

Hureaulite, $Mn_5^{2+}(H_2O)_4[PO_3(OH)]_2[PO_4]_2$: Its Atomic Arrangement

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Abstract

Hureaulite, $Mn_5^{2+}(H_2O)_4[PO_3(OH)]_2[PO_4]_2$, a 17.594(10), b 9.086(5), c 9.404(5), β 96.67(8)°, $Z = 4$, space group $C2/c$, is one of the more persistent low temperature transition metal phosphate hydrates derived from hydrothermal attack of triphylite-lithiophilite. The structure was solved by Patterson and difference synthesis and least-squares refinement converged to $R(hkl) = 0.058$ for 3500 reflections.

The structure is based on an octahedral edge-sharing pentamer of point symmetry 2 which has composition $M_5\phi_{22}$. It further links at six corners to produce an open octahedral framework of composition $M_5\phi_{15}$, where $\phi = 4$ water molecules + 14 oxygens associated with the $[PO_4]^{3-}$ tetrahedra. One tetrahedron, $[PO_3(OH)]$, possesses a free hydroxyl group situated in a pocket in the structure. This pocket may spatially accommodate an intermediate-sized cation, extending interest to the series $Mn_5^{2+}(H_2O)_4[PO_3(OH)]_2[PO_4]_2 - X^{2+}Mn_5^{2+}(H_2O)_4[PO_4]_2[PO_4]_2$ and may explain the excess of larger cations in some analyses. Me-O averages are Mn(1)-O 2.19, Mn(2)-O 2.16, Mn(3)-O 2.21, P(1)-O 1.54 and P(2)-O 1.54 Å.

Hureaulite characteristically occurs very late in the secondary phosphate paragenetic sequence. Since nearly all iron is oxidized to the Fe^{3+} state before its crystallization, most natural hureaulites are Mn-rich compounds although extensive (Mn,Fe) solution is known for synthetic material.

Introduction

Hureaulite is one of the more persistent and widespread phases of the aquated first transition series phosphates associated with hydrothermally attacked triphylite-lithiophilite crystals in granite pegmatites. Interest is added to the species as a result of numerous reports on its synthesis and the recent discovery of the isotype sainfeldite, $Ca_5(H_2O)_4[AsO_3(OH)]_2[AsO_4]_2$ (Pierrot, 1964). Sainfeldite crystallized from arsenate-bearing solutions derived from mine waters acting upon arsenides and subsequently reacting with carbonates associated with late stage fissures. The sainfeldite clearly is a post-mine product and formed close to room temperature.

To understand the labyrinthine world of aquated transition metal phosphates, three-dimensional crystal structure analysis is necessary. The underlying goal in these studies is to establish the nature of the polyhedral clustering of the transition metal octahedra and the role of water and hydroxyl groups in these structures. Only in this manner can an unambiguous structural classification evolve and a link be established between the clusters in the crystal and those which existed in the solution from which the crystals grew.

Experimental

A superior single crystal of hureaulite, slightly elongate prismatic in shape, averaging 0.1 mm in thickness and 0.2 mm in length, was selected from a personally collected sample from the White Elephant pegmatite, between Custer and Pringle, South Dakota. The crystal was mounted parallel to the c -axis and 4200 reflections were gathered on a PICKER automated diffractometer utilizing graphite monochromatized $MoK\alpha$ radiation ($\lambda = 0.7093$ Å). The very small mosaic spread ($\pm 0.18^\circ$) and least-squares refinement of 12 reference reflections guaranteed high quality data. Cell parameters resulting from the refinement appear in Table 1. Twenty second background counting times were taken at each side of the reflection, with a scan rate of $1.0^\circ/\text{minute}$ and half-angle scans of 1.8° . Shells of reflections were gathered to maximum $2\theta = 75^\circ$.

The data were processed by conventional computational procedures to obtain a table of $|F(\text{obs})|$. No absorption correction was applied on account of the favorable size and shape of the crystal ($\mu = 48.6 \text{ cm}^{-1}$); omega-scans about selected reflections revealed that such a correction would be minimal. Remaining were 3500 symmetry independent reflections including the averaged symmetry equivalent data.

Solution of the Structure

The hureaulite heavy atoms were located by three-dimensional Patterson synthesis. Included were three non-equivalent manganese and two non-equivalent phosphorus atoms. Routine inspection of the Pat-

TABLE 1. Hureaulite. Crystal Cell Contents¹

a (Å)	17.594 (10)
b (Å)	9.086 (5)
c (Å)	9.404 (5)
β	96.67 (8) ^o
space group	$C2/c$
Z	4
formula	$(Mn_{0.74}Fe_{0.26})_5(H_2O)_4[PO_3(OH)]_2[PO_4]_2$
specific gravity	3.17
density (calc.) gm/cm^3	3.24

¹ Sample from White Elephant pegmatite, Custer, South Dakota. Octahedral cations determined from ARL electron probe analysis. The specific gravity was obtained with a Berman microbalance.

terson map revealed that one Mn atom was confined to the 2-fold rotor at 0, y , $1/4$ since all potential positions at inversion centers, also of equipoint rank number 4, were vacant. Since this atom has only one degree of freedom, the Mn(1)-Mn(2) and Mn(1)-Mn(3) vectors could be located without difficulty. The solutions of Mn(2) and Mn(3) were further obtained by tabulating the Harker lines as solutions in $\pm (2x, 2y, 2z)$ followed by a search for the inversion peaks at the intersections of these solutions. When the Mn(1), Mn(2) and Mn(3) atoms were found, all Mn-Mn' vectors were located and eliminated. The P(1) and P(2) atoms were located by examining strong vectors remaining within a shell of radius 3.7 Å from the origin, corresponding to the sum of Mn-O (2.2 Å) and P-O (1.5 Å) distances. The solutions for the P atoms were obtained from the solutions of the Mn atoms. It was a delightful way to spend two hours on a rainy afternoon.

Two cycles of atom coordinate refinement of the three Mn and two P atoms converged to

$$R(hkl) = \frac{\sum ||F(obs) - F(calc)||}{\sum |F(obs)|} = 0.41.$$

All ten oxygen atoms were located by subsequent difference synthesis.

Refinement

Refinement of the atomic coordinates and isotropic thermal vibration parameters proceeded without difficulty, using a local version of the ORFLS program for IBM 7094 computers by Busing, Martin and Levy (1962). Scattering curves for Mn^+ , P^{3+} and O^- were obtained from the tabulations of MacGillavry and Rieck (1962). Final full-matrix atomic parameter and isotropic thermal vibration parameter re-

finement converged to $R(hkl) = 0.058$ for all 3500 reflections.

Final atomic coordinate parameters and isotropic thermal vibration parameters are given in Table 2 and a list of $|F(obs)| - F(calc)$ appears in Table 3.²

Geometry and Topology of the Hureaulite Structure

Condensation of the octahedral modules. The underlying feature of the rather complicated hureaulite structure is an octahedral edge-sharing pentamer. Such a pentamer belongs to the homologous series $M_r\phi_{4r+2}$ where M = octahedral core and ϕ = octahedral vertex of which there are r cores and $4r + 2$ vertices. This homologous series is identical to the connected tree of edge-sharing hexagons without loops or circuits and, in hureaulite, has the composition $M_5\phi_{22}$. As idealized in Figure 1, the pentamer has point symmetry 2. Individual pentamers are further condensed to symmetry equivalent pentamers via corner sharing through the O(5) and O(10) atoms, and Figure 1 reveals that four O(5) and two O(10) atoms are associated with each pentamer. This fusion of pentamers results in a very loose and open octahedral framework of formal composition $M_5\phi_{18}$, where

² To obtain a copy of Table 3, order NAPS Document Number 2024 from Microfiche Publications, Division of Microfiche Systems Corporation, 305 East 46th Street, New York, N.Y. 10017. Please remit in advance \$1.50 for microfiche or \$5.00 for photocopies. Please check the latest issue of this journal for the current address and prices.

TABLE 2. Hureaulite: Atomic Coordinates and Isotropic Thermal Vibration Parameters*

Atom	x	y	z	$B(\text{Å}^2)$
Mn(1)	0	0.10238 (8)	3/4	0.69 (1)
Mn(2)	0.31696 (3)	.08821 (6)	-.31470 (6)	.67 (1)
Mn(3)	.17453 (3)	-.02833 (6)	-.13408 (6)	.74 (1)
P(1)	.41723 (5)	.32038 (9)	-.09009 (9)	.66 (1)
P(2)	.16098 (5)	.26066 (9)	-.37176 (9)	.60 (1)
O(1)	.3455 (2)	.2278 (3)	-.1338 (3)	1.13 (4)
O(2) = (OH) ⁻	.4884 (2)	.2150 (3)	-.0796 (3)	1.24 (4)
O(3)	.4231 (2)	.4331 (3)	-.2072 (3)	1.11 (4)
O(4)	.4156 (1)	.3915 (3)	.0558 (3)	1.05 (4)
O(5)	.1638 (1)	.2357 (3)	-.5331 (3)	1.00 (3)
O(6)	.0760 (1)	.2655 (3)	-.3407 (3)	.96 (3)
O(7)	.2019 (1)	.4040 (3)	-.3257 (3)	1.01 (4)
O(8)	.2024 (1)	.1326 (3)	-.2885 (3)	.93 (4)
O(9) = H ₂ O	.4213 (2)	-.0081 (3)	-.3463 (3)	1.70 (5)
O(10) = H ₂ O	.2599 (1)	.0796 (3)	.0310 (3)	1.09 (4)

* Estimated standard errors in parentheses refer to the last digit.

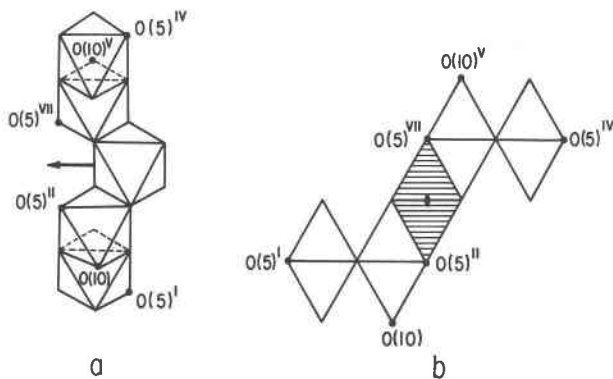


FIG. 1. Idealizations of the octahedral pentamer in hureaulite. a. Down the z^* -direction, showing the 2-fold rotor and the six points of corner-fusion to other symmetry equivalent pentamers. b. Down the y^* direction showing the 2-fold rotor. Unshaded octahedra are all above (or all below) the plane of the ruled octahedron.

$\varnothing_{18} = 4O_H + 14O_P$, O_H being water molecules and O_P oxygen atoms associated with the $(PO_4)^{3-}$ tetrahedra. All water molecules in hureaulite are bonded to the transition metals, so behave as ligand groups. Since there are no "zeolitic" water molecules in the structure, the formula should be written $Mn_5^{2+}(H_2O)_4[PO_3(OH)]_2[PO_4]_2$. One oxygen atom associated with the P(1) atom is not bonded to any transition metal and remains an $(OH)^-$ group in an open pocket in the structure and participates in hydrogen bonding. Thus, hureaulite is an acid crystal. Of the oxygen atoms associated with P(1), O(3) and O(4) bond to two, O(1) to one, and O(2) to no transition metals. For P(2), O(5), O(7), and O(8) bond to two and O(6) to one transition metal. Figure 2 reveals the rather elegant structure down the z^* direction.

The phosphate tetrahedra further knit the octahedral pentamers together by bridging to symmetry equivalent pentamers generated by the c -axial glide operation and the inversion centers at $1/4, 1/4, 0$; *etc.* But no $\cdots O-P-O-M \cdots$ bonds cross the a -axis at $x = 0, 1/2$; this promotes the good $\{100\}$ cleavage observed for hureaulite.

The acid pocket. The $O(2) = (OH)^-$ groups point into an open pocket in the structure whose center is on the 2-fold rotor at $1/2, y, 3/4$; *etc.*, where $y \sim 0$. Two geometrically plausible hydrogen bonds can be described, as revealed in Figure 3. The bonds $O(9)-H \cdots O(6)'''$ 2.703 Å and $O(2)^v-H \cdots O(9)$ 2.714 Å occur within the pocket. But O(2) does not appear to receive any bonds, since the second nearest distance is $O(9)-H \cdots O(2)$ 3.330 Å. Accordingly,

O(2) is interpreted as an acid portion of the structure, with the P(1) tetrahedral group written as $[PO_3(OH)]^{2-}$.

A curious and potentially important feature of the acid pocket is its spatial properties. From our Fourier syntheses, we concluded that the site is empty, at least in the crystal we studied. In addition, a probe analysis showed only Fe and Mn were present as large cations and these totalled to 4.96 in the formula unit. Defining its approximate center as the empty position X in Figure 2, there exist six bonds occurring pairwise to O(2), O(6) and O(9) with a polyhedral shape resembling a distorted octahedron. These $X-O$ distances include $X-O(9)$ 1.56, $X-O(2)$ 2.55 and $X-O(6)$ 2.71 Å. O(9) is a terminal water molecule, bonded to Mn(2), the terminus pointing into the pocket. Allowing some flexural freedom for O(9) and some "sliding" of X along the two-fold rotor, it is not difficult to conceive partial to complete replacement of X by intermediate-sized cations, such as Li^+ , Na^+ , Ca^{2+} , *etc.*, neutralizing the acid character of the crystal. This argument is advanced further to explain two analyses where an excess of larger cations is reported.

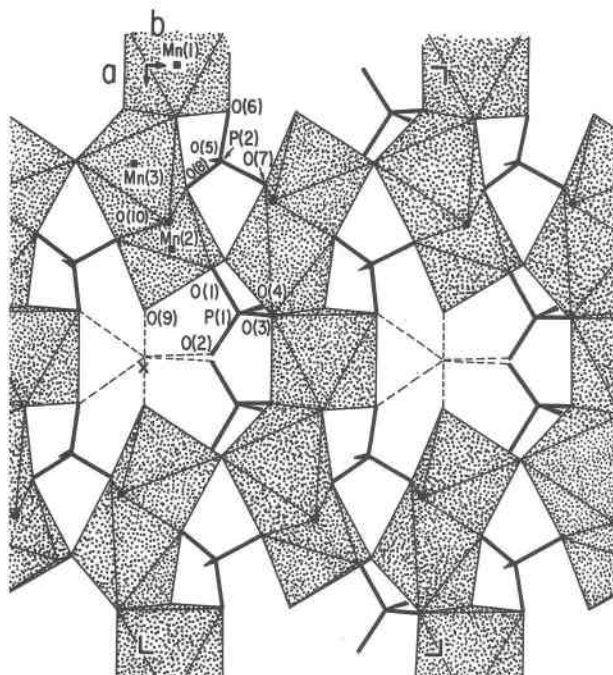


FIG. 2. The hureaulite structure down the z^* -direction. Remaining symmetry equivalent polyhedra in the cell are generated by the c -glide operation. Points of fusion of the pentamers are drawn as black dots. The MnO_6 octahedra are stippled and the $(PO_4)^{3-}$ tetrahedra appear as P-O spokes. The $X-O$ bonds are dashed in.

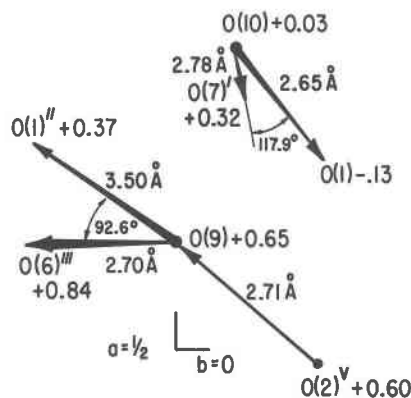


FIG. 3. Proposed hydrogen bonding scheme for hureaulite. Arrows point to the oxygen acceptors. Heights are given as fractional co-ordinates of the z-axis.

Hydrogen bonds. The O(9) and O(10) water molecules are donors of hydrogen bonds. Probable contributions by O(10) are O(10)-H...O(7)' 2.78 and O(10)-H...O(1) 2.65 Å with an angle O(7)'-O(10)-O(1) 117.9°. O(9) is more difficult to assess. The geometrically most compatible configuration is O(9)-H...O(6)''' 2.70 and O(9)-H...O(1)''' 3.50 Å with an angle O(6)'''-O(9)-O(1)''' 92.6°. It may be argued that O(2) receives as well as donates a bond from O(9), but the angle O(6)'''-O(9)-O(2) 140.3° is way out of range, even for a distorted tetrahedral angle.

It appears that the most likely acceptors of hydrogen bonds would be O(1) and O(6), further substantiated by the electrostatic valence balance calculations in Table 4 and the polyhedral interatomic distances in Table 5. Disregarding the contributions by hydrogen bonds, both O(1) and O(6) are severely undersaturated with respect to coordinating cations, with $\Delta\Sigma = -0.42$. But the Me-O(1) and Me-O(6) distances are not among the shortest for their polyhedra, so their degree of undersaturation is probably relieved by the hydrogen bond contributions.

Polyhedral distances. The Me-O averages are Mn(1)-O 2.19, Mn(2)-O 2.16, Mn(3)-O 2.21, P(1)-O 1.54 and P(2)-O 1.54 Å, which compare favorably with the Mn-O 2.22 and P-O 1.57 Å averages based on the tables of Shannon and Prewitt (1969) and the numerous recently refined manganese phosphate structures. In addition, Table 5 reveals that shared octahedral edges are among the shortest individual polyhedral distances, about 10 percent shorter than the polyhedral edge averages.

Hureaulite Paragenesis in Light of Its Crystal Structure

Hureaulite was originally named by Alluaud (1826) and described by the mining engineer Dufrenoy (1829) and its first analysis was undertaken by Vauquelin (1825). Material occurred sparingly from Hureaux, Haute Vienne, France, and later from La Vilate near Chanteloube, as described by Des Cloizeux (1858) who also presented crystal drawings. Subsequent occurrences include the famous Branchville pegmatite, Fairfield Co., Connecticut (Brush and Dana, 1890); the Strickland quarry, Portland, Connecticut (Schairer, 1926); and the Stewart mine, Pala, California (Schaller, 1912). Fisher (1964), in his study of lithian hureaulite ("bastinite", Fisher, 1946) from the Custer Mountain lode, near Custer, South Dakota, established the synonymy of "palaite" (Schaller, 1912) with the species; and Strunz (1954) relegated "baldaufite" and "wenzelite" from Hagendorf, Bavaria, to varietal status. "Pseudopalaite" of de Jesus (1933) from Mangualde, Portugal, was also shown to be hureaulite by Mason (1941) who adds Eräjärvi, Finland, as a new location. Indeed, few minerals have enjoyed such a reputation for obfuscation in the literature!

Recently, hureaulite has been recorded and noted from many localities and the species is one of the more persistent of the transition metal phosphate hydrates. Roberts and Rapp (1965) record six localities from the Black Hills, and one of us (P.B.M.) has collected specimens at nearly every pegmatite where altered triphylite-lithiophilite crystals and their hydration products are in evidence. It was common in the altered triphylite crystals at the

TABLE 4. Hureaulite. Electrostatic Valence Balances (Σ) of Cations about Anions

		Σ
O(1)	P(1) + Mn(2)	1.58
O(2)=(OH) ⁻	P(1)	1.25
O(3)	P(1) + Mn(1) + Mn(3)	1.92
O(4)	P(1) + Mn(1) + Mn(3)	1.92
O(5)	P(2) + Mn(2) + Mn(3)	1.92
O(6)	P(2) + Mn(1)	1.58
O(7)	P(2) + Mn(2) + Mn(3)	1.92
O(8)	P(2) + Mn(2) + Mn(3)	1.92
O(9)=H ₂ O	Mn(2)	0.33
O(10)=H ₂ O	Mn(2) + Mn(3)	0.67
	Sum:	15.01

TABLE 5. Hureaulite: Polyhedral Interatomic Distances*

Mn(1) octahedron		Mn(2) octahedron		Mn(3) octahedron	
2 Mn(1) -0(3)'' 2.116 Å		Mn(2) -0(9) 2.087 Å		Mn(3) -0(5)'' 2.129 Å	
2 -0(4)' 2.216		-0(8) 2.097		-0(8) 2.158	
2 -0(6) 2.232		-0(1) 2.134		-0(3)'' 2.170	
average 2.188 Å		-0(7)'' 2.181		-0(4)' 2.208	
		-0(5)' 2.198		-0(10) 2.256	
2 0(3)''-0(4)' 2.729		-0(10)'' 2.258		-0(7)'' 2.331	
1 0(3)''-0(3)'' 2.909		average 2.159		average 2.209	
2 0(4)' -0(6) 3.025					
2 0(3)''-0(6) 3.053		0(7)''-0(10)'' 2.778		0(7)''-0(10) 2.650	
2 0(4)' -0(6) 3.211		0(7)''-0(8) 2.807 ^a		0(3)'' -0(4)' 2.729 ^a	
1 0(6) -0(6) 3.337		0(8) -0(10)'' 2.832		0(7)''-0(8) 2.807 ^a	
2 0(4)' -0(3)'' 3.416		0(1) -0(8) 2.890		0(3)'' -0(8) 2.855	
average 3.093		0(7)''-0(9) 2.963		0(8) -0(10) 3.095	
		0(9) -0(10)'' 3.010		0(5)'' -0(7)'' 3.111	
		0(9) -0(5)'' 3.043		0(4)' -0(10) 3.113	
		0(1) -0(7)'' 3.070		0(3)'' -0(5)'' 3.129	
		0(1) -0(5)'' 3.134		0(4)' -0(8) 3.195	
		0(5)' -0(8) 3.270		0(5)'' -0(10) 3.347	
		0(1) -0(9) 3.315		0(4)' -0(5)'' 3.422	
		0(5)'' -0(10)'' 3.399		0(3)'' -0(7)'' 3.931	
		average 3.043		average 3.115	

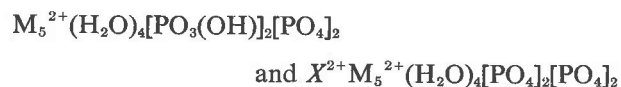
P(1) tetrahedron		P(2) tetrahedron		Distances to X, the center of the vacant acid pocket	
P(1) -0(3) 1.517 Å		P(2) -0(7) 1.527		2 X-0(9) 1.56	
-0(4) 1.520		-0(8) 1.538		2 -0(2) 2.55	
-0(1) 1.531		-0(5) 1.540		2 -0(6)'' 2.71	
-0(2) 1.571		-0(6) 1.556			
average 1.535		average 1.540			
0(1) -0(3) 2.457		0(7) -0(8) 2.490			
0(2) -0(4) 2.494		0(5) -0(8) 2.503			
0(1) -0(2) 2.509		0(5) -0(7) 2.507			
0(3) -0(4) 2.521		0(5) -0(6) 2.525			
0(2) -0(3) 2.523		0(6) -0(8) 2.528			
0(1) -0(4) 2.531		0(6) -0(7) 2.537			
average 2.506		average 2.515			

*The primed superscripts refer to the following transformations performed on the parameters in Table 2: $' = 1/2 - x, 1/2 - y, z$; $'' = x, y, 1/2 + z$; $''' = 1/2 - x, 1/2 + y, 1/2 - z$; $'''' = 1/2 + x, 1/2 + z$; $v = x, y, 1/2 - z$; $v' = 1/2 + x, 1/2 + y, z$; $v'' = x, y, z$. Estimated standard errors: M-0, P-0 \pm 0.003 Å; 0-0' \pm 0.004 Å.

^aOctahedral shared edges.

Fletcher and Palermo No. 1 pegmatites, N. Groton, New Hampshire, and from a pegmatite at Coosa Co., Alabama (P.B. Leavens, pers. comm.).

Of considerable interest are the analysis by Volborth (1954) on hureaulite from Viitaniemi, Eräjärvi, central Finland, and the analysis reported by Fisher (1964) on the lithian hureaulite from the Black Hills. Both analyses suffer faults: Volborth's material was contaminated with minor morinite (but he reports only a trace of Al_2O_3 !) and the water determination was by difference, and Fisher's analyses are crude. Table 6 presents these analyses and computations of cations based on 16 tetrahedra (= P + Be) in the former and the crystal cell in the latter analysis. The ratios Σ large cations: ΣT cations are 1.46 and 1.47 respectively, and extend our interest to the series



with ratios of 1.25 and 1.50 respectively. This peculiar series is possible because the acid pocket in the structure at $1/2, \sim 0, 1/4$ of equipoint rank number 4 is dimensionally suitable for intermediate-sized cations like Na^+, Li^+, Ca^{2+} , etc. Thus, Volborth suggested the composition $CaMn_5(PO_4)_4 \cdot 4H_2O$ for his compound which is, in effect, a neutral salt. To confirm the existence of a neutral salt for hureaulite, a most careful analysis of cations and water content or a difference synthesis on the structure of Volborth's material would be necessary.

Paragenetically, hureaulites are either products of hydrothermal attack on primary phosphates, particularly the triphylite-lithiophilite series, or the reaction products of Mn-rich phosphatic solutions during the late hydrothermal stage which were independent of the existence of some parent phase. Of interest is the synthesis of hureaulite-type compounds by Klements *et al.* (1970). By hydrolysis of metal chloride and sodium dihydrogen phosphate solutions at intermediate pH, they were able to synthesize mixed crystals of $Mn^{2+}, Fe^{2+} (Co^{2+}, Zn^{2+}, Cd^{2+}, \text{ and } Cu^{2+})$ hureaulites. Solid solution of Fe^{2+} in Mn^{2+} appears limited with maximum reported 35 percent replacement, which is the upper limit reported in the analysis of hureaulite from Hureaux. But most natural hureaulites occur in assemblages where the mineral is clearly contemporary to or postdates the appearance of the basic ferric phosphates such as strengite, rockbridgeite, etc., and are consequently low in Fe^{2+} content compared with the triphylite parent phase. Where lithiophilite is the parent phase, hureaulite forms directly as druses upon the parent without the appearance of the ferric compounds.

TABLE 6. Hureaulite: Analyses with Excess Large Cations

	1		2		
	Weight percent	Cations (T=16)	Weight percent	Cations in cell	
Na_2O	2.92	2.7			
Li_2O	-	-			
CaO	8.58	4.4	2.1 \pm 0.3	4.1	
MgO	-	-	not > 0.7	0.4	
MnO	38.85	15.7	not > 1.7	1.2	23.5
FeO	1.44	0.6	37.	15.3	
BeO	1.35	1.4	6.	2.5	
P_2O_5	36.35	14.6	16.0	43 \pm 3; 33 \pm 3	
$H_2O(-)$	0.04				
$H_2O(+)$	10.00				
rem.	0.75				
	(100.28)				

¹Analysis of Volborth (1954). T = $Be^{2+} + P^{5+} = 16$. $H_2O(+)$ was determined by difference.

²Fisher (1954), computed using his a 17.64 Å, b 9.13, c 9.49, θ 96°30' and specific gravity = 3.21. The two independent analyses for P are in conflict.

This is the paragenesis typical for Branchville, Connecticut, and Custer Mountain, South Dakota, pegmatites. Strunz (1954) observed that hureaulite from Hagendorf Süd has an Fe:Mn ratio of 1:3 whereas that of the parent triphylite was nearly 3:1. Consistent with the synthetic studies on hureaulite, the species evidently appears at the final stages after oxidation of iron to the ferric state and after precipitation of such species as rockbridgeite, leucophosphite and strengite. For the hureaulite in this study (Table 1), the Fe:Mn ratio is based on electron probe analysis and the White Elephant parent phase was unquestionably an iron-rich triphylite. It is concluded, as it was by Strunz, that the manganese content of the solution is enriched as the ferric iron is removed by precipitation at higher temperature. What ferrous iron remains enters into solution at the final stage in the predominantly manganese-rich hureaulite and is limited to a Fe:Mn \sim 1:3 ratio as observed in the synthetic studies.

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