American Mineralogist, Volume 66, pages 176–181, 1981

Polymorphism in $Cu_5(PO_4)_2(OH)_4$

GERALD L. SHOEMAKER AND EDWARD KOSTINER[1]

Institute of Materials Science and Department of Chemistry
University of Connecticut
Storrs, Connecticut 06268

Abstract

Three polymorphs of $Cu_5(PO_4)_2(OH)_4$ have been synthesized by hydrothermal techniques. One of these (PM) is the synthetic analog of pseudomalachite; the other two (PPM and QPM) have only recently been found as minerals. The crystal structures of the three are very similar, consisting of layers of edge-sharing, copper-containing polyhedra linked in the third dimension by phosphate tetrahedra and hydrogen bonds. The copper layers contain frameworks which may be derived from a layer of close-packed, edge-sharing octahedra (as observed in brucite) from which one third of the octahedra have been removed as edge-sharing pairs. This model successfully predicted the existence of the QPM polymorph and can be extended to show the possibility of a fourth polymorph. All three polymorphs can be grown within a single hydrothermal run and have been found to coexist within a mineral specimen. The distribution of the polymorphs depends in a complex fashion upon several factors, including composition of the reaction mixture, temperature, pressure, ease of nucleation, and rate of crystal growth.

Introduction

The structures of three polymorphs of $Cu_5(PO_4)_2(OH)_4$, pseudomalachite (PM), PPM, and QPM, have been described (Ghose, 1963; Shoemaker *et al.*, 1977, 1981; Anderson *et al.*, 1977). Single-crystal X-ray studies have shown that these polymorphs exhibit striking similarities (Table 1). The polymorphs exhibit similar unit-cell volumes (doubling QPM to two asymmetric units) and therefore have similar densities and similar oxygen-packing densities (volume/oxygen). In addition, the shortest unit-cell translations are very similar in length. The space groups of the first two polymorphs are equivalent, $P2_1/glide$, but the higher symmetry is not present in the third polymorph.

The structural model

Structurally, the short unit-cell translation in each polymorph corresponds to the separation between two-dimensional layers of edge-sharing, copper-containing polyhedra. The layers are interconnected by phosphate tetrahedra which share two vertices in each layer. Since the interlayer structures are functionally equivalent, it becomes apparent that the important differences between the structures lie within the copper-containing sheets. The copper polyhedra are essentially equivalent throughout the polymorphs, in general consisting of four short bonds plus one or two longer bonds which form characteristically elongated octahedral sites. (The minor differences in copper polyhedra will be discussed more fully below.) Therefore, the major structural difference has to lie in the pattern of sharing of polyhedral edges to form the extended two-dimensional sheets. We have determined that the relationship between the PM and PPM structures can be seen by the following analysis and were able to predict the existence of other possible polymorphs (including QPM) by an extension of this analysis.

The structures of PM and PPM can be derived from a simple two-dimensional (close-packed) layer of edge-sharing octahedra (as observed in brucite or in CdI_2) by removal of one third of the octahedral sites as edge-sharing pairs (Fig. 1). In place of these pairs of octahedra a new, elongated octahedral site can be formed by the twisting of octahedra in the remaining structural framework (see Fig. 3 in Anderson *et al.*, 1977). The new site, which maintains inversion symmetry, is occupied by the copper atoms designated

---

[1] Author to whom correspondence should be addressed.

0003–004X/81/0102–0176$02.00

Table 1. Unit-cell data for $Cu_5(PO_4)_2(OH)_4$ polymorphs

PM	PPM	QPM
$P2_1/c$	$P2_1/a$	$P\bar{1}$
a = 4.4728(4) Å	c = 4.461(1) Å	a = 4.445(1) Å
b = 5.7469(5)	b = 10.684(2)	b = 5.873(1)
c = 17.032(3)	a = 9.186(2)	c = 8.668(3)
β = 91.043(7)°	β = 92.31(1)°	β = 90.35(2)° α = 103.62(2)° γ = 93.02(1)°
V = 437.7 Å^3	V = 437.5 Å^3	V = 219.6 Å^3 (2 x V = 439.2 Å^3)
Z = 2	Z = 2	Z = 1
D_{cal} = 4.367 g cm^{-3}	D_{cal} = 4.370 g cm^{-3}	D_{cal} = 4.354 g cm^{-3}
Vol/O = 18.24 Å^3	Vol/O = 18.23 Å^3	Vol/O = 18.30 Å^3

Cu(1) in each polymorph. During the distortion of the framework, oxygen atoms near the ends of this site move close enough together to be bridged by the edge of a phosphate tetrahedron and thereby become the sites of attachment of the phosphate groups, which link the sheets in the third dimension. In the ideal model the layers stack directly over one another so that the attachment sites are directly superimposed. In reality the layers shift slightly from direct superposition. A measure of this shift is contained in the deviation of the unit-cell angle β (and γ in QPM) from 90°.

On the basis of this model, the topological difference between the structures of the polymorphs lies in the manner of removal of the pairs of octahedral sites. Four of the simplest ways of removing one third of the octahedra are shown in Fig. 2. The first two of these correspond to the idealized frameworks of PPM and PM. The remaining two frameworks represent arrangements which were hypothesized as other possible polymorphs. A halving of the unit-cell volume is expected in the two remaining arrangements. A newly discovered phase was found growing intermixed with PM and PPM. It was similar in appearance to PM and PPM and had a unit cell with half their volume but with a similar short translation. This phase proved to be the anticipated third polymorph. The early Patterson and electron density maps revealed that the new phase (QPM) was one of the predicted frameworks, shown specifically in Figure 2d (Shoemaker *et al.*, 1981).

Properties of the remaining net

A polymorph based on the fourth framework (XPM, Fig. 2c) remains to be discovered. A few features of the expected framework can be predicted. The polymorphs discovered thus far have manifested the symmetry which is inherent in the undistorted, idealized framework, specifically, $P2_1/glide$ for the first two frameworks and $P\bar{1}$ for the third framework. The highest symmetry contained in the remaining framework as an ideal layer is $P\bar{1}$; therefore the remaining polymorph is expected to show triclinic symmetry.

The width of the unit cell shown in Figure 2c corresponds to the width of two copper octahedra sharing an edge. In PM and QPM the similar dimension (b in both compounds) has an average value of 5.8Å. By combining this value with the average interlayer separation for the three known polymorphs, 4.46Å, and the average volume of the asymmetric unit, 129Å^3, a value for the width of the cell parallel to c^* can be estimated at ~8.5Å. The final unit-cell edge may be expected to be approximately 8.5/sinα. Thus, the unit-cell edges of the undiscovered polymorph may be estimated roughly as a = 4.46, b = 5.8, c = 8.5/sinαÅ, where the axes of the expected triclinic unit cell are defined as shown in Figure 2c. Of course, distortions of the framework can alter the symmetry and placement of components so that the unit-cell size may be a multiple of the smallest possible cell.

In addition to exhibiting the correct space groups of the known polymorphs, the idealized models also correctly portray the number of unique copper sites and the site symmetries. The model predicts that the remaining polymorph will have three crystallographically distinct copper atoms. Only one of these will lie on an inversion center [the Cu(1) site] while the other two will contain an inversion center in a

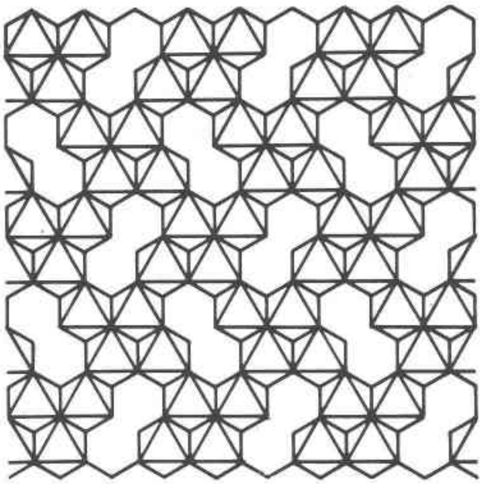

Fig. 1. A two-dimensional framework created by removing one third of the octahedra as edge-sharing pairs from a close-packed layer of octahedra.

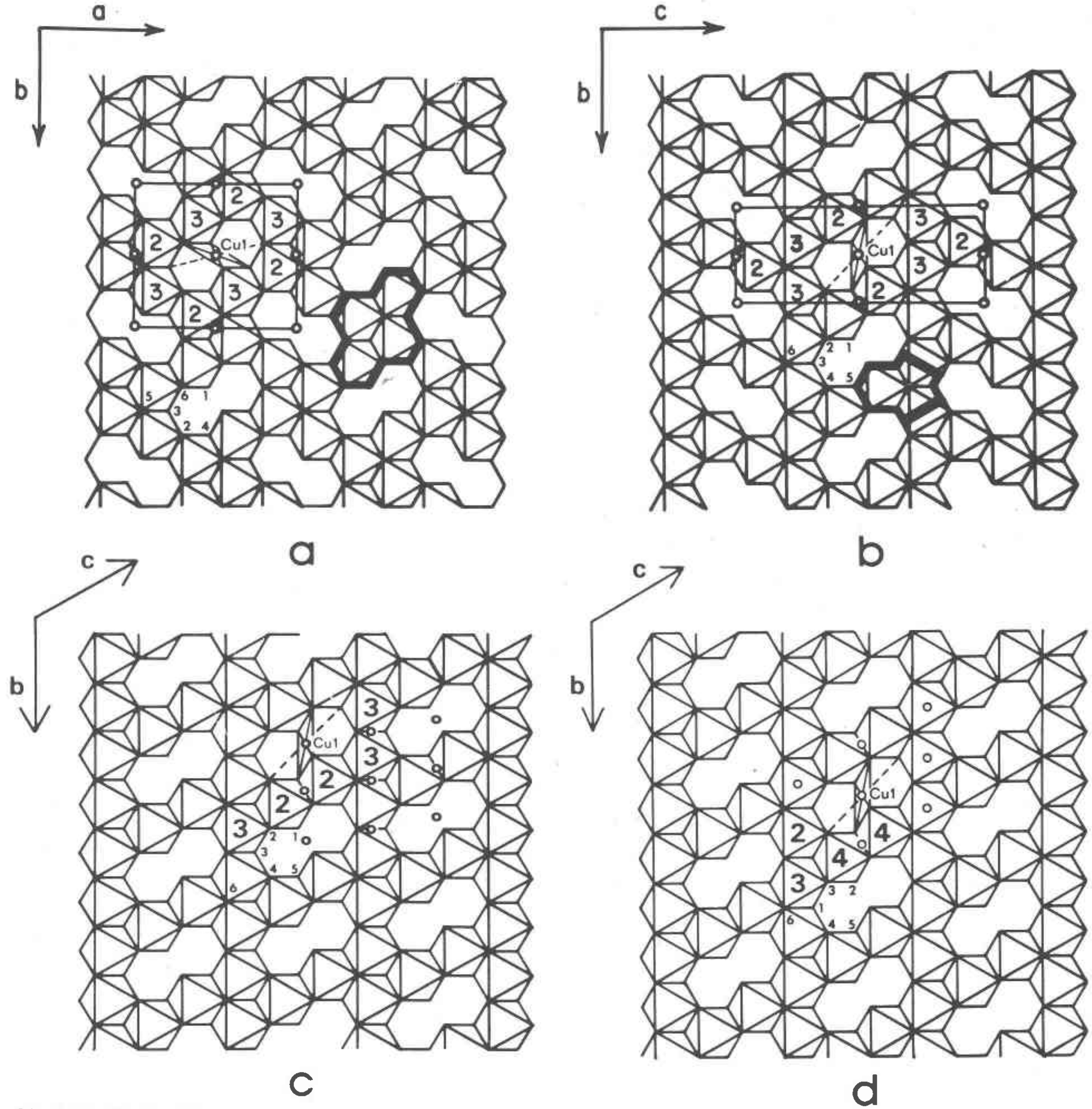

Fig. 2. The idealized frameworks of the $Cu_5(PO_4)_2(OH)_4$ polymorphs: (a) PPM, (b) PM, (c) XPM, (d) QPM. Large numbers identify the copper polyhedra, small numbers the oxygen atom positions, and small circles the locations of inversion centers. The nature of the Cu(1) site is shown.

polyhedral edge. As in the other polymorphs, there will be six unique oxygen atom positions in the asymmetric unit.

An interesting feature of these frameworks is that they can be constructed with perfect octahedra until the distortion occurs which creates the Cu(1) site and the site for attachment of the phosphate tetrahedron. A variety of cations which favor octahedral coordination might be expected to fit into such an undistorted framework, but since distortion can easily cause stretching of the polyhedra it might be expected to favor those ions which readily accept the four short plus one or two longer bonds common to the divalent copper-containing structures. A two-dimensional framework of edge-sharing copper octahedra like that of PPM has been observed in the mineral veszelyite, $(Cu,Zn)_2ZnPO_4(OH)_3 \cdot 2H_2O$ (Ghose *et al.*, 1974). In this compound the unique Cu(1) sites do not contain copper atoms, but instead are the loci of hydrogen atoms bonded to water molecules which complete framework copper polyhedra. In addition, the ends of the special site are not bridged by the edges of tetrahedral PO_4^{3-} or ZnO_4^{6-} groups. Distortion of the framework copper sites is observed in the veszelyite structure, even though it is possible to create the two-dimensional framework from undistorted octahedra as is demonstrated in Figure 2a.

Characteristics of the copper sites

The basic similarities of the frameworks result in the appearance of copper and oxygen sites which have similar characteristics. As expected, Cu(1) sites which are derived from the centers of the holes in the idealized frameworks show similar polyhedral characteristics (each site has inversion symmetry) (Table 2).

From Figure 2 it can be seen that the Cu(2) site in PM should be similar to Cu(4) in QPM (bonds listed in equivalent orders) (Table 3). In the undiscovered polymorph the Cu(1) environment is expected to be similar to the Cu(1)'s given above and the Cu(2) environment (as numbered in Fig. 2c) similar to the Cu(2) and Cu(4) sites in PM and QPM, respectively.

Another feature common to all the polymorphs is the occurrence of one oxygen site that interacts only weakly with three copper atoms and strongly with the phosphorus atom. One of the copper atom bonds lies in almost direct opposition to the phosphorus–oxygen bond and this interplay usually leads to a very long copper–oxygen distance, generally lengthened to the extent that the significance of the bond is questionable (Table 4). A similar situation is expected in XPM for the interaction of the Cu(2)–O(4)–P atoms.

Table 2. Cu(1) environment in the three polymorphs

PM			PPM			QPM		
Cu(1)-O(1)	2x	1.884Å	Cu(1)-O(1)	2x	1.915Å	Cu(1)-O(2)	2x	1.918Å
OH(5)	2x	2.007	OH(6)	2x	1.984	OH(5)	2x	2.040
O(4)	2x	2.757	O(3)	2x	2.723	O(4)	2x	2.580
Angles:								
equatorial								
O-Cu-OH		86.9°	O-Cu-OH		83.6°	O-Cu-OH		84.05°
pyramidal								
O-Cu-O		88.0°	O-Cu-O		85.1°	O-Cu-O		86.11°
O-Cu-OH		83.2	O-Cu-OH		83.4	O-Cu-OH		83.70

Table 3. Cu(2) (PM) *vs.* Cu(4) (QPM)

PM		QPM	
Cu(2)-O(2)	1.939 Å	Cu(4)-O(3)	1.932 Å
OH(6)	1.958	OH(6)	1.967
OH(5)	1.974	OH(5)	1.952
OH(5)	1.985	OH(5)	1.975
O(1)	2.395	O(2)	2.427
O(4)	2.755	O(4)	2.825

Hydrogen bonding

The oxygen position just described has been significantly valence-deficient in each of the known polymorphs and has become the prime candidate for hydrogen acceptor bonds. This is also expected for O(4) in XPM. Of course a key factor is that in all polymorphs this site is flanked by hydroxyl groups, O(5) and O(6), which lie near to it in the adjacent copper-containing layers. In PM O(4), which achieves 1.58 v.u., is 3.044 and 3.009Å from O(5) and O(6), respectively; in PPM the corresponding distances from O(3) (1.55 v.u.) are 2.941 and 3.147Å and in QPM O(4) (1.56 v.u.) is 2.935 and 3.017Å from O(5) and O(6).

Growth and equilibria between $Cu_5(PO_4)_2(OH)_4$ polymorphs

The determination of the conditions for growth of the members of the polymorphic series involves the interaction of many factors including: (1) composition of the reactant mixture, (2) temperature, (3) pressure, and (4) order or rate of product formation. Other factors are suggested by the results but are more difficult to demonstrate on the basis of current experimental data. These effects can be placed in a general category concerning hydrothermal transport, including: (5) the ease of nucleation, (6) the rate of crystal growth following nucleation, and (7) a factor which falls into a highly hypothetical category, the possible formation of complex species in hydrothermal solution which act as precursors favoring the precipitation of a particular structure.

Table 4. Nearly linear Cu–O–P in the three polymorphs

PM		PPM		QPM	
O(4)-P	1.511 Å	O(3)-P	1.515 Å	O(4)-P	1.512 Å
O(4)-Cu(2)	2.755 Å	O(3)-Cu(2)	2.916 Å	O(4)-Cu(4)	2.825 Å
angle:	172.5°		170.65°		176.70°

While operating within temperature, pressure, and final pH ranges in which all three polymorphs are observed, changes in the starting composition have been found to result in pronounced effects on the product distribution. For example, within moderate temperature ranges, the use of aqueous $NaHCO_3$ with $Cu_3(PO_4)_2$ nutrient seems to favor the formation of PM while the use of a K_2HPO_4 mineralizer with libethenite (Cu_2PO_4OH) seems to favor the initial production of PPM, and a K_3PO_4 mineralizing solution with either $Cu_3(PO_4)_2$ or libethenite appears to favor the formation of QPM.

A series of experiments was designed to test the effects of temperature on the spatial and quantitative distribution of the polymorphs. A set of conditions was found which produced all three polymorphs in the same capsule from a charge of 77 mg synthetic libethenite and 105 mg K_2HPO_4 in 0.5 ml H_2O run for 7 days. For each subsequent experiment in the series a similar charge of libethenite, K_2HPO_4, and water was loaded into two gold capsules of about 12 cm total length placed end-to-end in a hydrothermal bomb oriented horizontally during the growth experiment. The relative amounts of reactants in the capsules were held constant for the series, in which the main variable was temperature. At the end of an experiment the contents of each capsule were analyzed according to spatial distribution. Any unattached crystals were removed. Then the capsule was divided into sections according to distance from the hot end, and the crystals which adhered to the walls in each section were collected and analyzed by visual and X-ray techniques. PM and QPM were always found toward the cooler regions of the capsules and PPM in the hot region. When the experiment was carried out at progressively lower temperatures PM and QPM were found closer to the warmer end of the bomb. In the lowest-temperature experiments only QPM was found in the coolest zone.

The distribution of products along the walls of the growth capsule can be a function of several factors. Primarily, the point at which a phase is deposited along a temperature gradient is expected to reflect the temperature dependence of its solubility in the fluid phase. (In an experiment of infinite duration such a distribution might be observed.) However, these results may be affected by the ease of nucleation and the rate of crystal growth on the nuclei. In all cases the PM crystal aggregates seemed to be more numerous but significantly smaller than the QPM aggregates. The greater numbers of PM crystals may reflect a relative ease of nucleation of this phase onto the gold surface and the smaller crystallite size may simply be a function of the great number of nuclei. On the other hand, the noted tendency for QPM to twin during growth may have contributed to relatively rapid growth of the QPM crystallites, once nuclei were formed.

In one pair of experiments, where all conditions except pressure were matched, both visual inspection and X-ray examination tentatively indicated an increase in the relative amount of QPM over PM in the lower-pressure experiment (1.2 kbar *vs.* 2.7 kbar), in line with the commonly observed tendency for lower-density phases to grow at lower pressures.

Our experiments clearly illustrate a tendency for certain combinations of nutrient and mineralizer to favor the initial formation of specific products. At 300°C and approximately 3 kbar pressure, libethenite plus aqueous KOH produces only PM and QPM while libethenite plus aqueous K_2HPO_4 produces primarily PPM. Indeed, PPM is the favored product of the initial reaction of aqueous K_2HPO_4 with libethenite over a wide range of temperatures.

During a reaction between malachite, $Cu_2(OH)_2CO_3$, and ammonium monohydrogen phosphate at 270°C, 3.7 kbar, all three polymorphs were formed, but their order of appearance was reversed with respect to the temperature gradient. In this experiment (which was run in vertical orientation) little or no transport was observed. Instead, a lump of material was recovered which had an upper crust of well-crystallized PPM over a powder composed of PM and QPM along with CuO and Cu_2O. By thermal gradients alone PM and QPM would be expected to occur on top (toward the cooler end). However, PPM seemed to be the phase favored by primary contact with the solution, while PM and QPM were found in an environment where solution interaction would have been moderated by a high powder-to-solution ratio (possibly resulting in a local variation in pH or in concentration of some reacting species).

Discussion

The picture of stability and growth of the $Cu_5(PO_4)_2(OH)_4$ polymorphs remains cloudy. It seems clear that there are two factors to consider in hydrothermal reactions: the preferred formation of one polymorph during the initial reaction and the subsequent rates of transport and deposition of the various polymorphs. The first factor has been discussed, but the second factor needs further exposition.

As indicated earlier, the physical separation of the polymorphs by hydrothermal transport and deposition along a temperature gradient can be a complex matter involving solubilities, nucleation, and crystal growth rates. The seventh factor concerning formation of complex species which favors the deposition of a particular structure from solution may be important. Ballman and Laudise (1963) define a mineralizer as a substance which increases the rate of crystal growth from an aqueous solution. They further state that a mineralizer may act in part by altering the structure of complex species in the solution in a way that favors transport or crystal growth.

Ruszala (1977) briefly explored the possibility that certain structural units may be transported in hydrothermal systems and that this may favor the growth of crystals which incorporate such units. If such a system is operant in these experiments, the eventual distribution of the polymorphs may be controlled by the presence of structural subunits in the fluid phase. The concentration of these subunits might be influenced by temperature and pressure and by changes in concentration which accompany reaction in the nutrient. There may be a solution-based precursor for each polymorph. If so, then the distribution of the polymorphs must depend upon the rates of formation and transport and the solubilities of these precursors. If, on the other hand, there is only one species in solution from which all of the structures precipitate, then the polymorphic distribution rests solely upon the relative solubilities of each structure and their rates of nucleation and crystal growth.

Mineralogical occurrence

We obtained mineral specimens of the known copper orthophosphates from the mineralogical collection of Harvard University. X-ray examination of a green phase found on the surface of a cornetite-containing specimen (Harvard #90308) revealed that it contained a mixture of all three $Cu_5(PO_4)_2(OH)_4$ polymorphs. More work is necessary to properly categorize the PPM and QPM as new mineral species. Our investigation has been hampered by extremely small quantities of sample and possible poor crystallinity of the available material. A subsequent paper will present the refined powder X-ray diffraction patterns of synthetic PM, PPM, and QPM and an analysis of a naturally-occurring specimen.

Acknowledgments

We thank Dr. Carl Francis for samples from The Harvard University Mineralogical Museum. This work was supported in part by the University of Connecticut Research Foundation.

References

Anderson, J. B., Shoemaker, G. L., Kostiner, E., and Ruszala, F. A. (1977) The crystal structure of synthetic $Cu_5(PO_4)_2(OH)_4$, a polymorph of pseudomalachite. American Mineralogist, 62, 115–121.

Ballman, A. A, and Laudise, R. A. (1963) Hydrothermal growth. In J. J. Gilman, Ed., The Art and Science of Growing Crystals, p. 231–251. Wiley, New York.

Ghose, S. (1963) The crystal structure of pseudomalachite, $Cu_5(PO_4)_2(OH)_4$. Acta Crystallographica, 16, 124–128.

Ghose, S., Leo, S. R., and Wan, C. (1974) Structural chemistry of copper and zinc materials. Part I. Veszelyite, $(Cu,Zn)_2ZnPO_4(OH)_3 \cdot 2H_2O$: a novel type of sheet structure and crystal chemistry of copper–zinc substitution. American Mineralogist, 59, 573–581.

Ruszala, F. A. (1977) The Hydrothermal Synthesis and Crystal Growth of Hydroxyphosphates. Ph.D. Thesis, University of Connecticut, Storrs, Connecticut.

Shoemaker, G. L., Anderson, J. B., and Kostiner, E. (1977) Refinement of the crystal structure of pseudomalachite. American Mineralogist, 62, 1042–1048.

Shoemaker, G. L., Anderson, J. B., and Kostiner, E. (1981) The crystal structure of a third polymorph of $Cu_5(PO_4)_2(OH)_4$. American Mineralogist, 66, 169–175.

Manuscript received, May 29, 1980;
accepted for publication, August 19, 1980.