

LIPSCOMBITE: A NEW SYNTHETIC "IRON LAZULITE"*

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ABSTRACT

Lipscombite, a synthetic iron phosphate mineral, was obtained both by the partial oxidation of ferrous phosphate and by the combination of suitable ferrous and ferric salts. It forms black, flat tetragonal bipyramids with a dark green streak. It has a defect structure with a variable number of Fe in its unit cell. The ferrous iron of lipscombite can be easily replaced by other divalent metals. No regular decrease in the unit cell size was detected with decreasing sizes of replacing ions. The replacement of ferric iron by aluminum takes place only partially, and with difficulty, resulting in isodimorphism. Another compound, ferrous ferric lazulite, monoclinic (?), with the formula $\text{Fe}^{++}\text{Fe}_2^{+++}(\text{PO}_4)_2(\text{OH})_2$ was also synthesized.

Ferrous ferric lazulite changes to lipscombite between 110 and 290° C. Above 290° C. lipscombite contains no divalent iron. It changes to "iron berlinite" (FePO_4 , quartz isotype) and hematite around 560° C., above which an unknown compound forms at the expense of both hematite and iron berlinite. If ferrous phosphate is only partially oxidized, lipscombite is obtained. However, if ferrous phosphate is heated in air, it is dehydrated and oxidized to an amorphous ferric phosphate below 110° C. This product crystallizes at about 560° C. to hematite, a ferric orthophosphate (cristobalite isotype), and the unknown compound mentioned above. The ferric orthophosphate (cristobalite isotype) is converted to iron berlinite (quartz isotype) below 650° C. X-ray data for iron berlinite, ferrous ferric lazulite, and various compounds with lipscombite structure are given.

INTRODUCTION AND ACKNOWLEDGMENTS

During the investigation of the stability relations of iron oxides (Gheith, 1951), a black compound forming small shiny crystals was obtained as a result of contamination with phosphorus. Its x-ray powder pattern is similar but not quite identical to that of lazulite. The crystal structure of this "iron lazulite" was found by Katz and Lipscomb (1951) to be tetragonal.² Another compound, indistinguishable from the former on the basis of general appearance and qualitative analysis, was found to form under apparently identical conditions. Its x-ray powder pattern, however, corresponds practically line for line to that of lazulite and differs only in having spacings corresponding to a larger unit cell. This compound, probably monoclinic, changes to the tetragonal compound at elevated temperatures. The tetragonal "iron lazulite" is herewith named "lipscombite" (pronounced lips-kum-ite), after Professor William N. Lipscomb of the University of Minnesota. The monoclinic (?) compound will be referred to as "ferrous ferric lazulite."

* Most of this study constitutes part of a thesis submitted by the writer to the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree.

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² "Iron lazulite" was the name used by Katz and Lipscomb. Most of the investigation was carried out before Pecora and Fahey announced their discovery of scorzalite. $\text{Fe}^{++}\text{Al}_2(\text{PO}_4)_2(\text{OH})_2$, in 1949.

Professor J. W. Gruner was the first to obtain this material, note its resemblance to lazulite and suggest the name lipscombite for it. The writer is indebted to him for his guidance throughout this research and for his critical reading of the manuscript. He also wishes to thank Professor Lipscomb and Dr. Katz for helpful suggestions. Financial aid by the Wakfia Fahmia through the Egyptian Government is gratefully acknowledged.

SYNTHESIS OF LIPSCOMBITE AND FERROUS FERRIC LAZULITE

Crystals of linear dimensions of the order of .1 mm. were prepared. They are black and shiny and gem-like in appearance. Some of them resemble slightly flattened bipyramids, almost octahedra, showing no twinning as far as can be determined from its external shape. Under the microscope the crystals are opaque, and most of them show square outlines.³ The smallest crystals, however, and the thin edges of the larger crystals, appear very dark green in transmitted light, with only slight pleochroism. The extinction angle measured from a square edge is 45°. Accurate determination of the refractive indices was not possible, but they were found to be higher than 1.670 and lower than 1.80 in well crystallized lipscombite containing 12.33% FeO. The birefringence is strong.

Although lazulite ($\text{MgAl}_2(\text{PO}_4)_2(\text{OH})_2$) and scorzalite (theoretically $\text{Fe}^{++}\text{Al}_2(\text{PO}_4)_2(\text{OH})_2$), are known to be monoclinic, Katz and Lipscomb (1951) showed that lipscombite is tetragonal. Using Mo K radiation and the Weissenberg *x*-ray spectrometer they showed that the unit cell is body centered, group $D_4^{10} - I 4_1 2$, $a = 5.37 \text{ \AA}$, $c = 12.81 \text{ \AA}$.

The methods of formation of lipscombite and ferrous ferric lazulite (Table 1) fall broadly within two classes. The first class is the partial oxidation of ferrous phosphate under controlled laboratory conditions. Heating of ferrous phosphate in air even at temperatures as low as 100° C. results in its oxidation and dehydration. The product of such treatment is a yellow amorphous ferric phosphate that shows no ferrous iron on chemical analysis. The second class comprises the complex combination and double decomposition of simpler compounds supplying the required elements. Table 1 shows 16 selected experiments from over 100 trials to prepare lipscombite under various laboratory conditions. It indicates that no prediction can be made as to whether the product will be lipscombite or ferrous ferric lazulite. Both substances apparently form under identical conditions.

To determine the effect of the composition of starting materials on the

³ These most probably are the flattened tetragonal bipyramids (103) lying on one of their faces.

TABLE 1. EXPERIMENTS ON THE FORMATION OF LIPSCOMBITE AND FERROUS FERRIC LAZULITE

Exp. No.	Starting Materials	Experimental Detail	Temp. ° C.	Press. lb./in. ²	pH ¹	Duration	Product		Streak	
							Form	% FeO	Name	Ridgway's No.
456	Fe ^{'''} phosph. + H ₂ O	Sealed tube	108	23	7	2 days	Beta*	14.62	Olivaceous black (3)	23 ^{'''} m
86	Fe ^{'''} phosph. + H ₂ O in CO ₂ atmosphere ²	Sealed tube	180	153	2	4 days	Alpha*	17.54	Dusky dull green	37 ^{'''} m
99 B	Fe ^{'''} phosph., dry	Tightly packed in corked vial	105	—	—	1 day	Beta*	12.33	Dull greenish black (2)	33 ^{'''} m
458	Fe ^{'''} phosph. + H ₂ O + 5 drops conc. H ₂ SO ₄	Sealed tube	108	23	1	2 days	Beta*		Dusky bluish green	41 ^{'''} m
461	Fe ^{'''} phosph. + H ₂ O + 5 drops dil. NaOH	Sealed tube	108	23	9	2 days	Beta*		Olivaceous black (3)	23 ^{'''} m
12	Fe ^{'''} phosph. + artif. lepidocrocite (3:1) + H ₂ O	Sealed tube in bomb	188	183	7	2 days	Beta*		Deep slate green	33 ^{'''} k
64	Fe ^{'''} phosph. + artif. goethite + H ₂ O; in CO ₂ atmosphere	Open tube in bomb	180	153	5 ³	14 days	Alpha*	17.53	Dusky olive green	25 ^{'''} m
27	Fe ^{'''} phosph. + Fe ₂ (SO ₄) ₃ solution	Open tube in bomb	185	2000 ⁴	4	10 days	Beta*		Deep slate green	33 ^{'''} k
13	Powdered vivianite + artif. lepidocrocite + H ₂ O	Sealed tube in bomb	185	171	7	10 days	Beta*		Dull greenish black (1)	29 ^{'''} m
463	Fe ^{'''} phosph. + FeSO ₄ (1:5) + H ₂ O	Sealed tube	108	23	4	2 days	Beta*		Dull blackish green	29 ^{'''} m
145	Fe ^{'''} phosph. + FeSO ₄ (6:1) + H ₂ O	Open tube in bomb	170	132	5	2 days	Beta*		Light danube green	35 ^{'''} k
82-1	Fe ^{'''} phosph. + FeSO ₄ (2:1) + H ₂ O	Boil	100	—	5	20 min.	Beta*	9.54	Bottle green	37 ^{'''} m
56	Fe ^{'''} phosph. + FeSO ₄ (1:1) + H ₂ O	Boil	100	—	4	1 hour	Beta*	1.55	Andique green	33
52	Fe ^{'''} phosph. + FeSO ₄ (1:6) + H ₂ O	Sealed tube in bomb	185	171	3	11 days	Alpha*		Myrtle green	41 m
42	Fe ^{'''} phosph. + FeSO ₄ sol. + NaOH (in sealed tube) ⁵	In bomb	180	153	10 ³	13 days	Alpha*	17.50	Dusky bluish green	41 ^{'''} m
465	Fe ^{'''} phosph. + FeSO ₄ (1:5) + H ₂ O	Sealed tube in bomb	180	153	3	3 days	Alpha*		Myrtle green	41 m

¹ pH of solution at beginning of experiment.² A small amount of air entered the tube during sealing.³ This pH value is that of the solution at the end of the experiment.⁴ A tank of medical nitrogen supplied the necessary pressure.⁵ A light colored phosphate with an unidentified powder pattern formed a crust on top of the lipscombite. Several unidentified patterns were kindly examined by Professor F. H. Frondel. They did not correspond to any of the phosphates on file at Harvard.⁶ Three NaOH pellets were placed in a separate small, thin walled tube. At 180° C. the bomb was shaken vigorously to break this tube.

* Alpha indicates the monoferric (?) ferrous ferric lazulite; beta indicates lipscombite.

formation temperature of lipscombite, a series of 9 experiments were performed in pyrex tubes. In each tube were placed 2.245 gm. of finely powdered ferric phosphate and 25 cc. of water, to which were added known amounts of ferrous sulfate. The tubes, one third full of air, were sealed and placed in an oven at constant temperature. If at the end of 2 days no change had taken place, the temperature was raised 2° C. and kept constant for the next 2 days. As soon as lipscombite formed in any of the tubes, it was taken out and the heating process continued for the remaining tubes. The formation of lipscombite can easily be detected by its dark bluish green color. The products were x-rayed and found to be lipscombite, sometimes with a small amount of an unidentified compound. The results as shown in Table 2 indicate that the higher the ratio

TABLE 2. EFFECT OF COMPOSITION ON FORMATION TEMPERATURE OF LIPSCOMBITE

Ratio $\frac{\text{gm. FeSO}_4 \cdot 7\text{H}_2\text{O}}{\text{gm. Fe}'''\text{ Phosph.}^1}$	Lowest Temp. of Formation ° C.	Ratio $\frac{\text{gm. FeSO}_4 \cdot 7\text{H}_2\text{O}}{\text{gm. Fe}'''\text{ Phosph.}^1}$	Lowest Temp. of Formation ° C.
0.122	— ²	4.54	65
0.532	— ²	5.23	63.5
1.216	— ²	5.87	61.5
2.426	72	6.88	80 ?
3.64	67		

¹ Eimer and Amend's "precipitated pure insoluble ferric phosphate" was used. No definite formula can be given.

² The temperature was gradually raised from 72° C. to 135° C., but the product was a gray colored unknown phosphate and not lipscombite.

of ferrous to ferric iron in the starting materials, the lower is the temperature of formation of lipscombite. Furthermore, the rate of change of this formation temperature is greater at lower concentrations of ferrous iron.

CHEMICAL ANALYSIS AND FORMULA OF LIPSCOMBITE AND FERROUS FERRIC LAZULITE

Chemical Analysis of Lipscombite

The crystal structure of lipscombite as determined by Katz and Lipscomb (1951) is a defect structure with the unit cell containing: 4P, 4 OH, 16 O, and "about 7Fe distributed randomly" in eight equivalent positions. Table 3 shows the chemical analysis of two samples prepared by two different methods (Table 1). The high H₂O percentage in the analysis is to be expected, as the material is an extremely fine powder, and cannot be heated at 110° C. for any length of time, as partial oxidation

of the ferrous iron is liable to take place.⁴ It was assumed in the calculations that the amount of phosphorus present represents $2P_2O_5$, i.e., 4P per unit cell. The other oxide ratios were calculated on this basis.

Of the 36 negative charges per unit cell (16 O and 4 OH), 20 are compensated by the 4P. The remaining 16 must be compensated by Fe. The positive charges due to iron were, therefore, calculated and adjusted to 16. From these the number of both Fe^{++} and Fe^{+++} per unit cell was obtained (Table 3, last column). To maintain the tetragonal symmetry

TABLE 3. CHEMICAL ANALYSIS AND NUMBER OF IRON IONS PER UNIT CELL IN LIPSCOMBITE

	Weight %	Molecular Ratios	No. of Oxide Molecules	+Charges on Fe	Charges on Fe, Adjusted to 16	Metal Ions Per Unit Cell
Experiment 56						
Fe_2O_3	54.86	.3430	2.660	15.960	15.689	5.23
FeO	1.55	.0216	.167	.314	.311	.16
P_2O_5	36.63	.2582	2.000			
H_2O+	6.01					
H_2O-	.03					
Total	99.08					
Experiment 99 B						
Fe_2O_3	46.68	.2920	2.325	13.950	13.38	4.46
FeO	12.33	.1718	1.369	2.738	2.62	1.31
P_2O_5	35.62	.2508	2.000			
H_2O	5.53					
Total	100.16					

Analysis of Exp. 56 and Fe^{++} determination of Exp. 99 B are by Mr. Lee Peck. The rest is by the writer aided by Mr. S. Khalafallah, Univ. of Minnesota.

it must be assumed that the vacant cation positions (2.61 in the first case and 2.23 in the second) are distributed statistically over the whole lattice.

The 16 positive charges due to iron per unit cell can, theoretically, be supplied by as little as $5\frac{1}{3} Fe^{+++}$ or as much as $8Fe^{++}$ with no change in the x -ray powder pattern, but with the formula correspondingly changing from $Fe_8^{+++}(PO_4)_6(OH)_6$ to $Fe_4^{++}(PO_4)_2(OH)_2$. It was possible to prepare lipscombite with no ferrous iron at all. Its x -ray powder pattern (J 12,

⁴ In finely powdered samples it is sometimes impossible to get rid of all the nonessential water even by heating for a considerable length of time at $110^\circ C$. (Kolthoff and Sandell, p. 299).

TABLE 4. X-RAY POWDER DATA FOR LIPSCOMBITE AND FERROUS FERRIC LAZULITE AS COMPARED TO LAZULITE

(See Figure 2)

Unfiltered iron radiation. Radius of camera = 57.3 mm.

Lipscombite of Exp. 99 B (with 12.33% FeO)			Lipscombite of Exp. J 12 (with no FeO)			Ferrous ferric lazulite of Exp. 86 (17.54% FeO)			Ferrous ferric lazulite of Exp. 52			Lazulite* (Graves Mt.)	
<i>hkl</i>	<i>d</i> Å	<i>I</i>	<i>d</i> Å	<i>I</i>	<i>d</i> Å	<i>I</i>	<i>d</i> Å	<i>I</i>	<i>d</i> Å	<i>I</i>	<i>d</i> Å	<i>I</i>	
101	4.864	1	4.885	1	6.296	f	6.404	f	6.16	w			
	3.669	2.5	3.684	2.5	5.288	f	5.376	f					
	3.544	1	3.522	2	4.793	2	4.845	2.5			4.72	m	
103	3.329	10+	3.329	10+	3.661	2	3.708	1.5	3.60	vwv			
004	3.200	7	3.183	8	3.548	f							
	2.880	f	2.859	f	3.310	10+	3.332	10+	3.23	s (b)			
200	2.616	2	2.584	3	3.212	5	3.257	5	3.14	m			
	2.544	f	2.507	f	3.157	4	3.186	5	3.07	m			
202	2.422	1	2.276	3	2.882	f	2.908	f					
	2.299	2.5	2.239	1			2.665	f					
213	2.267	f	2.035	5	2.612	2.5	2.618	3	2.55	m			
	2.056	5.5	1.872	1.5	2.413	1 b	2.431	1	2.34	vw			
	2.036	1.5	1.825	2	2.325	4	2.329	4	2.26	w			
	1.862	1	1.754	1.5	2.290	1.5	2.290	1.5	2.22	w			
	1.845	2	1.665	4	2.053	4	2.117	f	2.05	vw			
	1.773	1	1.631	f	2.028	3	2.063	3.5	2.01	w			
017	1.747	1	1.589	5.5 b	1.859	2.5 b	2.031	2	1.977	mw (b)			
206	1.664	5	1.451	1	1.833	1	1.867	1.5					
008	1.604	6 b	1.421	1	1.778	1	1.831	1	1.807	w			
	1.449	1.5	1.379	f	1.754	1	1.788	f	1.787	vw			
	1.441	1	1.358	f	1.727	f	1.752	f	1.684	vw			
	1.374	1	1.305	1	1.680	4	1.684	4.5	1.618	w			
			1.289	2	1.659	4	1.663	4.5	1.600	w			
			1.227	1.5	1.613	5.5 b	1.614	6 b	1.568	m (b)			
			1.202	1.5 b	1.587	1	1.589	1.5	1.538	w			
					1.458	1	1.481	f	1.407	w			
					1.441	1	1.465	1	1.389	vw			
					1.389	1	1.442	1	1.274	m			
				1.374	f	1.391	f	1.185	vw				
				1.356	f	1.376	f	1.113	vwv				
				1.306	5	1.354	f						
						1.308	5.5						

* The x-ray data for lazulite are after Pecora and Fahey (1950, p. 11); filtered Cu radiation.

b=broad, f=faint.

Table 4) shows minor differences from that of lipscombite containing both ferrous and ferric iron. The product forms small olive yellow crystals (Ridgway 23") with a primrose yellow streak (23" d). The light color suggests the absence of Fe in two different valence states. Under the microscope the small crystals have square outlines and very high relief, the refractive indices being higher than 1.83. With the nicols crossed the material shows beautiful abnormal interference colors, and no extinction. Trials to prepare the other end member, namely lipscombite with 8Fe⁺⁺ and no Fe⁺⁺⁺ in the unit cell were not successful.

Theoretical and Observed Densities of Lipscombite

The density of finely crystallized lipscombite cannot be determined accurately since it cannot be freed from water without partial oxidation. Katz and Lipscomb, however, determined the density of a rather coarsely crystalline sample. Using a sink or float method in a thalium malonate-thalium formate solution they found the density to be 3.8.

TABLE 5. VARIATION OF THE CALCULATED DENSITY OF LIPSCOMBITE WITH INCREASING FERROUS IRON CONTENT

Total No. of Fe per Unit Cell	No. of Fe ⁺⁺ per Unit Cell	No. of Fe ⁺⁺⁺ per Unit Cell	% Ratio Fe ⁺⁺ :Total Fe	Calculated Density
5½	½	5	9.09	3.395
6	2	4	33.33	3.520
6½	3½	3	53.85	3.646
7	5	2	71.43	3.771
7½	6½	1	92.86	3.897

Based on the dimensions of unit cells of several samples, the writer obtained the theoretical densities shown in Table 5. These represent density changes with variation in ferrous iron content. The relation between the density and the ratio of ferrous to total iron follows very nearly a straight line (Fig. 1). If well crystallized samples whose densities can be determined accurately are found in nature, Fig. 1 can be used to determine their approximate composition. As an example, the synthetic lipscombite sample with a density of 3.8 (Katz and Lipscomb, 1951) is seen from the figure to have a ferrous to total iron ratio of 77.8%.⁵

⁵ As iron supplies 16 positive charges per unit cell, therefore:

$$K(77.8 \times 2 + 22.2 \times 3) = 16$$

$$K = \frac{16}{(77.8 \times 2 + 22.2 \times 3)} = 0.72$$

$$\text{No. of Fe}^{++} \text{ per unit cell} = 77.8 \times 0.72 = 5.60$$

$$\text{No. of Fe}^{+++} \text{ per unit cell} = 22.2 \times 0.72 = 1.60$$

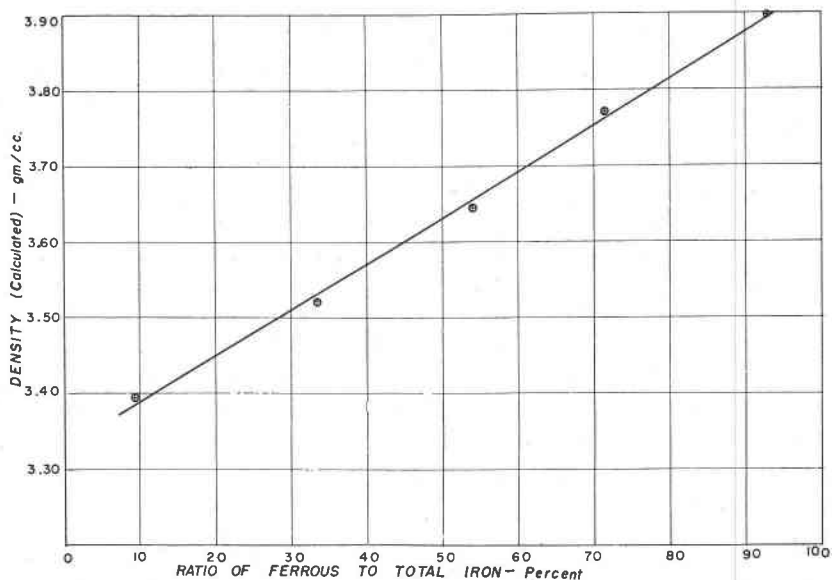


FIG. 1. Variation of the density of lipscombite with increasing ferrous iron content.

Chemical Composition of Ferrous Ferric Lazulite

The ferrous iron content of ferrous ferric lazulite shows only very limited variations as contrasted to that of lipscombite. Three ferrous ferric lazulite samples gave the values shown in Table 6.

TABLE 6. FERROUS AND FERRIC IRON CONTENT OF FERROUS FERRIC LAZULITE

	Exp. No. 42	Exp. No. 64	Exp. No. 86
FeO*	17.50	17.53	17.54
Fe ₂ O ₃ *	Not determined	42.74	41.82

* Ferrous iron determinations were made by Mr. Lee Peck; ferric iron by the writer.

A complete chemical analysis of ferrous ferric lazulite was not possible. As it gives an x-ray powder pattern very similar to that of lazulite and scorzalite $(\text{Mg, Fe}^{++})\text{Al}_2(\text{PO}_4)_2(\text{OH})_2$, the theoretical chemical analysis

TABLE 7. CALCULATED CHEMICAL ANALYSIS OF $\text{Fe}^{++}\text{Fe}_2^{+++}(\text{PO}_4)_2(\text{OH})_2$

Fe ₂ O ₃	FeO	P ₂ O ₅	H ₂ O+
40.79	18.35	36.26	4.60

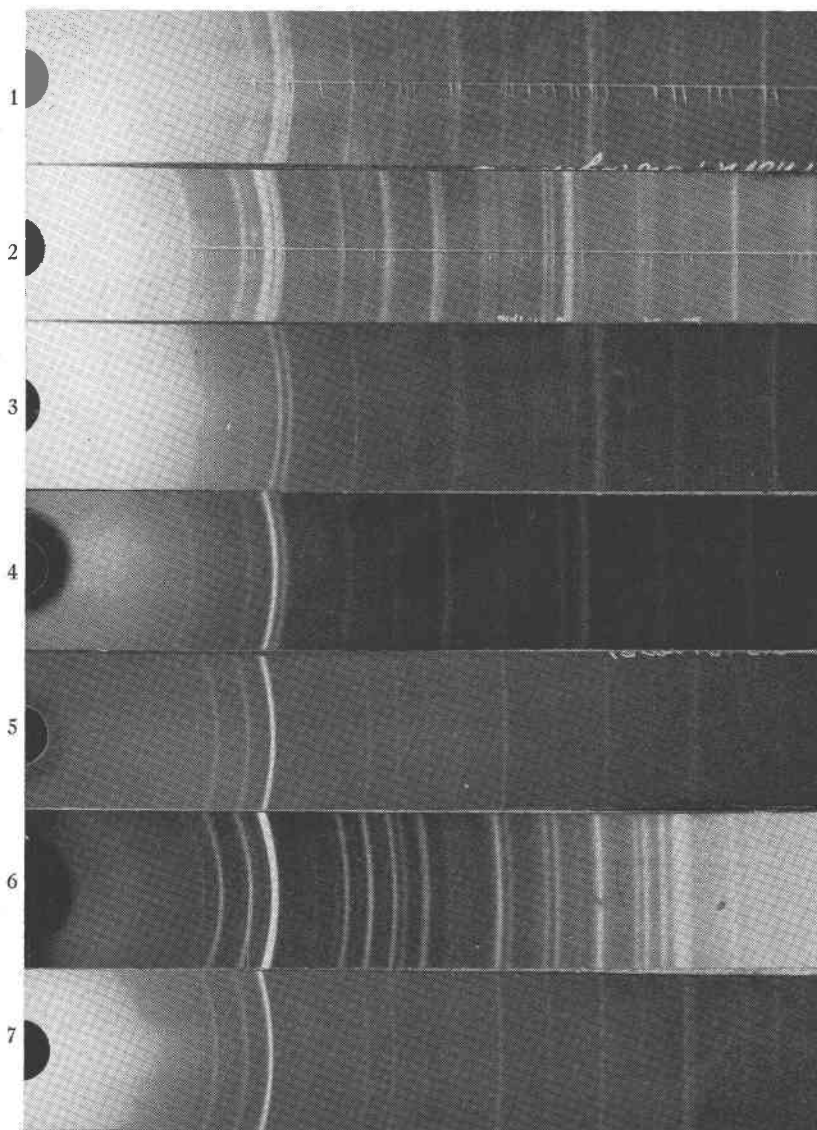


FIG. 2. Powder photographs (unfiltered iron radiation, radius of camera = 57.3 mm.)
From top to bottom: 1. Lazulite; Matterhorn, Switzerland. 2. Ferrous ferric lazulite.
3. U. S. National Museum sample #R5611 (supposed berlinite). 4. Lipscombite. 5. Quartz;
natural. 6. Iron berlinite; lines not agreeing with berlinite are hematite lines. 7. Berlinite;
synthetic.

for an iron lazulite with the formula $\text{Fe}^{++}\text{Fe}_2^{+++}(\text{PO}_4)_2(\text{OH})_2$, was calculated and is given in Table 7. This formula most probably represents the composition of ferrous ferric lazulite.

HEAT TREATMENT OF LIPSCOMBITE AND FERROUS FERRIC LAZULITE

Differential thermal analysis did not yield any satisfactory reproducible results when applied to these synthetic iron phosphates. It was therefore decided to heat various samples at constant temperatures. Five samples were chosen, including ferrous phosphate (Eimer and Amend), two ferrous ferric lazulite and two lipscombite samples, each prepared by a different method (Table 1). Each sample was heated in a loosely covered crucible at a given temperature for three days. A small amount was then removed for x -raying and the rest of the sample heated at a higher temperature for the next three days. This treatment covered the range from 110° C. to 1000° C., but no changes occurred above 735° C.

The results as shown in Table 8 indicate that ferrous ferric lazulite changes to lipscombite between 110 and 290° C. This transition is rather sluggish, and is always accompanied by the oxidation of ferrous iron. The lipscombite structure, which contains only trivalent iron at temperatures higher than 290° C., seems to be stable up to about 560° C. At this temperature or slightly below it, a transformation of lipscombite to a phosphate, FePO_4 , with a quartz-like structure, and to hematite proceeds slowly. As berlinite is AlPO_4 with a quartz structure, the corresponding FePO_4 is here named "iron berlinite." The x -ray powder data for this product are given in Table 12 and in Fig. 2. In the unit cell of lipscombite the minimum ratio of the number of Fe to P is $5\frac{1}{3}:4$. This means there is always an excess Fe over P above the ratio needed for the formation of FePO_4 . Hematite and iron berlinite, therefore separate simultaneously upon heating lipscombite.

Table 8 also shows that at about 650° C., or higher, a compound with an unidentified structure coexists with iron berlinite and hematite. This compound is referred to as unknown "A".⁶ From the progressive changes in the colors of the products along with the approximate determination of the relative amounts of the components as seen in the x -ray photographs, this unknown "A" seems to form at the expense of both hematite and iron berlinite.

Heating of ferrous phosphate in air yields an *amorphous* ferric phos-

⁶ It is significant to mention here that a sample of powdered vivianite, $\text{Fe}_3\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$, heated at 1000° C., gave an x -ray photograph showing iron berlinite, unknown "A" and very little hematite. These are exactly the same products obtained by heating any of the samples of Table 8 above 735° C.

TABLE 8. THE HEAT TREATMENT OF LIPSCOMBITE, FERROUS PHOSPHATE AND FERROUS FERRIC LAZULITE.
A.—Up to 425° C.

Starting Material	110° C.		290° C.		359° C.		425° C.	
	Color	X-ray	Color	X-ray	Color	X-ray	Color	X-ray
Ferrous ferric lazulite of Exp. 86	Dark bluish green	Ferrous ferric lazulite	Dark olive yellow	Lipscombite	Dark olive yellow	Lipscombite ¹	Dark olive yellow	Lipscombite ¹
Ferrous ferric lazulite of Exp. 64	Dark green	Ferrous ferric lazulite	Yellowish brown	Lipscombite	Light brown	Lipscombite ¹	Orange brown	Lipscombite ¹
Ferrous phosphate (Eimer and Amend)	Yellow	Amorphous	Orange yellow	Amorphous	Yellowish brown	Amorphous	Yellowish brown	Amorphous
Lipscombite of Exp. 99 B	Greenish black	Lipscombite	Olive brown	Lipscombite	Brown	Lipscombite, v. sharp pattern	Brown	Lipscombite
Lipscombite of Exp. 82-1	Green	Lipscombite	Yellow	Lipscombite	Orange yellow	Lipscombite	Dark orange	Lipscombite

¹ Product has one extra line at $d = 6.520$ with $I = 1$ to 1.5.

TABLE 8—(continued)
B.—Up to 1000° C.

Starting Material	560° C.		650° C.		735° C.	
	Color	X-ray	Color	X-ray	Color	X-ray
Ferrous ferric lazulite of Exp. 86	Dark brown	Lipscombite; Iron faint	Dark brown	Lipscombite, v. faint; Iron berlinite; Unknown "A"; Hematite, v. little	Reddish buff	Iron berlinite; Unknown "A"; Hematite, v. little
Ferrous ferric lazulite of Exp. 64	Dark brown	Lipscombite	Dark reddish brown	Lipscombite; Hematite	Red	Iron berlinite; Unknown "A"; Hematite
Ferrous phosphate (Eimer and Amend)	Dark brown	Ferric orthophosphate (crystalite isotype); Unknown "A"; Hematite, little	Light brown	Iron berlinite; Hematite, v. little	Light brown	Iron berlinite; Unknown "A"; Hematite, v. little
Lipscombite of Exp. 99 B	V. dark brown	Lipscombite; Iron Hematite, little	Deep red	Iron berlinite; Hematite; Unknown "A"; v.v. little	Reddish buff	Iron berlinite; Unknown "A"; Hematite, v. little
Lipscombite of Exp. 82-1	Deep red	Lipscombite; v. faint; Iron berlinite; Hematite, faint	Red	Iron berlinite; Hematite; v.v. little	Reddish buff	Iron berlinite; Unknown "A"; Hematite, v. little

¹ Unknown "A" was always obtained with hematite and/or iron berlinite. This unknown has the following x-ray data:

$d \text{ \AA}:$	3.09	2.45	2.01
$I:$	10+	2	3
		3.5	5
			1.63

phate even below 110° C. At about 560° C. this amorphous product crystallizes to an iron phosphate with a cristobalite structure. The excess iron forms hematite or combines in part with some phosphorus to form the unknown "A". Between 560 and 650 °C. this ferric orthophosphate— FePO_4 (cristobalite isotype) undergoes a complete transformation to iron berlinite.

It is to be noted that ferric orthophosphate (cristobalite isotype) formed only from the crystallization of the amorphous ferric phosphate. When no amorphous intermediate product forms, the phosphate with a cristobalite structure is not obtained. A striking analogy can be drawn between these transformations and those among corresponding modifications of silica. Sosman (1927, p. 105) states that silica *glass* when heated below 870° C. with fluxes or "mineralizers," converts first to one of the unstable forms (here ferric orthophosphate (cristobalite isotype)) and later changes further to quartz (here iron berlinite).

Oxidation of Ferrous Iron in Lipscombite and Ferrous Ferric Lazulite

Table 8 shows that the oxidation of ferrous iron in lipscombite is apparently not accompanied by any structural changes discernible in an *x*-ray powder photograph. This oxidation, therefore, must take place without the addition of any oxygen, but rather by removing the H ions of the OH groups. Such a process was proposed by Starke (1939) in connection with the oxidation of synthetic magnetite.⁷

TABLE 9. VARIATION OF IRON CONTENT OF FERROUS FERRIC LAZULITE UPON HEATING

	At Room Temp.	Heated at 290° C.	Heated at 425° C.
X-ray data	Ferrous Ferric Lazulite	Lipscombite	Lipscombite
FeO	17.54	0.2?	0.00
Fe ₂ O ₃	41.95	61.26	61.63
Total iron as Fe	43.02	42.99	43.10

The ferrous ferric lazulite is the product of Exp. 86. FeO determinations made by Mr. Lee Peck; Fe₂O₃ by the writer.

The oxidation of the ferrous iron of ferrous ferric lazulite on the other hand, is accompanied by a slight rearrangement of the structure resulting in lipscombite. Depending on *x*-ray evidence alone it cannot be said with certainty whether oxygen is added or H removed from the OH

⁷ Frondel (1949) found that a similar process of oxidation takes place in rockbridgeite $\text{Fe}^{++}\text{Fe}_6^{+++}(\text{PO}_4)_4(\text{OH})_8$, laubmannite $\text{Fe}_3^{++}\text{Fe}_6^{+++}(\text{PO}_4)_4(\text{OH})_{12}$ and dufrenite $\text{Fe}^{++}\text{Fe}_4^{+++}(\text{PO}_4)_3(\text{OH})_6 \cdot 2\text{H}_2\text{O}$.

groups. Determination of ferrous and ferric iron content of the original and the oxidized products (Table 9), does not at first sight seem to solve the problem. When the weight per cent of FeO and Fe_2O_3 was recalculated as weight per cent of Fe , it was clearly seen that no oxygen was added during the oxidation. Any addition of oxygen should have resulted in a corresponding decrease of the percentage of Fe .

ISOMORPHOUS SUBSTITUTION IN LIPSCOMBITE

Replacement of Iron by Divalent Metals

Lipscombite can be easily synthesized by heating powdered ferric phosphate in a ferrous sulfate solution (Table 1). If, however, other divalent metal sulfates are used, and the experiment performed in sealed tubes, or in bombs at temperatures usually higher than those required when ferrous sulfate is used, the lipscombite produced has a relatively

TABLE 10. REPLACEMENT OF IRON BY DIVALENT METALS IN LIPSCOMBITE¹

Exp. No.	Starting Materials	Experimental Detail	Temp. ° C.	Duration	Streak	
					Ridgway's	
					Name	No.
57-C	Ferric phosphate + CoSO_4 solution	Boil	100	3 hours	Raw sienna	17 i
58-4	Ferric phosphate + MnSO_4 solution	Sealed tube in bomb	180	7 days	Cream color	19' f
58-1	Ferric phosphate + MgSO_4 solution	Sealed tube in bomb	180	7 days	Pale green-yellow	27 f
58-2	Ferric phosphate + MgSO_4 solution (10 cc.) + FeSO_4 solution (2 cc.)	Sealed tube in bomb	180	7 days	Niagara green	41'' b
58-3	Ferric phosphate + $\text{MgH}_2(\text{PO}_4)_2$ + water	Sealed tube in bomb	180	7 days	Pale green-yellow	27 f
59	Ferric phosphate + NiSO_4 solution	Sealed tube in bomb	180	1 day	Citron green	25'' b
66-3	Ferrous phosphate + NiSO_4 solution	Sealed tube in bomb	180	22 days	Civette green	31' k

¹ All products were x-rayed and found to have a lipscombite structure.

light color (Table 10). This indicates that other divalent ions have replaced Fe^{++} ions, for almost without exception, crystals containing a given element in two different valence states are dark in color. X-ray data for magnesian lipscombite (of Exp. 58-1) are given in Table 12. Nickelian lipscombite (of Exp. 59) gave an identical powder pattern. Replacement of Fe^{++} by other divalent metals of various ionic radii does not result in any regular changes in the unit cell size.

Replacement of Iron by Aluminum

Over 40 experiments were performed in an attempt to synthesize

lazulite, scorzalite, and the aluminian and chromian analogues of lipscombite. The products in most cases were berlinite and/or some unidentified compounds. Four experiments, however, yielded a product with lipscombite structure. The fact that x -ray data (Table 12) show a smaller unit cell than lipscombite containing iron alone, and that iron and aluminum are the only metal ions present in the starting materials (Exp. 69, Table 11), indicate that aluminum has, at least partially, replaced iron.⁸ A chemical analysis is not possible, as this product always has either berlinite or a compound with an alunite structure mixed with it (Table 11).

TABLE 11. REPLACEMENT OF Fe^{+++} BY Al^{+++} IN LIPSCOMBITE

Exp. No.	Starting Materials	Experimental Detail	Temp. ° C.	Duration	Products	
					Color	X-Ray Data
67 A	$\text{Al}_2(\text{SO}_4)_3(\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ + Fe^{+++} phosphate + H_2O	Sealed tube in bomb	180	21 days	V. light green	Lipscombite: with smaller unit cell than that containing iron alone Compound with alunite structure
68 A	$\text{Al}_2(\text{SO}_4)_3(\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ + Fe^{+++} phosphate + 7 drops H_3PO_4 + H_2O	Sealed tube in bomb	180	12 days	Light pistachio green	Lipscombite: as in 67 A Berlinite
69	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ + Fe^{+++} phosphate + H_2O	Sealed tube in bomb	180	21 days	Pistachio green	Lipscombite: with smaller unit cell (measured, Table 12) Compound with alunite structure
75	Al phosphate + $\text{Fe}_2(\text{SO}_4)_3$ + H_2O (all trivalent ions)	Sealed tube in bomb	180	12 days	Cream color	Lipscombite: with smaller unit cell, v. small amount Berlinite

A Mineral with a Structure Similar to Lipscombite

An x -ray powder photograph of the U. S. National Museum sample No. R5611 showed a structure very similar to that of lipscombite (Fig. 2, and Table 12). The sample was labelled berlinite, Westana, Sweden. This mineral, however, is biaxial and contains aluminum. It has the following properties: Color, very light greenish white to almost colorless. Luster vitreous. Hardness about 7. Refractive indices for yellow light: $\alpha = 1.627 \pm .002$, $\beta = 1.643 \pm .002$, $\gamma = 1.648 \pm .002$. Birefringence moderate to weak ($\gamma - \alpha = .021$). Optically negative. $2V = 40^\circ$ (calculated), moder-

⁸ The difficulty of the replacement of Al by Fe^{+++} in the lazulite-scorzalite series is pointed out by the fact that none of the ten samples examined by Pecora and Fahey had over 0.9% Fe_2O_3 (Dr. W. T. Pecora, personal correspondence, 1949).

TABLE 12. X-RAY DATA FOR IRON BERLINITE, TWO SYNTHETIC AND ONE NATURAL COMPOUNDS WITH LIPSCOMBITE STRUCTURE

(Unfiltered iron radiation. Radius of camera = 57.3 mm.)

(See Fig. 2)

Iron berlinite		Magnesian Lipscombite of Exp. 58-1		Al-containing lipscombite (+faint alunite structure) of Exp. 69		U.S.N.M. No. R5611 Supposed berlinite Westana, Sweden	
<i>d</i> Å	<i>I</i>	<i>d</i> Å	<i>I</i>	<i>d</i> Å	<i>I</i>	<i>d</i> Å	<i>I</i>
4.887	1	5.155	f	5.508	2 ¹	5.018	f
4.422	6	3.726	3.5	3.600	1.5	4.627	.5
3.844	5	3.570	1.5	3.452	1.5 ²	3.515	2
3.471	10+	3.349	10+	3.362	f ³	3.408	1.5
2.789	3.5	3.212	8	3.254	10+	3.349	f
3.624	f	2.894	f	3.134	8	3.192	10+
2.529	5 ⁴	2.622	3.5	2.975	7 ³	3.074	9
2.379	5	2.551	f	2.546	3	2.778	1
2.312	2	2.303	3	2.481	f	2.512	5
2.192	3.5	2.264	f	2.256	2 ³	2.329	1
2.087	f	2.056	5	2.251	1.5	2.212	1
2.047	f	2.038	1.5	2.108	f	2.156	.5
1.886	4	1.878	1.5	2.012	5	2.106	1
1.729	2	1.843	3	1.989	2.5	1.985	5
1.701	1.5 ⁴	1.766	2 b	1.914	3 ³	1.953	4
1.588	3	1.673	4	1.841	1	1.790	3
1.511	f	1.600	5 b	1.807	1	1.778	1
1.427	4 b	1.456	1.5	1.758	1 ³	1.710	1
1.412	f	1.435	1	1.727	f	1.679	1.5
1.341	1	1.384	f	1.636	5	1.608	3.5
1.295	f	1.372	f	1.569	6 b	1.597	2.5
1.243	f	1.341	1	1.518	f	1.548	6.5 b
1.232	f	1.301	3	1.494	2.5 b ³	1.536	3
1.215	f	1.233	1	1.426	1.5	1.468	.5
		1.211	1	1.410	f	1.392	2.5 b
				1.393	f	1.328	1.5
				1.357	f	1.297	f
				1.332	f	1.268	1.5
				1.287	2	1.260	6
				1.277	2		

¹ Probably common to both alunite and aluminum-containing lipscombite.² Common to both alunite and aluminum-containing lipscombite.³ Alunite reflection.⁴ Common to both iron berlinite and hematite.

ate as observed in comparison to muscovite. No pleochroism. This mineral can be easily distinguished from lazulite and scorzalite by its lighter color, weaker birefringence, smaller optic angle and absence of pleochroism.

SOME THEORETICAL CONSIDERATIONS

The lipscombite series presents a complicated case of isomorphism in which definite chemical names indicating definite formulas cannot be given. It is believed that the presence of Al in place of Fe above a certain ratio results in a monoclinic rather than a tetragonal compound. Furthermore the "lipscombite series" ranging from the tetragonal magnesium ferric phosphate to the tetragonal ferrous ferric phosphate, is itself isomorphous with the lazulite-scorzalite series through partial replacement of ferric iron by aluminum, i.e., we have a case of isodimorphism.

The problem becomes even more interesting when the unit cell constants for lipscombite are recalculated. Instead of taking the tetragonal unit cell of lipscombite (Katz and Lipscomb, 1951), a unit cell with the same orientation as Berry's (1948) new unit cell of lazulite is used. The results are:

	a_0	b_0	c_0	β
Lipscombite	7.002	7.593	7.002	114°31'
Lazulite	7.12	7.24	7.10	118°55'
Scorzalite	7.15	7.32	7.14	119°00'

Again if the conventional orientation of the monoclinic prismatic so-called orthogonal pseudo-hexagonal morphological cell is used (Dana, *System of Mineralogy*, 1952), the following constants are obtained:

Lipscombite	$a:b:c$	1:1:1.687	β	90°
Lazulite	$a:b:c$.9750:1:1.6483	β	90°46'

Variations in the composition and properties of lipscombite as outlined in this paper may offer an explanation for some of the strange chemical analyses of "dufrenite-like" minerals, which do not afford a rational formula. Dufrenite itself has the formula $\text{Fe}''\text{Fe}'''_4(\text{PO}_4)_3(\text{OH})_5 \cdot 2\text{H}_2\text{O}$ (Frondel, 1949).

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