

**THE  $C2/m$  DISORDERED STRUCTURE OF PASCOITE,  $\text{Ca}_3[\text{V}_{10}\text{O}_{28}]\cdot 17\text{H}_2\text{O}$ :  
BONDING BETWEEN STRUCTURAL UNITS AND INTERSTITIAL COMPLEXES  
IN COMPOUNDS CONTAINING THE  $[\text{V}_{10}\text{O}_{28}]^{6-}$  DECAVANADATE POLYANION**

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ABSTRACT

The atomic arrangement of pascoite has been solved and refined to  $R = 0.0257$  using three-dimensional data obtained with  $\text{MoK}\alpha$  X-radiation and a CCD detector. The mineral crystallizes in space group  $C2/m$ ,  $a$  19.5859(6),  $b$  10.1405(3),  $c$  10.9110(3) Å,  $\beta$  120.815(1)°. The atomic arrangement of pascoite was previously presented in two possible space-groups, consistent with a  $C2/m$  disordered model and a  $C2$  ordered model. The earlier authors preferred the ordered model, but noted the ambiguity of the solution. Using CCD data and locating the hydrogen atoms allow us to assign the  $C2/m$  disordered model to the atomic arrangement. The structural unit, or anionic portion of the atomic arrangement in pascoite, is the decavanadate polyanion  $(\text{V}_{10}\text{O}_{28})^{6-}$ , similar to the decavanadate group found in hummerite and numerous synthetic vanadates. Linking the decavanadate groups together are interstitial groups, formed of the cationic group  $\{\text{Ca}_3(\text{H}_2\text{O})_{17}\}^{6+}$ . All oxygen atoms in the interstitial complex occur as  $(\text{H}_2\text{O})$  groups, in contrast to the structural unit, which is devoid of hydrogen atoms. There are two distinct Ca atoms in the interstitial complex. The disorder that occurs in the coordinating oxygen atoms leads to an average coordination of  $\text{Ca1O}_7$  for the Ca1 atom, although the disordered coordinating oxygen atoms yield possible  $\text{Ca1O}_6$ ,  $\text{Ca1O}_7$ , and  $\text{Ca1O}_8$  coordinations. The Ca2 atom, in  $\text{Ca2O}_7$  coordination, also bonds to disordered oxygen atoms. Examination of the structure of compounds with the decavanadate polyanion structural unit and with simple mono-, di-, and trivalent cations in the interstitial complex demonstrates that the sum of bonds emanating from the interstitial cations correlates with the number of  $(\text{H}_2\text{O})$  groups per cation.

*Keywords:* pascoite, crystal structure, hydrogen bonding, decavanadates.

SOMMAIRE

Nous avons déterminé l'agencement des atomes dans la pascoïte, et nous l'avons affiné jusqu'à un résidu  $R$  égal à 0.0257 en utilisant des données tridimensionnelles obtenues avec rayonnement  $\text{MoK}\alpha$  et un détecteur de type CCD. Ce minéral cristallise dans le groupe spatial  $C2/m$ ,  $a$  19.5859(6),  $b$  10.1405(3),  $c$  10.9110(3) Å,  $\beta$  120.815(1)°. L'agencement des atomes de la pascoïte était antérieurement présenté en deux groupes d'espace possibles, un modèle désordonné conforme au groupe  $C2/m$  et un modèle ordonné  $C2$ . Les auteurs antérieurs ont préféré le modèle ordonné, mais ont souligné l'ambiguïté de la solution. Avec des données CCD et la possibilité de bien situer les atomes d'hydrogène, nous avons pu conclure que le modèle désordonné  $C2/m$  est le bon. L'unité structurale, c'est-à-dire la portion anionique de la structure, est le polyanion décavanadate  $(\text{V}_{10}\text{O}_{28})^{6-}$ , que l'on retrouve dans la hummerite et de nombreux vanadates synthétiques. Ce sont les groupes interstitiels qui joignent les groupes décavanadate; ils contiennent le groupe cationique  $\{\text{Ca}_3(\text{H}_2\text{O})_{17}\}^{6+}$ . Tous les atomes d'oxygène du complexe interstitiel font partie de groupes  $(\text{H}_2\text{O})$ , contrairement à l'unité structurale, qui est dépourvue d'atomes d'hydrogène. Il y a deux atomes de Ca dans le complexe interstitiel. Le désordre qui affecte les atomes d'oxygène mène à une coordination moyenne de  $\text{Ca1O}_7$  pour l'atome Ca1, quoique les atomes d'oxygène désordonnés peuvent faire partie de coordinences  $\text{Ca1O}_6$ ,  $\text{Ca1O}_7$ , et  $\text{Ca1O}_8$ . L'atome Ca2, en coordination  $\text{Ca2O}_7$ , est aussi lié à des atomes d'oxygène désordonnés. Un examen des structures de composés possédant comme unité structurale le polyanion décavanadate et des cations mono-, bi-, et trivalents simples dans le complexe interstitiel démontre que la somme des liaisons émanant du complexe interstitiel montre une corrélation avec le nombre de groupes  $(\text{H}_2\text{O})$  par cation.

(Traduit par la Rédaction)

*Mots-clés:* pascoïte, structure cristalline, liaisons hydrogène, décavanadates.

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## INTRODUCTION

Interest in synthetic and natural vanadium oxide compounds has recently been rekindled (Hughes *et al.* 2002, and references therein). Schindler *et al.* (2000a, b) provided a summary of the crystal-chemical aspects of vanadium by examining the structural chemistry of natural and synthetic phases. Those authors offered a crystal-chemical approach to the composition and occurrence of vanadium minerals that describes these compounds by two component parts: the *structural unit*, the anionic portion of the structure that consists of polyhedra of higher bond-valence, and the interstitial complex, the cationic portion of the structure that contains alkali and alkaline-earth cations and (H<sub>2</sub>O) and (OH) groups. They also described the role of H<sub>2</sub>O groups in vanadium minerals, predicted the range in Lewis basicity for different structural units, and demonstrated the efficacy of the valence-matching principle in evaluating the structures of complex vanadium-hydrate minerals.

Hughes *et al.* (2002) used the approach proffered by Schindler *et al.* (2000a) to evaluate the atomic arrangement of hummerite, K<sub>2</sub>Mg(V<sub>5</sub>O<sub>14</sub>)•8H<sub>2</sub>O. That phase contains a *structural unit* formed of the [V<sub>10</sub>O<sub>28</sub>]<sup>6-</sup> decavanadate polyanion, the decavanadate structural group found in pascoite and numerous synthetic compounds (Griffen 1990). The study of hummerite led us to re-examine the atomic arrangement of pascoite. That arrangement was not well defined, as the only previous structural study (Swallow *et al.* 1966) did not reveal hydrogen atom positions nor did it offer a definitive space-group. Candidate space-groups *I2* and *I2/m* both yielded realistic structure-models, with nearly identical *R* values, that correspond to ordered and disordered models, respectively. Because of the insight into hydrogen bonding in vanadium oxysalts

that would result, we undertook this study of the atomic arrangement of pascoite.

## EXPERIMENTAL

A sample of pascoite was selected from Harvard specimen #91449, from Minasragra, Peru, the same specimen that was the source of the material used for the morphological, chemical, and unit-cell data in Palache *et al.* (1951). The crystal was mounted on a Bruker Apex CCD diffractometer equipped with graphite-monochromated MoK $\alpha$  radiation. Refined cell-parameters and other crystal data are listed in Table 1. Redundant data were collected for a sphere of reciprocal space, and absorption was corrected using semi-empirical methods as implemented in the programs SADABS (Bruker AXS, Inc. 2003). Data were integrated and corrected for Lorentz and polarization factors using the Bruker program SAINTPLUS (Bruker AXS, Inc. 2003).

The structure was solved using Direct Methods and difference Fourier maps, as implemented in the Bruker SHELXTL v. 6.14 (Bruker AXS, Inc. 2000) package of programs; neutral-atom scattering factors and terms for anomalous dispersion were employed throughout the solution and refinement. Refinement was performed with anisotropic thermal parameters for all non-hydrogen atoms, and the structure was refined on F<sup>2</sup>. In Table 2, we list the atom parameters, and in Table 3, we present selected interatomic distances. Tables 4 and 5 contain anisotropic thermal parameters and observed and calculated structure factors, respectively. Copies of Tables 4 and 5 are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

The initial solution was undertaken without knowledge of the earlier solution proffered by Swallow *et al.* (1966). Their solution was undertaken in the non-conventional space-groups *I2* and *I2/m*; those authors tentatively concluded that the ordered *I2* model was correct, although they noted that their conclusion that the mineral crystallized in the acentric alternative was not definitive. Our solution was successfully undertaken in the conventional centric space-group *C2/m*, but subsequently the acentric ordered *C2* model was evaluated, and the results of that evaluation are offered below.

## THE ARRANGEMENT OF ATOMS

Hawthorne (1983) recognized two distinct parts of complex mineral structures: (a) the *structural unit*, usually the anionic portion of the structure that contains bonds of higher bond-valence, and (b) the *interstitial complex*, usually the cationic part of the structure, with bonds of lower bond-valence between alkaline and alkaline-earth cations and (H<sub>2</sub>O), (OH), or Cl groups. There is perhaps no mineral group more illustrative of

TABLE 1. CRYSTAL DATA AND RESULTS OF THE REFINEMENT OF THE STRUCTURE OF PASCOITE

Crystal size: 0.10 × 0.11 × 0.13 mm			
Ca <sub>3</sub> [V <sub>10</sub> O <sub>28</sub> ]•17H <sub>2</sub> O; Z = 2			
Unit cell by least squares (space group: <i>C2/m</i> , 7,845 reflections):			
<i>a</i> 19.5859(6)	<i>b</i> 10.1405(3)	<i>c</i> 10.9110(3) Å	$\beta$ 120.815(1)°
Frame width, scan time, number of frames: 0.20°, 15 s, 4500			
-27 ≤ <i>h</i> ≤ 27;	-14 ≤ <i>k</i> ≤ 14;	-15 ≤ <i>l</i> ≤ 15;	2 $\theta$ ≤ 60°
Temperature: 20°C			
Detector distance: 5 cm			
Effective transmission: 0.901461 - 1.000			
<i>R</i> <sub>int</sub> (before - after SADABS absorption correction): 0.0287 - 0.0156			
Measured reflections, full sphere: 20,777			
Refined parameters: 186, refined on F <sup>2</sup>			
<i>R</i> 1 = 0.0257 for 2743 <i>F</i> <sub>o</sub> > 4 $\sigma$ ( <i>F</i> <sub>o</sub> ) and 0.0267 for all 2844 data			
w <i>R</i> 2 = 0.0671, GooF = <i>S</i> = 1.119			
Largest difference peaks: +0.57, -0.62 e <sup>-</sup> • Å <sup>-3</sup>			

the bipartite nature of many mineral structures than the numerous alkali and alkaline-earth vanadium oxide hydrates. Schindler *et al.* (2000a) applied Hawthorne's (1983) observations to such vanadium minerals and elucidated the nature of the bonding between the two distinct parts of the structure. Below, we describe the structural unit and the interstitial complex in pascoite.

### The structural unit

The  $(V_{10}O_{28})^{6-}$  decavanadate polyanion in pascoite is depicted in Figure 1. The polyanion is formed of ten distorted, edge-sharing octahedra. In addition to hummerite, the decavanadate polyanion is found in numerous synthetic vanadate compounds, as discussed by Griffen (1990).

Schindler *et al.* (2000b) defined the vanadyl bond as a  $V^{5+}-O$  bond of less than 1.74 Å in length. Each of the vanadium octahedra in pascoite contains one vanadyl bond except the V1 octahedron, which contains two vanadyl bonds. In V2, V3 and V4, the vanadyl bond is *trans* to the long V–O bond, with four equatorial bonds to oxygen approximately perpendicular to the

vector formed by the two *trans* bonds; such a disposition of bonds is typical of the decavanadate unit in other structures. Oxygen atoms of the decavanadate polyanion bond to Ca and H atoms of the interstitial complex to link the structural unit and the interstitial unit. Atoms O1 and O5, the "apical" oxygen atoms of the decavanadate polyanion (Fig. 1), bond to Ca atoms of the interstitial complex, whereas other oxygen atoms of the decavanadate polyanion [except O2 and O3] bond to the interstitial complex through hydrogen bonding. Oxygen atoms O2 and O3 only bond to vanadium atoms of the polyanion.

As noted by Hughes *et al.* (2002), one oxygen atom of the decavanadate group is of particular interest. Oxygen atom O2 (Fig. 1) bonds to six vanadium atoms, a particularly unusual coordination for oxygen and even more unusual where coordinated to a pentavalent cation. In each octahedron, the bond to O2 is the longest in

TABLE 3. SELECTED BOND-DISTANCES AND VALENCE SUMMATIONS (*vu*) IN PASCOITE

Cation Bond	Distance	<i>vu</i>	Cation Bond	Distance	<i>vu</i>
V1 -O4	1.687(1)	1.37	V2 -O5	1.622(2)	1.63
-O4	1.687	1.37	-O6	1.803(1)	1.00
-O3	1.907(1)	0.75	-O6	1.803	1.00
-O3	1.907	0.75	-O3	2.013(1)	0.57
-O2	2.1339(9)	0.41	-O3	2.013	0.57
-O2	2.1339	0.41	-O2	2.221(1)	0.32
Mean	1.909	Σ=5.06	Mean	1.913	Σ=5.09
V3 -O1	1.623(2)	1.63	V4 -O9	1.598(1)	1.74
-O7	1.804(1)	1.00	-O8	1.827(1)	0.94
-O7	1.804	1.00	-O6	1.878(1)	0.82
-O3	2.008(1)	0.57	-O7	1.882(1)	0.81
-O3	2.008	0.57	-O4	2.070(1)	0.49
-O2	2.220(2)	0.32	-O2	2.312(1)	0.25
Mean	1.911	Σ=5.09	Mean	1.928	Σ=5.05
Ca1 -O13A	2.247(5)	0.47	Ca2 -O12B	2.340(4)	0.36
-O13A	2.247	0.47	-O12B	2.340	0.36
-O11	2.365(3)	0.34	-O14	2.368(2)	0.34
-O11	2.365	0.34	-O14	2.368	0.34
-O10	2.407(3)	0.30	-O15	2.383(2)	0.32
-O10	2.407	0.30	-O1	2.443(2)	0.28
-O13B	2.567(4)	0.20	-O12A	2.438(4)	0.28
-O13B	2.567	0.20	-O12A	2.438	0.28
-O13B	2.567	0.20	-O5	2.463(2)	0.26
-O13B	2.567	0.20	Mean 2 × O12A	2.414	2.10
Mean O <sub>6</sub>	2.340	Σ=2.22	Mean 2 × O12B	2.386	2.26
Mean O <sub>7</sub>	2.418	Σ=2.15	Mean O12A +		
Mean O <sub>8</sub>	2.477	Σ=2.08	O12B	2.400	2.18
<b>Hydrogen bonding</b>					
D-H	<i>d</i> (D-H)	<i>d</i> (H..A)	<i>d</i> (D..A)	A	
O10-H10	0.829	1.898	2.704	O13B	
O11-H11	0.799	2.368	3.136	O14	
O12B-H12B	0.823	1.987	2.770	O7	
O12A-H12A	0.495	2.610	2.844	O5	
O13A-H13A	0.726	2.560	2.687	O6	
O13B-H13B	0.855	1.635	2.490	O12A	
O13B-H13B	0.855	2.178	2.997	O12B	
O14-H14A	0.790	1.916	2.695	O3	
O14-H14B	0.746	2.268	2.973	O12A	
O14-H14B	0.746	2.291	2.833	O13B	
O15-H15	0.797	2.045	2.833	O4	

TABLE 2. ATOM POSITIONS IN PASCOITE

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	Occ.
<b>Atoms of the <math>(V_{10}O_{28})^{6-}</math> Structural Unit</b>					
V1	1/2	0.33651(4)	0	0.01878(9)	V <sub>1</sub>
V2	0.54184(2)	1/2	0.79952(4)	0.01806(9)	V <sub>2</sub>
V3	0.65968(2)	1/2	0.12557(4)	0.01982(10)	V <sub>3</sub>
V4	0.38252(2)	0.34975(4)	0.67524(3)	0.02917(9)	V <sub>4</sub>
O1	0.72992(11)	1/2	0.0882(2)	0.0276(4)	O <sub>1</sub>
O2	0.55118(10)	1/2	0.14160(18)	0.0175(3)	O <sub>2</sub>
O3	0.41518(7)	0.37824(12)	0.03121(13)	0.0185(2)	O <sub>3</sub>
O4	0.44846(8)	0.23734(14)	0.85724(15)	0.0260(3)	O <sub>4</sub>
O5	0.61929(11)	1/2	0.7822(2)	0.0254(4)	O <sub>5</sub>
O6	0.48079(8)	0.36781(14)	0.68558(14)	0.0236(3)	O <sub>6</sub>
O7	0.68615(8)	0.63212(15)	0.25285(14)	0.0271(3)	O <sub>7</sub>
O8	0.34433(12)	1/2	0.5690(2)	0.0324(5)	O <sub>8</sub>
O9	0.34214(10)	0.2333(2)	0.56159(18)	0.0452(4)	O <sub>9</sub>
<b>Atoms of the <math>\{Ca_3(H_2O)_7\}^{6+}</math> Interstitial Complex</b>					
Ca1	0	1/2	1/2	0.0397(2)	Ca <sub>1</sub>
Ca2	0.76544(3)	1/2	0.90375(6)	0.02429(11)	Ca <sub>2</sub>
O10	0.8632(2)	1/2	0.4389(4)	0.0714(10)	O <sub>10</sub>
H10	0.8736(19)	0.440(3)	0.400(3)	0.05 <sup>#</sup>	H <sub>10</sub>
O11	0.9871(2)	1/2	0.2723(3)	0.0747(11)	O <sub>11</sub>
H11	0.9572(16)	0.554(3)	0.218(3)	0.05 <sup>#</sup>	H <sub>11</sub>
O12A*	0.7143(2)	0.6970(4)	0.7557(4)	0.0356(7)	O <sub>12</sub>
O12B*	0.7257(2)	0.6418(4)	0.7095(4)	0.0464(9)	O <sub>12</sub>
H12A <sup>§</sup>	0.7503(15)	0.712(2)	0.739(3)	0.05 <sup>#</sup>	H <sub>12</sub>
H12B	0.6926	0.6736	0.7140	0.05 <sup>#</sup>	H <sub>12</sub>
O13A*	0	0.7216(5)	1/2	0.074(3)	O <sub>13</sub>
O13B*	0.9218(3)	0.7063(5)	0.3643(6)	0.0647(12)	O <sub>13</sub>
H13A	0.9608(15)	0.737(3)	0.440(3)	0.05 <sup>#</sup>	H <sub>13</sub>
H13B <sup>§</sup>	0.8752	0.7400	0.3234	0.05 <sup>#</sup>	H <sub>13</sub>
O14	0.83935(13)	0.67191(19)	0.0643(2)	0.0468(5)	O <sub>14</sub>
H14A	0.8672(16)	0.728(3)	0.063(3)	0.05 <sup>#</sup>	H <sub>14</sub>
H14B	0.8330(19)	0.689(3)	0.124(3)	0.05 <sup>#</sup>	H <sub>14</sub>
O15	0.8824(2)	1/2	0.8880(5)	0.0752(12)	O <sub>15</sub>
H15	0.9065(16)	0.562(2)	0.886(3)	0.05 <sup>#</sup>	H <sub>15</sub>

\* Half-occupied position. § Position fixed at value from difference Fourier.  
# Fixed value.

\* Atoms in italics are in half-occupied positions.

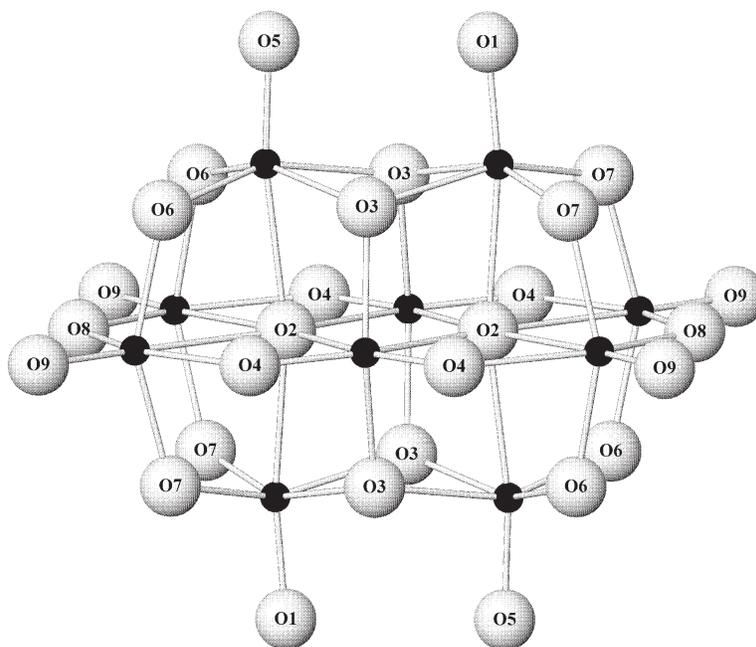


FIG. 1. The  $(V_{10}O_{28})^{6-}$  decavanadate unit in pascoite.

the polyhedron, and thus the V–O bond valence is the lowest in each polyhedron. The bond valence for O2, 1.96 valence units (*vu*), demonstrates that despite the unusual coordination for O2, the efficacy of the valence-matching principle is maintained.

#### *The interstitial complex*

The decavanadate polyanionic structural units in pascoite are connected by the  $\{Ca_3(H_2O)_{17}\}^{6+}$  interstitial complex. All oxygen atoms in the interstitial complex occur as  $(H_2O)$  groups, in contrast to the decavanadate polyanion, which is devoid of hydrogen atoms.

There are two distinct Ca atoms in the interstitial complex, and the disorder that occurs in the coordinating oxygen atoms is of interest. The coordination of Ca1 is complex, and is depicted in Figure 2. Ca1 is bonded solely to  $(H_2O)$  molecules, including four in fully occupied positions [O10 2 and O11 2]. In addition to these four bonds, Ca1 bonds to partially occupied, disordered O13 atoms. Oxygen O13 disorders into two sites of differing ranks, which could also be described as two distinct half-occupied positions. O13A is a half-occupied site in the  $(0, y, \frac{1}{2})$  special position (rank = 4), and O13B is a half-occupied site in the  $(x, y, z)$  general position (rank = 8). Thus O13 contributes six possible oxygen sites, but only two, three, or four of those sites will be filled in any Ca1 polyhedron. The sites corre-

spond to the coordinating atoms in the acentric alternative with the addition of the mirror plane.

At any specific Ca1 site, the central cation bonds to the four fully occupied oxygen sites, O10 2 and O11 2, forming an equatorial plane (Fig. 2). In addition, the Ca1 cation bonds to some combination of the two half-occupied O13X sites, forming the “apices” of the polyhedron; Figure 2 depicts the possible ligands for the “apical” bonds. Ca1 can bond to two *trans* O13A atoms, yielding  $Ca1O_6$  coordination. Alternatively, the central Ca1 atom can bond to one O13A on one side of the equatorial plane and two O13B atoms on the opposite side, yielding  $Ca1O_7$  coordination. Finally, the central cation can bond to two O13B atoms on both sides of the equatorial plane, resulting in  $Ca1O_8$  coordination. Bond-valence calculations allow all three possibilities for Ca1 coordination (Table 3); the half-occupied nature of the O13X sites yields the average coordination of  $Ca1O_7$ . The possibility of such disorder was recognized by Swallow *et al.* (1966).

The Ca2 cation also is bonded to disordered oxygen atoms, forming a  $Ca2O_7$  polyhedron. Ca2 bonds to O1, O5, O14 ( $\times 2$ ), and O15; in addition, Ca2 bonds to two O12X oxygen atoms, either the O12A or O12B atoms. The central cation can bond to two O12A atoms, two O12B atoms, or one O12A and one O12B atoms, completing the  $Ca2O_7$  polyhedron. Bond distances and valence sums for the three possibilities are offered in Table 3.

*The space group of pascoite*

In their description of the atomic arrangement, Swallow *et al.* (1966) noted the difficulty in distinguishing between two candidate space-groups for the phase; we reiterate that difficulty here. In their non-conventional setting of the cell, they attempted to distinguish between space groups  $I2$  and  $I2/m$ , and ultimately accepted the acentric alternative, although they noted that “the space group might conceivably be  $I2/m$  with structural disorder”. They reported that the final  $R$  indices for the two candidate space-groups were “virtually the same”, and that the final difference-maps in each space group were inconclusive regarding the true symmetry. In the conventional cell setting offered in this work, their two alternative cells yield space groups  $C2$  and  $C2/m$ ; the superior data collected with the CCD detector in this work allow us to distinguish between the two candidate space-groups, and the refinement of those data lead us to the alternative conclusion from that offered by Swallow *et al.* (1966). Below, we support our conclusion that the correct space-group of pascoite is the centric alternative,  $C2/m$ , which, as suggested by Swallow *et al.*, does indeed display extensive structural disorder. However, we do not de-emphasize the difficulty in conclusively determining the space group in

such cases as pascoite. Marsh (1986, 1994, 1995) has written extensively on the topic, and noted the difficulty, if not impossibility, of distinguishing the correct space-group between examples as  $C2$  and  $C2/m$  on the basis of diffraction data. However, he noted that “in cases where diffraction data do not provide a clear choice between centrosymmetric and noncentrosymmetric space-group, it is better to opt for the centrosymmetric description even though disorder may result. The disorder model implies that the crystal is a composite of two or more molecular structures that cannot be distinguished from one another” (Marsh 1986).

As noted by Swallow *et al.* (1966), the principal difference between the two candidate space-groups is disorder among the Ca1 (our nomenclature) ligation (Fig. 2). In the acentric alternative proffered by those authors, Ca1 is bonded to seven oxygen atoms. In the  $C2/m$  alternative offered here, Ca1 is disordered, and bonded to six, seven, or eight oxygen atoms, with an *average* coordination of  $\text{Ca1O}_7$  (Fig. 2), yielding the proscribed formula for pascoite. Refinement of the atom arrangement with the current dataset in the acentric alternative,  $C2$ , provided difficulties in identifying hydrogen atom positions, and also yielded one non-positive definite atom. Because all H atoms could not be located in the  $C2$  acentric alternative, both

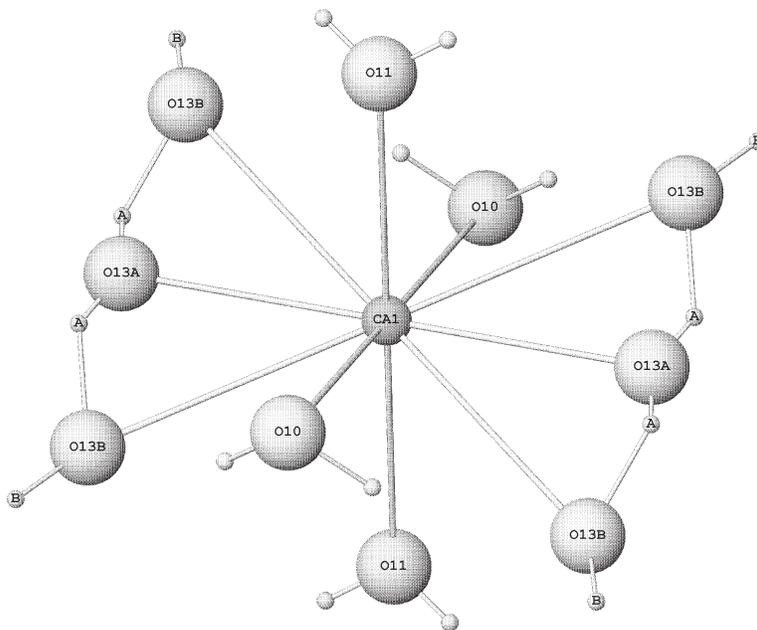


Fig. 2. The Ca1 polyhedron in pascoite. Oxygen atom O13 is disordered into two half-occupied sites, O13A and O13B, and a hydrogen associated with O13B (H13B, Table 2) is also half-occupied. On either “side” of the equatorial plane defined by O10 and O11, either the O13A site *or* the pair of O13B sites is occupied. Thus, Ca1 can be 6-, 7-, or 8-coordinated with oxygen, with an average of  $\text{Ca1O}_7$ . Hydrogen atom “x” = H13A, hydrogen atom “y” = H13B.

structures were refined using only non-hydrogen atoms for comparison of the two structure alternatives. Under these conditions, the *C2* alternative, equivalent to the *I2* structure proffered by Swallow *et al.* (1966) and with its additional degrees of freedom, yields an *R* value of 3.71%, with one atom with non-positive-definite thermal parameters. The centric alternative reported here as the correct structure yielded an *R* value of 2.92% with no atoms having non-positive-definite thermal parameters. Perhaps most definitive is the refinement of a racemic twinning in the acentric alternative. The twin scale-factor refined to within  $1\sigma$  of 0.50 [0.47(5)], essentially yielding the centric *C2/m* model. We thus conclude that the *C2/m* structure offered here is the correct arrangement of atoms for pascoite, and that the disordered alternative of Swallow *et al.* (1966) is the correct arrangement.

#### Hydrogen atoms in pascoite

As noted previously, hydrogen atom positions were not located in the original study of Swallow *et al.* (1966). However, as noted subsequently, an understanding of the hydrogen bonding in the phase is fundamental to understanding the bonding between the decavanadate polyanion and the interstitial complex in pascoite.

All hydrogen atoms were successfully located in difference maps. The positions of the hydrogen atoms were subsequently refined to yield O–H bond lengths within  $2\sigma$  of 0.82 Å, the expected O–H distance in X-ray-diffraction studies; the value of the isotropic displacement factor  $U_{11}$  ( $= 0.05 \text{ \AA}^2$ ) was fixed. The scheme of hydrogen bonds is given in Table 3, and the hydrogen bonding between the decavanadate polyanion and the interstitial complex in pascoite is discussed subsequently. The interatomic distances in Table 3 also reveals disordered atoms that would not exist as nearest neighbors, such as O13B and O12A, which yield a value of  $d(\text{H}\dots\text{A})$  of 1.64 Å, unrealistically short for a hydrogen bond. Although all H atoms were located in difference maps, difficulties exist because some H atoms [*e.g.*, H(3*x*)] are clearly disordered owing to bonding to two different disordered atoms, and at least one H atom [H(3*y*)] is in a half-occupied position.

#### SPACE-GROUP SYMMETRIES AND INTERSTITIAL COMPLEXES IN COMPOUNDS WITH THE $[\text{V}_{10}\text{O}_{28}]^{6-}$ DECAVANADATE POLYANION

Table 5 lists the interstitial cations, space-group symmetries, number of anions in the structural unit per bond from the interstitial cations, and the number of (H<sub>2</sub>O) groups per interstitial cation in selected compounds that contain the  $[\text{V}_{10}\text{O}_{28}]^{6-}$  structural unit. In Table 5, we consider only structures that contain simple mono-, di-, and trivalent cations, and no complex

cationic groups such as (NH<sub>4</sub>)<sup>+</sup> and (H<sub>3</sub>O)<sup>+</sup> or organic molecules in the interstitial complex.

Inspection of Table 5 indicates that the structures of all of the compounds are centric. This observation further supports the arguments offered above that space-group symmetry *C2/m* is the correct one for pascoite. The most common space-group symmetry is *P*, but many structures also show space-group symmetries belonging to point group *2/m*. The structure of Al<sub>2</sub>[V<sub>10</sub>O<sub>28</sub>](H<sub>2</sub>O)<sub>25</sub> (Punte *et al.* 1988) alone has an orthorhombic space-group, *Cmma*.

#### Number of (H<sub>2</sub>O) groups versus number of emanated bonds in the interstitial complex

All compounds listed in Table 5 have the  $[\text{V}_{10}\text{O}_{28}]^{6-}$  structural unit in common. That decavanadate polyanion (Fig. 1) can be seen as an anionic sphere on which bond-valence acceptors occur at the outer layer. These bond-valence acceptors are “exterior” oxygen atoms that accept only one or two bonds from vanadium atoms, including <sup>11</sup>O1, <sup>11</sup>O5, <sup>11</sup>O9, <sup>12</sup>O4, <sup>12</sup>O6, <sup>12</sup>O7, and <sup>12</sup>O8, whereas <sup>16</sup>O2 and <sup>13</sup>O3, oxygen atoms in the interior of the decavanadate group, do not accept any bonds emanating from the interstitial complex. Interstitial cations around the decavanadate ion must

TABLE 5. INTERSTITIAL CATIONS, SPACE GROUP, THE NUMBER OF ANIONS IN THE STRUCTURAL UNIT PER BOND FROM THE INTERSTITIAL CATIONS AND THE NUMBER OF H<sub>2</sub>O GROUPS PER INTERSTITIAL CATION IN SELECTED MINERALS AND SYNTHETIC COMPOUNDS WITH THE  $[\text{V}_{10}\text{O}_{28}]^{6-}$  STRUCTURAL UNIT

Interstitial cations	Space group	Anions per bond	H <sub>2</sub> O groups per cation	Ref.
Ca <sub>1</sub> (pascoite)	<i>C2/m</i>	1.33	5.67	[1]
K <sub>2</sub> Mg <sub>2</sub> (hummerite)	<i>P1</i>	0.88	4	[2]
Na <sub>6</sub>	<i>P1</i>	0.74	3	[3]
Nd <sub>2</sub>	<i>P2<sub>1</sub>/b</i>	1.56	14	[4]
Rb <sub>2</sub> Mg <sub>2</sub>	<i>P1</i>	0.88	4	[5]
Yb <sub>2</sub>	<i>P1</i>	1.75	12	[6]
Al <sub>2</sub>	<i>Cmma</i>	2.33	12.25	[7]
Sr <sub>3</sub>	<i>C2/c</i>	1.12	7.33	[8]
Ba <sub>3</sub>	<i>P1</i>	1.04	6.33	[9]
K <sub>6</sub>	<i>P2<sub>1</sub>/n</i>	0.57	1.5	[10]
Eu <sub>2</sub>	<i>P1</i>	1.75	12	[11]
K <sub>2</sub> Ba <sub>2</sub>	<i>P2<sub>1</sub>/a</i>	0.78	2	[12]
Y <sub>2</sub>	<i>P1</i>	1.75	12	[13]
K <sub>2</sub> Zn <sub>2</sub>	<i>P1</i>	0.88	4	[14]
Na <sub>2</sub> Ni <sub>2</sub>	<i>P2<sub>1</sub>/c</i>	1.08	5.5	[15]
La <sub>2</sub>	<i>P2<sub>1</sub>/c</i>	1.56	13	[16]
Na <sub>2</sub> Ni	<i>P1</i>	0.93	4.6	[17]
K <sub>2</sub> Co <sub>2</sub>	<i>P1</i>	0.88	4	[18]
CuNa <sub>4</sub>	<i>P1</i>	0.93	4.6	[19]
Cu <sub>3</sub>	<i>P1</i>	1.56	8	[19]
K <sub>2</sub> Na <sub>2</sub>	<i>P1</i>	0.64	1.67	[20]
K <sub>2</sub> Ni <sub>2</sub>	<i>P1</i>	0.88	4	[21]

[1] this work, [2] Hughes *et al.* (2002), [3] Durif *et al.* (1980), [4] Saf'yanov & Belov (1976), [5] Avtamonova *et al.* (1990), [6] Rivero *et al.* (1985), [7] Punte *et al.* (1988), [8] Nieto *et al.* (1993), [9] Kamenar *et al.* (1996), [10] Xu *et al.* (1997); [11] Naruke *et al.* (1999), [12] Rastsvetaeva (1999), [13] Navaza *et al.* (2000), [14] Yakubovich *et al.* (2002), [15] Higami *et al.* (2002), [16] Peng *et al.* (2002), [17] Sun *et al.* (2002), [18] Lee *et al.* (2003), [19] Iida & Ozeki (2003), [20] Lee & Joo (2003), [21] Khan *et al.* (2001).

either directly bond to those acceptors or they require interstitial ( $\text{H}_2\text{O}$ ) groups, which distribute the emanated bond-valence of the cations to the anions of the structural unit. Schindler & Hawthorne (2001) showed that there are three different types of ( $\text{H}_2\text{O}$ ) groups in the interstitial complexes of oxysalt minerals: A) A transformer ( $\text{H}_2\text{O}$ ) group accepts only one bond and from it emanate two hydrogen bonds; B) a non-transformer ( $\text{H}_2\text{O}$ ) group accepts two bonds and from it emanate two bonds, and C) a reverse transformer ( $\text{H}_2\text{O}$ ) group accepts three bonds and from it emanate two bonds. Transformer and non-transformer ( $\text{H}_2\text{O}$ ) groups are very common in oxysalt minerals, whereas reverse transformer ( $\text{H}_2\text{O}$ ) groups rarely occur.

Let us consider six monovalent cations in [6]-coordination around the decavanadate ion. Each cation must not bond to many ( $\text{H}_2\text{O}$ ) groups, because there are overall  $6 \times 6 = 36$  bonds emanating from the interstitial cations but there are only 22 bond-valence acceptors (out of 28 anions); hence for a stable structure, we predict that the number of ( $\text{H}_2\text{O}$ ) groups per cation will be small. For example, the structure of  $\text{Na}_6[\text{V}_{10}\text{O}_{28}](\text{H}_2\text{O})_{18}$  contains four Na in [6]-coordination and two Na in [7]-coordination (Durif *et al.* 1980). The overall number of bonds that emanates is 38, and there are only three ( $\text{H}_2\text{O}$ ) groups per interstitial cation.

The situation will be completely different if two trivalent cations ( $^{[6]}M^{3+}$ ) occur in the interstitial complex around the decavanadate ion. The overall number of bonds from the interstitial cations would be only twelve in contrast to 22 bond-valence acceptors. The twelve  $M^{3+}\text{-O}$  bonds have average bond-valence of 0.50 *vu* that must be distributed to the 22 bond-valence acceptors. Hence, each cation must bond to a large number of transformer ( $\text{H}_2\text{O}$ ) groups (maximum six) in

order to produce a higher number of bonds with a lower average bond-valence. Furthermore, a high number of non-transformer ( $\text{H}_2\text{O}$ ) groups must be present in order to distribute the bonds to all bond-valence acceptors. For example, the structure of  $\text{Al}_2[\text{V}_{10}\text{O}_{28}](\text{H}_2\text{O})_{25}$  contains two  $\text{Al}^{3+}$  in [6]-coordination. The overall number of bonds from the interstitial cations is only twelve, but there are 12.5 ( $\text{H}_2\text{O}$ ) groups per cation.

In this way, there must be a correlation between the sum of bonds emanating from interstitial cations and the number of ( $\text{H}_2\text{O}$ ) groups per cation in the interstitial complex. Schindler & Hawthorne (in prep.) found this type of correlation for uranyl oxysalt minerals with sheet structural-units. They normalized the number of bonds emanating from interstitial cations to the overall number of anions in the structural unit. This approach has the advantage that one can compare structural units with a different number of anions. Schindler & Hawthorne further show that this type of correlation only exists between the data of compounds with structural units of identical degree of polymerization (*i.e.*, framework, sheet, chain and cluster).

Figure 3 shows a plot of the number of anions in the structural unit per emanated bonds from the interstitial cations *versus* the number of ( $\text{H}_2\text{O}$ ) groups per interstitial cation for the compounds in Table 5. It is apparent that the data points follow a linear trend ( $R^2 = 0.83$ ) in which the quality of the correlation decreases with a higher number of ( $\text{H}_2\text{O}$ ) groups in the interstitial complexes. However, the high value of the correlation does still cause surprise if one considers that distortion of cation polyhedra (*e.g.*, Jahn–Teller distortion of  $\text{Cu}^{2+}$ -bearing polyhedra), the effective ionic radii of interstitial cations and the variable space between the decavanadate ions also control the overall number of ( $\text{H}_2\text{O}$ ) groups in the interstices.

This correlation confirms the predictive nature of the number of interstitial ( $\text{H}_2\text{O}$ ) groups for a given combination of interstitial mono-, di-, and trivalent cations with specific coordination numbers. This issue will be discussed elsewhere.

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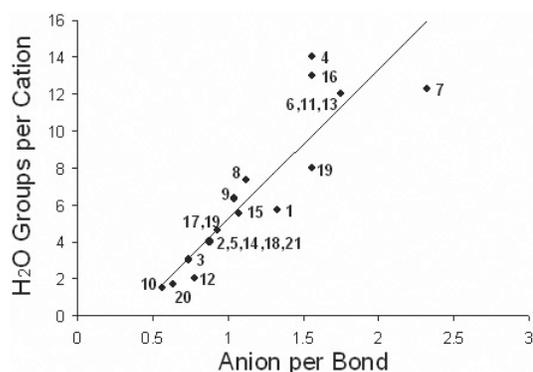


FIG. 3. The number of anions in the  $[\text{V}_{10}\text{O}_{28}]^{6-}$  structural unit per bonds emanated from the interstitial cation (Anions / Bonds) *versus* the number of interstitial ( $\text{H}_2\text{O}$ ) groups per interstitial cation ( $\text{H}_2\text{O}$ -Groups / Cation) for all minerals and synthetic phases listed in Table 5. Numbers correspond to references listed in Table 5.

## REFERENCES

- AVTAMONOVA, N.V., TRUNOV, V.K. & MAKAREVICH, L.G. (1990): Specifying the crystal structures of magnesium hexadecaquadecavanadates with potassium, ammonium and rubidium. *Izvest. Akad. Nauk SSSR, Neorg. Mat.* **26**, 350-356.
- BRUKER AXS, INC. (2000): SHELXTL v. 6.14 Software Package. Madison, Wisconsin, U.S.A.
- BRUKER AXS, INC. (2003): SaintPlus v. 6.45 Software Package. Madison, Wisconsin, U.S.A.
- DURIF, A., AVERBUCH-POUCHOT, M.T. & GUITEL, J.C. (1980): Structure d'un d cavanadate d'hexasodium hydrat . *Acta Crystallogr.* **B36**, 680-682.
- GRIFFEN, D.T. (1990): The crystal structure of hummerite, with comments on the crystallochemical stability of the decavanadate isopolyanion. *Brigham Young Univ., Geology Studies* **36**, 1-14.
- HAWTHORNE, F.C. (1983): Graphical enumeration of polyhedral clusters. *Acta Crystallogr.* **A39**, 724-736.
- HIGAMI, T., HASHIMOTO, M. & OKEYA, S. (2002):  $(\text{Ni}(\text{H}_2\text{O})_6)_2(\text{Na}(\text{H}_2\text{O})_3)_2(\text{V}_{10}\text{O}_{28})\cdot 4(\text{H}_2\text{O})$ . *Acta Crystallogr.* **C58**, 144-146.
- HUGHES, J.M., SCHINDLER, M., RAKOVAN, J. & CURETON, F.E. (2002): The crystal structure of hummerite,  $\text{KMg}(\text{V}_5\text{O}_{14})\cdot 8\text{H}_2\text{O}$ : bonding between the  $[\text{V}_{10}\text{O}_{28}]^{6-}$  structural unit and the  $\{\text{K}_2\text{Mg}_2(\text{H}_2\text{O}_{16})\}^{6+}$  interstitial complex. *Can. Mineral.* **40**, 1429-1435.
- IIDA, A. & OZEKI, T. (2003):  $\text{Cu}_3\text{V}_{10}\text{O}_{28}\cdot 24(\text{H}_2\text{O})$  and  $\text{CuNa}_4\text{V}_{10}\text{O}_{28}\cdot 23(\text{H}_2\text{O})$ . *Acta Crystallogr.* **C59**, 41-44.
- KAMENAR, B., CINDRIC, M. & STRUKAN, N. (1996):  $\text{Ba}_3(\text{V}_{10}\text{O}_{28})\cdot 19(\text{H}_2\text{O})$ . *Acta Crystallogr.* **C52**, 1338-1341.
- KHAN, M.I., TABUSSUM, S. & ZHENG, C. (2001): Mixed-metal oxide phases containing decavanadate clusters: synthesis and crystal structures of  $((\text{H}_2\text{O})_2\text{K}-\text{mue}-(\text{H}_2\text{O})_3-\text{M}(\text{H}_2\text{O})_3)_2(\text{V}_{10}\text{O}_{28})$ . *J. Cluster Sci.* **12**, 583-594.
- LEE, U. & JOO, H.-C. (2003): Potassium-sodium double salt of decavanadate,  $\text{K}_4\text{Na}_2(\text{V}_{10}\text{O}_{28})\cdot 10(\text{H}_2\text{O})$ . *Acta Crystallogr.* **E59**, 122-124, Structure Reports Online.
- \_\_\_\_\_, JUNG, Y.-H. & JOO, H.-C. (2003): Dipotassium bis(hexaaquacobalt(II)) decavanadate tetrahydrate. *Acta Crystallogr.* **E59**, 72-74, Structure Reports Online.
- MARSH, R.E. (1986): Centrosymmetric or noncentrosymmetric? *Acta Crystallogr.* **B42**, 193-198.
- \_\_\_\_\_. (1994): The centrosymmetric-noncentrosymmetric ambiguity: some more examples *Acta Crystallogr.* **A50**, 450-455.
- \_\_\_\_\_. (1995): Some thoughts on choosing the correct space group. *Acta Crystallogr.* **B51**, 897-907.
- NARUKE, H., YAMASE, T. & KANEKO, M. (1999): X-ray structural characterization of  $[\text{Eu}(\text{H}_2\text{O})_8]_2[\text{V}_{10}\text{O}_{28}]\cdot 8(\text{H}_2\text{O})$ . *Bull. Chem. Soc. Jap.* **72**, 1775-1779.
- NAVAZA, A., CHEVRIER, G., KIAT, J.-M. & BARAN, E.J. (2000): Neutron diffraction structure of  $\text{Y}_2\text{V}_{10}\text{O}_{28}\cdot 24(\text{H}_2\text{O})$  at 297 and 60 K. *J. Chem. Crystallogr.* **30**, 545-555.
- NIETO, J.M., SALAGRE, P. & MEDINA, F., SUEIRAS, J.E. (1993): Structure of  $\text{Sr}_3\text{V}_{10}\text{O}_{28}\cdot 22\text{H}_2\text{O}$ . *Acta Crystallogr.* **C49**, 1879-1881.
- PALACHE, C., BERMAN, H. & FRONDEL, C. (1951): *Dana's System of Mineralogy* **2** (7th ed.). John Wiley & Sons, New York, N.Y. (p. 1055).
- PENG, X.-H., LI, Y.-Z., CAI, L.-X., WANG, L.-F. & WU, J.-G. (2002): A novel polyoxometalate supramolecular compound:  $(\text{La}(\text{H}_2\text{O})_9)_2(\text{V}_{10}\text{O}_{28})\cdot 8(\text{H}_2\text{O})$ . *Acta Crystallogr.* **E58**, 111-113, Structure Reports Online.
- PUNTE, G., RIVERO, B.E. & RIGOTTI, G. (1988): Aluminium decavanadate 25-hydrate. *Acta Crystallogr.* **C44**, 216-219.
- RASTSVETAeva, R.K. (1999): Crystal structure of new potassium-barium decavanadate. *Kristallografiya* **44**, 1027-1028 (in Russ.).
- RIVERO, B.E., PUNTE, G. & RIGOTTI, G. (1985): Dytterbium decavanadate 24-hydrate,  $(\text{Yb}_2\text{V}_{10}\text{O}_{28})(\text{H}_2\text{O})_{24}$ . *Acta Crystallogr.* **C41**, 817-820.
- SAF'YANOV, YU.N. & BELOV, N.V. (1976): Crystal structure of neodymium decavanadate  $\text{Nd}_2\text{V}_{10}\text{O}_{28}(\text{H}_2\text{O})_{28}$ . *Dokl. Akad. Nauk SSSR* **227**, 1112-1115.
- SCHINDLER, M. & HAWTHORNE, F.C. (2001): A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals. I. Theory. *Can. Mineral.* **39**, 1225-1242.
- \_\_\_\_\_, \_\_\_\_\_ & BAUR, W.H. (2000a): A crystal-chemical approach to the composition and occurrence of vanadium minerals. *Can. Mineral.* **38**, 1443-1456.
- \_\_\_\_\_, \_\_\_\_\_ & \_\_\_\_\_ (2000b): Crystal-chemical aspects of vanadium: polyhedral geometries, characteristic bond-valences and polymerization of (VOn) polyhedra. *Chem. Mater.* **12**, 1248-1259.
- SUN, Z.-G., LONG, L.-S., REN, Y.-P., HUANG, R.-B., ZHENG, L.-S. & NG, S.W. (2002): Tetradecaquatetrasodium hexaaquanickel(II) decavanadate(V) trihydrat. *Acta Crystallogr.* **E58**, 34-36, Structure Reports Online.
- SWALLOW, A.G., AHMED, F.R. & BARNES, W.H. (1966): The crystal structure of pascoite,  $\text{Ca}_3\text{V}_{10}\text{O}_{28}\cdot 17\text{H}_2\text{O}$ . *Acta Crystallogr.* **21**, 397-405.
- YAKUBOVICH, O.V., ANAN'EVA, E.N., DIMITROVA, O.V. & URUSOV, V.S. (2002): Refinement of the crystal structure of  $\text{K}_2\text{Zn}_2\text{V}_{10}\text{O}_{28}\cdot 16(\text{H}_2\text{O})$ . *Dokl. Akad. Nauk* **384**, 334-340 (in Russ.).
- XU, J.-N., YANG, G.-Y., SUN, H.-R., WANG, T.-G. & XU, J.-Q. (1997): Synthesis and crystal structure of  $\text{K}_6\text{V}_{10}\text{O}_{28}\cdot 9(\text{H}_2\text{O})$ . *Huaxue Yanjiu Yu Yingyong (Chem. Research and Application)* **9**, 576-581.

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