FRONDELITE AND THE FRONDELITE-ROCKBRIDGEITE SERIES[1]

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ABSTRACT

The name frondelite is given to the mineral of composition $Mn''Fe_4'''(PO_4)_3(OH)_5$, isostructural and isomorphous with rockbridgeite, the ferrous iron analogue. The type locality of frondelite is the Sapucaia pegmatite, Municipio of Conselheiro Pena, Minas Gerais, Brazil, where it occurs in association with triphylite and other iron-manganese phosphates. It occurs in brown botryoidal masses with a radiating fibrous structure. It is orthorhombic with cleavages (100) excellent; (010) good; (001) fair. Hardness 4.5; sp. gr. 3.476; $\alpha=1.86$, $\beta=1.88$, $\gamma=1.893$; absorption in shades of orange Z>Y>X; 2V medium; dispersion $r>v$, strong. Orthorhombic, tentative space group $B22_1$ or $B22_12$ (D_2^5); $a_0=13.89$, $b_0=17.01$, $c_0=5.21$ Å.

The frondelite-rockbridgeite series is represented by frondelite, $Mn''Fe_4'''(PO_4)_3(OH)_5$ from the Sapucaia pegmatite, Brazil, manganoan rockbridgeite $(Fe''Mn'')Fe_4'''(PO_4)_3$-$(OH)_5$, from the Fletcher quarry, North Groton, New Hampshire, and rockbridgeite $Fe''Fe_4'''(PO_4)_3(OH)_5$ from Rockbridge County, Va. Ferrous iron may oxidize to ferric iron. At Fletcher quarry green rockbridgeite $(Fe'', Mn'')Fe_4'''(PO_4)_3(OH)_5$ oxidizes readily to brown rockbridgeite, $(Fe''', Mn'')Fe_4'''(PO_4)_3(OH)_5$.

The variation of unit cell and optical properties are discussed. Three new analyses are given.

INTRODUCTION

In the summer of 1947 it was the privilege of the author to examine some phosphate minerals collected in 1945 by William T. Pecora of the U. S. Geological Survey from the Sapucaia pegmatite, Municipio of Conselheiro Pena, Minas Gerais, Brazil. One of these, a dark-brown, radially fibrous mineral occurring as crusts, botryoidal and drusy masses, appeared to resemble minerals previously grouped together as dufrenite. Dr. Clifford Frondel was at that time studying the dufrenite group, and kindly permitted use of his type material as standards for identification purposes. The mineral was found to be isostructural with rockbridgeite, $Fe''Fe_4'''(PO_4)_3(OH)_5$, now being described by Clifford Frondel. A chemical analysis showed the fibrous mineral to be the manganous end member, and the name frondelite is proposed for the mineral of composition $Mn''Fe_4''(PO_4)_3(OH)_5$. Frondelite is found in association with other iron-manganese pegmatite phosphates: triphylite, vivianite, and a member of the heterosite-purpurite series. The Sapucaia pegmatite and its minerals will be described in a forthcoming paper by W. T. Pecora and others.

PHYSICAL AND OPTICAL PROPERTIES

Frondelite from the Sapucaia pegmatite, Brazil, occurs as crusts and as botryoidal and drusy masses, showing in cross section a radiating

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fibrous structure. The fibers are parallel to the *c* crystallographic direction. Frondelite is orthorhombic; (100) is an excellent cleavage, (010) good, and (001) fair. The hardness is $4\frac{1}{2}$, the specific gravity 3.476. The luster is dull to vitreous. It is brittle, with an uneven fracture.

In the frondelite-rockbridgeite series frondelite is brown; rockbridgeite green. An intermediate member, manganoan rockbridgeite from the Fletcher quarry, North Groton, New Hampshire, is green where fresh,

TABLE 1. OPTICAL PROPERTIES OF THE FRONDELITE-ROCKBRIDGEITE SERIES

		Unoxidized		Oxidized
	Frondelite (7.74 MnO, no FeO) Sepucaia Pegmatite (Lindberg)	Rockbridgeite (5.51 FeO, 3.73 MnO) Fletcher Quarry, N. H. (Frondel)	Rockbridgeite (6.14 FeO, 0.40 MnO) Rockbridge County, Va. (Frondel)	Rockbridgeite (MnO 4.10, no FeO) Fletcher Quarry, N. H. (Lindberg)
Indices				
α	1.860	1.875	1.873	1.915
β	1.880	1.880	1.880	1.927
γ	1.893	1.897	1.895	1.939
Pleochroism				
X	pale yellow brown	pale yellow brown	pale brown	pale yellow brown
Y	orange brown	bluish green	bluish green	orange brown
Z	orange brown	dark bluish green	dark bluish green	orange brown
Absorption	Z>Y>X	Z>Y>X	Z>Y>X	Z>Y>X
Optic sign	negative	positive	positive	
2V	moderate	moderate	moderate	large
Dispersion	$r>v$	$r<v$		$r>v$, if positive
Orientation				
X	$=c$			
Extinction	parallel			

but readily oxidizes to brown radiating fibers. Rockbridgeite from Chanteloube, France, is brown in color. All known members of the series occur as radiating fibers.

The optical properties for rockbridgeite and frondelite are summarized in Table 1. The indices of refraction of frondelite were determined upon a small homogeneous fraction which was representative of the bulk of the larger sample. A small portion of the bulk sample may have been partly oxidized (as is substantiated by chemical analysis); a few grains gave values of γ as high as 1.93, and correspondingly high α and β.

Most grains show parallel extinction; a false extinction angle was noted by Frondel,[2] which was probably due to the radiating character of the material.

Table 1 clearly shows that the differences in indices of refraction between frondelite and rockbridgeite are not as large as the differences between green unoxidized and brown oxidized rockbridgeite that occur together at Fletcher quarry, North Groton, New Hampshire.

Rockbridgeite from Chanteloube, France, has variable indices of refraction; the lowest index for α observed was 1.865; the highest index for γ observed was 1.895. The sample is probably largely unoxidized, although some portions of the sample are very much altered. The MnO content is 3.53 per cent.

Chemical Composition

In Table 2 are given the chemical analyses and ratios of various members of the frondelite-rockbridgeite series. Columns 1 through 4 give the

Table 2. Chemical Analyses of the Frondelite-Rockbridgeite Series

	1	2	3	4	5 Analysis	5 Ratios	6 Analysis	6 Ratios	7 Analysis	7 Ratios
FeO	6.144	6.06	0.99	2.66	5.51	.0767	none		none	
MnO	0.403	0.24	2.24	2.84	3.73	.0526	4.10	.0578	7.74	.1091
MgO	0.762	2.16		trace	0.25	.0062	trace		0.20	.0050
CaO	1.124			trace	none		none		0.02	.0004
ZnO					0.16	.0020	0.16	.0020		
Na_2O					0.24	.0039	0.23	.0037	0.98	.0158
K_2O					trace		trace		0.12	.0013
Fe_2O_3	50.845	50.89	55.84	55.00	50.31	.3150	55.20	.3457	48.85	.3058
Mn_2O_3					none		0.32	.0020	1.75	.0122
Al_2O_3	0.212	0.29		trace	0.24	.0024	0.35	.0034	1.31	.0128
P_2O_5	31.761	31.66	32.86	30.43	32.43	.2284	31.67	.2231	31.28	.2203
H_2O	8.531	8.35	7.96	8.06	7.42	.4119	6.98	.3875	7.52	.4174
Rem.	0.115	0.20		(1.01)	0.07		0.16		0.32	
Total	99.987	99.85	99.89	100.00	100.36		99.17		100.09	
Sp. Gr.					3.474		3.490		3.476	

1. Rockbridge County, Va. Campbell analyst. Rem. is insol. On dufrenite from Rockbridge County, Va. J. L. Campbell, *Am. J. Sci.*, 3rd Series, 22, 65 (1881).
2. Rockbridge County, Va. Massie analyst. Rem. is SiO_2. On the composition of dufrenite from Rockbridge County, Va. F. A. Massie, *Chemical News*, 42, 181 (1880).
3. Palermo, N. H. Gonyer analyst. The dufrenite problem. Clifford Frondel, *Amercian Mineralogist*, **34**, 528.
4. Polk County, Arkansas. Hallowell analyst. Rem. not determined but largely SiO_2. The dufrenite problem. Clifford Frondel, *American Mineralogist*, **34**, 528.
5. Fletcher quarry, North Groton, N. H. Lindberg analyst. Unoxidized. Rem. insol.
6. Fletcher quarry, North Groton, N. H. Lindberg analyst. Oxidized. Rem. insol.
7. Frondelite, type locality. Sapucaia pegmatite, Brazil. Lindberg analyst. Rem. insol. Spectrographic analysis by K. J. Murata showed in addition .OX% Li, Be, Zn.

[2] Frondel, Clifford, The dufrenite problem: *Am. Mineral.*, **34**, 524 (1949).

analyses of members of the rockbridgeite series, as reported by Frondel.[3] Columns 5 and 6 represent new chemical analyses of fresh and oxidized rockbridgeite from Fletcher quarry. In column 7 are given data for frondelite from the Sapucaia pegmatite, Brazil.

The molecular weight of the unit cell of frondelite may be derived from the formula,

$$M = \frac{\text{Vol. (in A}^3) \times \text{density}}{1.6604}.$$

The volume of frondelite, as derived from *x*-ray studies, discussed later in this paper, is 1231 Å³. The molecular weight of the unit cell is 2577. In Table 3, column 4, the number of atoms of each kind per unit cell is found by multiplying the ratios from Table 2 by 0.01 to convert from a

TABLE 3. FORMULA OF FRONDELITE

	Frondelite, Sapucaia Pegmatite					Rockbridgeite, Fletcher Quarry					
						Unoxidized			Oxidized		
	Ratios	Oxygen equiva-lent	Metal equiva-lent	Atoms per cell		Ratios	Atoms per cell		Ratios	Atoms per cell	
FeO						.0767	1.94				
MnO	.1091	.1091	.1091	2.812		.0526	1.33		.0578	1.47	
MgO	.0050	.0050	.0050	.129		.0062	0.16	3.74	—		
CaO	.0004	.0004	.0004	.010	3.83	—	—		—		1.70+1.80=3.51
ZnO						.0020	0.05		.0020	.05	
Na_2O	.0158	.0158	.0316	.814		.0039	0.20		.0037	.19	
K_2O	.0013	.0013	.0026	.067		—			—		
Fe_2O_3	.3058	.9174	.6116	15.761		.3150	15.94		.3457	17.53	
Mn_2O_3	.0122	.0366	.0244	.629	17.05	—	—	16.06	.0020	.10	17.80−1.80=16
Al_2O_3	.0128	.0384	.0256	.660		.0024	.12		.0034	.17	
P_2O_5	.2203	1.1050	.4406	11.354	11.35	.2284	11.56	11.56	.2231	11.31	11.31
H_2O	.4174	.4174	.8348	21.508	21.51	.4119	20.85	20.85	.3875	19.65	19.65

per cent to a fraction scale, and then multiplying by 2577. The formula so derived is $4Mn''Fe_4'''(PO_4)_3(OH)_5$, which also fits the requirement of a minimum of four molecules per unit cell imposed by the space groups $B22_1$ or $B22_12$.

The ratios derived for frondelite show a small deficiency of R″, suggesting the possibility that some R‴ may occupy positions equivalent to R″. Phosphate is a little low and water a little high, but closer agreement to theoretical values are shown in the analyses of rockbridgeite from Fletcher quarry.

Two samples of rockbridgeite from the Fletcher quarry, North

[3] Frondel, Clifford, The dufrenite problem: *Am. Mineral.*, **34**, 528 (1949).

Groton, New Hampshire, were prepared, one of green unoxidized fibers and a second of brown oxidized fibers which correspond to $(Fe'', Mn'')Fe_4'''(PO_4)_3(OH)_5$ and $(Fe''', Mn'')Fe_4'''(PO_4)_3(OH)_5$. The Fe''/Mn'' ratio for the unoxidized sample is 1.46 (3/2). During oxidation the following changes occur: (1) oxidation of all the FeO to Fe_2O_3 and a minor amount of MnO to Mn_2O_3, (2) a relative increase in MnO, (3) a decrease in total iron and in phosphate, and (4) a decrease in water content. In the oxidized portion the excess of R_2O_3 over that required by the formula above is calculated to RO in order to obtain the ratios tabulated. The cell volume for rockbridgeite was not determined precisely by Weissenberg photographs, but approximately by powder photographs; the weight of the unit cell is 2531 for unoxidized material and 2535 for oxidized material. Ratios so derived are given in Table 3.

Frondelite is easily fusible to a magnetic globule. It is soluble in dilute HCl, but insoluble in HNO_3 and H_2SO_4; the Na_2CO_3 fusion is insoluble in HNO_3 but soluble in HCl; the $KHSO_4$ fusion is soluble in H_2SO_4. It yields water when heated in a closed tube.

The specific gravities were determined by the use of an Adams-Johnston pycnometer of fused silica. The slightly higher specific gravities than those reported by Frondel on rockbridgeite from the Fletcher quarry may possibly be due to removal of lighter fractions with methylene iodide in the course of purification of the author's samples. The specific gravities reported are representative of the sample analyzed.

The analyses of the minerals composing the rockbridgeite-frondelite series, as represented by analyses from Rockbridge County, Virginia, Fletcher quarry, New Hampshire, and the Sapucaia pegmatite, Brazil, establish the unoxidized series represented by $R''Fe_4'''(PO_4)_3(OH)_5$, with $R''=Fe$ for rockbridgeite from Rockbridge County, $R''=Fe/Mn=3/2$ for rockbridgeite from Fletcher quarry, and $R''=Mn$ for frondelite. Analyses of material from the Palermo pegmatite,[4] New Hampshire; from Polk County, Arkansas; and from the Fletcher quarry, New Hampshire, establish an oxidation sequence in which partial or complete oxidation of ferrous iron to ferric iron is followed by a minor amount of oxidation of MnO to Mn_2O_3. This follows the generally accepted plan of oxidation of all iron-manganese phosphate minerals, as described by Brian Mason,[5] in which iron oxidizes first, and may or may not be followed by oxidation of manganous manganese.

[4] As used in this paper the term Palermo pegmatite serves only as a convenient means of reference and is not to be considered a stratigraphic name.

[5] Minerals of the Varutrask pegmatite. XXIII Some iron-manganese phosphate minerals and their alteration products, with special reference to material from Varutrask. Brian Mason. *Geol. Fören. Förhandl.*, **63,** 165–168 (1941).

X-RAY DATA

Single crystal rotation and Weissenberg pictures were taken about a cleavage fragment of frondelite so oriented that (1), (100) and (010) were in a zone parallel to the rotation axis ($=c$); (2), (100) and (001) were in a zone parallel to the rotation axis ($=b$); and (3), (010) and (101) were in a zone parallel to the rotation axis $=[10\bar{1}]$. All three orientations showed C_{2l} symmetry on the zero layer of the Weissenberg photographs; the first layer pictures were not equally well developed about both axes; hence it was not possible to differentiate between C_{2l} and C_l symmetry. An orthorhombic mineral is indicated. An extremely small cleavage fragment was chosen to minimize the effect of the radiating fiber structure; however the zero and first layers of the Weissenberg picture rotated around the fiber axis $=c$ showed the spots representing a single plane spread out as a thin line through a distance of several degrees. The Weissenberg pictures around other axes showed this effect far less, but the various levels of the rotation pictures around these axes were represented by small arcs rather than discrete points. The d values, however, could be measured accurately from the Weissenberg pictures; $a=13.89$, $b=17.01$, and $c=5.21$ Å. The volume of the unit cell is 1231 $(\text{Å})^3$.

An examination of the projections on (hkl) showed $h+l$ even, k even or odd; on $(0kl)$ l even, k even or odd; on $(h0l)$ $h+l$ even, h odd if l odd; on $(hk0)$ h even, k even or odd, on $(h00)$ h even, on $(0k0)$ k even and on $(00l)$ l even; therefore the tentative space group is $B22_1$ or $B22_12$ (D_2^5). This space group requires a minimum of four molecules per cell.

The single crystal x-ray photographs were taken with copper radiation, nickel filter, on a very small irregular cleavage fragment, and it is possible that some of the extinctions observed may have been due to absorption, thus indicating a higher symmetry. The possibility of absorption is verified by unequal development of spots around the two axes on the first layer pictures, making it impossible to differentiate between C_{2l} and C_l symmetry. The powder photograph taken with iron radiation was therefore indexed to see whether all lines could be accounted for by indices consistent with the chosen space group. Since more than one solution to the equation

$$d_{hkl}^2 = \frac{1}{\dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2}}$$

is possible, an exhaustive list of possibilities is not given, nor is the possibility of alternate indices not fitting the space group considered. The approximate cell dimensions of various members of the rockbridgeite-

TABLE 4. POSSIBLE INDICES FOR REFLECTIONS OCCURRING ON POWDER PHOTOGRAPH OF FRONDELITE
IRON RADIATION, MANGANESE FILTER

d observed	Indices for reflections also observed on Weissenberg photographs				Additional possible indices			
	Index	Theory	Index	Theory	Index	Theory	Index	Theory
8.59Å	020	8.51						
6.90	200	6.94						
6.46					210	6.431		
4.86	101	4.88						
4.69	111	4.69						
4.36					230	4.393		
4.23	040	4.25						
3.61	240	3.626						
3.441	400	3.473	301	3.461				
3.381	311	3.391	410	3.403				
3.195	321	3.205	420	3.214				
3.045	250	3.054						
2.949	430	2.960			331	2.954		
2.825	060	2.835						
2.779	151	2.791						
2.679	440	2.690			341	2.685		
2.597	002	2.605						
2.444	501	2.451	202	2.439[a]				
2.415	351	2.421	212	2.414				
2.340					222	2.345		
2.292	270	2.294			610	2.294		
2.234					232	2.224		
2.175	171	2.175						
2.121	080	2.126			242	2.115		
2.064	412	2.069			052	2.068		
2.030					422	2.024		
1.979	252	1.983						
1.957	181	1.949			432	1.956		
1.913					062	1.918		
1.849	701	1.852	262	1.849				
1.723					272	1.722		
1.694					123	1.689		
1.659	490	1.661			2.10.0	1.653		
1.598	1.10.0	1.606	323	1.597	143	1.597		
1.562					333	1.563		
1.537					153	1.537		
1.492	292	1.494						
1.472	353	1.468			1.11.1	1.474	163	1.473
1.411	4.11.0	1.413			3.11.1	1.412	363	1.410[b]
1.394					2.10.2	1.395		
1.360	1.12.1	1.361						
1.312	4.12.0	1.312			3.12.1	1.312		
1.259	1.13.1	1.263						
1.252					234	1.249		
1.223	4.13.0	1.224			10.02	1.226	2.12.2	1.226[c]
1.214					0.14.0	1.215	414	1.216[d]
1.189					434	1.192		
1.148					3.14.1	1.146	1.11.3	1.151

Additional indices:
[a] 161, 2.452, 450, 2.432.
[b] 492, 1.414.
[c] 244, 1.226.
[d] 1.10.3, 1.211.

TABLE 5. X-RAY POWDER SPACING DATA FOR THE ROCKBRIDGEITE-FRONDELITE SERIES
IRON RADIATION, MANGANESE FILTER

Rockbridgeite (6.14 FeO, 0.40 MnO) Rockbridge, County, Va.		Rockbridgeite (5.51 FeO, 3.73 MnO) Fletcher quarry, N. H.		Frondelite (MnO 4.10, no FeO) Fletcher quarry, N. H.		Frondelite (MnO 7.74, no FeO) Sapucaia pegmatite	
Intensity	*d*-Å	Intensity	*d*-Å	Intensity	*d*-Å	Intensity	*d*-Å
1	8.36	1	8.56	1	8.52	1	8.59
2	6.94	2	6.87	1	6.85	2	6.90
1	6.46			1	6.43	1	6.46
1	4.85	1	4.83	1	4.80	1	4.86
1	4.67	1	4.67			2	4.69
1	4.34	1	4.34			1	4.36
1	4.20	1	4.22	1	4.22	1	4.23
4	3.58	4	3.59	4	3.60	4	3.61
2	3.431	2	3.435	2	3.426	2	3.441
5	3.391	5	3.367	5	3.357	5	3.381
10	3.186	10	3.192	10	3.181	10	3.195
3	3.017	3	3.035	3	3.033	3	3.045
1	2.934	1	2.938	1	2.931	1	2.949
		1	2.811			1	2.825
3	2.763	3	2.770	3	2.773	3	2.779
2	2.670	2	2.673	2	2.661	2	2.679
2	2.589	2	2.587	2	2.597	2	2.597
		3	2.434	3	2.439	3	2.444
4	2.415	4	2.413	4	2.402	2	2.415
				1	2.332	1	2.340
2	2.269	2	2.279	2	2.282	2	2.292
1	2.26	1	2.220	1	2.196	1	2.234
1	2.169	1B	2.171			1	2.175
2	2.106	2	2.109	1	2.112	2	2.121
		1	2.060	1	2.060	2	2.064
2	2.019	1	2.021	1	2.02	2	2.030
3	1.966	2	1.971	2	1.976	3	1.979
						2	1.957
1	1.930			1	1.942	1	1.939
		1	1.914				
1	1.897	1	1.908			1	1.913
3	1.836	3	1.841	3	1.842	3	1.849
1	1.731					1	1.756
1	1.709	2	1.718	2	1.717	2	1.723
2	1.688	2	1.689	2	1.691	2	1.694
2	1.637	2	1.650	2	1.654	2	1.659
5	1.592	5	1.596	5	1.594	5	1.598
		1	1.570				
2	1.551	1	1.558	2	1.558	2	1.562
		2	1.535	2	1.534	2	1.537
1	1.513	1	1.517				
1	1.478	1	1.485	1	1.487	1	1.492
1	1.455	1	1.471	1	1.471	1	1.472
		1	1.406	1	1.406	1	1.411
1	1.393	1	1.393	1	1.388	1	1.394
						1	1.360
				1	1.305	1	1.312
2	1.255	1	1.256	1	1.255	1	1.259
1	1.244	1	1.249	1	1.249	1	1.252
		1	1.219	1	1.225	1	1.223
				1	1.206	1	1.214
		1	1.187			1	1.819
		1	1.148	1	1.144	1	1.148

frondelite series may be obtained from the powder photograph. These are: $a=13.73$, $b=16.82$, and $c=5.18$ Å for rockbridgeite from Rockbridge County, Va., $a=13.76$, $b=16.94$, and $c=5.19$ Å for rockbridgeite from Fletcher quarry, N. H., and $a=13.72$, $b=16.94$, and $c=5.19$ Å for the oxidized rockbridgeite at Fletcher quarry.

In Table 5 are listed the *x*-ray powder spacing data for frondelite and data for members of the frondelite-rockbridgeite series. The material from the Sapucaia pegmatite represents the manganous end member. Rockbridgeite from Rockbridge County, Virginia, represents the ferrous iron end member; the unoxidized material from Fletcher quarry, New Hampshire, has a Fe''/Mn'' ratio of 3/2. The difference in cell size between the various members of the series is not easily observed by inspection of powder pictures, but careful measurements show a slightly smaller cell for the ferrous iron member than for the manganous end member.

Summary

Frondelite, $Mn''Fe_4'''(PO_4)_3(OH)_5$, occurs as brown radiating fibers at the Sapucaia pegmatite, Brazil. It is isomorphous with rockbridgeite $Fe''Fe_4'''(PO_4)_3(OH)_5$ from Rockbridge County, Virginia. An intermediate member of the series $(Fe'', Mn'')Fe_4'''(PO_4)_3(OH)_5$ with $Fe''/Mn'' = 3/2$ occurs at Fletcher quarry, New Hampshire; the latter oxidizes to $(Fe''', Mn'')Fe_4'''(PO_4)(OH)_5$.

Acknowledgments

The writer is indebted to colleagues in the Geochemistry and Petrology Branch, U. S. Geological Survey, particularly William T. Pecora for collecting the frondelite, K. J. Murata for spectrographic analysis, and Joseph J. Fahey, George T. Faust, Joseph M. Axelrod, and Michael Fleischer for critical reading of the manuscript.