THERMOCRYSTALLIZATION OF RICHELLITE TO PRODUCE A LAZULITE STRUCTURE (CALCIUM LIPSCOMBITE)

DUNCAN McCONNELL, *Ohio State University, Columbus, Ohio.*

ABSTRACT

Richellite, a calcium-iron hydrated phosphate, appears to be virtually amorphous. In this respect it resembles several other poorly defined natural phosphates. However, after heating at 500° C. for 30 minutes, it crystallizes to produce a tetragonal substance which seems to be a calcium lipscombite with a 5.18, c 12.61 Å, and a unit-cell content $(Ca_{1.3}Fe^{2+}_{0.7})$ $(Fe^{3+}_{3-3}Al_{0.7})$ $(PO_4)_4$ $(OH, F)_4$.

The analysis, necessarily based solely on powder diffraction methods and chemical calculations, indicates a third tetragonal variant of the lazulite-type structure. Several enigmas concerning these lipscombite structures persist.

INTRODUCTION

In some respects the "amorphous" phosphate minerals have not attracted the attention that they deserve. Collophane, one of the commonest so-called amorphous substances, always produces the recognizable powder diffraction pattern of an apatite (McConnell, 1942a) whereas some other phosphatic precipitates indicate no better atomic organization than most commercial glasses.

Griphite from the type locality proved to be cubic, rather than "amorphous" (McConnell, 1942b), but another similar substance produced a cubic powder diffraction pattern—also that of a garnetoid—only after heating (Jaffe, 1946).

Most of the "amorphous" phosphates under consideration are fairly high in their water contents and consequently have low densities. Their inability to crystallize during geological time seems to be related to their retentivity of water in quasistable combination. This relationship is implied, at least, by the fact that some such substances can be induced to crystallize—presumably with more or less expulsion of water—by heating at temperatures above 300° C.

Similarly, it should be noted that synthetic calcium phosphate precipitates may produce, under some circumstances, very poor powder diffraction patterns, but these precipitates frequently yield good to excellent apatite-like diffraction patterns after hydrothermal treatment, after aging in contact with the parent solution, or after heating the dry preparation (Klement, 1936). However, under other circumstances (McConnell, Frajola and Deamer, 1961) carbonate hydroxyapatite (dahllite) will form crystals which, though quite small, will produce many of the interference maxima of the apatite structure.

In view of the inadequacy of present knowledge it is not possible to re-

late this subject to the more general principles of thermodynamics. The present report is concerned merely with some observations on richellite, a calcium-containing hydrated iron phosphate.

Acknowledgments

Crystallographic Data

The richellite sample, as received, consisted of very light brownish flecks with subvitreous luster. This material produced two very diffuse, broad diffraction bands, the spacings (d about 15 Å and 5.4 Å) of which are not similar to any obtained after heating the substance. The color of the heated powder closely resembles that of goethite.

After heating at 500° C. for 30 minutes and cooling slowly, a series of powder diffraction maxima were obtained for richellite that can be indexed as tetragonal (Table 1). The calculated and experimental interplanar spacings are in good agreement except for the first three maxima and a reflection of moderate intensity (d 2.98). It is possible that an impurity (*i.e.*, a second phase) may have resulted from the thermal crystallization. The powder diffraction pattern of heated richellite is compared with that of synthetic lipscombite (Ext. 99B, Gheith, 1953) in Fig. 1.

In order to compare analogous structural units, it is necessary to select a pseudo-cell that is common to all. In Table 2, "monoclinic data" are given for richellite, lipscombite, manganoan lipscombite and lazulite (using the pseudohexagonal orientation). (Body centering of the tetragonal cell of lipscombite produces halving of a' and b' of the "monoclinic" (pseudohexagonal) cell, Table 2.)

Crystal-Chemical Data

In order to obtain comparisons involving crystallochemical relations among these substances, it becomes necessary to assume that the same number of oxygen atoms occurs in comparable volumes of the monoclinic pseudo-cells, despite the fact that their symmetrical arrangements

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TABLE 1. POWDER DIFFRACTION DATA

(Fe radiation; $r = 57.3$ mm)

hkl	Richellite (Heated)			Lipscombite (Synthetic)[1]	
	$d_{(calc.)}$	$d_{(expt.)}$	I	$d_{(expt.)}$	I
002	6.30	5.99(?)	5	—	
100	5.18	—		—	
101	—	—		4.83	4
003	4.20	4.35	5	—	
102	4.00	4.14	5	—	
110	—	—		3.67	6
111	3.52	3.58	6	—	
103	3.29	3.24	9	3.33	>10
004	3.152	3.15	6	3.20	8
—	—	2.98	3	—	
113	2.763	2.74	3	—	
200	2.592	2.57	2	2.60	5
201	2.539	—		—	
202	2.397	2.415	1	—	
114	2.390	—		2.42	2
211	2.280	—		—	
105	2.268	2.271	5	2.297	5
213	2.030	2.027	5	2.050	8
204	—	—		2.030	4
220	1.833	1.831	3	1.859	1
116	—	—		1.844	3
301	1.712	1.710	4	1.739	2
215	1.707			—	
107	1.702			—	
310	1.650	1.640	5	1.659	8
312	1.587	1.590	7	1.614	6
224	1.585			—	
008	1.576			1.601	9
207	1.479	1.477	<1	—	
321	1.429	1.433	3	1.447	4
—	—	1.388	<1	—	
323	1.361	1.364	<1	1.373	
400	1.296	1.297	3	1.307	6

[1] Unfiltered radiation. Diffraction maxima caused by β radiation and known impurities are omitted. The β reflection for (103) coincides with the α reflection of (110).

are obviously slightly different. According to the structural proposal of Katz and Lipscomb (1951) the number of oxygens is 20 (of which 4 are hydroxyls), the number of P atoms is 4, and the number of equivalent positions for larger cations is 8, of which they say merely 7 are occupied in lipscombite. Written in the usual form, then, their structural formula

TABLE 2. COMPARISONS OF CRYSTALLOGRAPHIC DATA

	Richellite (Heated)	Gheith's Preparation 99B	Lipscombite (Synthetic)	Manganoan Lipscombite	Lazulite[2]
Reference	This work	This work	Katz & Lipscomb (1951)	Lindberg (1962)	Berry (1948)
Symmetry	—[3]	—	$I4_12$	$P4_12_12$	$P2_1/n$
Dimensions					
a (Å)	5.18	5.23	5.37	7 40	7.12
b					7.24
c	12.61	12.81	12.81	12.81	7.10
vol. (Å³)	338.4	350.4	369.4	701.5	320.4
Monoclinic pseudo-cell[1]					
a' (Å)	14.58	14.79/2	14.89/2	14.79	7.12
b'	14.58	14.79/2	14.89/2	14.79	7.10
c'	7.33	7.40	7.59	7.40	7.24
$\beta'(\gamma)$	119°42′	120°	118°41′	119°58′	118°55′
vol. (Å³)	338.4×4	350.4	369.4	350.7×4	320.4

[1] This pseudohexagonal orientation is such that $a'=b'=c/\sin \beta'/2$, $c'=a\sqrt{2}$ (or for manganoan lipscombite $c'=a$), and $\tan \beta'/2=c/c'$.

[2] The dimensions, a 7.16, b 7.26, c 7.24, β 120°40′, for lazulite from Minas Gerais, Brazil were obtained by Lindberg and Christ (1959), who also give dimensions for isostructural scorzailte and barbosalite.

[3] The space group is apparently limited to certain primitive types involving 4 or $\bar{4}$.

for lipscombite is $2[(A, B)_{4-x}(PO_4)_2(OH)_2]$, whereas the formula commonly written for lazulite is $2[AB_2(PO_4)_2(OH)_2]$. The difference, of course, involves whether there are, in fact, 8 or merely 6 symmetrical positions assigned to $A+B$, A being Mg, Fe^{2+}, etc. and B being Al,
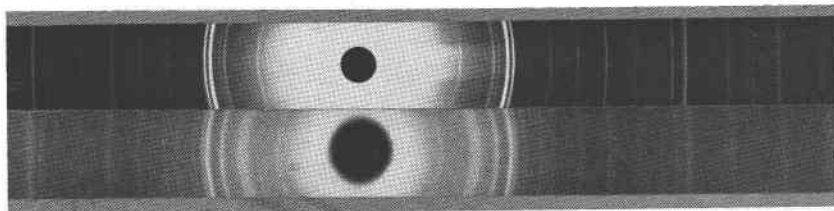

FIG. 1. Powder diffraction pattern of lipscombite (Gheith's preparation 99B) using unfiltered Fe radiation (above) compared with that of heated richellite using filtered Fe radiation (below).

TABLE 3. CONTENTS OF UNIT CELL OF MANGANOAN LIPSCOMBITE

(Analysis by Lindberg)

Ions	Ionic ratios	Ratios of charges	Charges $\Sigma = 40$	Unit-cell contents
Mn^{2+}	0.1115	0.2230	1.76	0.88 ⎫
Fe^{2+}	0.0522	0.1044	0.82	0.41 ⎬ 6.28
Fe^{3+}	0.6322	1.8966	14.96	4.99 ⎭
P^{5+}	0.4706	2.3530	18.56	3.71
H^+	0.4940	0.4940	3.90	3.90
		5.0710	40.00	

Fe^{3+}, etc. It should be possible to distinguish between these two possibilities on the basis of the chemical analyses.

In an attempt to ascertain the contents of the unit cells of these lipscombite-like substances, the calculations are based on the pseudo-cells, having volumes approximating 350 Å^3 and containing 20 oxygen atoms (Tables 3, 4 and 5). With the exception of heated richellite, however, it should be noted that the hydroxyl ions are not assumed to be 4, but are calculated from the water determinations of the analyses.

Probably the most reliable chemical data are those obtained by Lindberg (1962) for manganoan lipscombite (Table 3). Relegating the 40 charges of the 20 oxygen atoms to the various cations (including hydrogen) gives 6.28 for the total of divalent and trivalent metals (rather than 7) and small deficiencies for both P and OH.

Similar calculations for the analysis of Gheith's material of experiment 99B (Table 4) yield merely 5.80 for the metallic ions and a deficiency in P which is approximately one-fourth of the excess of H, suggesting the substitution of (H_4O_4) for PO_4. That is, $3.85 + (4.71 - 4)/4 = 4.03$.

TABLE 4. CONTENTS OF UNIT CELL OF SYNTHETIC LIPSCOMBITE

(Analysis by Gheith, Expt. 99B)

Ions	Ionic ratios	Ratios of charges	Charges $\Sigma = 40$	Unit-cell contents
Fe^{2+}	0.1718	0.3436	2.63	1.32 ⎫ 5.80
Fe^{3+}	0.5840	1.7520	13.43	4.48 ⎭
P^{5+}	0.5016	2.5080	19.23	3.85
H^+	0.6144	0.6144	4.71	4.71
		5.2180	40.00	

TABLE 5. CONTENTS OF UNIT CELL OF HEATED RICHELLITE

Oxides	Wt. %	Mol. ratios	Ions	Ionic ratios	Ratios of charges	Charges $\Sigma = 40$	Unit-cell contents
CaO	7.19	0.1282	Ca^{2+}	0.1282	0.2564	2.73	1.37
Al_2O_3	3.64	0.0357	Al^{3+}	0.0714	0.2142	2.28	0.76 }6.09
Fe_2O_3[1]	29.67	0.1858	Fe^{3+}	0.3716	1.1148	11.87	3.96
P_2O_5	25.49	0.1796	P^{5+}	0.3592	1.7960	19.12	3.82
H_2O^+	23.63[2]	—	H^+	—		(4.00)[2]	
HF	0.96	—					
					3.3814	40.00	

[1] Ferrous iron is not reported.

[2] The water content of a hydrogel is meaningless with respect to such calculations; the hydroxyl content is assumed to be 4.

Comparable calculations for richellite (Table 5) are based on analysis 4, (*Dana's System*, ed. 7, p. 957). This analysis shows the greatest amounts of metallic oxides and the least amount of fluorine among the four existing analyses of richellite. There is, again, a deficiency of P, but it becomes necessary to assume the hydroxyl content is 4 inasmuch as the water content of the heated material is unknown. The number of metallic ions under these circumstances is 6.09, and they occur in the approximate ratios 2:6:1 for Ca:Fe:Al. Assuming that about one-sixth of the iron of richellite is present in the divalent condition, the unit cell contents can be written as

$$(Ca_{1.3}Fe^{2+}{}_{0.7})(Fe^{3+}{}_{3.3}Al_{0.7})(PO_4)_4(OH, F)_4.$$

DISCUSSION AND CONCLUSIONS

Although the unit cell of heated richellite has *a* and *c* dimensions similar to those of lipscombite, it is primitive, rather than body centered, and its symmetry seems to be fairly low because of reflections from (111), (113) and possibly (003), (102) and (207), as shown in Table 1. Thus the product of thermocrystallization of richellite appears to be a third tetragonal variant of the lazulite-type structure.

Among these tetragonal variants, however, richellite would be expected to have the largest unit-cell volume in view of the comparative radii of the divalent cations: Ca 0.99, Mn^{2+} 0.80, and Fe^{2+} 0.74 (for C.N. = 6; Ahrens, 1952). Lipscombite would be expected to have the smallest unit-cell volume. From Table 2 it is apparent, not only that the volume of manganoan lipscombite is smaller than that of lipscombite, but that richellite has the smallest volume. These apparent anomalies

may be related to the substitution of (H_4O_4) groups for PO_4 groups inasmuch as this type of substitution seems to have a significant tendency to cause expansion of the lattice.

It is noticeable that the numbers for total metallic ions for manganoan lipscombite, Gheith's synthetic lipscombite (Expt. 99B), and richellite are 6.28, 5.80 and 6.09, respectively, when calculated directly from the analyses by the electrostatic valency method by assuming that the unit cell contains 20 oxygen atoms. The concordance with the usually accepted formula for lazulite obtains if the total number of metallic ions is 6, as is suggested by the calculations (Table 3–5), which give an average of 6.06.

It seems probable, as indicated by Katz and Lipscomb (1951), that a single set of 8 equivalent positions should be assigned to iron atoms in the lipscombite structure determined by them. What seems improbable is that merely 7 of these positions should be occupied.

Their postulation of the occupancy of merely 7 of these positions was based solely on a determination of the specific gravity and the necessity for assuming that iron is present in both the ferric and ferrous states. Nevertheless, their calculation contains another, though not apparent, assumption: namely, that all phosphorus positions necessarily are occupied by phosphorus.

Obviously, if all 8 positions are occupied by iron atoms, all 8 would have to be divalent. However, all 8 positions can be filled and trivalence can occur to the same extent that PO_4 is substituted by (H_4O_4). Although the change in molecular weight arising from the loss of a P atom is not as great as that of addition of a Fe atom, the calculation involving 8 Fe and one P substituted by H_4 matches the experimental specific gravity better than does the calculation involving 7 Fe atoms.

If these assumptions are correct, the structural formula for the substance with space group $I4_12$ should be

$$A^{2+}{}_{8-x}B^{3+}{}_x(PO_4)_{4-x}(H_4O_4)_x(OH)_4.$$
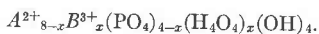
Alternative explanations should be considered in connection with structural proposals which involve defects as significant as the absence of one among 8 metallic cations.

In view of the data presented, it is tentatively concluded that thermal treatment of richellite produces a calcium lipscombite. Although the chemical and diffraction data lack the desired precision, the implied relationships can hardly be regarded as fortuitous. Several enigmas arise which cannot be resolved by the application of powder diffraction methods, and single-crystal methods do not appear to be applicable to heated richellite. Finally, the "invalidity of calcium lazulite" which has been postulated by Pecora and Fahey (1950) may require re-examination.

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