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HARRISONITE, A WELL-ORDERED SILICO-PHOSPHATE WITH A LAYERED CRYSTAL STRUCTURE[1]

JOEL D. GRICE

Mineral Sciences Section, Canadian Museum of Nature, Ottawa, Ontario K1P 6P4

ANDREW C. ROBERTS

Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8

ABSTRACT

The crystal structure of harrisonite, a new silico-phosphate mineral species, ideally $Ca(Fe^{2+},Mg)_6(SiO_4)_2(PO_4)_2$, has been determined and refined to indices R = 2.5% and R_w = 2.1%. The structure is rhombohedral $R\bar{3}m$, with cell parameters (hexagonal) *a* 6.248(1), *c* 26.802(7) Å, *V* 906.0(4) Å^3, and with Z = 3. D(calc) is 4.01 g/cm^3. The structure analysis determined the centrosymmetric space-group, the valence state of the Fe atom, the lack of H atoms, the number of O atoms, and the ideal order of Si and P atoms. The crystal structure is comprised of three distinct (00*l*) types of layers: a $[FeO_6]^{10-}$ corundum-type layer, a layer of $[SiO_4]^{4-}$ independent tetrahedra, and a $[Ca(PO_4)_2]^{4-}$ slab of $[CaO_6]^{10-}$ polyhedral trigonal antiprisms with six apical $[PO_4]^{3-}$ tetrahedra. The structure is unique if compared to other layered phosphate, arsenate or vanadate structures.

Keywords: harrisonite, silico-phosphate, crystal structure, order, layers, unique structure.

SOMMAIRE

La structure cristalline de la harrisonite, silico-phosphate nouvellement découvert de composition idéale $Ca(Fe^{2+},Mg)_6(SiO_4)_2(PO_4)_2$, a été affinée jusqu'à un résidu R de 2.5% (R_w = 2.1%). Sa structure est rhomboédrique $R\bar{3}m$, et ses paramètres réticulaires (maille hexagonale) sont *a* 6.248(1), *c* 26.802(7) Å, *V* 906.0(4) Å^3, Z = 3. La densité calculée est 4.01. Nous avons utilisé les résultats de l'affinement pour déterminer le groupe spatial centrosymétrique, la valence du fer, l'absence d'atomes d'hydrogène, le nombre d'atomes d'oxygène, et la répartition ordonnée des atomes de Si et P. La structure cristalline comprend trois sortes de feuillets de type (00*l*), soit un feuillet $[FeO_6]^{10-}$ de type corindon, un plan de tétraèdres $[SiO_4]^{4-}$, et une couche de composition $[Ca(PO_4)_2]^{4-}$ contenant des antiprismes polyédriques trigonaux $[CaO_6]^{10-}$ ayant six tétraèdres apicaux $[PO_4]^{3-}$. En comparaison de la structure en feuillets de phosphates, arsenates et vanadates connus, la structure semble unique.

(Traduit par la Rédaction)

Mots-clés: harrisonite, silico-phosphate, structure cristalline, agencement ordonné, feuillets, structure unique.

INTRODUCTION

Harrisonite, described by Roberts *et al.* (1993) from Arcedeckne Island, off northern Boothia Peninsula, District of Franklin, Arctic Canada, is one of the few known silico-phosphate minerals. The solution of the crystal structure of harrisonite not only provided essential information for the establishment of its chemical formula and the confirmation of its crystallography, but it also provided further information on the crystal chemistry of silico-phosphates.

EXPERIMENTAL

One of the two crystals of harrisonite used in the optical study also was found to be suitable for the collection of intensity data (cotype material with National Mineral Collection of Canada catalogue number 59685). The roughly equant fragment measures 0.12 × 0.12 × 0.09 mm. Single-crystal precession photographs yielded space-group choices $R\bar{3}m$, $R3m$ and $R32$. Intensity data were collected on a fully automated Nicolet R3m four-circle diffractometer operated at 50 kV, 35 mA, with graphite-monochromated Mo$K\alpha$ radiation. A set of 25 intense reflections was used to orient the crystal and subsequently to

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TABLE 1. POSITIONAL AND THERMAL PARAMETERS (X100, Å^2) FOR HARRISONITE

Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ca	0	0	0	0.66(5)	0.66(5)	2.06(9)	0	0	0.33(2)	1.13(5)
Fe	0.4969(1)	0.9938(1)	0.0950(1)	0.65(2)	0.70(3)	1.01(3)	-0.02(2)	0.01(1)	0.35(1)	0.78(2)
Si	0	0	0.8623(1)	0.56(5)	0.56(5)	0.62(7)	0	0	0.28(2)	0.58(4)
P	0	0	0.6802(1)	0.66(5)	0.66(5)	0.54(7)	0	0	0.33(2)	0.62(4)
0(1)	0	0	0.1988(2)	0.9(1)	0.9(1)	0.7(2)	0	0	0.48(7)	0.9(1)
0(2)	0	0	0.6224(2)	0.9(1)	0.9(1)	0.8(2)	0	0	0.43(7)	0.8(1)
0(3)	0.1429(2)	0.2858(5)	0.1183(1)	0.8(1)	0.8(1)	1.2(1)	0.2(1)	0.11(5)	0.38(7)	0.92(8)
0(4)	0.7979(2)	0.5958(5)	0.0362(1)	1.3(1)	0.8(1)	0.8(1)	-0.0(1)	0.02(5)	0.43(7)	1.04(9)

Temperature factors are of the form: exp $[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+.....2U_{12}hka^*b^*)]$.

refine the cell dimensions based on a hexagonal setting: a 6.248(1), c 26.802(7) Å. Two asymmetric sets of intensity data were collected up to $2\theta = 60°$ using a θ:2θ scanning mode, with scan speeds inversely proportional to intensity, varying from 4 to 29.3°/minute. Of the 752 intensities collected, 378 are unique, and 334 are considered observed $[F > 4\sigma(F)]$.

Reduction of the intensity data, structure determination and structure refinement were accomplished by means of the SHELXTL (Sheldrick 1976) package of computer programs. Data reduction included correction for background, scaling, Lorentz and polarization and linear absorption, $\mu = 7.27$ mm^{-1} for Mo$K\alpha$ radiation. For the absorption correction, a set of 11 intense diffraction maxima in the range 8 to 58° 2θ was chosen for ψ-diffraction-vector scans after the method of North *et al.* (1968). The ψ-scan set of intensity data was used to refine an ellipsoidal, empirical absorption-correction. The absorption correction reduced the merging R of the ψ-scan data set from 3.3% to 2.2%. When the absorption correction was applied to the entire set of intensity data, the transmission factors ranged from 0.572 to 0.653. The merged R for the symmetry-related reflections is equal to 2.0%.

CRYSTAL-STRUCTURE ANALYSIS

The phasing of a set of normalized structure-factors gives a mean value $|E^2 - 1|$ of 0.968, indicative of the centrosymmetric space-group $R\bar{3}m$. The E-map coordinates were assigned to appropriate scattering curves, Ca, Fe, Si and two O atoms, but the structure would only refine to $R = 46\%$. Similarly, modeling of the E-sharpened Patterson map, with peaks assigned to Ca, Fe, Si and one O atom, refined to only $R = 59\%$. From these attempts, it became evident that the solution to the crystal structure of harrisonite was going to require a different approach than these standard methods.

The idealized formula for harrisonite, $Ca(Fe^{2+},Mg)_6(SiO_4)_2(PO_4)_2$, with $Z = 3$, when applied in space group $R\bar{3}m$, requires that all cations be placed in special positions. The Ca atom must be at the origin, $3a$ 0,0,0. If we assume that Si and P occupy distinct atomic sites, the Si and P atoms would require positions with six-fold site symmetry of the type $6c$ $0,0,z$. As there are 18 (Fe,Mg) atoms per unit cell, this position requires a site symmetry $18m$ $x,\bar{x},z$ (given the restrictions in $c/3$ outlined below). The intensities of the $00l$ reflections show the 006 and 009 reflections to be very strong, indicating a pronounced subperiodicity of $c/6$ and $c/9$ in addition to the $c/3$ layering imposed by the rhombohedral lattice centering. The $c/6$ subperiod is produced by dividing each $c/3$ layer into approximate halves with equal scattering power. The reader should realize that 1/9 of the harrisonite c dimension is approximately 3 Å, which is a reasonable cation– cation or oxygen–oxygen distance. The intermediate layer at height 1/12 was assigned to the Fe atom in $x,\bar{x},z$ with $x \sim 0.5$. This trial structure, with atoms placed at 0, 1/9, 1/6 and 1/3 along the z axis plus the intermediate level Fe atom at height 1/12, refined to give a residual R of 29%. From this initial

TABLE 2. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR HARRISONITE

		Ca polyhedron	
Ca -O(4)	2.393(2) x6	O(4) -O(4)'	75.2(1) x6
Ca -O(3)	3.528(3) x6	O(4) -O(4)''	104.8(1) x6
		Fe polyhedron	
Fe -O(1)	2.120(3)	O(1) -O(3)	99.3(1) x2
Fe -O(2)	2.232(3)	O(3) -O(3)'	123.0(1)
Fe -O(3)	2.031(3) x2	O(2) -O(3)	84.2(1) x2
Fe -O(4)	2.294(3) x2	O(4) -O(1)	85.2(1) x2
Mean	2.167	O(4) -O(2)	88.4(1) x2
		O(4) -O(3)	85.3(1) x2
		O(4) -O(4)'	64.9(1)
		Si tetrahedron	
Si -O(1)	1.640(5)	O(1) -O(3)	108.5(1) x3
Si -O(3)	1.631(2) x3	O(3) -O(3)'	110.4(1) x3
Mean	1.633		
		P tetrahedron	
P -O(2)	1.550(5)	O(2) -O(4)	113.2(1) x3
P -O(4)	1.545(2) x3	O(4) -O(4)'	105.5(1) x3
Mean	1.548		

refinement, the final sites of the atoms and the assignment of the appropriate scattering curves could be derived from a series of difference-Fourier maps.

In the final least-squares refinement, the sites of the four cations and the four O atoms were refined with anisotropic temperature-factors; the Fe atom site had an amount of Mg added to the scattering factor consistent with that reported in Roberts *et al.* (1993). A weighting scheme inversely proportional to $\sigma^2(F)$ and an additional isotropic extinction-correction resulted in final residual indices R of 2.5% and R_w of 2.1%. The final residuals of $R = 3.4\%$ and $R_w = 3.2\%$, without correction for extinction, indicate the significance of this correction for harrisonite, which presumably has a high degree of crystal perfection. The final positional and thermal parameters are given in Table 1, and selected bond-lengths and angles, in Table 2. A table listing the observed and calculated structure-factors has been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The analysis of the crystal structure of harrisonite permitted the calculation of bond-valence sums for the various atomic sites based on the constants of Brown (1981). The sums are: Ca atom 1.79, (Fe,Mg) atom 2.00, Si atom 3.97, P atom 4.91, O(1) atom 2.05, O(2) atom 2.02, O(3) atom 1.90, and O(4) atom 1.99 *v.u.* These calculations allow the assignment of the correct valence to the Fe^{2+} atoms. They also indicate that there are no H atoms associated with any of the O ions, including those in the anionic groups (SiO_4) and (PO_4), as there are for the silico-phosphate mineral attakolite (Grice & Dunn 1992). The resultant structural formula for harrisonite is $Ca(Fe^{2+}_{5.3}Mg_{0.7})_{\Sigma 6}(SiO_4)_2(PO_4)_2$, with $Z = 3$. It should be mentioned that the bond-valence sum for the Ca atom, 1.79 *v.u.*, is somewhat low for regular, six-fold coordination in an antiprism, but if the summation is extended to include the six additional O atoms at a distance of 3.53 Å, the sum becomes 1.90 *v.u.* The ten-fold coordination of the Ca atom in attakolite (Grice & Dunn 1992) extends out to 3.25 Å, and this makes a realistic polyhedron. The potential twelve-fold coordination in harrisonite seems less likely in that the six additional O atoms are quite distant, but the polyhedron is still possible because the outer O atoms are not shielded by the inner sphere of O atoms. The coordination of the Fe site is best described as a flattened trigonal antiprism; the bond angles (Table 2) are not close to that of an octahedron. It is evident from the results of the electron-microprobe analyses, bond-valence sums and scattering power of each of the two tetrahedral sites, that the Si atoms and P atoms are essentially ideally ordered. Mean Si–O bond distances of 1.633 Å and mean P–O bond distances of 1.548 Å fall within the ranges of bond distances for Si–O, 1.59 – 1.63 Å, and P–O, 1.45 – 1.56 Å (Ondik & Smith 1968).

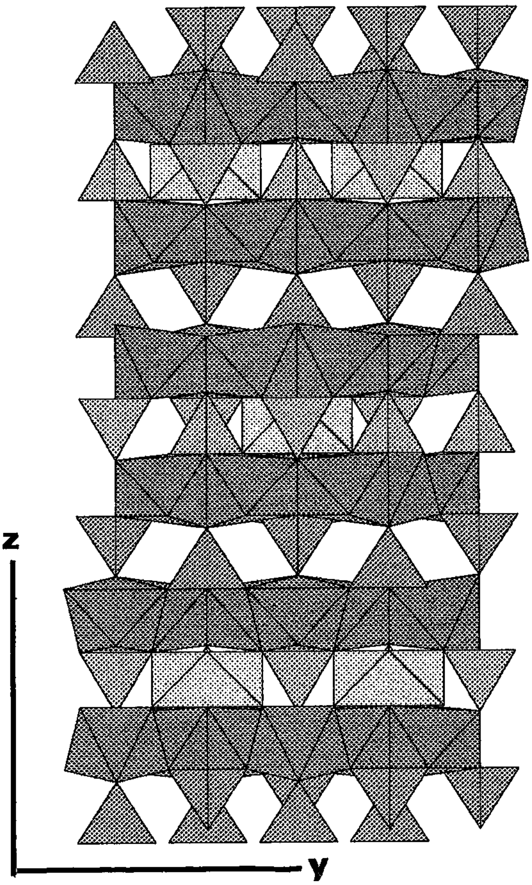

FIG. 1. A (100) projection of the layered structure of harrisonite, with dark-shaded $[SiO_4]^{4-}$ tetrahedra, lighter-shaded $[PO_4]^{3-}$ tetrahedra, light-stippled $[CaO_6]^{10-}$ polyhedra, and dark-stippled $[FeO_6]^{10-}$ polyhedra.

The layering in the crystal structure of harrisonite is shown in Figure 1. As predicted by the trial structural model, there are twelve layers within the *c* repeat unit. Within each subunit (1/3 of the hexagonal *c* dimension) or the rhombohedral cell itself, there are four layers; two $[FeO_6]^{10-}$, one $[SiO_4]^{4-}$ and one $[Ca(PO_4)_2]^{4-}$. The $[FeO_6]^{10-}$ layers (Fig. 2) are essentially like those of the corundum structure, in which 1/4 of the "octahedral" sites are holes. These holes are capped above and below by either $[SiO_4]^{4-}$ tetrahedra or $[CaO_6]^{10-}$ polyhedra (Figs. 1, 3). The $[SiO_4]^{4-}$ layer consists of independent $[SiO_4]^{4-}$ tetrahedra with alternating apical directions between layers of $[FeO_6]^{10-}$. The $[FeO_6]^{10-}$ layers are puckered at the $[SiO_4]^{4-}$ apical join. The $[Ca(PO_4)_2]^{4-}$ layer (Fig. 4) consists of

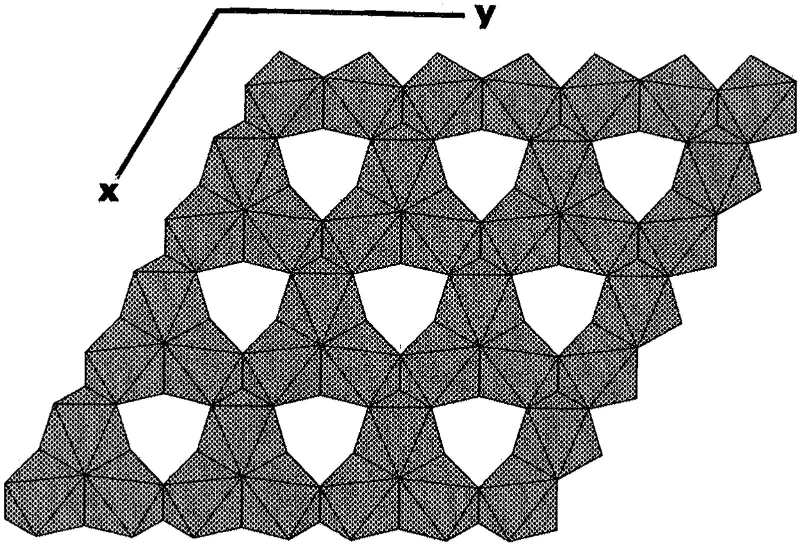

FIG. 2. A z-axis projection of the structure of harrisonite showing the corundum-type $[FeO_6]^{10-}$ layer.

independent $[PO_4]^{3-}$ tetrahedra cross-linked by $[CaO_6]^{10-}$ polyhedral trigonal antiprisms flattened along the z axis. The flattening nicely accommodates the height of a $[PO_4]^{3-}$ tetrahedron in such a way that around each $[CaO_6]^{10-}$ polyhedron, there are three $[PO_4]^{3-}$ tetrahedra pointing up, based at the lower apices and interspersed with three $[PO_4]^{3-}$ tetrahedra pointing down from their placement at the upper apices. This layer closely resembles that described by Moore (1973) for the crystal structure of merwinite, in which $[MgO_6]^{6-}$ octahedra are surrounded by six $[SiO_4]^{4-}$ tetrahedra, with apices alternating up and down. Moore (1973) described this basic topological unit as a "pinwheel".

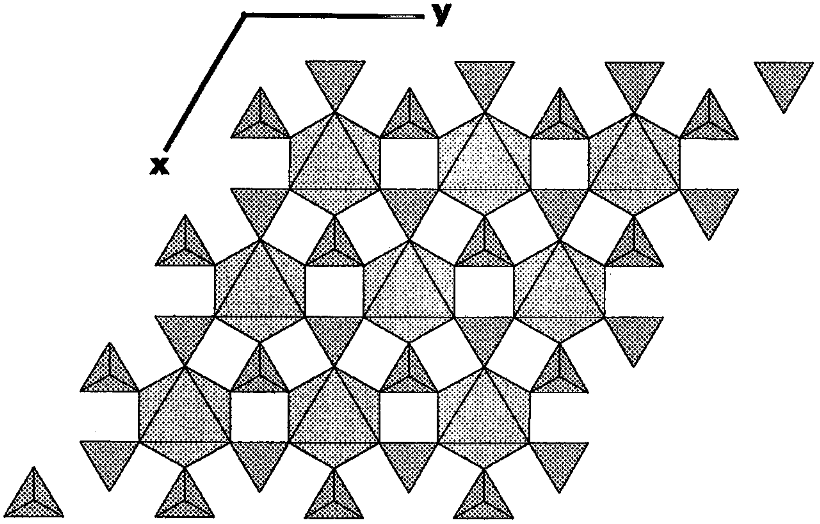

FIG. 3. A z-axis projection of the $[Ca(PO_4)_2]$ structural layer, which is composed of $[CaO_6]^{4-}$ polyhedral trigonal antiprisms connecting $[PO_4]^{3-}$ tetrahedra.

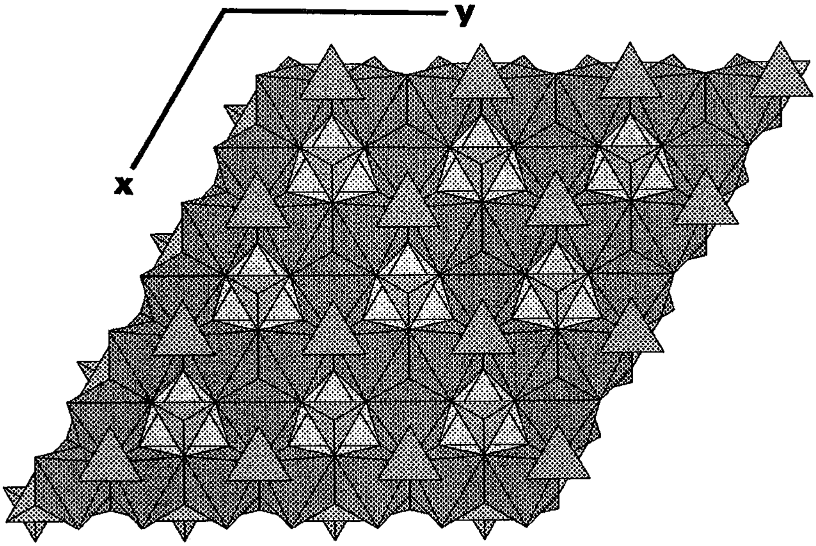

FIG. 4. A z-axis projection of the structure of harrisonite. The $[FeO_6]^{10-}$ layer has $[SiO_4]^{4-}$ tetrahedra capping the top of the layer holes and $[CaO_6]^{10-}$ polyhedra underlying the holes.

The layers within the crystal structure of harrisonite resemble layers in other minerals, but the overall structure seems unique in comparison to the compilation of phosphate, arsenate and vanadate structures reported by Kostov & Breskovska (1989).

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