Paulkerrite
a new titanium phosphate from arizona

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ABSTRACT

Paulkerrite is a new mineral from near Hillside, Yavapai County, Arizona, having the ideal composition $KTi(Mg,Mn)_2(Fe^{+3},Mg,Al,Ti)_2(PO_4)_4(OH)_3 \cdot 15H_2O$. It occurs as an alteration product of triplite associated with bermanite and minute crystals of leucophosphite, phosphosiderite and strengite. It is orthorhombic, space group *Pbca,* with $a = 10.49(7)$, $b = 20.75(13)$, $c = 12.44(2)$ Å, $Z = 4$. The name is in honor of Professor Paul Kerr, former Professor of Mineralogy at Columbia University.

INTRODUCTION

As part of a description of bermanite, Hurlbut (1936) gave partial descriptions of some unidentified phosphates which occur as microcrystals associated with bermanite, but which occur in such small quantities as to preclude their identification with the methods then available. A re-examination of bermanite by Leavens (1967) provided identifications for some of the unknown phosphates. Of particular interest to us was the light brown and most abundant of these minutely crystallized species, which Hurlbut had referred to as *unidentified phosphate #2.* Our examination of this mineral indicated it was probably a new species and our subsequent study has verified this initial observation.

We are pleased to name this new titanium-bearing phosphate *paulkerrite* in honor of the late Professor Paul F. Kerr of Columbia University, in recognition of his voluminous contributions to mineralogy and the education of mineralogists. A biography of Paul Kerr was published by Holmes (1965) in a *Festschrift* in the *American Mineralogist,* upon Professor Kerr's retirement. Holotype material is preserved in the Smithsonian Institution. The mineral and the name were approved by the I.M.A. Commission on New Minerals and Mineral Names. Type material is preserved at the Smithsonian Institution (cat. no. NMNH R7778 and NMNH 120405).

PHYSICAL and OPTICAL PROPERTIES

Paulkerrite is light yellowish brown, grading to nearly colorless. It has a colorless streak. It is highly transparent and, due to the thinness of some crystals, it can easily be overlooked upon casual observation. However, the crystal habit, discussed below, is relatively invariant and permits easy identification, at least in all crystals that we have observed. The luster is vitreous on crystal faces and cleavage and fracture surfaces. Paulkerrite is not discernibly fluorescent in ultraviolet radiation. The hardness (Mohs) is approximately 3. There is a perfect {100} cleavage, which is easily produced. The fracture is even. The density, measured using heavy-liquid techniques, is 2.36(4) g/cm^3, in excellent agreement with the calculated value of 2.36 g/cm^3.

Optically, paulkerrite is biaxial negative, $2V \cong 80°$ (Hurlbut, 1936), but β could not be determined on our crystals due to twinning, small size and mosaic texture. The indices of refraction are $\alpha = 1.598(4)$, $\beta = 1.624$(calc) and $\gamma = 1.643(4)$. Dispersion is strong, $r > v$; orientation is $X = c$, $Z = a$. Paulkerrite is non-pleochroic. These optical parameters compare well with those reported by Hurlbut (1936) ($\alpha = 1.591$, $\beta = 1.615$, $\gamma = 1.639$, $2V = 80°$, $r > v$) although all three indices are slightly higher. The differences may be due to slight variations in cation content or in the oxidation state of Fe and/or Mn.

CHEMISTRY

Paulkerrite was chemically analyzed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a beam current of 0.025 μA. After first being checked for homogeneity with a small beam-spot, the mineral was analyzed using a large-diameter beam-spot in order to minimize loss of H_2O through volatilization. Standards used were hornblende (K,Ti), maricite (Fe), montgomeryite (Al,Mg,P), manganite (Mn) and fluorapatite (F). There was inadequate material for the direct determination of H_2O; it was calculated by difference. The oxidation state of Fe was determined by microchemical tests which showed Fe^{+3} to be dominant and Fe^{+2} to be present but subordinate in amount. Mn was assigned to Mn^{+2} based on calculation of the Gladstone-Dale relationship, which for the formula with Mn^{+2} gives $K_C = 0.270$, and for that with Mn^{+3} gives 0.277, as compared with a value of $K_P = 0.263$ as calculated from values for physical properties.

A wavelength-dispersive microprobe scan indicated the absence of any additional elements with atomic number greater than 8. The resultant analysis yields: $K_2O = 4.4$, $Al_2O_3 = 1.6$, $Fe_2O_3 = 12.2$, $MnO = 7.1$, $MgO = 4.6$, $TiO_2 = 9.8$, $P_2O_5 = 29.4$, $F = 0.9$, $[H_2O] = 30.5$, sum = 100.4, less $O = F = 0.4$, sum = 100.0%. Calculation of unit cell contents, using the unit cell parameters and observed density, yields: $K_{3.59}Mg_{4.39}Fe^{+3}_{5.88}Al_{1.20}\ Mn^{+2}_{3.85}Ti_{4.72}P_{15.94}$

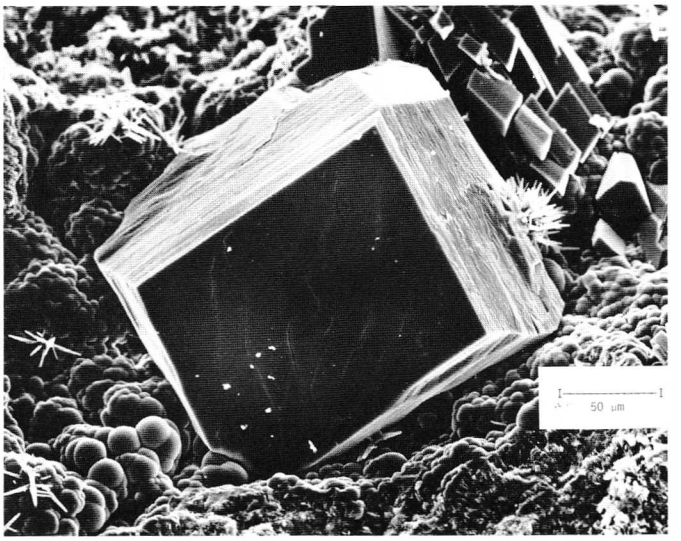

Figure 1. **Tabular paulkerrite crystal from Arizona.**

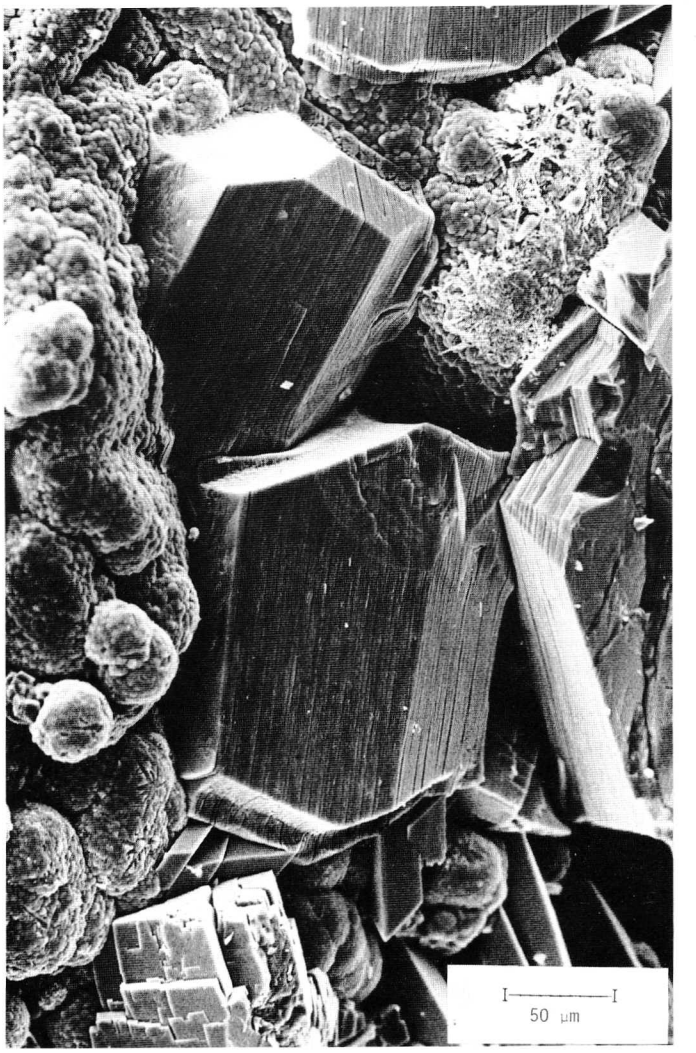

Figure 2. **Equant paulkerrite crystals showing traces of the perfect cleavage.**

$F_{1.82}H_{130.31}$, which we interpret as: $K_{3.59}Ti_{4.0}(Mg_{4.15}Mn^{+2}_{3.85})_{8.0}(Fe^{+3}_{5.88}Mg_{0.24}Al_{1.20}Ti_{0.72})_{8.04}(PO_4)_{15.94}(F_{1.82}OH_{10.55})_{12.37}\cdot 59.9H_2O$. The idealized formula of paulkerrite is **$KTi(Mg,Mn)_2(Fe^{+3},Al,Ti,Mg)_2(PO_4)_4(OH)_3\cdot 15H_2O$.** This ideal formula is written so as to be compatible with the formula for the isostructural mineral mantienneite, $KMg_2Al_2Ti(PO_4)_4(OH)_3\cdot 15H_2O$ (Fransolet, in preparation).

The space group *Pbca* has only two special positions of rank 4 in addition to the general equipoint of rank 8. This formula assumes that K and Ti occupy those equipoints. Given only the chemical data for paulkerrite, it is not clear as to whether Ti, Mg or Mn occupy a special equipoint. We therefore have used the isostructural

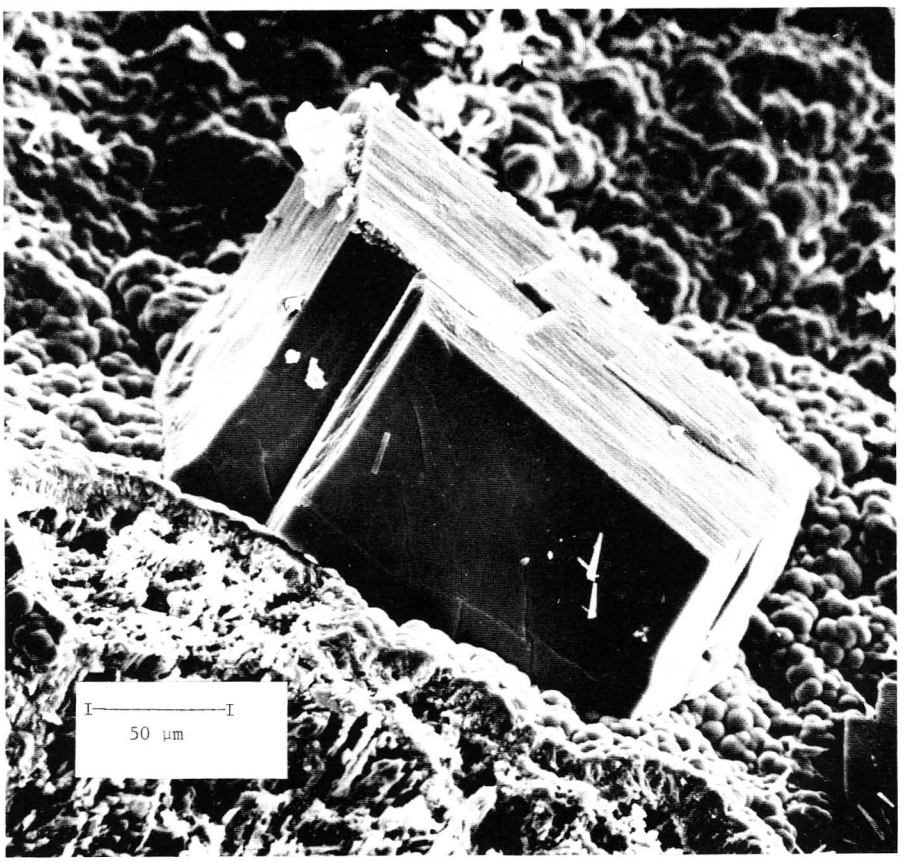

Figure 3. **Sharp, tabular paulkerrite crystals which lack the {100} pinacoid.**

relation with mantiennite, for which the special site occupancy of Ti appears to be clear-cut, as a reference for deriving site assignments for paulkerrite.

The sum of approximately 12 F + OH per cell requires some explanation, as it apparently requires that 4 OH occupy a special site of rank 4 and none are available. As with mantienneite (Fransolet, in preparation) we propose solid solution of some OH with H_2O, implying that at least some H_2O is directly coordinated to an octahedrally coordinated cation. The hydrogen-containing portion of the formula might then be better written as $(OH,F)_2(OH,H_2O)_2 \cdot 14H_2O$. This is an awkward expression, however, and we prefer to write the formula as above with the status of hydrogen being determined in the future through a crystal structure analysis.

Lastly, we note that the valence states for Fe and Mn are not precisely known. There is a small proportion of Fe^{+2} and some Mn may be Mn^{+3}. The formula is affected only in small adjustments in the relative amounts of OH versus H_2O, when such adjustments in valence are considered. The overall form of the formula is unchanged.

CRYSTALLOGRAPHY

Morphology

Paulkerrite occurs as 0.2-mm euhedral crystals which are either equant or flattened on {010}. The crystals are elongate parallel to [001]. The forms present are {010}, {100} and {111}. Tabular crystals have large dominant {010} faces, as shown in Figure 1. More equant crystals, shown in Figure 2, have well-developed {111} dipyramids, giving the crystals a stouter habit. Growth features parallel to the {010} cleavage are well illustrated on the crystals shown in Figure 2, lending to them a layered aspect. The {100} pinacoid is not always present, as shown in Figure 3.

X-Ray Crystallography

Weissenberg and precession photographs show that paulkerrite is orthorhombic, space group *Pbca*. Least-squares refinement of Gandolfi camera powder diffraction data, obtained using Si as an internal standard, and FeKα radiation, yielded the lattice parameters a = 10.49(7), b = 20.75(13), and c = 12.44(2) Å. Reflections having $h + k + l = 2N + 1$ are generally very weak in intensity or not observable except for the reflection 111. The structure is therefore pseudo-body centered. In addition reflections parallel to b^* are somewhat diffuse, indicating the presence of some kind of stacking disorder in that direction. Except for 111, indices are assigned to reflections in the powder pattern assuming that only reflections with h + k + l = 2N are observable, by analogy with the single-crystal patterns.

There are several aspects to the data, especially the X-ray diffraction data, which indicate that the cell parameters and/or formula may be subject to revision. The interpretation of the powder diffraction data is not entirely satisfactory in that the agreement between d(obs) and d(calc) is not as good as is generally true for other well-defined minerals. For example, the agreement for 233, 312, 323 and 411 is not especially good. Furthermore, the indexed powder data leads to lattice parameters with relatively high standard errors. In order to determine if this was due to some peculiar feature of the specific powder photograph, a second Gandolfi photograph, obtained using a different specimen, was obtained and measured, but without improved results. Furthermore, the diffuse nature of single-crystal diffraction patterns (parallel to b^*) coupled with the {010} cleavage and layered aspect of the crystals, implies that the structure is layered parallel to {010} and that there must be some sort of stacking disorder. Such disorder implies that there must be domains with cell parameters and symmetries different from those of the average crystal. In a general and unspecified way, the substructure-superstructure relation defined by pseudo-body centering and the near equality of a and $b/2$ also imply the possibility of submicroscopic domains having a structure differing from the average. These data in turn imply that the composition, with cations distributed as consistent with equipoint requirements for space group *Pbca,* may not be entirely accurate if units of structure possess some other symmetry. We have examined the crystals and data carefully for additional features which might serve to provide a firmer basis for our concerns, but can find none. Further definition of these relations must await either a structure analysis (which may provide ambiguous results due to the disorder parallel to [010]) or high resolution transmission electron microscopy and electron diffraction data (which is difficult to obtain due to the small crystal size and good cleavage).

Table 1. **X-ray powder diffraction data for paulkerrite.***

I/I_o	d (Obs)	d (Calc)	hkl	I/I_o	d (Obs)	d (Calc)	hkl
90	10.3	10.4	020	10	2.814	2.824	341
80	7.46	7.47	111	20	2.624	2.623	400
100	6.20	6.22	002	10	2.563	2.585	323
20	5.22	5.25	200	10	2.512	2.547	411
		5.19	040	5	2.322	2.340	314
		5.18	112				
				5	2.187	2.191	442
1	4.72	4.71	211	5	2.117	2.111	433
		4.68	220	10	2.069	2.073	006
1	4.37	4.36	141	20	1.980		
30	3.95	3.96	231	2	1.864		
40	3.75	3.74	222	2	1.831		
70	3.13	3.11	004	5	1.713		
5	3.05	3.02	312	2	1.663		
20	2.979	2.979	024	1	1.608		
40	2.872	2.944	233	1	1.566		

* Data obtained using a 114.6-mm diameter Gandolfi camera, FeKα radiation, and Si as an internal standard. Intensities visually estimated.

OCCURRENCE

Paulkerrite occurs at the type locality for bermanite, the 7 U 7 Ranch, about 40 km west of Hillside, Yavapai County, Arizona. The dominant phosphate mineral at the locality is triplite, which was found in a pegmatite knot as described by Hurlbut (1936). The massive triplite, frequently weathered black by oxidation of the manganese, is dissected by numerous fractures which are lined with secondary phosphates, chiefly bermanite, $Mn^{+2}Mn_2^{+3}(PO_4)_2(OH)_2 \cdot 4H_2O$, which occurs in crystals up to several mm in size. In addition to the rather abundant bermanite, a number of other secondary Fe^{+3} and Mn phosphates occur in association, including light blue crystals of phosphosiderite, magenta-colored leucophosphite crystals, glassy pink strengite crystals, deep violet massive phosphosiderite, and colorless-to-white acicular sprays of switzerite as identified using powder X-ray diffraction techniques. Randomly distributed among these late-stage phosphates are paulkerrite crystals. Next to bermanite, they are the most abundant of the species listed here. Only bermanite and switzerite are younger than paulkerrite in this paragenesis. Paulkerrite crystals are evenly distributed on the fracture surfaces in triplite and show no preferential association with other species. The source of Ti is enigmatic. We know of no work on this pegmatite other than Hurlbut's description and no TiO_2 was reported in the analysis by Gonyer (*in* Hurlbut, 1936) of the host triplite. Other than paulkerrite, no titanium-bearing minerals were found in the specimens we examined. It is still possible that the triplite contains a very small amount of Ti which became concentrated in paulkerrite, or that the source of titanium may have been through supergene alteration of minerals of the country rock.

We have found paulkerrite crystals on many of the specimens labeled bermanite from the type locality which were available to us. Hence, it might be almost as abundant as bermanite at this locality, albeit in very small crystals.

ACKNOWLEDGMENTS

We are indebted to Professor André-Mathieu Fransolet for providing us with data on the mineral mantienneite so that a comparison with data on paulkerrite could be made, and for reviewing the manuscript. We also thank Richard W. Thomssen and Abraham Rosenzweig for helpful reviews of the manuscript.

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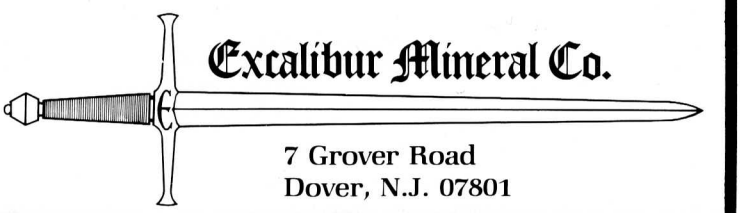

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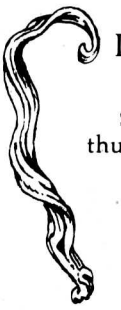

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