Crystal structure and crystal chemistry of melanovanadite, a natural vanadium bronze

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ABSTRACT

The crystal structure of melanovanadite from Minas Ragra, Peru, has been determined in space group $P\bar{1}$. The triclinic unit cell (nonstandard) has $a = 6.360(2)$, $b = 18.090(9)$, $c = 6.276(2)$ Å, $\alpha = 110.18(4)°$, $\beta = 101.62(3)°$, $\gamma = 82.86(4)°$, $V = 662.5$ Å³. A subcell with $b' = b/2$ was found by crystal-structure analysis to contain $CaV_4O_{10} \cdot 5H_2O$. The subcell has a layer structure in which the vanadate sheet consists of corner-shared tetrahedral VO_4 and double square-pyramidal V_2O_8 groups, similar to that previously found in synthetic CsV_2O_5. Refinement of the full structure ($R = 0.056$) showed that the Ca atom, which half-occupies a general position in the subcell, is 90% ordered at one of these sites in the whole unit cell. Bond length–bond strength estimates indicate that the tetrahedra contain V^{5+}, and the square pyramids, V^{4+}. The measured density is 2.55 g/cm³; the calculated density is 2.53 g/cm³. Heating experiments show that four H_2O are lost at 75°C, two more H_2O are lost at 95°C, and all water is lost between 200 and 250°C, at which point the crystals become amorphous to X-rays.

INTRODUCTION

Melanovanadite was discovered in splendid black crystals at Minas Ragra, Cerro de Pasco, Peru, by W. S. Hutchinson in 1920 and was recognized as a new mineral species and named by Lindgren (1921). A detailed description was published by Lindgren et al. (1922), who concluded that melanovanadite is monoclinic, with original composition $Ca_2V_{10}O_{25}$. They found that the mineral absorbed considerable amounts of water on exposure to humid air.

Only three reports concerning melanovanadite have appeared since: an X-ray diffraction study by Barnes and Qurashi (1952), who showed that the crystals are triclinic with a pronounced superstructure; a report by Bayliss and Hughes (1985), who gave powder-diffraction and crystallographic data; and a note by Barth and Berman (1930), who gave optical data. All these studies were made on type material from Peru. Melanovanadite is also reported in association with duttonite at the Peanut mine, Montrose County, Colorado, by Thompson et al. (1956) and is mentioned as occurring at several other localities in the Colorado Plateau by Weeks et al. (1959). No other occurrences have been reported in the literature.

Melanovanadite has all the characteristics of a vanadium bronze: mixed valences for V, perfect prismatic cleavage, dark color, low cation content, and variable water content. Its true chemical composition and crystal-chemical nature have remained unclear since its first description by Lindgren (1921). We now report our determination of the crystal structure of melanovanadite and investigate its crystal-chemical relationship to other va-

nadium bronzes. Studies of the system $CaO\text{-}V_2O_4\text{-}V_2O_5$ at temperatures above 600°C (Bouloux et al., 1974; Volkov et al., 1975) have not revealed any compound analogous to melanovanadite.

CRYSTAL-STRUCTURE ANALYSIS OF MELANOVANADITE

Crystallography

Using type material (Peru; U.S. National Museum specimen no. 138067), crystallographic data (Table 1) were derived from precession photographs and least-squares analysis of Guinier-Hägg powder data, using a nonstandard triclinic setting to simplify the definition of the sub-

TABLE 1. Crystallographic data for melanovanadite

	Barnes and Qurashi (1952)*	Bayliss and Hughes (1985)*	This work
Crystal system	triclinic	triclinic	triclinic
Space group	P1	P$\bar{1}$ or P1	P$\bar{1}$
a (Å)	6.36(1)	6.357(2)	6.360(2)
b (Å)	17.99(2)	17.993(9)	18.090(9)
c (Å)	6.28(1)	6.274(2)	6.276(2)
α (°)	110.4(2)	110.37(2)	110.18(4)
β (°)	101.8(3)	101.60(2)	101.62(3)
γ (°)	82.9(3)	82.97(4)	82.86(4)
V (Å³)	658	657.9(4)	662.5(4)
D_{calc} (X-ray; g/cm³)			2.53
D_{meas} (g/cm³)	(3.477)**	2.83–2.90	2.55

* Unit cells of these workers transformed to our setting. The transformations (our setting to BQ and BH) are $\bar{1}00/011/00\bar{1}$ (reciprocal); $\bar{1}00/010/01\bar{1}$ (direct).
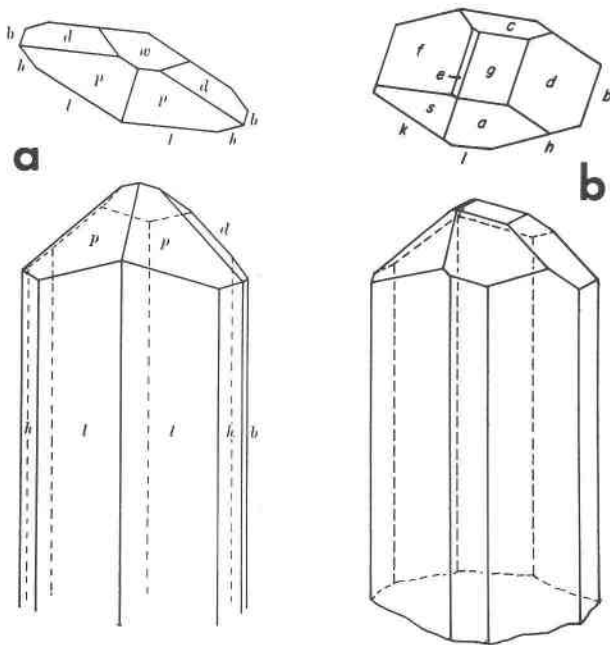
** From Lindgren et al. (1922).

Fig. 1. Crystal habit of melanovanadite, (a) according to Palache (reproduced from Lindgren et al., 1922) and (b) according to our measurement. See Table 2 for form indices.

TABLE 2. Crystal morphology of melanovanadite

System, class: Triclinic, $\bar{1}$
Axial elements:
  $a:b:c = 0.3516:1:0.3469$
  $\alpha, \beta, \gamma = 110.18°, 101.62°, 82.86°$
  $v_1, v_2 = 0.05596, 0.9369$
Polar elements:
  $x'_0, y_0 = 0.2056, 0.3560$
  $p'_0, q'_0 = 1.0751, 0.3703$
  $\nu = 86.58°$

Observed forms (Fig. 1):

Palache*		This work: angles to [10$\bar{1}$]		
	hkl	hkl	ρ	ϕ
b	010	b	010	90.0	0.0
d	032	d	$\bar{1}$21	41.4	1.3
d	0$\bar{3}$2	f	$\bar{1}$41	38.2	179.1
g	012	g	$\bar{1}$01	18.0	2.3
g	0$\bar{1}$2	e	$\bar{1}$21	13.0	178.5
h	230	h	121	90.0	52.3
l	210	l	101	90.0	79.4
l	2$\bar{1}$0	k	1$\bar{2}$1	90.0	75.2
p	111	a	$\bar{1}$00	50.6	274.4
p	1$\bar{1}$1	s	0$\bar{4}$2	53.7	114.2
w	$\bar{1}$01	c	001	53.6	65.9

Crystal elements (in setting of Palache*):
  Palache* $a:b:c = 0.4737:1:0.5818$
                $\alpha, \beta, \gamma = 90, 88.63, 90$
  This work $a:b:c = 0.4706:1:0.5766$
                $\alpha, \beta, \gamma = 92.08, 90.78, 87.26$

* In Lindgren et al. (1922).

cell. In this setting, all reflections with k odd are very weak and sparse, and more diffuse than those with k even.

Palache (in Lindgren et al., 1922) described the morphology in a nearly orthogonal monoclinic unit cell (Fig. 1a). If we associate his **a**, **b**, and **c** axes with our [$\bar{1}$01], [011], and [10$\bar{1}$] directions, respectively, we can compare his morphological parameters with our data as shown in Table 2. The crystals do not give sharp optical signals (as noted by Palache), but a typical habit found on our specimen could be clearly defined (Fig. 1, Table 2). Because a difference of 5 or 10 water molecules would lead to large changes in the b ratios, it seems most probable that Palache also measured crystals with a degree of hydration similar to ours.

Experimental procedure

The Peruvian specimen contains large crystals (1 to 2 mm) of melanovanadite, which show perfect (010) cleavage. These crystals give the best X-ray patterns, much better than those given by crystals from the Colorado Plateau localities, but even the best crystals showed considerable mosaic spread. The typical diffractometer peak profiles are well-defined but extend over about 2.1° 2θ. Two groups of intensity data were measured in one hemisphere of the reciprocal lattice with a modified Picker automatic diffractometer system, using Zr-filtered Mo$K\alpha$ radiation. Those reflections with k even were measured up to 2θ = 60°; those with k odd, only up to 2θ = 30° as beyond this angle, no reflections of this type could be detected. Absorption corrections were calculated (lath-shaped cleavage fragment 0.25 × 0.11 × 0.05 mm, μ = 31 cm^{-1}) and applied along with the usual geometric corrections. In the k-even group, 2115 reflections were measured and averaged to 1901 nonequivalent terms, of which

1676 with $F^2 > 2\sigma(F^2)$ were used for the structure analysis. In the k-odd group, 266 independent reflections were measured, of which 176 had $F^2 > 2\sigma(F^2)$. The 221 reflection was monitored every hour, and the data were corrected for a small amount of X-ray drift.

Structure analysis

The great dominance of the subcell ($\Sigma|F_{ev}|$ = 52 300, $\Sigma|F_{od}|$ = 2560) showed that the major features contained in one-half of the unit cell are only slightly varied in the other half. Therefore the structure was solved for the subcell (which contains the elements of one vanadate layer and one interlayer component), using only the k-even data. A combination of MULTAN calculations, Fourier syntheses, and structure-factor calculations led to a vanadate-layer structure that was chemically satisfactory. The positions of 2 V atoms, 10 O atoms and 5 H$_2$O molecules, plus that of a half-occupied Ca atom site, were established. A least-squares refinement of this structure (based on $|F_{ev}|$ only) in isotropic mode converged smoothly to the conventional reliability index R_{ev} = 0.097, and in anisotropic mode, to R_{ev} = 0.061. This result is given in Table 3. The thermal ellipsoids so obtained, especially of the H$_2$O molecules, were influenced as much or more by the differences in the two halves of the supercell as by the thermal motions.

To determine the nature of the superstructure, we turned to the k-odd reflections. A Patterson map made with F_{od}^2 terms only, interpreted as being derived from a correction map to be added to the F_{ev} electron-density map,

TABLE 3. Structure and isotropic thermal parameters for melanovanadite

Atom	x	y	z	U (Å)
		Average layer (subcell refinement)		
V(1)	0.6717(2)	0.0460(1)	0.6969(2)	0.104(4)
V(2)	0.2179(2)	0.0207(1)	0.8564(2)	0.104(4)
O(1)	0.0386(9)	0.0016(4)	0.2832(9)	0.12(2)
O(2)	0.2126(10)	0.1098(4)	0.0437(10)	0.15(2)
O(3)	0.6806(11)	0.1367(4)	0.7150(11)	0.16(2)
O(4)	0.6830(8)	0.0489(3)	0.0113(8)	0.12(2)
O(5)	0.3740(8)	0.0166(3)	0.6366(8)	0.12(2)
		Layer A		
V(1A)	0.6707(4)	0.0468(2)	0.6985(5)	0.110(11)
V(2A)	0.2174(4)	0.0205(2)	0.8558(5)	0.090(12)
O(1A)	0.0388(16)	0.0002(7)	0.2811(17)	0.15(3)
O(2A)	0.2176(17)	0.1097(7)	0.0444(20)	0.17(2)
O(3A)	0.6761(16)	0.1392(5)	0.7218(16)	0.14(2)
O(4A)	0.6851(15)	0.0486(6)	0.0117(17)	0.13(3)
O(5A)	0.3742(15)	0.0149(7)	0.6353(16)	0.12(3)
		Layer B		
V(1B)	0.6726(4)	0.5453(2)	0.6957(5)	0.095(11)
V(2B)	0.2185(4)	0.5211(2)	0.8571(5)	0.114(11)
O(1B)	0.0387(14)	0.5031(6)	0.2858(16)	0.12(3)
O(2B)	0.2050(15)	0.6090(7)	0.0453(15)	0.14(3)
O(3B)	0.6856(17)	0.6332(7)	0.7067(18)	0.18(2)
O(4B)	0.6817(16)	0.5490(7)	0.0111(16)	0.13(3)
O(5B)	0.3713(16)	0.5186(7)	0.6362(16)	0.12(2)
		Interlayer atoms		
Ca(1)	0.2220(7)	0.2423(3)	0.3166(7)	0.131(4)
Ca(2)	0.2262(52)	0.7409(23)	0.3235(55)	0.131
O(6)	0.0205(19)	0.7508(8)	0.0109(22)	0.19(1)
O(7)	0.0833(18)	0.1674(7)	0.4962(16)	0.19(2)
O(8)	0.5852(17)	0.2089(7)	0.2561(21)	0.21(2)
O(9)	0.0759(20)	0.6709(7)	0.5171(21)	0.21(2)
O(10)	0.5980(20)	0.7111(8)	0.2908(18)	0.21(2)

indicated that the superstructure arises mainly because of an ordering of the Ca atoms. Starting with an empty unit cell, structure factors for the k-odd reflections were calculated when 2 Ca atoms were inserted in the full cell at a position corresponding to one of the equivalent sites in the subcell. Least-squares treatment of this atom gave $R_{od} = 0.22$. The subsequent Fourier synthesis (k odd only) indicated a strong displacement of the O(8) atoms from their subcell positions; least-squares analysis led to $R_{od} = 0.20$. Next, O(6) was displaced from its position on a subcell center of symmetry; $R_{od} = 0.175$. Similar treatment of O(7) led to $R_{od} = 0.165$, but this procedure produced no further improvement through adjustment of other atoms.

Next, the entire data set was used to further refine the interlayer structure. Holding the parameters of the layer atoms fixed at the values obtained from the subcell refinement, least-squares analysis of the interlayer structure with anisotropic thermal parameters gave $R = 0.071$. Appreciable electron density was found at the now-vacant alternate Ca site, indicating some degree of disorder in the Ca distribution. A least-squares analysis of the Ca population at the two sites, with the major site anisotropic and the minor site isotropic, led to $R = 0.066$. Least-squares analysis of the occupancies of the H_2O sites indicated no departure from unity.

Finally, all parameters for the whole structure in *isotropic* mode were refined, yielding $R = 0.081$. This step was followed by the refinement of anisotropic thermal parameters [except Ca(2)] with position parameters held fixed: $R = 0.058$. A final round varying x, y, and z parameters led to $R = 0.056$, and $R_w = 0.061$. Severe cross-correlation of anisotropic thermal parameters with the position parameters made joint refinement impractical. The rather large standard errors (~0.015 Å for layer oxygen atoms) result from strong correlations between the two halves of the supercell, although as executed, the refinement remained stable. It is felt that the effect of the

TABLE 4. Anisotropic thermal parameters (Å²) for melanovanadite

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
			Layer A			
V(1A)	0.011(2)	0.020(2)	0.006(2)	0.000(2)	0.006(4)	0.006(2)
V(2A)	0.006(2)	0.011(2)	0.007(2)	−0.001(2)	0.001(2)	0.002(2)
O(1A)	0.022(8)	0.031(7)	0.007(6)	0.007(6)	0.012(6)	0.006(5)
O(2A)	0.026(7)	0.019(7)	0.040(9)	−0.004(5)	0.004(6)	0.017(6)
O(3A)	0.031(6)	0.005(5)*	0.026(6)	0.002(4)	0.004(5)	0.011(4)
O(4A)	0.015(7)	0.016(9)	0.018(8)	−0.005(6)	−0.004(6)	−0.004(6)
O(5A)	0.010(6)	0.026(6)	0.005(6)*	0.003(5)	0.004(5)	0.002(4)
			Layer B			
V(1B)	0.010(2)	0.011(2)	0.006(2)	0.000(2)	0.001(2)	0.004(2)
V(2B)	0.016(2)	0.021(2)	0.003(2)	0.007(2)	0.006(2)	0.002(2)
O(1B)	0.008(7)	0.025(6)	0.008(6)	−0.001(5)	−0.002(5)	0.007(5)
O(2B)	0.023(6)	0.032(10)	0.006(6)	0.006(6)	0.010(5)	−0.005(6)
O(3B)	0.032(7)	0.041(8)	0.023(6)	−0.013(6)	0.002(6)	0.009(6)
O(4B)	0.021(8)	0.024(10)	0.005(7)	0.010(6)	0.010(6)	0.006(6)
O(5B)	0.011(6)	0.029(6)	0.008(7)	−0.006(5)	0.001(6)	0.009(5)
			Interlayer atoms			
Ca(1)	0.021(1)	0.015(1)	0.016(1)	−0.001(1)	0.006(1)	0.003(1)
O(6)	0.045(6)	0.021(4)	0.047(5)	0.004(4)	0.008(4)	0.015(4)
O(7)	0.054(8)	0.034(9)	0.016(5)	0.012(7)	0.018(5)	0.006(5)
O(8)	0.032(7)	0.035(9)	0.065(6)	−0.006(6)	0.026(6)	−0.017(6)
O(9)	0.057(9)	0.017(8)	0.062(9)	−0.005(7)	0.030(8)	0.011(7)
O(10)	0.059(9)	0.046(10)	0.026(6)	0.002(6)	−0.002(6)	−0.006(6)

* Calculated value augmented by 0.5σ to make atom positive definite.

TABLE 6. Bond lengths D (Å) and O–V–O angles (°) in melanovanadite and synthetic CsV$_2$O$_5$

V coordination polyhedra Atoms	D (V–O) ±0.015	Bond angles, ±0.3				D (CsV$_2$O$_5$)* ±0.005
		O–V–O(1)	–O(4)'	–O(5)	–O(5)'	
V(1A)–O(3A)	1.631	109.4	104.4	111.3	107.2	1.616
–O(1A)	1.934		86.5	139.1	87.8	1.918
–O(4A)	1.939			87.5	148.0	1.947
–O(5A)	1.964				76.6	1.944
–O(5A)'	1.986					2.012
V(1B)–O(3B)	1.580	108.1	106.3	110.5	106.0	
–O(1B)	1.921		87.7	141.0	86.7	
–O(4B)	1.948			86.9	147.4	
–O(5B)	1.965				77.5	
–O(5B)'	1.985					
		O–V–O(1)	–O(4)	–O(5)		
V(2A)–O(2A)	1.639	109.5	110.9	110.0		1.626
–O(1A)	1.703		108.2	107.0		1.722
–O(4A)	1.719			111.1		1.708
–O(5A)	1.832					1.843
–O(4A)'	2.987					
V(2B)–O(2B)	1.626	108.3	111.2	111.2		
–O(1B)	1.728		107.1	106.0		
–O(4B)	1.734			112.3		
–O(5B)	1.833					
–O(4B)'	2.958					

Ca coordination				O–O D < 3.00 Å	
Atoms	D (Ca–O) ±0.013	Atoms	D (Ca–O) ±0.03	Atoms	D (O–O) ±0.02
Ca(1)–O(6)	2.340	Ca(2)–O(6)	2.18	O(6)–O(2B)	2.75
–O(7)	2.374	–O(7)	2.59	–O(3A)	2.80
–O(8)	2.386	–O(8)	2.56	–O(2A)	2.87
–O(10)	2.402	–O(10)	2.39	O(7)–O(1A)	2.88
–O(2A)	2.418	–O(2B)	2.42	–O(2A)	2.93
–O(3B)	2.456	–O(3A)	2.45	–O(10)	2.95
–O(9)	2.464	–O(9)	2.41	O(8)–O(4A)	2.83
				–O(2A)	2.93
Avg.	2.406	Avg.	2.43	O(9)–O(1B)	2.89
				O(10)–O(4B)	2.90

* From Waltersson and Forslund (1977).

positional parameters on the structure factors is much greater than that of the thermal parameters, and therefore the strategy described above has led to a structure that is true within limits that are probably about two times those expressed by the standard errors.

Unit weights were used throughout the analysis. These gave a goodness of fit of 2.71. When weights derived from counting statistics were used, this value decreased slightly to 2.55. The differenc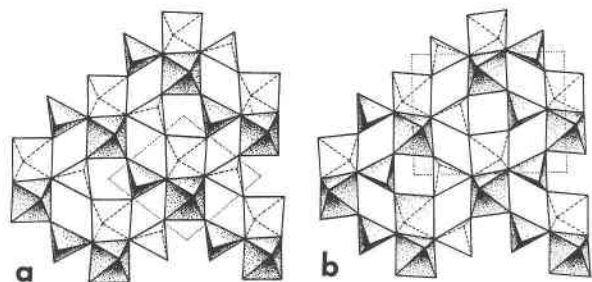e is not considered significant, and the parameters obtained with unit weights are accepted. The last anisotropic cycle left two oxygen atoms nonpositive-definite, but not significantly so. The last cycle of the weighted calculation ended with eight atoms unacceptably nonpositive-definite. One source of error stems from the broadness of the reflection profiles, which led to some difficulties with interference with strong neighboring reflections. As a consequence, a few reflections had to be excluded from the least-squares process because of their anomalously high $\Delta|F|$ values. Whatever the source of errors in the data set, the errors are not primarily related to counting statistics. Because of the large mosaic character of the reflections, no extinction correction was calculated. A detailed examination of the strong intensities showed no evidence of this effect.

The XTAL system (Stewart and Hall, 1985) was used for all machine computations. Atomic scattering factors and absorption factors used were obtained from *International Tables for X-ray Crystallography* (Ibers and Hamilton, 1974).

In Table 3 are listed the final structure and isotropic thermal parameters, and Table 4 gives the anisotropic thermal parameters for melanovanadite. Table 5 contains
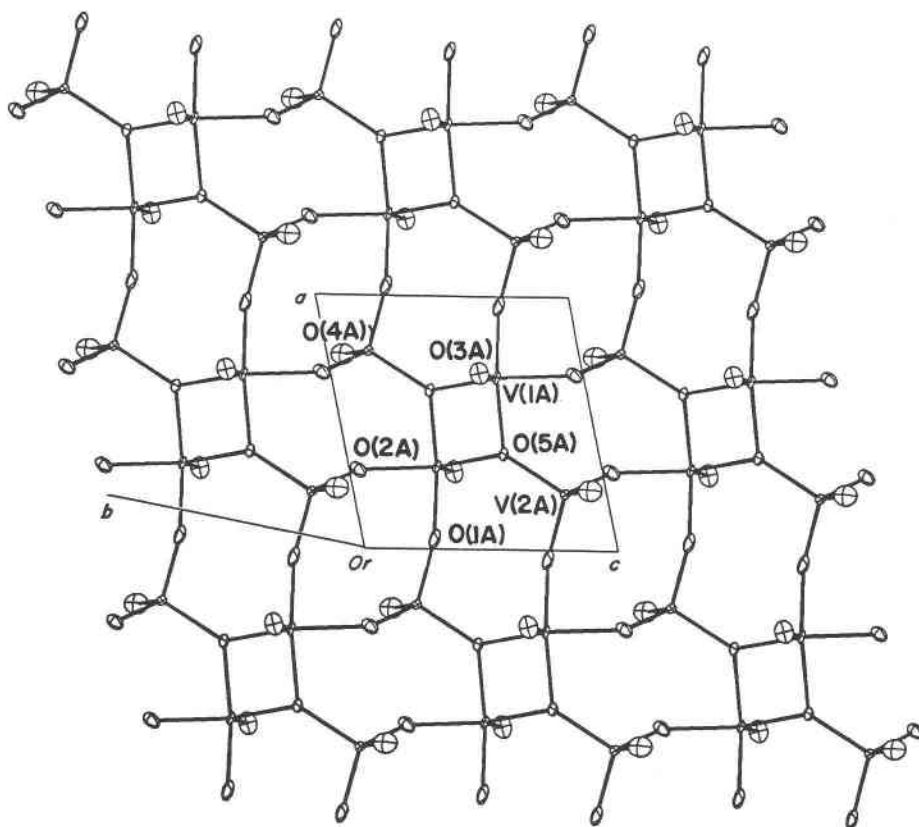

Fig. 2. Polyhedral representation of the vanadate layer in (a) melanovanadite and (b) synthetic CsV$_2$O$_5$.

Fig. 3. The vanadate layer A of melanovanadite ($y \approx 0$) viewed normal to the layer, showing 50% probability ellipsoids.

the observed and calculated structure factors,[1] and Table 6 gives selected interatomic distances.

CRYSTAL STRUCTURE OF MELANOVANADITE

Vanadate layer

As shown in Figure 2a, the layer unit contains two VO_4 tetrahedra and one V_2O_8 double square-pyramid group, linked by corner sharing into a sheet. The tetrahedral group is nearly regular: the average deviation of the O–V–O angles from 109.5° is 1.2°. Figure 3 shows a view of one of the two independent layers. The V(1) atom is displaced somewhat from the center toward O(3), which is the unlinked oxygen atom. The average length for this bond is 1.63 Å, compared to 1.75 Å for the bonds to bridging oxygen atoms. Figure 4 presents a stereoscopic edge view of the structure showing how the Ca atoms are joined to the layer oxygen atoms and the water molecules.

Figure 5 shows the double V_2O_8 group [V(1) atoms], which lies at a crystallographic center of symmetry in both layers. A similar configuration is found in other van-

adate compounds; for example, carnotite (Appleman and Evans, 1965), CsV_3O_8, and KV_3O_8 (Evans and Block, 1966). As usual the apical V(1)–O(3) bond length to the unlinked oxygen atom is significantly shorter than the other bonds in the group (averages of 1.61 vs. 1.97 Å). The two square bases, which share an edge, are nearly coplanar: the average displacement of oxygen from the best (least-squares) plane is 0.2 Å.

The linkage of VO_4 and V_2O_8 groups in the layer is the same as that found by Mumme and Watts (1971) in orthorhombic CsV_2O_5. The configuration of the layer is compared for the two structures in Figure 2. An essential difference occurs in the arrangement of the unlinked apices of the VO_4 tetrahedra and VO_5 square pyramids up and down away from the plane of the layer. In melanovanadite, continuous chains of alternating tetrahedra and square pyramids parallel to the triclinic **a** axis with all vertices pointing up are joined to similar parallel chains with all vertices pointing down. In CsV_2O_5, the chains with vertices pointing in one direction follow a zig-zag course parallel to the monoclinic **c** axis, conforming to the **c** glide plane in the structure. No significant differences between melanovanadite and CsV_2O_5 (refined by Waltersson and Forslund, 1977) are apparent for the bonds shown in Figure 5 and listed in Table 6.

[1] To obtain a copy of Table 5, order Document AM-87-341 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.
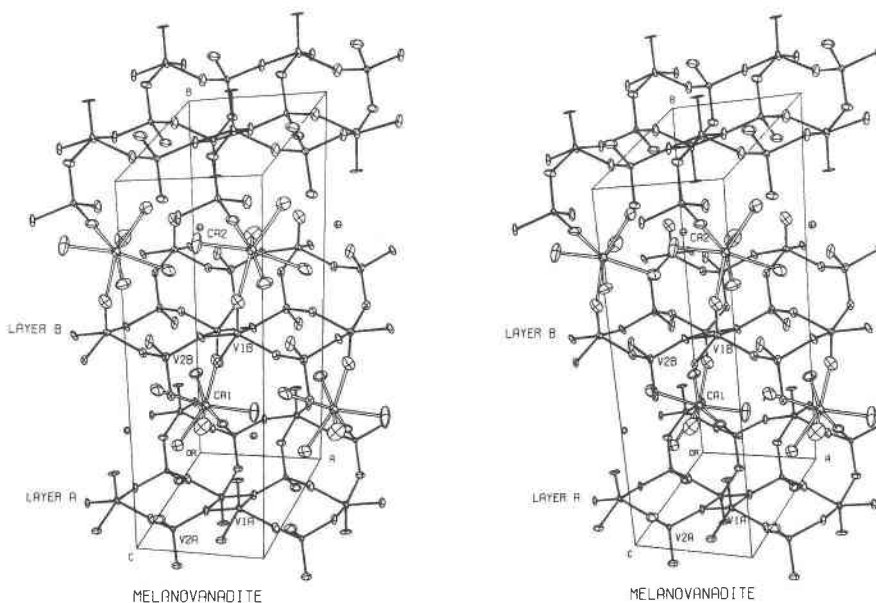
Fig. 4. Stereoscopic edge view of layer structure of melanovanadite, showing how a Ca ion is coordinated to one terminal oxygen atom of each adjacent layer, and 5 H_2O molecules. The unlinked site labeled Ca2 is 10% occupied. Atoms are shown as 50% probability thermal ellipsoids.

Interlayer structure

The vanadate layers are separated by Ca ions and H_2O molecules in a highly ordered arrangement (Fig. 6). The Ca ions are in 7-fold coordination with two vanadate-layer oxygen atoms (a tetrahedral apex of one layer and a pyramidal apex of the other layer) and five H_2O molecules. If $2Na^+$ were to replace Ca^{2+}, the cation site in the subcell would be fully occupied, and no superstructure would occur. As it is, the site is only half-occupied by Ca^{2+} on average, but resolves into two independent sites when the **b** axis is doubled. (In the superstructure, the symmetry centers in the vanadate layer are retained, but those in the Ca-H_2O layer are eliminated.) Our structure analysis has shown that Ca is ordered largely but not completely at one of the new sites. The site occupancy for one site is 0.90(2), and for the other 0.12(3). If one site is occupied and an adjacent site is vacant, some adjustment of the positions of the surrounding H_2O molecules may be expected and was easily detected in the refinement of the interlayer structure based on the odd reflections alone. The Ca–O distances range from 2.35 to 2.50 Å and average 2.41 Å, an entirely normal distribution. The weakly occupied site has distances to seven corresponding oxygen atoms ranging from 2.30 to 2.56 Å and averaging 2.43 Å, and thus no significant shrinkage of the space available to the site seems to occur. On the other hand, there is no possibility of inserting an extra H_2O molecule at this site.

Several O–O distances involving H_2O molecules are somewhat shorter than normal van der Waals contacts, but many of these are within one Ca-coordination polyhedron and therefore would not usually be interpreted as H bonds.

VALENCE OF V

Until this study was completed, the only information about the composition of melanovanadite available was that of Lindgren et al. (1922). These authors reported two chemical analyses, with Ca:V atomic ratio of 0.181 and 0.197, respectively, but our structure analysis clearly indicates a ratio close to 0.25. We measured this ratio in a JEOL scanning-electron microscope fitted for energy-dispersive X-ray (EDX) fluorescence analysis. Three melanovanadite cleavage crystals were tested against a lath of synthetic $Ca_2V_2O_7$, where all exposed surfaces tested were flat, uniform, and normal to the electron beam. The EDX peaks for Ca and V were integrated to establish an intensity ratio equivalent to the atomic ratio Ca:V = 1:2, which was used to determine the atomic ratio in other crystal plates. The crystal of melanovanadite used for structure analysis yielded Ca:V ratios of 0.243, 0.247, 0.252 (avg. 0.247). Another Peruvian crystal gave 0.248. A crystal from the Colorado Plateau gave ratios of 0.234, 0.247, 0.240. No other cations were detected in these measurements. Some variation in the ratio is possible, of course, if the V valence can vary, but it is most probable that the original analyses were not correct.

For Ca:V = 0.25, the charge per unit of vanadate layer V_4O_{10} is -2, and the average V valence is $+4.5$, the same as in synthetic CsV_2O_5. The fact that in CsV_2O_5 (Waltersson and Forslund, 1977) the average V–O distance of 1.718 Å in the tetrahedron is substantially less than 1.882 Å in the square pyramid (referred to as a trigonal bipyramid by Mumme and Watts, 1971) led Mumme and Watts to conclude that the tetrahedron contains V^{5+} and the square pyramid contains V^{4+}. Waltersson (1976) has made an exhaustive study of the application of various
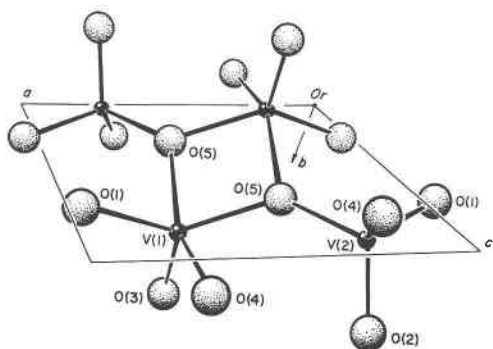
Fig. 5. One unit of the melanovanadite layer in oblique view.

TABLE 7. Bond-number estimates of valence in melanovanadite

	V(1)		V(2)			Σ s(O)	
	A	B	A	B	Ca	A	B
O(1)	0.63	0.66	1.32	1.22		1.96	1.88
O(2)			1.62	1.69	0.28	1.90	
O(3)	1.67	1.96			0.26		2.22
O(4)	0.62	0.61	1.26	1.20		1.88	1.81
O(5)	0.58	0.57	0.88	0.88		1.99	1.99
O(6)					0.34		
O(7)					0.31		
O(8)					0.30		
O(9)					0.25		
O(10)					0.29		
Σ s(V, Ca)	4.04	4.34	5.08	4.99	2.03		

Note: V–O: $s = 10^{(1.791 - D)}/0.722$ (Waltersson, 1976). Ca–O: $s = 10^{(1.880 - D)}/0.944$ (Brown, 1981).

empirical bond-valence functions to a wide range of ox-ovanadium compounds. Using the Pauling semilogarithmic function $D_i = D_1 - 2k \log_{10} s_i$ (where D_i is the bond length to a neighboring atom, D_1 is the bond length of unit strength, and s_i is the valence number for that bond), he found that the best overall consistency with expected valence sums for V was obtained with $D_1 = 1.791$ Å, $k = 0.361$. Based on Waltersson's function, the various bond-valence numbers and their sums are set forth in Table 7. The sums for tetrahedral and square-pyramidal V confirm the conclusions of Mumme and Watts (1971) and Waltersson and Forslund (1977) that the former contains V^{5+} and the latter contains V^{4+}. The corresponding valence sums in CsV_2O_5 are 5.22 and 4.24, respectively.

In Table 7, we note that Σ s for V(1B) and for O(3) are especially high. This circumstance is certainly related to the abnormally short bond length for V(1B)–O(3). Whereas this length was the consistent outcome of all least-squares computations for the full cell, it seems probable that the true bond length is somewhat longer.

THERMAL PROPERTIES OF MELANOVANADITE

As noted in the Introduction, Lindgren et al. (1922) reported that their original sample, "kept for several months in a warm dry atmosphere," was found to be "practically anhydrous" (0.42% total H_2O measured). An
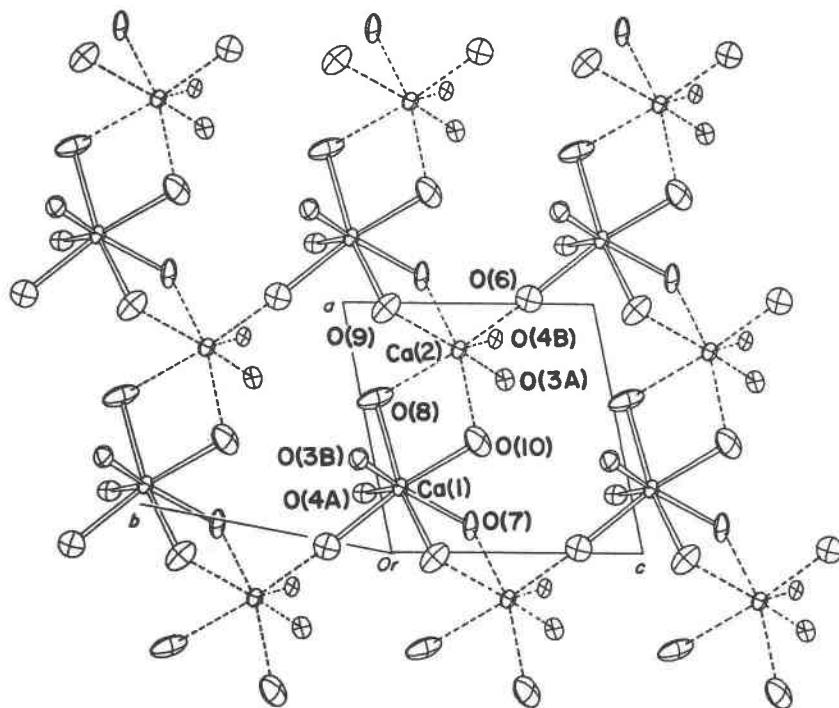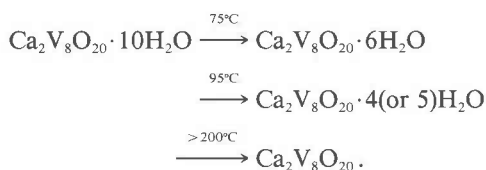

Fig. 6. Interlayer arrangement of Ca and H_2O molecules in melanovanadite in the region above layer A ($y \approx \frac{1}{4}$). Dashed bonds are associated with the (mostly) unoccupied cation sites. Atoms are represented by 50% probability ellipsoids.

exposed sample was later found to yield H_2O in a closed-tube test. When this sample was dried in a dessicator, it lost 10.26% H_2O; a sample heated to 105°C lost 10.7%. The total H_2O content was found to be 16.6%.

In a heating experiment on 22.2 mg of melanovanadite crystals, we found that 10.4% was lost at 95°C, a further 0.9% at 120°C, and a total of 20.4% at 250°C. The "minus" H_2O is thus in agreement with Lindgren et al. (1922), but the total H_2O is greater. Assuming the unit-cell content as found by crystal-structure analysis to be $Ca_2V_8O_{20} \cdot nH_2O$, the first stage of H_2O loss corresponds to $n = 5.7$, and the total H_2O loss to $n = 11.5$. The sample heated to 250°C was amorphous to X-rays.

We also made a heating experiment with a Guinier-Lenne apparatus, which records dynamically the change in the X-ray powder pattern as the sample is heated. In the range 30–200°C, we found two phase changes, one at 75°C, and another at 95°C. Discontinuous changes occurred in the X-ray pattern at these points, although close relationships in some features of the patterns were evident. Of particular interest is the strong 040 line, which measures the interlayer spacing. In the unheated material, this spacing is 4.236 Å, corresponding to an interlayer spacing of 8.47 Å. At 75°C, the interlayer spacing drops to 7.4 Å and at 95°C to 7.2 Å and then remains nearly constant up to 200°C. If the layer unit area remains relatively unchanged over this temperature range ($665/8.5 = 78.2$ Å^2), the first change corresponds to a volume change of 86 Å^3, and the second to about 16 Å^3. If the molecular volume of water is 20 Å^3, these changes may be represented as follows:

$$Ca_2V_8O_{20} \cdot 10H_2O \xrightarrow{75°C} Ca_2V_8O_{20} \cdot 6H_2O$$
$$\xrightarrow{95°C} Ca_2V_8O_{20} \cdot 4(or\ 5)H_2O$$
$$\xrightarrow{>200°C} Ca_2V_8O_{20}.$$

The uncertainty of estimates of n in these experiments is probably >1.

If the molar volume of anhydrous $Ca_2V_8O_{20}$ is $663 - (10 \times 20) = 463$ Å^3, then a density of about 2.9 g/cm^3 may be estimated. Our measurement of the density of the amorphous product of heating to 250°C was 2.95 g/cm^3. The value of 3.477 g/cm^3 reported for original material by Lindgren et al. (1922) suggests again that their analytical samples were not pure.

Finally, there is the question as to whether the hydrated crystals, which have evidently been the subject of study ever since the discovery of melanovanadite, should be regarded as a species different from the original anhydrous mineral. We leave this question open but with the suggestion that the hydrated form ($n = 10$) may appropriately be given a separate or modified name.

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