American Mineralogist, Volume 63, pages 863–868, 1978

The crystal chemistry of sherwoodite, a calcium 14-vanadoaluminate heteropoly complex

HOWARD T. EVANS, JR. AND JUDITH A. KONNERT

U.S. Geological Survey
Reston, Virginia 22092

Abstract

The crystal structure of sherwoodite (tetragonal, space group $I4_1/amd$; a = 28.06, c = 13.56A) has been determined from 848 counter-measured intensity data (Mo$K\alpha$ radiation). Difficulties with disorder and variability of crystal water as well as poor crystal quality prevented refinement below R = 0.22, but the essential structure is clearly revealed. Aluminum is found to play an essential role as the nucleus atom in the heteropoly complex molecule found in the structure: 14-vanadoaluminate, $(AlV_{14}O_{40})^{n-}$. There are 8 molecules in the unit cell joined by Ca^{2+} ions into chains along body diagonals, cross-linked to form an open framework of zeolitic character. The remaining Ca atoms and H_2O molecules could not be resolved and are presumably in disordered array in the intermolecular channels. The vanadium is partially reduced, and the ideal formula that best fits the determined structure and chemical analysis is $Ca_{4.5}(AlV^{V}_{12}V^{IV}_{2}O_{40})\cdot 28H_2O$. The molecule has $4/mmm$ symmetry and consists of 14 VO_6 octahedra condensed by edge-sharing around the central AlO_6 octahedron. The V–O distances vary from 1.58 to 2.36A.

Introduction

In 1958, Thompson *et al.* published a description of a new calcium vanadate mineral which was found at the Peanut Mine, Montrose County, Colorado. This rare species occurs as soft, greenish-black, tetragonal crystals up to 1 mm on fracture surfaces in Colorado Plateau sandstones bearing partially-oxidized vanadium minerals. The discrete nature of the mineral species was clearly established by its characteristic physical and crystallographic properties, but a wholly satisfactory chemical description could not be given. The best formula that could be derived from a microchemical analysis and crystallographic studies was $Ca_3V_8O_{22}\cdot 15H_2O$. The analysis also showed minor amounts of Al, Fe, and Mg. Thompson *et al.* (1958) recognized that the true chemical nature of sherwoodite could only be learned from a crystal structure analysis.

Such a structure determination has now been undertaken. Although still incomplete, it has clearly revealed that sherwoodite contains isolated molecules of a 14-vanadoaluminate heteropoly complex. The mineral is the first known occurrence in nature of this type of chemical complex. Although experimental difficulties have prevented full refinement of the structure of this mineral to a degree that is nowadays considered desirable, the results obtained at this point are considered to be sufficiently noteworthy to warrant making this preliminary report.

Experimental procedure

A flat, square fragment of a euhedral crystal 0.07 × 0.06 × 0.025 mm in size (from the Peanut Mine) was used for structure analysis. Precession photography confirmed the earlier space-group determination, given as $I4_1/amd$ (No. 141). Careful measurement of the 20.0.0 and 0.0.12 reflections in the plus and minus 2θ regions on the Picker automatic diffractometer using Mo$K\alpha$ radiation gave cell constants a = 28.06(3) and c = 13.56(2)A for this crystal. Intensities were measured for all allowed independent reflections with $2\theta < 45$ degrees; of 1783 measured, 848 had $F > 3\sigma$ based on counting statistics, and were used for the structure analysis.

The reflection 962 was used to monitor the primary beam during the run, and the intensity of this reflection showed somewhat greater than expected variation. As a consequence (and because of difficulties encountered in the structure refinement) the data set was measured a second time, but with no apparent

0003-004X/78/0910-0863$02.00

improvement. Toward the end of the second run the monitor reflection intensity suddenly dropped to less than one third its nominal value. A day later, it had recovered its full strength. It seems clear that the crystal reacts to humidity changes in the manner of a zeolite. Absorption corrections were calculated assuming a rectangular parallelopiped having the dimensions given above, and a linear absorption coefficient $\mu = 45$ cm^{-1}. Corrections applied to the data varied from 1.25 to 1.75. In addition to the Lorentz and polarization factors, dispersion corrections were applied using the coefficients of Cromer and Liberman (1970). In the structure factor computations, the neutral atom scattering factors of Doyle and Turner (1968) were used.

The data set used for the structure analysis is recognized to be of inferior quality for the following reasons: (1) the crystals are very soft and give irregular and broadened reflection profiles; (2) the water content of the crystal was subject to change during the counter run, causing changes in intensities. These factors, in addition to the problem of accounting for disordered cations and water molecules in the structure, will make it difficult to improve the structure determination described in the following section.

Crystal structure analysis

The first data set was normalized to E values and was treated by the symbolic addition procedure (Karle and Karle, 1966) in an attempt to find a consistent set of phases. Such a set was eventually obtained and used to prepare the sharpened electron density function (E map). In this way, 6 prominent peaks were found in the asymmetric unit, corresponding to 128 atoms in the unit cell. Fourteen peaks were clustered around the site 8(c) at the origin of the cell, with $2/m$ symmetry. Additional peaks in 16(g) on a twofold axis with $x = 0.133$ continued the arrangement of peaks in a network of dense rods intersecting at the sites 8(c) and leaving large open spaces in the cell volume.

At this point we recognized that the 14 peaks around 8(c) formed an elongated rhombic dodecahedron that was very similar to that found recently by Moore (1974) for a synthetic heteropoly complex, $K_7(MnV_{13}O_{38})\cdot 18H_2O$ (Flynn and Pope, 1970), where one of the outer vertexes of the dodecahedron is absent. [An exactly analogous structure of $K_7(NiV_{13}O_{38})\cdot 18H_2O$ has since been published by Kobayashi and Sasaki, 1975.] Such a molecule was clearly visible in our electron density maps, complete with all the oxygen atoms. The peak at 16(g) was somewhat less dense than the others (assumed to be vanadium) and was readily assigned to Ca, which finds itself in very favorable square antiprism coordination with 8 oxygen atoms from two adjacent polyvanadate molecules at distances close to 2.4A.

A peak at the 8(c) site at the center of the group of 14 vanadium atoms had a density about half that of vanadium. It was octahedrally coordinated to 6 oxygen atoms at a distance of about 1.9A. A glance at the chemical analysis given by Thompson *et al.* (1958) shows the presence of 2.7 percent Al_2O_3 (see Table 4), thus providing Al as an ideal candidate for this central site. After four cycles of least-squares refinement (using unit weights) of the Ca, Al, 5 V and 12 O atoms thus identified in the asymmetric unit, the conventional reliability factor converged to $R = 0.223$. The corresponding electron density synthesis shows these atoms (the molecules) clearly and sharply, except for O(1). This atom appears as a broad, elongated peak linked to the V(1) peak, with a maximum near to 0, 0.096, 0.380, while the least-squares analysis invariably converges at 0, 0.087, 0.362. (No useful information was provided by the difference map.) The latter site is unreasonably close to V(1) (<1.3A); therefore, the former peak maximum site at a distance of 1.59A from V(1) is accepted instead.

Little detail is revealed in the intermolecular region. One weak peak appears in site 16(f) x, 0, 0 with $x = 0.300$, which suggests a possible site for some occupancy by Ca^{2+} or H_2O species. When Ca^{2+} is refined at 50 percent occupancy at this position, convergence is reached with $x = 0.307(4)$ and $U = 0.19(4)$, with no significant improvement in R. All attempts to place H_2O molecules at low concentrations of electron density in this region also failed to yield any conclusive result. We believe that the contents of the intermolecular region are strongly affected in a zeolitic manner by external humidity conditions, and that the structure here has actually changed during the course of the data measurement. Presumably, the data measurement could be improved by enclosing the crystal in an atmosphere of constant humidity. Such a procedure might result in some further resolution of the intermolecular material, but to judge from other experience with crystals of this type (see below), extensive disorder probably would still prevail.

The best parameters for the atoms in the molecular framework are listed in Table 1. The observed and calculated structure factors from the last cycle are

Table 1. Structure and temperature parameters for sherwoodite

Space group: $I4_1/amd$, no. 141; origin at (c) (2/m).
Unit cell: a = 28.06(3)Å, c = 13.56(2)Å; Z = 8.

Atom	Equipoint	Unit cell fractions			Ångström units			ū, Å
		x	y	z	x	y	z	
Al	8(c)	0	0	0	0	0	0	0.23(3)
V(1)	16(h)	0	0.0698(7)	0.2758(16)	0	1.96(2)	3.74(2)	0.23(1)
V(2)	32(i)	0.0570(4)	-0.0149(4)	0.1940(9)	1.60(1)	-0.42(1)	2.63(1)	0.16(1)
V(3)	32(i)	0.0563(4)	0.0852(4)	0.0841(8)	1.58(1)	2.39(1)	1.15(1)	0.14(1)
V(4)	16(h)	0	-0.1015(6)	0.1131(12)	0	-2.58(2)	1.54(2)	0.16(1)
V(5)	16(f)	0.1159(5)	0	0	3.25(1)	0	0	0.13(1)
O(1)*	16(h)	0	0.096	0.380	0	2.70(10)	5.15(10)	0.22
O(2)	32(i)	0.049(2)	0.017(2)	0.298(3)	1.37(4)	0.47(4)	4.05(4)	0.19(3)
O(3)	32(i)	0.050(2)	0.099(2)	0.192(3)	1.41(4)	2.79(4)	2.61(4)	0.21(3)
O(4)	16(h)	0	-0.059(2)	0.207(5)	0	-1.65(6)	2.80(6)	0.18(5)
O(5)	16(h)	0	0.031(2)	0.122(4)	0	0.86(5)	1.65(5)	0.12(5)
O(6)	16(h)	0	0.111(2)	0.021(4)	0	3.12(4)	0.29(5)	0.06(7)
O(7)	32(i)	0.097(2)	-0.053(2)	0.221(3)	2.72(4)	-1.48(4)	3.00(4)	0.18(3)
O(8)	32(i)	0.096(2)	0.029(2)	0.120(3)	2.70(4)	0.81(4)	1.62(4)	0.19(3)
O(9)	32(i)	0.097(2)	0.120(2)	0.049(3)	2.72(4)	3.37(4)	0.66(4)	0.19(3)
O(10)	32(i)	0.049(2)	-0.131(2)	0.148(3)	1.37(4)	-3.67(4)	2.00(4)	0.18(3)
O(11)	32(i)	0.049(1)	-0.042(1)	0.044(2)	1.37(3)	-1.18(3)	0.60(3)	0.05(5)
O(12)	32(i)	0.151(2)	-0.041(2)	0.057(3)	4.24(4)	-1.16(4)	0.78(4)	0.18(3)
Ca	16(g)	0.1318(4)	-0.1182	0.125	3.70(1)	-3.32	1.70	0.17(2)

* Coordinates from electron density map.

listed in Table 2[1]. The various crystallographic calculations have been carried out using the XRAY72 and XRAY76 computer systems evolved by J. M. Stewart and his colleagues at the University of Maryland.

The 14-vanadoaluminate molecule

Sherwoodite is the hydrated calcium salt of the 14-vanadoaluminate heteropoly anion. The polyion has the ideal composition $[AlV_{14}O_{40}]^{n-}$. If the vanadium were fully oxidized n would be 7, but we know from the chemical analysis and the dark color of the crystals that the vanadium must be partially reduced. The vanadium atoms are all in more or less distorted oxygen octahedra, and the 15 octahedra in the molecule are condensed into a dense structure in which the oxygen atoms are in a cubic-close-packed arrangement (Fig. 1a). The whole edifice may thus be considered as a fragment of a NaCl type structure. The tendency of heteropoly and especially isopoly complexes to adapt to a limited NaCl structure has been previously noted by Evans (1966).

As shown in Figure 1b, the central AlO_6 octahedron shares all its edges with neighboring VO_6 octahedra: 4 equatorial, 4 with the next level of VO_6 octahedra above, and 4 below. This arrangement is capped at the top and bottom by 2 further VO_6 octahedra. Although the symmetry of the molecule required by the crystal space group is only $2/m$, it conforms closely to the ideal symmetry $4/mmm$. Using Cartesian axes x and y parallel to twofold axes through the vanadium atoms and z parallel to the fourfold axis, the molecule can be defined in terms of Al at the origin, 3 types of V, and 7 types of O, as shown in Table 3, in which the symmetry-ideal equivalent dimensions from Table 1 have been averaged. The corresponding coordinates found by Moore (1974) are also given. Table 4 shows bond lengths in the molecule derived from Table 3, and also the range of these lengths actually observed in the structure. The bond lengths vary primarily according to the number of metal atoms bonded to the oxygen atom in question. Of the 40 oxygen atoms in the molecule, $2(O_c)$ share 5V + Al (avg. V-O distance, 2.21A); $4(O_f)$ share 4V + Al (2.12A); $8(O_e)$ share 3V (1.90A); $8(O_b)$ share 2V (1.81A); and $18(O_a, O_d, O_g)$ are bonded to only one V (1.61A).

The temperature factors for the molecular cations are fairly large, but not more than expected for a molecular structure of this type, an open ionic framework of large polyanions joined by Ca^{2+} ions, with loosely bound cations and water molecules in the intermolecular regions. The largest vibrations are found for V(1) and O(1), the top and bottom VO groups in the complex, suggesting that there is considerable libration around the Al–V(1) axis. The large

[1] A copy of Table 2 may be obtained in microfiche by ordering Document AM-78-085 from the Business Office, Mineralogical Society of America, 1909 K Street NW, Washington, DC 20006. Please remit $1.00 in advance for the microfiche.

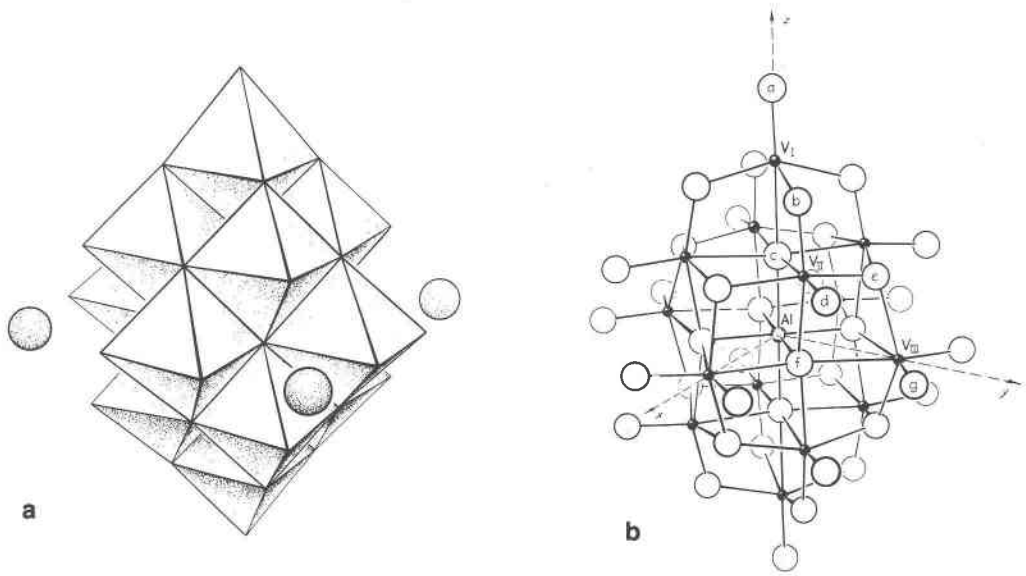

Fig. 1. The 14-vanadoaluminate molecule ion: (a) polyhedral representation with associated Ca^{2+} ions; (b) bonding configuration.

anisotropic thermal motions of these atoms have certainly distorted the definition of the V(1)–O(1) bond link. We have therefore somewhat arbitrarily chosen a site for O(1) that insures that the bond length is greater than 1.55A (see above).

The corresponding bond lengths found by Moore and by Kobayashi and Sasaki are also shown in Table 3 for comparison. The agreement among the three sets of bond lengths is excellent, except for V_{II}–O_b, which varies from 1.6 to 2.09A. This variation seems to be real, but at present we have no explanation for it.

The studies of the synthetic 13-vanadate complexes by Moore and Kobayashi and Sasaki convinced these scientists that the 13-fold stoichiometry is adapted to the crystallographic tetragonal point group symmetry *4/mmm* in each case (space group *I4/mmm*) by random location of the missing equatorial VO_6 octahedron on four positions around the 4-fold axis. We tested our structure for similar random orientations of a ($AlV_{13}O_{38}$) molecular group around the 8(*c*) site of *2/m* point symmetry, by varying the population parameters for V(4), V(5) in equatorial octahedra and V(1) in apical octahedra. These parameters in full isotropic least-squares analysis acquired the values 0.99, 0.91 and 0.94 (±0.06), respectively, without altering the *R* index. Thus, we find no evidence for less than 14 V atoms in our molecule.

Table 3. Cartesian coordinates of idealized polyvanadometallate ions

Atom designations refer to Fig. 1b.
Symmetry 4/mmm; coordinates in Å.

Atom	Multi-plicity	No. (Tab. 1)	$(AlV_{14}O_{40})^{9-}$ x	y	z	$(MnV_{13}O_{38})^{7-}$ * x	y	z
Al,Mn	1		0	0	0	0	0	0
V_I	2	1	0	0	4.22	0	0	4.20
V_{II}	8	2,3	1.59	1.59	2.13	1.60	1.60	2.06
V_{III}	4	4,5	0	3.24	0	0	3.32	0
O_a	2	1	0	0	5.81	0	0	5.82
O_b	8	2,3	1.37	1.37	3.70	1.32	1.32	3.78
O_c	2	5	0	0	1.86	0	0	1.83
O_d	8	7,9	2.71	2.71	2.06	2.73	2.73	2.09
O_e	8	4,6,8	0	2.70	1.72	0	2.64	1.83
O_f	4	11	1.35	1.35	0	1.29	1.29	0
O_g	8	10,12	1.38	4.21	0	1.28	4.34	0

* Dimensions from Moore(1974).

Intermolecular structure

The 14-vanadoaluminate molecules, which are tilted ~28° from the *c* direction in the mirror planes, are arranged in an elegant framework joined by Ca^{2+} ions, as depicted in Figure 2. The cation is clamped on a two-fold axis between two vanadoaluminate molecules in a square antiprism by 4 pairs of oxygen atoms at an average distance of 2.45A [2.45 to O(7), 2.55 to O(9), 2.38 to O(10), 2.40 to O(12); all ±0.04A]. Large channels, about 7A in diameter, run parallel to the *c* axis close to the 4_1 screw axes in the structure. Irregular side channels, 3 to 6A in section, connect the larger channels to each other along diagonal axes parallel to the *x*–*y* plane. As noted above, only one possible site for additional Ca could be found on the electron density map in this open region, but this indication is very weak and is not adjacent to any molecule. Also, no definite evidence for localized water sites could be found. It is appar-

Table 4. Bond lengths in idealized polyvanadometallate ions

Atom designations refer to Tab. 2 and Fig. 1b; lengths (d) in Å.

Atoms	$(AlV_{14}O_{40})^{9-}$ d(±0.05)	range	$(MnV_{13}O_{38})^{7-}$ d(±0.01)*	$(NiV_{13}O_{38})^{7-}$ d(±0.02)**
Al(Mn,Ni)-O_c	1.86		1.83	1.82
-O_f	1.91		1.82	1.89
V_I-O_a	1.59		1.62	1.54
-O_b	2.01	1.99-2.05	1.91	1.90
-O_c	2.36		2.37	2.40
V_{II}-O_b	1.61	1.53-1.69	1.77	2.09
-O_c	2.27	2.26-2.27	2.27	2.27
-O_d	1.58	1.58-1.59	1.60	1.59
-O_e	1.98	1.93-2.03	1.92	1.93
-O_f	2.16	2.13-2.19	2.11	2.09
V_{III}-O_e	1.85	1.75-1.90	1.95	1.95
-O_f	2.32	2.30-2.35	2.41	2.38
-O_g	1.69	1.67-1.71	1.64	1.62

* From Moore(1974).
** From Kobayashi and Sasaki(1975).

ently not possible to locate with certainty any of the intermolecular atoms with the data at hand. This situation is particularly unfortunate with respect to Ca, because the charge on the polyanion, and hence the oxidation state of V, is related to the population of Ca in the structure.

The elusive character of intermolecular material in structures of this type is often encountered. For example, Strandberg (1975), in his careful refinement of the cubic structure (see Allmann, 1976) of $H_3(PMo_{12}O_{40})\cdot 29$–$31H_2O$ was able to find only $6H_2O$ in the formula. In spite of this, partly because of the predominance of Mo scattering, he was able to reach $R = 0.047$. Clark and Hall (1976) had a similar experience with the same structure, arriving at $R = 0.099$. In contrast to the elegant model for the intermolecular water molecules proposed in the original description of this structure by Bradley and Illingworth (1936), these H_2O molecules are evidently moving at random in the intermolecular channels. Kobayashi and Sasaki (1975) reported the structure of $K_7(Ni^{IV}V_{13}O_{38})\cdot 18H_2O$ without locating $4K^+$ or any water molecules, giving $R = 0.089$. Moore (1974) had a similar experience with $K_7(Mn^{IV}V_{13}O_{38})\cdot 18H_2O$. In view of these experiments, it is quite likely that, even if we can acquire a data set from a stabilized crystal, it will not be possible to define clearly the intermolecular material in sherwoodite.

Chemistry of sherwoodite

Thompson *et al.* (1958) reported the composition of sherwoodite on the basis of a microanalysis (by Meyrowitz) of a 14 mg sample. We attempted an electron microprobe analysis of a sherwoodite crystal, but without success because of its extreme softness and high water content. Therefore, we can rely only on the published analysis (Table 5). In writing a formula, the Al and Fe were lumped together with V (and Mg with Ca) and written in ideal form as $Ca_3V_8O_{22}\cdot 15H_2O$. We now know that Al plays a specific role, but we may still assume that Fe_2O_3 together with one H_2O may replace V_2O_4 in the molecule. The new formulation is:

$$[Ca_2(AlV^{V}_{14-x-y}V^{IV}_{x}Fe_yO_{40}H_y)]$$
$$[(Ca,Mg)_{1.5+(x+y)/2}(H_2O)_{m-y/2}].$$

The left brackets contain the molecular framework component, and the right brackets contain the intermolecular material. It is difficult to reconcile this formula with the reported chemical analysis. The given weight percentage of CaO and Fe_2O_3 implies a value of x of 3.5 ($y = 0.2$) and a weight percentage of V_2O_4 of 13.9. On the other hand, the given weight percentage of V_2O_4 of 6.2 is consistent with 11.8 weight percent CaO + MgO. On the basis of our knowledge of the structure and the difficulties associated with such a microanalysis, we believe the actual composition to lie somewhere between these limits. If we assume an integral value for V^{IV}, namely $x = 2$, the expected composition is that shown in column 4 of Table 3. Here m is taken to be 28, but this value is uncertain and variable. The corresponding formula weight is 2065, which with 8 formula units per cell leads to a predicted density of 2.56, somewhat less (perhaps due to lost water) than the reported value of

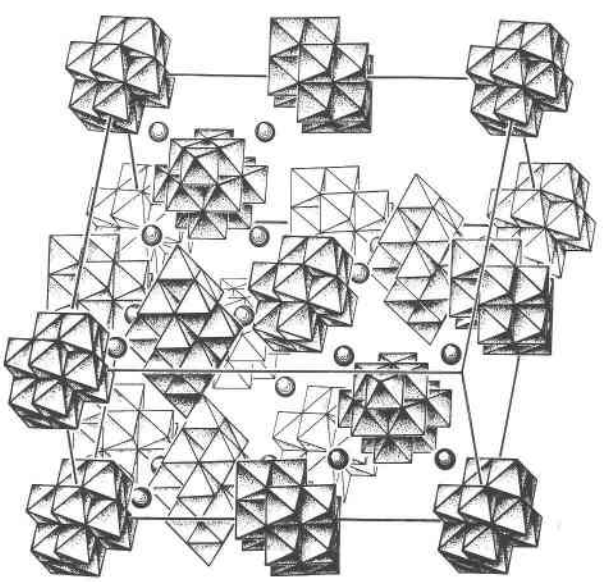

Fig. 2. The unit cell of sherwoodite, showing the 14-vanadoaluminate molecule ions linked by Ca^{2+} ions into a three-dimensional framework.

Table 5. Chemical composition of sherwoodite

(1) Analysis (weight percent) from Thompson, Roach, and Meyrowitz (1958).
(2) Moles contained in one formula unit: $Ca_{4.3}Mg_{0.2}(AlV^{V}_{11.8}V^{IV}_{2.0}Fe_{0.2}O_{40}H_{0.2})\cdot 27.9H_2O$.
(3) Weight percent calculated from (2).

Component	(1)	(2)	(3)
CaO	13.7	4.37	11.8
MgO	0.5	0.23	0.5
V_2O_5	52.1	5.90	52.0
V_2O_4	6.2	1.00	8.0
Fe_2O_3	0.8	0.10	0.8
Al_2O_3	2.6	0.50	2.5
H_2O	23.1	28.00	24.4
Total	100.0		100.0

2.8. Under the circumstances, the agreement of these calculated and observed data may be considered to be fairly good. The probable ideal formulation for sherwoodite is therefore $Ca_{4.5}(AlV^{V}_{12}V^{IV}_{2}O_{40})\cdot 28H_2O$.

Acknowledgment

We are most grateful to Dr. Paul B. Moore of the University of Chicago for letting us have the results of his structure study of $K_7(MnV_{13}O_{38})\cdot 18H_2O$ prior to publication. This information provided a valuable key to the solution of the sherwoodite structure.

References

Allmann, R. (1976) About the space group of $H_3Mo_{12}PO_{40}(H_2O)_{29-31}$; a discussion. *Acta Chem. Scand., A30,* 152.

Bradley, A. J. and J. W. Illingworth (1936) The crystal structure of $H_3PW_{12}O_{40}\cdot 29H_2O$. *Proc. R. Soc. Lond., A157,* 113–131.

Clark, C. J. and D. Hall (1976) Dodecamolybdophosphoric acid *circa* 30-hydrate. *Acta Crystallogr., B32,* 1545–1547.

Cromer, D. T. and D. Liberman (1970) Relativistic calculation of anomalous scattering factors for X-rays. *J. Chem. Phys., 53,* 1891–1898.

Doyle, P. A. and P. S. Turner (1968) Relativistic Hartree-Fock X-ray and electron scattering factors. *Acta Crystallogr., A24,* 390–397.

Evans, H. T., Jr. (1966) The molecular structure of the isopoly complex ion, decavanadate $(V_{10}O_{28})^{6-}$. *Inorg. Chem., 5,* 967–977.

Flynn, C. M., Jr. and M. T. Pope (1970) 1:13 Heteropolyvanadates of manganese(IV) and nickel(IV). *J. Am. Chem. Soc., 92,* 85–90.

Karle, J. and I. L. Karle (1966) The symbolic addition procedure for phase determination for centrosymmetric and noncentrosymmetric crystals. *Acta Crystallogr., 21,* 849–859.

Kobayashi, A. and Y. Sasaki (1975) Crystal structure of $K_7(Ni^{IV}V_{13}O_{38})\cdot 18H_2O$. *Chem. Lett.* (Japan), 1123–1124.

Moore, P. B. (1974) Crystal structure of $K_7(MnV_{13}O_{38})\cdot 18H_2O$. Samples for this study were kindly provided by Prof. M. T. Pope of Georgetown University, Washington, D.C. Unpublished work; private communication.

Strandberg, R. (1975) Multicomponent polyanions. 13. The crystal structure of a hydrated dodecamolybdophosphoric acid, $H_3Mo_{12}PO_{40}(H_2O)_{29-31}$. *Acta Chem. Scand., A29,* 359–364.

Thompson, M. E., C. H. Roach and R. Meyrowitz (1958) Sherwoodite, a mixed vanadium(IV)–vanadium(V) mineral from the Colorado Plateau. *Am. Mineral., 43,* 749–755.

Manuscript received, April 4, 1978; accepted for publication, May 17, 1978.