of the larger Eiserfelder Gangzug. There are also individual iron mines named Hollertszug near Dermbach, at Offhausen and at Herdorf in the Daaden-Kirchen area of this district.

Crystallography. None of the specimens from the localities listed afforded suitable material for either morphological or single-crystal *x*-ray study. With the exception of the crystals from the Wheal Phoenix, described below, the mineral occurs as crusts and botryoidal masses with a divergent fibrous structure. *X*-ray rotation photographs taken about the direction of elongation of seemingly single fibers gave powder patterns with very broadly marked intensity maxima unsuited for the measurement of the fiber period and indicating a considerable departure from parallelism of the individual fibrils. The Wheal Phoenix mineral is composed of tablets grouped together in subparallel, sheaf-like aggregates that are superficially altered to limonite. Cleavage fragments are markedly composite and it proved impossible to obtain usable single-crystal *x*-ray photographs. Some of the specimens of this mineral apparently were unaltered on the surface because Miers, in a note appended to the paper by Kinch and Butler in which this mineral was first described, gave some approximate crystallographic measurements. Miers described the crystals as orthorhombic tablets flattened on {010} and bevelled at the sides by small faces of {110}, {001} and a rounded brachydome. His best measurements gave 86°26′ for the prism angle ($\phi=46°47'$) and 12°45′ for the brachydome to the base. These measurements are fairly close to those obtained by Streng on relatively well developed crystals from the Rothläufchen mine, Waldgirmes, Hesse. Streng's crystallographic data, the best available for any of the dufrenite-like minerals, indicate his mineral to be orthorhombic. The crystals are cuboidal in habit with {100}, {010} and {011} as principal forms, the latter form more or less rounded, with small faces of {110} and {120}. His measured angles, tabulated below,

TABLE 1. PROVEN LOCALITIES FOR DUFRENITE

Siegen, Westphalia. (Dark olive green to olive brown radial fibrous crusts with a botryoidal surface on limonite.)

Hirschberg, Thuringia. (Radial fibrous aggregates of olive brown to greenish black color in limonite and quartz. Here taken as the type locality.)

Wheal Phoenix, Cornwall. (Sub-parallel aggregates and crusts of rectangular plates on limonite. Also as dark greenish black botryoidal crusts with a radial fibrous structure on limonite.)

Hauptmannsgrün, near Reichenbach, Saxony. (Dark greenish black botryoidal crusts with a fibrous structure, on limonite.)

Ullersreuth, Saxony. (Dark greenish black to olive green botryoidal crusts with a fibrous structure on limonite.)

Leobenstein, Thuringia. (Olive brown to greenish black radial fibrous masses on limonite.)

Rock Run, Cherokee Co., Alabama. (Thick radial fibrous crusts on limonite. Color dark greenish black; luster brilliant.)

Rothläufchen mine, Waldgirmes, Hesse. (This material, described by Streng, is probably but not certainly identical with dufrenite.)

give the ratio 0.873:1:0.426. Neither Miers' nor Streng's observations, if the latter are relevant, are sufficiently good to definitely establish the symmetry as orthorhombic.

	ϕ	ρ
010	0°00′	90°00′
100	90°00′	90°00′
110	48°52′	90°00′
120	29°47′	90°00′
011	0°00′	23°05′

Physical Properties. Dufrenite ordinarily occurs as botryoidal masses or crusts with a radial fibrous structure. The surface of the crusts sometimes is drusy and composed of sub-parallel grouped crystals with rounded or exfoliated terminations. Distinct crystals, such as those from the Wheal Phoenix and from Waldgirmes, are rare. The color is dark green or olive green grading to greenish black. The mineral alters readily, first by more or less complete oxidation of the ferrous iron present with an accompanying change in color to shades of olive brown to reddish brown but with retention of other properties, and finally becomes brown or yellow-brown with an ochreous consistency. The hardness is 3½ to 4½. The values reported for the specific gravity of so-called dufrenite vary over a wide range, no doubt due to the fibrous character of the mineral and to variation in the degree of alteration. Some of the measurements reported in the literature can not be ascribed to a definite species. These include the values 3.500–3.555 of Ullmann, 3.4987–3.5609 of Karsten and 3.534 of Diesterweg on Hollerter Zug material, and the value 3.872 of Bořicky on material from St. Benigna, Bohemia. New determinations on the microbalance of material known definitely to belong either to dufrenite or rockbridgeite are given in Table 2 together with values reported in the

TABLE 2. SPECIFIC GRAVITY OF DUFRENITE AND ROCKBRIDGEITE

Locality	Dufrenite		Locality	Rockbridgeite	
	New	Lit.		New	Lit.
Siegen	3.29		Rockbridge	3.37	3.383 3.454
Hirschberg	3.33	3.227	Palermo	3.33	
Wheal Phoenix, fibrous		3.08	Fletcher	3.45	
Wheal Phoenix, crystals		3.233	Herdorf	3.40	
Ullersreuth	3.34		Hagendorf	3.38	
Alabama	3.34		Ullersreuth	3.33	

literature for material from the same localities. The most representative value for the species is probably 3.34. Bořicky's value, 3.872, is entirely out of line and either is in error or does not represent the minerals at hand. The optical properties of dufrenite are described and tabulated on a following page in connection with the description of rockbridgeite.

Chemical Composition. Chemical analyses are available for only three of the occurrences here established as belonging to dufrenite proper (Columns 3, 4, 5 in Table 3). These are of the fibrous and crystallized types of the mineral from the Wheal Phoenix, Cornwall, described by Kinch and by Kinch and Butler, respectively, and of the material from Rock Run, Alabama, analyzed by Wells.[2] Kinch derived the formula $Fe''Fe'''_6(PO_4)_4(OH)_8 \cdot 4H_2O$ from his analysis after deducting the CaO and MgO as impurities. If these cations are taken to be essential constituents, as seems likely, the ratio of $RO:R_2O_3$ becomes significantly higher than that expressed by the formula (1.28:6 instead of 1:6). Kinch and Butler's analysis differs from that of Kinch in that it entirely lacks FeO

Table 3. Chemical Analyses of Dufrenite and of Some Related Minerals

	1.	2.	3.	4.	5.	6.
CaO			1.68	1.50		
MgO			0.17	tr.		
FeO			6.80		2.2	1.53
MnO	6.76					
Fe_2O_3	56.2	63.45	47.03	55.63	56.5	60.20
Al_2O_3			0.87			
P_2O_5	[27.84]	27.72	31.10	30.26	31.8	31.82
H_2O	9.2	8.56	11.47	10.62	9.1	8.03
Rem.			0.43	1.48	0.1	
Total	[100.00]	99.73	99.55	99.49	99.7	101.58
G			3.08	3.233		3.39

1. Huréaux (?), France. Vauquelin analysis. 2. Hollerter Zug, Westphalia. Karsten analysis. 3. Dufrenite, Wheal Phoenix, Cornwall. Fibrous type. Kinch analysis. Rem. is SiO_2. 4. Dufrenite, Wheal Phoenix. Crystals. Kinch analysis in Kinch and Butler. Rem. is SiO_2 0.53, CuO 0.95. 5. Dufrenite, Rock Run, Alabama. Wells analysis, 1939. Published by permission of the U. S. Geol. Survey. Rem. is SiO_2. 6. Dufrenite (?) Waldgirmes, Hesse. Streng analysis.

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[2] The writer is indebted to the U. S. Geological Survey for permission to use this hitherto unpublished analysis.

and nearly lacks other divalent cations that might substitute therefor. Since the two minerals are found by *x*-ray study to be structurally identical, it may be supposed that divalent iron was originally present in Kinch and Butler's material and was later oxidized to the ferric condition without accompanying structural changes of consequence. Wells' analysis of the Alabama material contains a small and irrational amount of FeO and also may be considered to be partly oxidized. On this assumption, all three analyses together with the analysis by Streng of the Waldgirmes mineral (which is apparently identical with true dufrenite on crystallographic grounds) may be arbitrarily calculated to a series of simple ratios between R_2O_3 and P_2O_5 with concomitant conversion of excess Fe_2O_3 to FeO. A selected set of relatively simple ratios calculated in this way is given in Table 4. The best formula for the mineral is taken as

$$Fe''Fe'''_4(PO_4)_3(OH)_5 \cdot 2H_2O$$

TABLE 4. SOME CALCULATED RATIOS FOR DUFRENITE ANALYSES

Analysis in Table 3	RO : R_2O_3 : P_2O_5			Calculated per cent FeO	Calculated per cent Fe_2O_3	Ideal formula
3. Kinch	1.28	3	2.17	Analysis ratio		
4. Kinch and Butler	0.90	3	2	4.09	51.08	$FeFe_6(PO_4)_4(OH)_8 \cdot nH_2O$
5. Wells	0.63	3	2	5.04	53.34	
6. Streng	0.918	3	2	7.39	53.69	
3. Kinch	2.98	7	5.06	Analysis ratio		
4. Kinch and Butler	3.24	7	5	7.15	47.68	$Fe_3Fe_{14}(PO_4)_{10}(OH)_{18} \cdot nH_2O$
5. Wells	2.48	7	5	7.98	50.08	
6. Streng	3.30	7	5	10.63	50.09	
3. Kinch	2.06	4	3	8.37	45.29	
4. Kinch and Butler	2.34	4	3	8.19	45.41	$FeFe_4(PO_4)_3(OH)_5 \cdot nH_2O$
5. Wells	1.88	4	3	10.12	47.70	
6. Streng	2.38	4	3	12.77	47.71	
3. Kinch	3.42	5	4	11.00	42.37	
4. Kinch and Butler	3.79	5	4	11.75	42.57	$Fe_2Fe_5(PO_4)_4(OH)_7 \cdot nH_2O$
5. Wells	3.18	5	4	12.84	44.72	
6. Streng	3.84	5	4	13.93	44.72	

This formula is preferred over $Fe''Fe'''_6(PO_4)_4(OH)_8 \cdot H_2O$, which is just about as satisfactory on an oxide-ratio basis, because it brings Wells' analysis better into line and gives also very exact ratios for Kinch's analysis. As already pointed out, the latter analysis, if taken as correct, contains too much RO, even before any correction for partial oxidation, to fit a formula based on $R_2O_3:P_2O_5=3:2$. It might also be noted that several analyses high in RO of dufrenite-like minerals that have been reported in the literature but which can not be associated with any definite species, for lack of *x*-ray data, also conform to the formula given. These analyses are described in a following section. The mineral beraunite, discussed beyond, may have the same formula as dufrenite and thus be dimorphous with that species.

The above line of interpretation is also taken in the case of the new minerals rockbridgeite and laubmannite, described beyond. The interpretation of all of these minerals as more or less oxidized compounds of both ferrous and ferric iron, rather than as straight ferric compounds as done earlier, is also indicated by the following more general considerations:

(1) Ca and Mg are often present in small but significant amounts which do not yield any simple or systematic numerical relation to Fe''' or P. This suggests that these cations were originally present in substitution for another divalent cation, presumably Fe'', that has since been "lost" by oxidation.

(2) Ferrous iron itself is commonly present in small and irrational amounts, and in some analyses reaches an apparent maximum of roughly 8 weight per cent FeO. This circumstance suggests that the low values of FeO represent cases of partial oxidation. The situation thus would be somewhat similar to that obtaining with vivianite.

(3) Manganese is sometimes present in small, irrational amounts in the divalent but not trivalent state. The non-oxidation of manganese from Mn'' to Mn''', while the original Fe'' has at the same time gone over to Fe''', would reflect the higher oxidation potential of this element relative to iron, a fact exemplified in the oxidation of lithiophilite-triphylite.

(4) Laubmannite, a new basic ferrous-ferric phosphate described beyond, is isostructural with the mineral andrewsite which is a basic phosphate of ferric iron and divalent copper. Laubmannite, however, contains a large excess of ferric over ferrous iron, and a formula analogous to that of andrewsite with Fe'' equivalent to Cu'' is obtained only when some ferric iron is converted to ferrous as argued in the case of dufrenite.

(5) Rockbridgeite may be isostructural with chenevixite, a basic arsenate of ferric iron and divalent copper, and ferrous iron would be structurally equivalent with the copper. Rockbridgeite affords rational formulas only when treated analogously to dufrenite and laubmannite.

Sjögrenite. The specimen from the Wheal Phoenix described earlier is part of the type material of Kinch and Butler and is of particular interest because of a knotty problem in nomenclature connected therewith. The specimen itself was acquired by the Harvard Museum in 1943 from Mr. Hugh A. Ford, a mineral collector and dealer, who had obtained it directly from Mr. F. A. Butler with the assurance that it was one of the original specimens described by him and Kinch. Kinch and Butler had found that the mineral differed somewhat in composition from that often attributed to dufrenite ($2Fe_2O_3 \cdot P_2O_5 \cdot 3H_2O$), a matter already discussed, but referred to it as "dufrenite?" and did not propose a new name. The closing sentence of their paper reads "Having regard to the conclusions we have so far arrived at, it is not our intention to propose a new name for this mineral." In the 10th International Geological Congress, held in Stockholm in 1910, the Hungarian mineralogist J. A. Krenner gave an informal talk, recorded by the Secretary of the meeting, P. Quensel, in the Procès-Verbaux, in which it was stated that Kinch and Butler's material has a domatic cleavage, inclined extinction and is triclinic. No measurements are cited and no statement is made of the authenticity of the specimens. Krenner proposed the new name sjögrenite after the Swedish mineralogist Hjalmar Sjögren. Krenner's name did not receive notice in the abstracting journals and general reference works until it was mentioned, without reference, thirty years later in Klockmann-Ramdohr's *Lehrbuch* (1942) and Strunz's *Tabellen* (1941). These works were not available in the United States until 1945 because of the war. In 1941, the present writer, unaware of Krenner's remarks and finding no prior use of sjögrenite proposed this name for a new member of the hydrotalcite group. In 1945, Quensel published a note drawing attention to the matter and urged retention of the name for the Wheal Phoenix mineral. The present study, however, proves that Kinch and Butler's mineral is identical with minerals earlier described as dufrenite including what is here considered to be the type material. In view of this, the writer would prefer to see the name sjögrenite preserved as a species designation for the carbonate-hydroxide mentioned rather than relegate it to the synonymy of dufrenite.

Krenner's statements definitely indicate that he examined chalcosiderite instead of dufrenite. Chalcosiderite has domatic cleavage, inclined extinction and is triclinic, in accordance with Krenner's description, and occurs not only at Wheal Phoenix but on some at least of the type specimens of the Wheal Phoenix dufrenite. Kinch and Butler do not specifically mention chalcosiderite as being present although this is inferred by their statement " . . . the evidence of certain specimens in the possession of the authors points pretty conclusively to the occasional origin of brilliantly crystallized chalcosiderite in the decomposition of this phosphate [dufrenite]." The writer's specimen of Kinch and Butler's material, however, contains chalcosiderite associated with the dufrenite; and a specimen labeled dufrenite from Wheal Phoenix in the Yale collection (Brush No. 975) consists entirely of chalcosiderite. The Wheal Phoenix dufrenite, as originally described, and confirmed here, has parallel extinction, no signs of domatic cleavage and morphologically appears to be orthorhombic. The writer feels that these facts alone are sufficient to invalidate the name sjögrenite as applied to a dufrenite-like mineral.

ROCKBRIDGEITE

About half of the specimens labelled "dufrenite" examined in the course of the present study were found to give an *x*-ray powder pattern entirely distinct from that of dufrenite proper. The powder pattern data are given in Table 16. This mineral is indistinguishable from dufrenite in its general appearance and has been confused with that species since earliest times. Material from four of the nine localities here recorded in Table 5 for this new species have already been described by others under the name dufrenite. These include the well-known occurrence in Rockbridge County, Virginia, here taken as the type occurrence because of the wide distribution of this material in collections.[3]

TABLE 5. PROVEN LOCALITIES FOR ROCKBRIDGEITE

Midvale, Rockbridge Co., Virginia. (Dark greenish black, compact fibrous masses. With limonite.)
Greenbelt, Maryland. (Dark greenish black to black radial fibrous crusts with a brilliant luster lining cavities in limonite concretions.)
Polk County, Arkansas. (Greenish brown to olive green radial fibrous crusts with limonite.)
Palermo mine, North Groton, New Hampshire. (Radial fibrous crusts and masses altering from triphylite in pegmatite. Color greenish black to olive green, bronze-brown, reddish brown.)
Fletcher mine, North Groton, New Hampshire. (Greenish black coarse radial fibrous masses as an alteration of triphylite in pegmatite.)
Near Herdorf, Westphalia. (Yellow brown to olive brown radial fibrous crusts on limonite.)
Kreuzberg, near Pleystein, Bavaria. (Greenish black fibrous masses as an alteration of triphylite in pegmatite.)
Hagendorf, Bavaria. (Radial fibrous masses of a dark olive green color as an alteration of triphylite in pegmatite.)
Ullersreuth, Saxony. (Radial fibrous masses of a dark brown to olive brown color in limonite.)

Physical Properties. Rockbridgeite is identical in appearance with the fibrous varieties of dufrenite. The mineral forms fibrous crusts and masses ranging from small-botryoidal shapes with a radial structure to thick crusts with a straight or sub-parallel fibrous or fine-columnar structure. Concentric color banding is sometimes observed in these aggregates, as in dufrenite. No single-crystals of the mineral have yet been found, and

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[3] The original material came from the outcroppings of a limonite deposit on South Mountain about one mile east of Midvale and ten miles east of Lexington in the Blue Ridge Mountains, Rockbridge County, Virginia. The specimens are ordinarily found labelled only Rockbridge County, Virginia. Several tons of the mineral are said to have been mined for distribution among collectors and dealers.

the aggregate character of the fibers is such as to prevent single-crystal *x*-ray study. Rockbridgeite is very similar chemically to dufrenite. Material in which the ferrous iron is more or less oxidized to ferric becomes dark reddish brown in color but the luster and hardness remain unimpaired. On further alteration the color turns brown or yellowish brown and the material becomes soft and ochreous as described beyond. The hardness is $3\frac{1}{2}$–$4\frac{1}{2}$. The specific gravities newly determined here or earlier reported are cited in Table 2. The values vary considerably due to the fibrous nature of the material and to variation in composition and in alteration. The best value for the essentially pure iron compound is probably 3.45. The specific gravity of rockbridgeite probably is slightly higher than that of dufrenite, as are the indices of refraction.

Optical Properties of Rockbridgeite and Dufrenite. The optical properties of these minerals as newly measured are listed in Tables 6 and 7. Optical data given earlier by Larsen and later summarized by Larsen and Berman for so-called dufrenite are given in Table 8; it is not certain to which species these data actually refer.

TABLE 6. OPTICAL PROPERTIES OF DUFRENITE (NEW DATA)

	Rock Run	Wheal Phoenix (crystals)	Hirsch-berg	Hirsch-berg	Siegen	Wheal Phoenix (fibrous)
nX	1.820	1.837	1.832	1.845	1.842	1.810
nY	1.830	1.845	1.837	1.855	1.850	1.813, varies
nZ	1.925	1.895	1.890	1.890	1.875	1.855
Pleochroism						
X	deep blue	pale yellow brown	deep bluish green	pale yellow brown	pale brown	pale yellow brown
Y	buff	pale brown to olive brown	pale yellow brown	yellow brown	brown	deep blue
Z	deep red brown, olive brown	dark brown, red brown	deep olive brown	dark brown, olive brown	dark brown	deep greenish blue
Absorption	Z>X>Y	Z>Y>X	Z>X>Y	Z>Y>X	Z>Y>X	Z>Y>X
Opt. sign	+	+	+	+	+	+
2V	small	small	very small	mod.	small	small to mod.
Dispersion	$r<v$	$r>v$	$r<v$	$r<v$	$r<v$	$r>v$

The optical characters of both rockbridgeite and dufrenite vary widely and are of little value for diagnostic purposes. Both minerals are marked by extreme dispersion, crossed, and show abnormal green, orange, red or ultrablue interference colors without sharp extinction in white light. The axial dispersion is usually $r<v$, but sometimes is $r>v$, and always is extreme. The pleochroism of both minerals is marked. Z is always the most strongly absorbed and X, less frequently Y, the least strongly absorbed direction. The absorption colors vary widely. Material with much divalent metal present, either Fe'' or Mn'' or both, shows intense blue, bluish green or olive-green absorption colors for Y and Z, with X yellowish brown. Oxidized material with little or no divalent metal lacks the blue to green tints and shows reddish brown, brown or olive-brown tints for Y and Z and pale yellow brown for X. The absorption may be so intense, even in small grains, to make accurate measurement of the indices or extinction angles impossible. The absorption becomes less marked as the extent of oxidation of Fe'' to Fe''' increases. Under the microscope, both dufrenite and rockbridgeite show one perfect cleavage with another less perfectly developed, both usually parallel to the fiber length, and sometimes traces of a third cleavage approximately at right angles to the other two. The vibration direction Z always is perpendicular to the best cleavage; either X or Y is parallel to the elongation. Dufrenite in some instances shows parallel extinction against cleavage lines in the plane of the best cleavage, taken as {010},

TABLE 7. OPTICAL PROPERTIES OF ROCKBRIDGEITE (NEW DATA)

	Fletcher mine, N. H.	Rockbridge Co., Va.	Palermo mine, N. H.	Ullers-reuth	Herdorf	Polk Co. Ark.
nX	1.875	1.873	1.875	1.847	1.914	1.838
nY	1.880	1.880	1.890	varies	varies	varies
nZ	1.897	1.895	1.920	1.945	1.935	1.915
Pleochroism						
X	pale brown	pale yellow brown	pale yellow brown	pale yellow brown	pale brown	pale yellow brown
Y	bluish green	bluish green	pale olive green	brown	brown	yellow brown to olive brown
Z	dark bluish green	dark bluish green	dark olive green	dark brown	dark brown	brown to olive brown
Absorption	Z>Y>X	Z>Y>X	Z>X>Y	Z>Y>X	Z>Y>X	Z>Y>X
Opt. sign	+	+		+, mostly		
2V	mod.	mod.	mod. to large	mostly small	mostly mod.	mostly mod.
Dispersion	$r<v$			$r<v$, mostly		$r>v$, mostly

and such plates when turned on edge show sharp parallel extinction. Some finely fibrous dufrenite, notably that from Siegen, shows extinction angles measured from the elongation up to 30° probably due to the subparallel or twisted aggregation[4] of the fibers. The crossed dispersion indicates that dufrenite is monoclinic or triclinic although the morphological evidence and parallel extinction previously mentioned indicates orthorhombic symmetry. Relatively perfect cleavage laths and fibers of rockbridgeite show definite extinction angles of about 3° to Y, together with

Table 8. Optical Properties of "Dufrenite" from Larsen (1921)

	Saxony			Ullersreuth	
	Type A	Type B	Type C	Type A	Type C
nX	1.830	1.830	1.840	1.840	
nY	1.840	1.840		1.845	
nZ	1.885	1.885		1.89	
Pleochroism					
X	bright green[a]	bright green	light yellow brown	pale yellowish	pale yellowish
Y	pale yellowish	pale yellowish	dark brown	dark reddish brown[b]	grass green
Z	dark reddish brown	dark reddish brown		dark reddish brown, dark green	
Absorption	Z>X>Y	Z>X>Y		Z>Y>X	
Opt. sign	+	−	+	+	+
2V	med. to large	large	small to large	varies; large	small
Dispersion	$r>v$	$r<v$	$r<v$	$r<v$	$r<v$
⊥ cleavage	Z	Z	Z	Z	Z
‖ elongation	Y	X	X	Y	X

[a] Brownish when 2V is small.
[b] Bright green when 2V is small.

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[4] A helicoidal type of aggregation in fibrous "dufrenite" from Rochefort-en-Terre, France, has been described by Lacroix.

crossed dispersion, and this substance apparently is monoclinic or triclinic.

The indices of refraction of both dufrenite and rockbridgeite vary widely. Rockbridgeite has in general higher values for the indices although both nX and nZ in single instances overlap the values for dufrenite. The birefringence seemingly varies markedly, ranging between 0.105 and 0.033 in dufrenite and between 0.098 and 0.024 in rockbridgeite. The values of the indices of refraction also vary markedly independently of the birefringence. It seems likely that both types of variation are due to varying degrees of oxidation or hydration of the material; the variation in birefringence may then be due to variation in these regards among different grains of a single sample. The indices of refraction given in Tables 6 and 7 were determined statistically so that the values for nX and nZ do not necessarily represent measurements on single grains and hence may not afford a measure of the true birefringence. The divergent optical character of the fibrous unaltered dufrenite from Wheal Phoenix and the thoroughly altered rockbridgeite from Herdorf is particularly interesting. Increasing oxidation of Fe'' to Fe''' apparently is accompanied by an increase in the values for the indices, especially nZ. Increasing hydration presumably has an opposite effect.

Chemical Composition. Four analyses are available for material known definitely to belong to the present species. These comprise two old analyses by Massie and by Campbell on what is termed the type material from Rockbridge County, Virginia, and two new analyses on material from Polk County, Arkansas, and the Palermo mine, New Hampshire, by Hallowell and Gonyer, respectively. The interpretation of these analyses presents a problem identical with that met with in dufrenite. The Palermo and Arkansas minerals contain small and irrational amounts of divalent cations, and the ferrous iron originally present is presumed to have been partially oxidized; the Rockbridge mineral may be essentially unaltered. The four analyses are cited in Table 9. These analyses as recalculated to some simple whole number ratios of R_2O_3 to P_2O_5, with accompanying conversion of excess Fe_2O_3 to FeO, are cited in Table 10. The most representative formula is probably:

$$Fe''Fe'''_6(PO_4)_4(OH)_8.$$

This formula meets the analysis ratios of the Rockbridge and the Arkansas material fairly closely. The fact that the two analyses of the Rockbridge material were made on separate samples and yet are in good agreement indicates that this material is unaltered. If this is so, the formula given is to be preferred over that based on a ratio of $R_2O_3:P_2O_5 = 4:3$, which requires a considerable conversion of Fe_2O_3 to FeO and

TABLE 9. CHEMICAL ANALYSES OF ROCKBRIDGEITE

	1.	2.	3.	4.
CaO	1.124			tr.
MgO	0.762	2.16		tr.
FeO	6.144	6.06	0.99	2.66
MnO	0.403	0.24	2.24	2.84
Fe_2O_3	50.845	50.89	55.84	55.00
Al_2O_3	0.212	0.29		tr.
P_2O_5	31.761	31.66	32.86	30.43
H_2O	8.531	8.35	7.96	8.06
Rem.	0.115	0.20		[1.01]
Total	99.897	99.85	99.89	[100.00]
G	3.382	3.454	3.33	

1. Rockbridge Co.. Va. Campbell analysis. Rem. is insol. 2. Rockbridge Co., Va. Massie analysis. Rem. is SiO_2. 3. Palermo mine, N. H. Gonyer analysis, 1948. 4. Polk Co., Ark. Hallowell analysis, 1948. Rem. not determined but largely SiO_2.

which also brings the Hallowell analysis out of line. The preferred formula, nevertheless, is unsatisfactory in that it is relatively high in divalent metals and in total metals relative to phosphorus and, further, the analysis of the Palermo mineral is widely divergent therefrom. The Palermo mineral conforms very closely to $Fe''Fe'''_7(PO_4)_5(OH)_8$.

The formula cited would make rockbridgeite the ferrous iron ana-

TABLE 10. SOME CALCULATED RATIOS FOR ROCKBRIDGEITE ANALYSES

Analysis in Table	RO : R_2O_3 : P_2O_5			Calculated per cent		Ideal formula
				FeO	Fe_2O_3	
1. Campbell	1.22	3	2.09	Analysis ratio		$FeFe_6(PO_4)_4(OH)_8 \cdot nH_2O$
2. Massie	1.32	3	2.08	Analysis ratio		
3. Gonyer	0.43	3	2	1.34	55.45	
4. Hallowell	1.14	3	2	5.94	41.36	
1. Campbell	3.24	7	5	7.19	49.68	$Fe_3Fe_{14}(PO_4)_{10}(OH)_{18} \cdot nH_2O$
2. Massie	3.55	7	5	7.35	49.45	
3. Gonyer	2.08	7	5	4.67	51.75	
4. Hallowell	3.86	7	5	9.01	47.94	
1. Campbell	2.33	4	3	9.33	47.30	$FeFe_4(PO_4)_3(OH)_5 \cdot nH_2O$
2. Massie	2.55	4	3	9.54	47.03	
3. Gonyer	1.65	4	3	6.88	49.29	
4. Hallowell	2.71	4	3	11.07	45.66	

logue of chalcosiderite, $Cu''Fe'''_6(PO_4)_4(OH)_8\cdot 4H_2O$, disregarding uncertainties as to the water content of the former mineral. The two species are not isostructural, however, since their *x*-ray powder photographs are totally unlike and their physical and crystallographic characters are also unlike. The *x*-ray pattern of rockbridgeite, on the other hand, resembles that of chenevixite and these two species may be isostructural. The formulae derived from the three available analyses of this mineral, however, are inconsistent both with each other and with rockbridgeite as seen from the accompanying tabulation.

$Fe''Fe'''_6(PO_4)_4(OH)_8$	(rockbridgeite)
$Cu''Fe'''_6(PO_4)_4(OH)_8\cdot 4H_2O$	(chalcosiderite)
$Cu''_5Fe'''_6(AsO_4)_6(OH)_{10}\cdot 8H_2O$	(chenevixite, New South Wales)
$Cu''_9Fe'''_{10}(AsO_4)_8(OH)_{24}\cdot 2H_2O$	(chenevixite, Tintic)
$Cu''_5Fe_4'''(AsO_4)_4(OH)_{10}\cdot 6H_2O$	(chenevixite, Cornwall)

It might also be considered that dufrenite and rockbridgeite are nonstoichiometric defect structures, but such an interpretation would be very speculative in lack of knowledge of the unit cell dimensions or crystal structure. The analyses themselves in most instances are probably not sufficiently accurate to permit more than an approximate formulation of the substances at best.

ISOMORPHOUS SUBSTITUTION IN DUFRENITE AND ROCKBRIDGEITE

The principal types of compositional variation in dufrenite and rockbridgeite are in the relative proportions of the divalent metals Fe, Mn, Ca, Mg and Cu, and in the proportions of Al and Fe'''. Significant amounts of Mn'' have not been reported in dufrenite, although an analysis by Schaller of an unidentified dufrenite-like mineral from Grafton, N. H., described beyond, may represent the manganese analogue of dufrenite. Vauquelin's old analysis (Table 3) of a brown fibrous manganese mineral from Huréaux (?) also might belong here. Both Ca and Cu'' substitute for Fe'' in dufrenite, with $Ca:Fe''=1:3.8$ in the fibrous material from Wheal Phoenix and $Cu:Fe''=1:10$ in the crystals from the same locality. It may be noted in this connection that laubmannite, $Fe''_3Fe'''_6(PO_4)_4(OH)_{12}$, described beyond, is isostructural and probably isomorphous with the copper analogue, andrewsite,

$$Cu''_3Fe'''_6(PO_4)_4(OH)_{12}.$$

Manganese is often present in rockbridgeite and a series extends up to at least $Mn'':Fe''=1:2$ in the Arkansas mineral analyzed by Hallowell. A significant amount of manganese also is present in the rockbridgeite from Palermo (Table 9) and in the unanalyzed material from the Fletcher mine; the rockbridgeite at both localities occurs as an alteration of triphylite in pegmatite. The unit cell dimensions as seen in *x*-ray powder photographs vary measurably with variation in the $Mn'':Fe''$ ratio, decreasing with increase in content of iron, and there also appears to be a slight variation in dimensions accompanying the oxidation of Fe'' to Fe'''. Aluminum may substitute for Fe''' in these minerals. A dufrenite-like mineral from Dandarragan, Western Australia, probably identical with true dufrenite and described in more detail beyond, has $Al:Fe'''=1:5.8$. An aluminian "dufrenite" from Rochefort-en-Terre, France, with 4.50 per cent Al_2O_3 has been analyzed by Pisani. Both dufrenite and rockbridgeite might well form a series to material with $Al>Fe'''$, analogous to the chalcosiderite-turquoise series. Trivalent manganese possibly also may substitute for ferric iron.

CHEMICAL ANALYSES OF DUFRENITE-LIKE MINERALS OF UNCERTAIN IDENTITY

At least 22 chemical analyses of dufrenite-like minerals have been reported in the literature. Most of these lack divalent iron. It has proven possible to associate some of these analyses with either dufrenite or rockbridgeite, as earlier discussed, but the others remain of uncertain affiliation. A few of the latter, however, contain relatively large amounts of divalent metals and hence are of particular interest in connection with the problem of formulation of these minerals. These analyses are described below.

A mineral from Grafton, New Hampshire, analyzed by Schaller (Column 1, Table 11) and labelled "near dufrenite" affords ratios agreeing almost exactly with the formula $(Mn, Fe, Ca)Fe'''_4(PO_4)_3(OH)_5 \cdot 1\frac{1}{2}H_2O$. This formula is identical with that proposed for dufrenite except that Mn'' and not Fe'' is the dominant divalent metal. The mineral hence would be the manganese analogue of dufrenite and entitled to species rank in its own right. It is not known, unfortunately, whether this mineral actually is isostructural with dufrenite; physical data are lacking, and the specimen itself has been lost.[5]

A so-called dufrenite described by Simpson from Dandarragan, Western Australia, is of interest because of its unusually high content of FeO and its bright green color, suggesting that it is essentially unoxidized. The analysis of this material (Column 2, Table 11) again conforms rather closely to the formula, $Fe''Fe'''_4(PO_4)_3(OH)_5 \cdot 2H_2O$, earlier proposed for dufrenite. The calculated ratios are $RO:R_2O_3:P_2O_5=1.78:4.02:3$, indicating a slight deficiency of divalent metals. The mineral occurs at Dandarragan as the petrifying substance of conifer-like wood fragments

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[5] W. T. Schaller, private communication, 1948.

embedded in a ferruginous sandstone associated with beds containing phosphatic coprolites.

The highest content of FeO found in a dufrenite-like mineral is that reported by Schnabel in material from the Hollerter Zug. A physical description of the mineral was not given. The analysis (Column 3, Table 11) does not afford a rational formula, and in fact contains too little P_2O_5 to yield ratios close to those of dufrenite or rockbridgeite. The analysis probably is erroneous, particularly in view of the high summation and non-determination of divalent metals other than Fe.

Another mineral from Grafton, New Hampshire, analyzed by Schaller and labelled "near dufrenite" may be mentioned here. The analysis (Column 4, Table 11) conforms approximately to the formula $(Ca, Fe, Mg)Fe'''_2(PO_4)_2(OH)_2 \cdot 2H_2O$. This formula differs entirely from those of other dufrenite-like minerals, both in content of CaO and in ratios, but is close to that of some mitridatite and to xanthoxenite. The specimen has been lost[5] and confirmatory tests cannot be made.

TABLE 11. SELECTED ANALYSES OF UNIDENTIFIED DUFRENITE-LIKE MINERALS

	1.	2.	3.	4.
CaO	0.99	0.64		5.71
MgO	0.12			3.48
MnO	5.51	0.20		0.45
FeO	3.69	8.34	9.97	6.98
Fe_2O_3	47.44	40.15	53.66	39.77
Al_2O_3		4.44		
P_2O_5	31.87	31.26	28.39	32.40
H_2O	10.31	14.39	8.97	11.53
Rem.		1.12		
Total	99.93	100.54	100.99	100.32

1. Grafton, N. H. Schaller analysis of material labelled "near dufrenite." 2. "Dufrenite," Dandarragan, Western Australia. Bowley analysis in Simpson. Rem. is CO_2 0.24, SiO_2 0.48, C 0.40. 3. "Dufrenite," Hollerter Zug. Schnabel analysis in Rammelsberg. 4. Grafton, N. H. Schaller analysis of material labelled "near dufrenite."

ALTERATION OF DUFRENITE AND ROCKBRIDGEITE

Both dufrenite and rockbridgeite alter readily, a fact early noted by Karsten for the material from the Hollerter Zug. Karsten showed the final product to consist principally of hydrated iron oxide with 2.45 per cent P_2O_5 in brown material and 1.98 per cent in yellow material. Later, Diesterweg made a more detailed chemical study of the alteration sequence of the Hollerter Zug material. His analyses, cited in Table 12, show that even the earliest stage of the alteration, from the original green to the reddish brown state, is marked by a slight loss of P_2O_5; *x*-ray study by the writer of similar material shows no discernible structural change accompanying the alteration. Diesterweg's analysis of the yellow end product shows a P_2O_5 content of about one-fourth that originally present. Laubmann also has contributed data on the alteration of "dufrenite" from Auerbach, Bavaria. His analyses (Table 12) again show a marked leaching of P_2O_5 increasing with the extent of alteration. Observations on the alteration of "dufrenite" from St. Benigna, Bohemia, have been reported by Bořicky. Finally, the writer has examined the soft, yellow alteration crusts with a pseudomorphous fibrous structure often present on the rockbridgeite from Rockbridge, Virginia. The analysis of this material, cited in Table 12, shows a large reduction in P_2O_5 but little change in the content of H_2O. The ratios of the analysis are very close to $Fe'''_5(PO_4)(OH)_{12}$, if the very small amount of RO is disregarded, but this is fortuitous since *x*-ray study shows that the substance is a gross mixture of an unidentified mineral with goethite. Under the microscope, the former mineral appears as non-pleochroic shreds and fibers with a yellow color and indices between 1.87 and 1.93.

TABLE 12. ANALYSES OF ALTERED "DUFRENITE" AND ROCKBRIDGEITE

	1.	2.	3.	4.	5.	6.	7.
Fe_2O_3	62.02	59.14	80.03	65.85	78.38	73.58	52.73
P_2O_5	27.71	25.20	6.25	20.11	5.66	13.69	15.90
H_2O	10.90	13.98	14.06	13.61	14.20	10.32	23.15
Rem.		2.33		0.78	1.70	2.56	7.31
Total	100.63	100.65	100.34	100.35	99.94	100.15	99.09

1. Hollerter Zug, Westphalia. Green material. Diesterweg analysis. 2. Hollerter Zug. Reddish material. Diesterweg analysis. Rem. is Mn_2O_3. 3. Hollerter Zug. Yellow material. Diesterweg analysis. 4. Auerbach, Bavaria. Greenish white. Hiller analysis in Laubmann. Rem. is insol. 0.20, FeO 0.58. 5. Auerbach, Bavaria. Brown end product. Hiller analysis in Laubmann. Rem. is insol. 0.37, FeO 1.33. 6. Rockbridge, Co., Va. Yellow-brown alteration product of rockbridgeite. Hallowell analysis, 1947. Rem. is CaO 0.55, MnO 0.26, Al_2O_3 1.75. 7. Azovskite. Taman Peninsula. Efremov analysis. Rem. is CaO 2.84, SiO_2 2.64, CO_2 0.15, MgO tr., Mn_2O_3 1.68. H_2O includes $H_2O-11.28$, $H_2O+11.87$.

In accordance with the above observations on natural material, it has been found that artificially prepared ferric phosphate is slowly decomposed with continuous removal of phosphate when washed with water or with solutions containing organic matter, alkalies or certain salts. The voluminous literature in this field has been summarized by Mellor.

Some of the difficulties encountered in interpreting the analyses of dufrenite and rockbridgeite might be attributed to a leaching of phosphate from the material in its natural state. It seems probable that the decomposition is initially a surface effect, and proceeds thereafter at an advancing interface, in which iron phosphate is hydrolyzed leaving hydrous iron oxide and yielding phosphate ion to the solution. The material would then consist of two phases, hydrous iron oxide and unaltered mineral in varying degree of admixture depending on the extent of attack. Alternately, it may be supposed that the process of leaching is akin to base exchange, in which (PO_4) is diffused and lost without destruction of the crystal structure. The crystal chemistry of the process is not obvious. The analyses of dufrenite and rockbridgeite can be recalculated on these bases by progressively adding P_2O_5, or deducting Fe_2O_3, until simple ratios are obtained between $R_2O_3:P_2O_5$ or $RO:R_2O_3:P_2O_5$. It proves impossible, however, in the case of both dufrenite and rockbridgeite to fit the analyses simultaneously to a single, simple formula.

The oxidation of the iron from the divalent to the trivalent state may perhaps be compensated electrostatically by the disruption of OH groups and loss of H from the structure, as recently suggested by A. N. Winchell for some basic compounds of divalent iron. In this mechanism, there is no gain or loss of oxygen and, since packing requirements and coordination would be maintained, a considerable change in the structure would not be expected. This mechanism has been found by Barnes to operate reversibly when hornblende is heated in air or in hydrogen.

A basic ferric phosphate which, if a valid species, might occur as an intermediate stage in the alteration of dufrenite or rockbridgeite has been described by Efremov under the name azovskite. This material occurs as dark brown, metacolloidal masses and veinlets in sedimentary iron ores on the Taman Peninsula, Sea of Azov, USSR. The analysis, cited in column 7 of Table 12, approximates the formula $Fe'''_3(PO_4)(OH)_6$, probably fortuitously. The material may be a hardened gel-mass of coprecipitated hydrous iron phosphate and hydrous iron oxide. It shows weak birefringence, perhaps due to strain, with a mean refractive index of about 1.758.

UNIDENTIFIED DUFRENITE-LIKE MINERALS

Several unidentified minerals that resembled dufrenite were encountered in the course of the study. The best defined of these comprised a substance forming radial fibrous crusts and botryoidal masses with a pure black color and dark olive green streak. Luster vitreous, shining. Hardness 4 to 4½. Specific gravity 3.51. Optically, the mineral is biaxial positive (+) with $n\text{X}\sim 1.82$ (deep blue), $n\text{Y}\sim 1.83$ (olive brown) and

$nZ \sim 1.88$ (very deep blue-green). There is one good cleavage, with Z perpendicular thereto, and another cleavage parallel to the elongation. The extinction angle of Y to the elongation is about 6°. Thick grains are nearly opaque. The dispersion is strong. This substance was found sparingly associated with reddingite in specimens from pegmatite at two localities, Hagendorf, Bavaria, and Vianua do Castelo, Maxedo, Portugal. The Hagendorf material is quite distinct from the rockbridgeite which occurs at this locality. The substance apparently is a basic phosphate of iron and manganese and is almost certainly a new species, but it is considered inadvisable to propose a new name in lack of a chemical analysis. The *x*-ray powder data for this mineral are listed in Table 16.

Another unidentified dufrenite-like mineral was found on a specimen from the Rothläufchen mine, Waldgirmes, Hesse. This is the locality from which Streng described the crystals of dufrenite (?) earlier discussed in connection with that species. The material comprises radial-fibrous crusts with a grayish green to yellow brown color and concentric color banding. The hardness is $4\frac{1}{2}$ and the specific gravity 3.23. Optically, the mineral is biaxial positive with $nX = 1.850$ (yellow to yellow brown), $nY = 1.855$ (yellow brown to olive brown), $nZ = 1.875$ (yellow brown to reddish brown and olive brown). The pleochroism is weak, in contrast to dufrenite and rockbridgeite. The dispersion is strong, and 2V is moderate. The extinction against the fiber length is nearly or quite parallel. The *x*-ray powder pattern, poor in quality, is listed in Table 14. It differs from those of dufrenite and rockbridgeite but resembles that of the black mineral from Hagendorf and Maxedo described above. One wonders if this substance represents Streng's mineral, is an altered form thereof, or is a separate species.

LAUBMANNITE AND ANDREWSITE

A specimen labelled dufrenite, from Shady, Polk County, Arkansas, was found to give an *x*-ray powder pattern identical with that of andrewsite. The latter species was described in 1871 by Maskelyne from the West Phoenix mine, Cornwall, England.[6] An analysis by Flight, cited in Table 13, approximates to the formula $(Cu, Fe)_3Fe'''_6(PO_4)_4(OH)_{12}$ with $Fe'' : Cu = 1 : 1.4$. Andrewsite occurs as green to bluish green botryoidal masses with a radial fibrous structure on limonitic vein material. Two authentic specimens were available for examination. Optically, the mineral has $nX \sim 1.813$ (pale yellowish green), $nY \sim 1.820$ (emerald green) and $nZ \sim 1.830$ (yellow to olive green). The dispersion is extreme,

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[6] The locality is given simply as Cornwall in the original description but Collins in his account of henwoodite says that this species is found at the West Phoenix mine [near Liskeard] associated with andrewsite.

crossed, with $r<v$, and anomalous interference colors without sharp extinction are obtained in white light. The axial angle is moderate to large.

The dufrenite-like mineral from Arkansas occurs as thick crusts with a parallel-fibrous structure upon limonite. The inner parts are brown inclining toward dark brown and greenish brown in color with concentric color banding. Hardness 3½ to 4, and specific gravity 3.33. The outermost parts of some of the crusts are somewhat altered, with a yellowish brown to grayish green color and reduced hardness. The optical properties are somewhat variable. The inner, fresh material is biaxial positive, with $nX=1.840$ (pale buff), $nY=1.847$ (greenish brown to olive green) and $nZ=1.892$ (reddish brown to olive brown). Absorption $Z>Y>X$. The dispersion is extreme, crossed, with $r<v$. 2V is variable but usually moderate. Crushed grains show one and perhaps two cleavages parallel to the fiber length. The x-ray powder patterns of this mineral and of andrewsite are listed in Table 16.

TABLE 13. CHEMICAL ANALYSES OF ANDREWSITE AND LAUBMANNITE

	1.	2.	3.	4.	5.
CuO	10.86	10.86	0.00	0.00	
CaO	0.09	0.09	1.14	1.14	
FeO	7.11	8.58	2.07	15.47	19.74
MnO	0.60	0.60	2.40	2.40	
Fe_2O_3	44.64	43.01	57.88	42.99	44.95
Al_2O_3	0.92	0.92	0.05	0.05	
P_2O_5	26.09	26.09	25.95	25.95	26.21
H_2O-	8.79	8.79	0.44	0.44	0.67
H_2O+			10.06	10.06	8.40
SiO_2	0.49	0.49			
Total	99.59	99.43	100.00	98.51	99.97
G	3.475		3.33		

1. Andrewsite, Cornwall. Flight analysis. $RO:R_2O_3=0.85:1$. 2. Andrewsite. Analysis 1 recalculated after converting enough Fe_2O_3 to FeO to make $RO:R_2O_3=1:1$. 3. Laubmannite, Shady, Polk Co., Arkansas. Hallowell analysis, 1948. Recalculated to 100 after deducting quartz from original sum of 100.14. With MgO 0.01. 4. Laubmannite. Analysis 3 recalculated after converting enough Fe_2O_3 to FeO to make $RO:R_2O_3=1:1$. With MgO 0.01. 5. Laubmannite (?) Nitzelbuch mine, Bavaria. Spengel analysis in Laubmann. $RO:R_2O_3:P_2O_5=2.98:3.04:2$.

A chemical analysis of the Arkansas mineral is cited in Table 13. Copper is entirely lacking, and there are not sufficient amounts of other divalent metals in its place to give the ratio $RO:R_2O_3=3:3$ indicated by the isostructural relation to andrewsite. The analysis as it stands affords

$RO:R_2O_3:P_2O_5=1:4.37:2.20$. It is considered that the mineral in its unoxidized state was the ferrous iron analogue of andrewsite and that most of the ferrous iron later oxidized to ferric. If enough Fe_2O_3 is converted to FeO to make $RO:R_2O_3=3:3$, the analysis appears as in column 4 of Table 13 and affords the simple ratio $RO:R_2O_3:P_2O_5=2.95:2.95:2$. The formula then is analogous to andrewsite:

Andrewsite	$(Cu, Fe, Mn)_3(Fe, Al)_6(PO_4)_4(OH)_{12}$
Laubmannite	$(Fe, Mn, Ca)_3Fe_6(PO_4)_4(OH)_{12}$.

The observed water content is slightly higher than that required by the formula, due probably to the fibrous nature of the material. As in the case of dufrenite and rockbridgeite, the oxidation of the iron from ferrous to ferric is apparently not accompanied by any structural changes discernible on an *x*-ray powder photograph. The name laubmannite is proposed for the species after the German mineralogist Heinrich Laubmann, who has made numerous contributions to the knowledge of the iron phosphates.

A mineral described by Laubmann in 1923 from the Nitzelbuch mine, Amberg-Auerbach district, Bavaria, may be identical with laubmannite in its unoxidized state. The mineral forms broad, radial fibrous bands and reniform crusts in limonite. Color dark green, with a very fresh appearance. Under the microscope the substance is said to have all the characters of "dufrenite." An analysis of the mineral by Spengel is cited in column 5 of Table 13. The ratios of the analysis yield the formula $Fe''_3Fe'''_6(PO_4)_4(OH)_{12}$ as found for the Arkansas mineral.

BERAUNITE

Beraunite is close to both dufrenite and rockbridgeite in composition, and its fibrous varieties resemble the reddish brown types of these minerals. Several specimens of beraunite were found erroneously labelled dufrenite. One of these, from Middletown, New Jersey, comprised discoidal concretions with a radial fibrous structure. The *x*-ray powder pattern and optical properties of this material were identical with those of beraunite from St. Benigna, Bohemia, and Eiserhausen, Nassau. A chemical analysis of the Middletown material is cited in Table 14. The analysis is of considerable interest because it reveals a small but significant

TABLE 14. CHEMICAL ANALYSIS OF MIDDLETOWN BERAUNITE

FeO	Fe_2O_3	Al_2O_3	P_2O_5	H_2O	Total	G
1.92	54.41	0.02	30.17	13.45	99.97	3.08

Hallowell analysis, 1948. Recalculated to original sum after deducting SiO_2 1.13 per cent.

content of ferrous iron, not hitherto reported in beraunite, that cannot be accommodated in any rational formula. This suggests that beraunite, like dufrenite and rockbridgeite, is properly a basic phosphate of both divalent and trivalent iron that is known ordinarily only in an oxidized condition. If the FeO is converted into Fe_2O_3, that is, oxidized, it is found that the ratios of the analysis then yield almost exactly the simple formula $Fe'''_5(PO_4)_3(OH)_6 \cdot 2H_2O$. This formula is identical with that derived from the three analyses of beraunite from St. Benigna reported by Tschermak and by Bořicky, aside from a slight deficiency in water. Since the Middletown material as presently constituted must be presumed to be the result of partial oxidation, a rational formula containing divalent iron must be sought for the original compound. A number of such formulae can be derived arbitrarily, depending only on the rational distribution of the available iron between FeO and Fe_2O_3, and no definite choice can be made between them. Since the amount of FeO present is likely to be small, the formulae $Fe''Fe'''_9(PO_4)_6(OH)_{11} \cdot 5H_2O$, with 5.03 per cent FeO, or $Fe''Fe'''_4(PO_4)_3(OH)_5 \cdot 3H_2O$, with 10.06 per cent FeO, seem the more probable. The original analysis and weight per cent composition of the several formulae mentioned above are compared in Table 15. The formula last mentioned above is identical with that proposed for dufrenite, aside from a slight apparent difference in water content, and the two species may be dimorphous.

TABLE 15. PERCENTAGE COMPOSITION OF VARIOUS BERAUNITE FORMULAE

	1.	2.	3.	4.
Fe	39.51	39.74	40.22	39.56
P	13.15	13.22	13.39	13.17
H	1.50	1.51	1.45	1.51
O	45.84	45.53	44.94	45.75
	100.00	100.00	100.00	100.00

1. $Fe'''_5(PO_4)_3(OH)_6 \cdot 2\frac{1}{4}H_2O$.
2. $Fe''Fe'''_9(PO_4)_6(OH)_{11} \cdot 5H_2O$.
3. $Fe''Fe'''_4(PO_4)_3(OH)_5 \cdot 2\frac{1}{2}H_2O$.
4. Analysis of Middletown beraunite.

The Middletown beraunite has a reddish brown color in bulk with a concentric color banding in shades of dark greenish brown. The streak is brownish yellow with a tinge of olive drab. The luster is vitreous and brilliant, inclining toward resinous on cross-fractures. The hardness is 3 to $3\frac{1}{2}$, and the specific gravity is 3.08. Optically, the mineral is biaxial

TABLE 16. X-RAY POWDER DATA FOR DUFRENITE, ROCKBRIDGEITE AND SOME RELATED MINERALS

(Iron radiation ($\lambda = 1.937$ Å), manganese filter. Low *d* values have been omitted in some instances)

Dufrenite		Rockbridgeite		Laubmannite		Andrewsite		Beraunite		Maxedo unknown		Waldgirmes unknown	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
12.33	3	8.41	1	12.14	2	5.98	1	10.32	10	7.00	2	9.61	1
6.90	1	6.90	2	5.04	5	5.52	1	9.60	1	4.86	3	7.97	3
6.54	1	4.83	1	4.38	2	5.01	5	7.20	3	4.66	3	6.97	3
6.10	1	4.64	1	4.12	3	4.54	1	4.80	4	4.37	1	6.41	1
5.59	1	4.34	1	3.81	1	4.35	2	4.39	2	4.21	1	5.20	5
5.05	9	4.19	1	3.63	1	4.16	3	4.09	1	3.59	2	4.84	1
4.84	1	3.58	3	3.40	5	4.02	1	3.73	2	3.40	10	4.15	1
4.40	3	3.43	1	3.22	10	3.78	2	3.41	5	3.19	10	3.71	6
4.15	4	3.37	2	3.18	10	3.55	1	3.28	1	3.02	1	3.46	8
4.04	1	3.18	10	3.01	4	3.42	3	3.18	3	2.93	½	3.30	2
3.79	1	3.02	3	2.88	4	3.22	10	3.06	8	2.76	2	3.18	10
3.67	2	2.94	1	2.64	2	3.19	3	2.82	1	2.68	1	3.03	2
3.54	1	2.85	1	2.44	3	3.01	3	2.72	3	2.59	2	2.80	3
3.42	9	2.76	3	2.11	6	2.89	3	2.56	3	2.42	8	2.76	1
3.24	8	2.67	2	2.06	2	2.79	1	2.48	1	2.34	½	2.59	3
3.17	10	2.59	3	2.01	2	2.65	2	2.41	1	2.27	1	2.44	5
3.01	4	2.42	5	1.96	1	2.60	1	2.31	2	2.18	1	2.30	1
2.88	5	2.33	1	1.73	3	2.50	1	2.22	1	2.15	1	2.13	1
2.81	2	2.26	2	1.61	2	2.44	5	2.10	2	2.11	2	2.07	2
2.64	3	2.23	1	1.58	3	2.34	1	2.06	1	2.07	1	1.97	1
2.58	2	2.16	1	1.53	1	2.24	1	1.99	2	2.03	1	1.92	1
2.50	1	2.11	1	1.49	1	2.17	2	1.97	1	1.97	3	1.87	1
2.44	5	2.06	3			2.12	8	1.92	4	1.92	1	1.84	1
2.38	1	2.02	2			2.07	1	1.87	1	1.90	1	1.75	1
2.29	2	1.96	3			2.02	2	1.81	1	1.86	1	1.71	3
2.23	2	1.94	1			1.96	2	1.79	1	1.83	2	1.62	5
2.16	1	1.90	2			1.87	1	1.74	1	1.80	1	1.58	1
2.11	6	1.84	3			1.83	1	1.71	1	1.74	1	1.55	2
2.07	4	1.80	1			1.76	1	1.70	1	1.72	1	1.53	1
2.02	1	1.75	1			1.73	4	1.67	1	1.71	1	1.47	1
2.00	1	1.71	1			1.69	2	1.65	1	1.68	1	1.41	1
1.95	3	1.69	2			1.67	2	1.61	3	1.64	2	1.29	3
1.92	1	1.64	2			1.62	5	1.59	1	1.61	2	1.16	1
1.86	1	1.59	8			1.59	4	1.56	1	1.59	4	1.14	1
1.83	1	1.55	1			1.54	1	1.53	1	1.56	1		
1.81	1	1.53	3			1.51	2	1.51	1	1.54	1		
1.77	1	1.51	1			1.49	1	1.49	1	1.51	1		
1.75	2	1.48	1			1.48	1	1.45	1	1.48	1		
1.73	3	1.46	1			1.46	2	1.32	1	1.46	2		
1.70	1	1.39	1			1.37	3	1.28	1	1.43	1		
1.68	2	1.29	3			1.34	3						
1.66	3	1.26	2			1.32	1						
1.63	2	1.24	1			1.29	2						
1.62	3	1.15	2			1.28	2						

positive with $nX=1.775$ (very pale yellow), $nZ=1.820$ (reddish to carnelian brown) and large 2V. The *x*-ray powder data are listed in Table 16.

Thermal Analyses of Beraunite, Rockbridgeite and Dufrenite. Satisfactory thermal analyses by the differential thermocouple method, using an Esterline-Angus recorder, could not be obtained. The best data indicate that the Middletown beraunite has an exothermic break peaking at about 625° C. and weak endothermic breaks peaking at about 220° and 340°. Rockbridgeite has an exothermic break near 650°, a weak endothermic break near 350° and possibly others. Dufrenite gave particularly bad records; an endothermic break is present at about 270° and other breaks are probably present. All three minerals begin to melt below 900°.

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