American Mineralogist, Volume 83, pages 889–895, 1998

Phosphovanadylite: A new vanadium phosphate mineral with a zeolite-type structure

MARJORIE D. MEDRANO,[1,*] HOWARD T. EVANS JR.,[2] HANS-RUDOLF WENK,[3] AND DAVID Z. PIPER[4]

[1] U.S. Geological Survey, 345 Middlefield Road, MS 999, Menlo Park, California 94025, U.S.A.
[2] U.S. Geological Survey, 12201 Sunrise Valley Drive, MS 954, Reston, Virginia 20192, U.S.A.
[3] Department of Geology and Geophysics, University of California, Berkeley, California 94720, U.S.A.
[4] U.S. Geological Survey, 345 Middlefield Road, MS 902, Menlo Park, California 94025, U.S.A.

ABSTRACT

Phosphovanadylite, whose simplified formula is $(Ba,Ca,K,Na)_x[(V,Al)_4P_2(O,OH)_{16}]\cdot 12H_2O$, is a new vanadium phosphate zeolite mineral found in the Phosphoria Formation at Monsanto's Enoch Valley Mine, Soda Springs, Idaho. Its formula in more detail is $(Ba_{0.38}Ca_{0.20}K_{0.06}Na_{0.02})_{\Sigma 0.66}[P_2(V_{3.44}Al_{0.46})_{\Sigma 3.90}O_{10.34}(OH)_{5.66}]\cdot 12H_2O$. The drusy mineral occurs as pale greenish-blue euhedral cubes (20–50 μm edge) coating phosphatic, organic-rich mudstone. The chemical composition determined by electron microprobe is (in weight percent) V-28.02, P-9.91, Al-1.97, Ca-1.31, Ba-8.28, Cd-0.09, Zn-0.34, Na-0.15, K-0.73, O-46.57, and F-0.03. The index of refraction is $n_D = 1.566$ (4) and specific gravity is 2.16 (3). The X-ray powder pattern shows strong reflections at 3.16 Å (422), 2.58 (600), 2.44 (620), and 7.73 (200), which are indexed on the basis of a cubic body-centered unit cell with a = 15.470 (4) Å. From the single-crystal structure analysis, its space group was determined to be $I\bar{4}3m$, $Z = 6$, and its structure consists of V_4O_{16} octahedral clusters linked to each other by P atoms to form a cubic lattice, creating cavities 7.0 and 5.5 Å in diameter where mainly H_2O resides. Final residual indexes are $R = 0.066$, $R_w = 0.061$, goodness-of-fit = 0.75, and 93 observations and 24 parameters.

INTRODUCTION

Phosphovanadylite, a new mineral species, was found while examining a newly dug trench located in one of the deepest areas of an open-pit mine at Monsanto's Enoch Valley Phosphate Mine (42°53′N, 111°25′W), Soda Springs, Idaho. It occurred as a thin, richly colored mineral coating on a small cluster of dark brown to black phosphatic organic rich mudstone rocks.

GEOLOGIC SETTING

The mineral and the mined phosphate ore are in sedimentary layers of the Meade Peak Member of the Permian Phosphoria Formation. This member consists of interbedded pelletal phosphorite, phosphatic mudstone, and shale with a few layers of dolomite (McKelvey et al. 1959). The upper and lower parts of the Meade Peak Member consist of phosphorite and phosphatic shale, which are separated by a middle part of shale that has a relatively low phosphate content.

Notable within the Meade Peak Member are discrete beds enriched in vanadium containing as much as 1 wt% V_2O_5 (McKelvey et al. 1986). One group of contiguous beds, called the vanadiferous zone, has been mapped and studied extensively for its economic potential. It is 0.6 to 4.5 m thick and is 1.5 to 3 m below the upper phosphatic-enriched part of the Meade Peak Member (Love 1961; McKelvey et al. 1986). It extends over an area of about 11 600 square kilometers in western Wyoming, southeastern Idaho, and northeastern Utah. Secondary vanadium minerals, sincosite [green, $Ca(VO)_2(PO_4)_2\cdot 5H_2O$], hewettite (red, $CaV_6O_{16}\cdot 6H_2O$), and pascoite (orange, $Ca_3V_{10}O_{28}\cdot 17H_2O$), have been identified from this zone (McKelvey et al. 1986). Other beds in the Meade Peak Member are also enriched in vanadium, but they are not as continuous nor as enriched as the vanadiferous zone (Medrano and Piper 1992, 1995; Piper and Medrano 1994).

The mineral identified in this study occurs in a thin discrete bed (no more than 15 cm in thickness) within the upper part of the lower phosphate beds, and it is considerably lower in the section than the vanadiferous zone. Sincosite was also identified in close proximity in the same thin bed.

PHYSICAL PROPERTIES

Phosphovanadylite is light greenish blue, transparent, with a non-metallic vitreous luster, and a very pale greenish-blue streak. Its color changed from light greenish blue to greenish black over a matter of a few months presumably due to oxidation of vanadium during exposure to air. The euhedral crystals are small cubes about 20 to 50 μm on edge (Fig. 1). Grain mounts show complete extinction

---

* E-mail: mmedrano@octopus.wr.usgs.gov

0003–004X/98/0708–0889$05.00

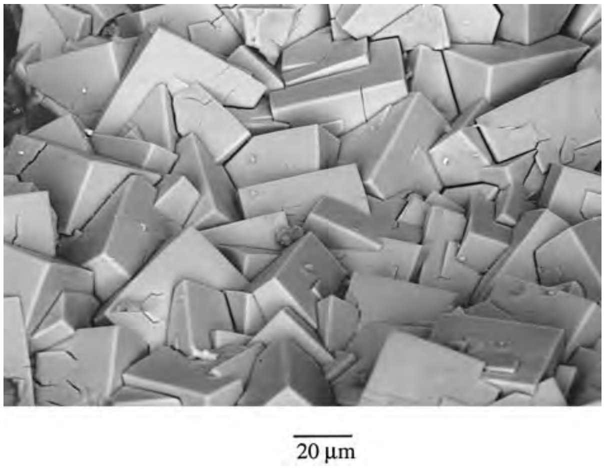

FIGURE 1. Scanning electron microscope micrographs showing the cubic habit of phosphovanadylite.

between crossed polars, confirming the mineral to be isotropic. The index of refraction, determined by oil immersion, is $n_D = 1.566$ (4). Specific gravity of 2.16 (3) was determined by the sink-swim method using a mixture of lithium metatungstate and water. A centrifuge was used because the crystals are very small.

X-RAY STUDY

An X-ray powder diffraction pattern was obtained with a Philips X-ray powder diffractometer, using monochromatic Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å), operating at 35 kV and 15 mA (Table 1). The pattern was indexed on the basis of a cubic body-centered unit cell with all reflections satisfying $h + k + l$ = even. The lattice parameter was refined from 25 reflections to $a = 15.470(4)$ Å (Burnham 1962). Reflections existed with $d < 1.87$ Å, but they were weak, diffuse, and partially overlapping.

CHEMICAL ANALYSIS

Single mineral grains were quantitatively analyzed with a ARL SEMQ electron microprobe equipped with eight wavelength spectrometers with an analytical range from Be to U. The operating voltage was 15 KeV at 30 nA, as measured on MgO. All the data were corrected for beam drift and standard count drift in real time, and the matrix was corrected using the PROBE CITZAF Phi-Rho-Z corrections (Donovan et al. 1992). All data were corrected for background using an iterative polynomial mean atomic number background correction. The count time was 10 s.

Due to the numerous and overlapping peaks in the microprobe scan, the scan was compared with the results from a qualitative bulk analysis by energy-dispersive X-ray fluorescence (XRF) of the rock coated by the mineral. The bulk analysis established those elements possibly present in the mineral in the 0.001 to 100% range. Using the microprobe analysis in conjunction with the XRF bulk analysis, it was determined that the mineral contains V, P, Al, Ba, Ca, K, Na, Zn, Cd, and F. The absence of U is notable as this element is significant in other vanadium minerals and is present in the host rock in the 10 to 100 ppm range.

TABLE 1. X-ray diffraction powder pattern of phosphovanadylite

hkl	d_{obs} (Å)	d_{calc}	I*
110	10.8	10.939	29
200	7.73	7.735	34
211	6.33	6.315	6
220	5.47	5.469	6
310	4.90	4.892	9
222	4.47	4.466	19
321	4.14	4.134	9
400	3.88	3.867	6
411	3.66	3.646	8
332	3.302	3.298	13
422	3.164	3.158	100
431	3.038	3.034	25
521	2.827	2.824	28
440	2.738	2.735	29
600	2.582	2.578	37
611	2.508	2.509	25
620	2.445	2.446	36
622	2.330	2.332	14
444	2.230	2.233	14
710	2.188	2.188	15
633, 721	2.106	2.105	17
642	2.065	2.067	7
800	1.933	1.934	24
554, 811	1.903	1.904	9
644, 820	1.873	1.876	17

* The intensity was determined from the peak height, then normalized to the largest peak (422).

Nine standards were used: (1) vanadium metal for V, (2) synthetic chlorapatite for P and Ca, (3) orthoclase MAD-10 for Al and K, (4) barite UC 5393 for Ba, (5) Cazadero albite for Na, (6) synthetic fluor-phlogopite for F, (7) ZnO for Zn, (8) CdS for Cd, and (9) MgO for O.

The results (Table 2) indicate the mineral is essentially a vanadium phosphate hydrate with minor amounts of Ca, Al, and Ba and traces of K, Na, Zn, Cd, and F. The elements sum to 97.13 wt%. The balance is attributed to H^+ in H_2O, which is required for charge balance. Each column of data represents an average of four to six analyses

TABLE 2. Electron microprobe analyses in weight percents

Element	Grain no. 1	Grain no. 2	Grain no. 3	Grain no. 4	Grain no. 5	Grain no. 6	Average
V	28.23	28.75	27.34	28.15	27.44	28.24	28.02
P	9.69	10.24	9.83	10.14	9.52	10.06	9.91
Al	1.93	1.94	2.21	1.95	1.85	1.94	1.97
Ca	1.71	1.64	0.88	1.10	1.29	1.24	1.31
Ba	8.41	8.81	7.79	8.40	7.68	8.58	8.28
Cd	0.06	0.01	0.15	0.11	0.18	0.00	0.09
Zn	0.10	0.04	0.90	0.20	0.80	0.00	0.34
Na	0.07	0.09	0.15	0.18	0.27	0.15	0.15
K	0.57	0.85	0.71	0.86	0.65	0.76	0.73
O*	46.51	45.75	47.02	45.37	47.84	46.95	46.57
F	0.00	0.05	0.08	0.05	0.02	0.00	0.03
Total	97.29	96.63	96.95	96.53	97.53	97.87	97.13

* These O analyses are semiquantitative due to interference from V$L\alpha 1$ and $L\beta 1$ lines.

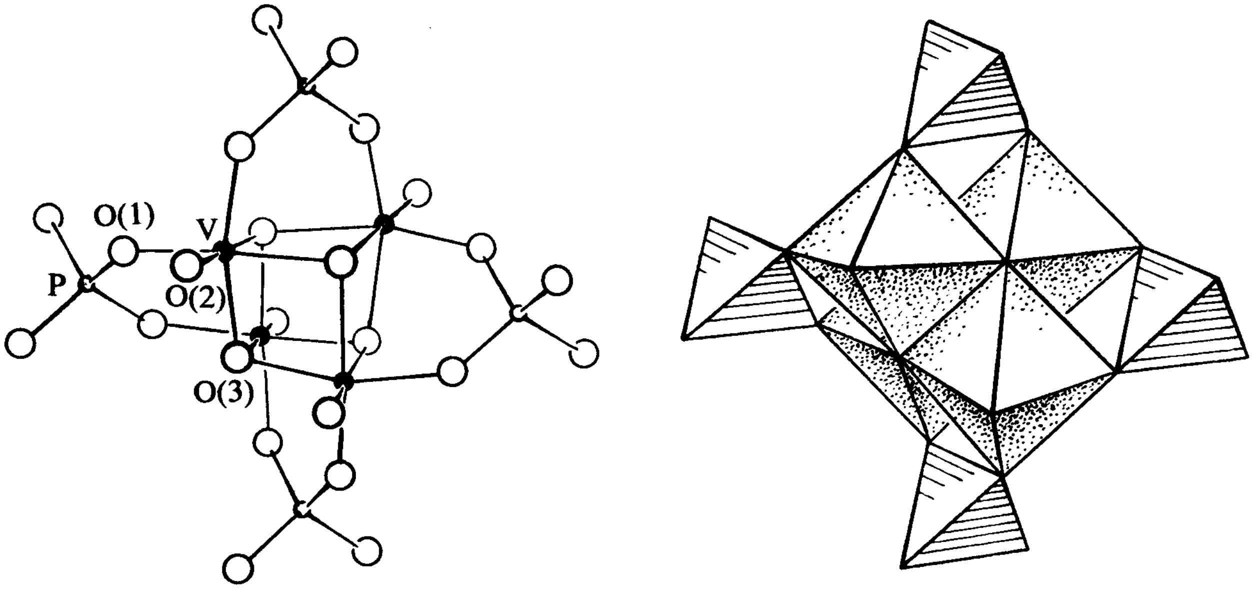

FIGURE 2. Two representations of the V_4O_{16} group, which links through phosphate groups to form the three-dimensional framework.

on each of six crystal grains from the polished section. The last column is an average of the averages for the six separate crystal grains.

Due to the carbon coating on the polished section, the scan displayed a small C peak. To eliminate the possibility that the deficiency in the totals could be attributed to C in the mineral, the scan of the C$K\alpha$ peak from our sample was compared to the C$K\alpha$ peak of a mineral known not to contain C. It is concluded that the mineral contains no C.

Quantitative analysis for O is precluded by a significant interference between the O$K\alpha$, V$L\alpha1$, and $L\beta1$ lines, despite applications of several correction factors. Nevertheless, the qualitative O data confirm that O is present in excess of that needed to balance the charge of cations present, even if the V were totally in the +5 valence state. With the elimination of the possible presence of C compounds and N compounds (from the initial scan), we assume then that the excess O must be charge balanced by H in the form of either H_2O or OH^-.

STRUCTURE ANALYSIS

One crystal with dimensions 0.04 × 0.04 × 0.02 mm^3 was mounted for X-ray intensity measurements on a NONIUS CAD4 automatic diffractometer. Because of the small size of the crystal, diffraction intensities were very weak, and were measured only to $2\theta < 40°$, using Mo$K\alpha$ radiation. An entire hemisphere in the reciprocal lattice was covered, yielding 3382 reflections. By carefully examining and comparing the reflections for symmetrical and statistical significance, it was established that the Laue symmetry is not $m3$ but $m3m$, thus limiting the possible space group to be either $Im3m$, $I\bar{4}3m$, or $I432$. Intensities were reduced to F values in the usual manner, but without absorption corrections (μ = 20 cm^{-1}, minimum transmission 0.93). Setting the minimum intensity for processing at 2σ (F) (based on counting statistics) yielded a data set of 182 observations. These data proved to be troublesome, producing ambiguous statistical averages and leading to a completely false structure on statistical phase analysis. Eventually, the whole data set was again thoroughly analyzed and culled by hand, making use of the fact that reflection redundancy was high, up to 22 times. Standard deviations were established on the basis of this averaging process and were then used rather than those based on counting statistics, which were found to be completely inadequate. In this way, 197 observations were listed, of which 93 were used for a new structure analysis.

Eliminating space group $Im3m$, which could not accommodate the 24 vanadium atoms predicted by the measured density, statistical methods (SIMPEL, Hall and Stewart 1988) led directly to a plausible but entirely unexpected structure in $I\bar{4}3m$. A phosphovanadate framework emerged consisting of V_4O_{16} clusters (Fig. 2) that are joined to each other by P atoms to form a cubic lattice. The clusters are located at the face centers and edge centers of the unit cell, leaving a large cavity at the origin (Fig. 3). This cavity is occupied zeoliticly by cations and H_2O molecules (see Fig. 4).

Among the remaining cations, Al was assigned to the vanadium site (see Table 3), thus filling the occupancy of this site. By Fourier analysis, three interframework sites were found for 56 H_2O molecules. One of these, O(4), on refinement became non-positive definite, thus indicating partial replacement by Ba. Another, O(5), attained a rather low U parameter, so Ca was deposited here. The atom O(6) adopted a higher value of U characteristic of

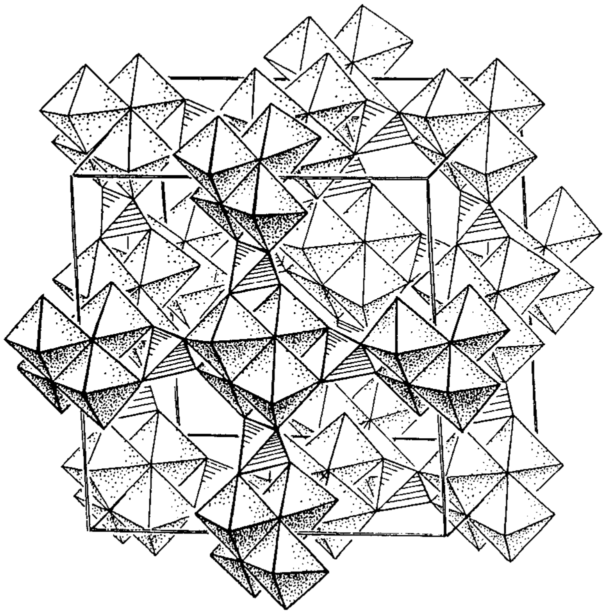

FIGURE 3. The cubic unit cell of the phosphovanadylite structure in polyhedral representation showing the framework only.

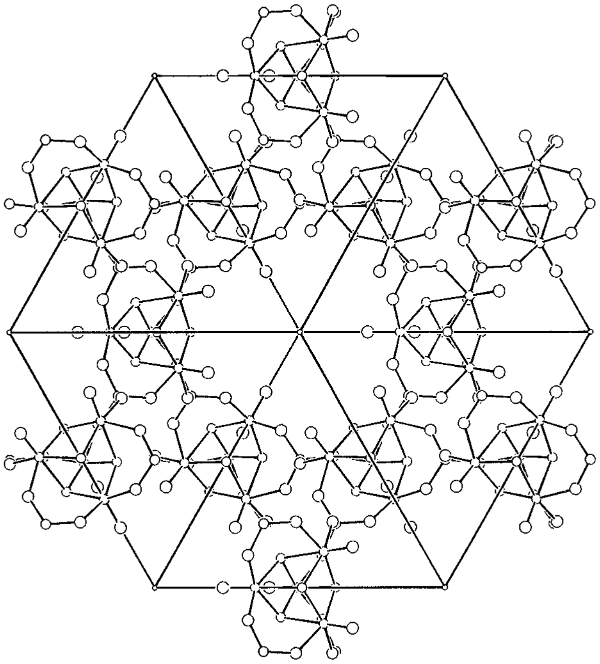

FIGURE 4. Projection of the framework of the phosphovanadylite structure down the cubic body-diagonal direction showing the large open passages.

zeolitic water. In the final model, O(4) contains Ba and K, and O(5) contains Ca. The population parameters for Al, Ba, Ca, and K were all constrained to be consistent with the analytical data (Table 4) and were not refined. Although these assignments are rather arbitrary, the displacement parameters all attained consistent and reasonable values.

Thus, about 52 H_2O molecules were accounted for. This number was less than expected, but a large space remained around the origin in which several small peaks were observed in the electron density map; this region is probably occupied by water in some sort of disorder. The density and analytical sum deficiencies suggest a total of about 72 H_2O.

Under the conditions described above, refinement converged (not including anisotropic terms for P and V) to the following critical points: $R = 0.066$, $R_w = 0.061$, goodness-of-fit = 0.75, and 93 observations and 24 parameters. Anisotropic refinement of V and P led to a reasonable result: P nearly isotropic, and V vibrating around an axis passing through the center of the V_4 cluster, with an axial ratio of about 0.5. As the parameter-observations ratio is quite low (0.3), the model was not elaborated further. (An attempt to refine in *I*432 led to no reasonable result.) All parameter shift/esd ratios were reduced to less than 0.1.

Table 3 shows the results of the structure analysis, and Table 5 shows the significant interatomic distances. The list of observed and calculated structure factors (Table 6[1]) has been deposited together with a table of bond angles (Table7[1]). All calculations were carried out with the programs of XTAL 2.4 (Hall and Stewart 1988) on a SUN 4/10 workstation.

CRYSTAL CHEMISTRY

The $P_2V_40_{16}$ cluster that forms the building block of the zeolitic framework in this mineral is evidently unique for vanadium. Nevertheless, the coordination of vanadium is entirely characteristic of octahedral V^{+4} with V displaced from the center of the octahedron toward one apex O, thus forming one short bond (1.59 Å) and one opposite long bond (2.3 Å, Table 5). Several questions concerning this new structure arise, which are discussed in the following sections.

Vanadium valency

The sum of the bond valencies *s* (Brown and Aldermatt 1985) in the VO_6 octahedron is 4.3, strongly indicating a reduced valence state for V atoms. Significantly, the crystals are a transparent blue color, characteristic of +4 valency. The crystals slowly become dark and opaque black on exposure to air through oxidation. We may safely assume that vanadium is in a purely quadrivalent state in fresh phosphovanadylite.

---

[1] For a copy of Tables 6 and 7, Document AM-98-013, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the *American Mineralogist* web site at http://www.minsocam.org.

TABLE 3. Atomic coordinates and isotropic temperature factors for phosphovanadylite

Atom	Site	*x*	*y*	*z*	*u**	*p*†
V	24(*g*)	0.4294(5)	0.4294	0.0828(8)	0.13(2)	0.87
P	12(*d*)	0.25	0.5	0.0	0.14(2)	
O(1)	48(*h*)	0.435(3)	0.307(2)	0.050(2)	0.16(3)	
O(2)	24(*g*)	0.420(2)	0.420	0.184(2)	0.17(3)	
O(3)	24(*g*)	0.558(2)	−0.558	0.066(3)	0.13(4)	
O(4)	24(*g*)	0.257(5)	0.257	−0.028(4)	0.30(4)	0.85
O(5)	8(*c*)	0.340(5)	0.340	0.340	0.32(11)	0.92
O(6)	24(*g*)	0.148(4)	0.148	0.314(6)	0.41(19)	
Al	24(*g*)	Same as V				0.13
Ba(5)	24(*g*)	Same as O(4)				0.07
Ba(6)	8(*c*)	Same as O(5)				0.08

* *u* is root-mean-square atomic displacement in angstroms.
† *p* is occupancy factor.

Role of aluminum

The microprobe analysis gives only about 21 V out of the expected 24; but three Al atoms are also found (Table 4). The Al most probably substitutes for V in the framework, in a comfortable octahedral environment (a normal Al-O distance is 1.95 Å). This substitution confers a small additional negative charge on the framework, which would otherwise be −6 per [$P_2V_4O_{16}$] group. This charge is balanced by the cations and OH groups replacing O in the framework (see below). This arrangement was assumed in the structure analysis (Table 3).

Cation distribution

The cation counts in the structure, based on the chemical analysis (Table 3), conform well with the site requirements in the crystal structure within the limitations of the structural and analytical uncertainties. The cations Ba and K are located in the model replacing H_2O at O(4), which is surrounded on three sides by framework O atoms, two O(2) atoms at 3.0 Å, and four O(3) atoms at 3.1 Å. Ca is placed with O(5), which is in contact with three framework atoms, and O(2) at 3.0 Å. Thus, the cations are all associated with the framework, lining the cavity at the origin.

TABLE 4. Recalculation for phosphovanadylite

Oxide	wt%*	M†	O‡	FW
V_2O_4	45.6(2)	20.6(1)	41.2(1)	1710
Al_2O_3	3.7(2)	2.7(2)	4.1(3)	139
P_2O_5	22.7(6)	12.0(3)	30.0(8)	851
BaO	9.2(5)	2.3(1)	2.3(1)	345
K_2O	0.9(1)	0.7(1)	0.4(1)	34
CaO	1.8(4)	1.2(3)	1.2(3)	69
Na_2O	0.2(2)	0.2(2)	0.1(1)	7
ZnO	0.4(4)	0.2(2)	0.1(1)	4
CdO	0.1(1)	0.0	0.0	
O total			79.5(4)	
Add framework H_2O			16.5	297
Subtotal			96	3473
Add zeolitic H_2O			72	1296
Total formula weight (FW)				4769

* Calculated from Table 2.
† Metal atoms per unit cell.
‡ O atoms per unit cell.

Oxygen and water

In the $P_2V_4O_{16}$ framework 96 O are needed per cell, but the cation chemistry provides only 79. Therefore it is necessary to add 17 H_2O to complete the complement. The framework must therefore carry 34 OH groups, but their locations can be only indirectly inferred. The 48 O(1) atoms are each shared between V and P, and are nearly saturated ($\Sigma s = 1.9$). The 24 O(2) atoms are associated with a single V atom in a short bond, ($s = 1.7$), which cannot accommodate an H atom. The 24 O (3) atoms are each shared with three V atoms and the valence sum for this O atom is 1.3; thus these atoms are available for 24 H atoms in the cell. The remaining 10 OH groups may be partly accounted for by terminal OH groups associated with the six Al atoms in the framework, but altogether the particular H locations are unclear.

CONCLUSIONS

The simplest formula for phosphovanadylite that can be derived from the structure analysis and chemical analysis (neglecting Zn and Cd) is $(\mathrm{Ba,Ca,K,Na})_x[(\mathrm{V,Al})_4\mathrm{P}_2(\mathrm{O,OH})_{16}]\cdot 12\mathrm{H_2O}$.

In more detail the formula becomes

$$(\mathrm{Ba}_{0.38}\mathrm{Ca}_{0.20}\mathrm{K}_{0.06}\mathrm{Na}_{0.02})_{\Sigma 0.66}$$
$$[\mathrm{P}_2(\mathrm{V}_{3.44}\mathrm{Al}_{0.46})_{\Sigma 3.90}\mathrm{O}_{10.34}\,(\mathrm{OH})_{5.66}]\cdot 12\mathrm{H_2O}$$

TABLE 5. Interatomic distances in phosphovanadylite

Atoms	*d*, Å	Atoms	*d*, Å
Framework			
V-O(1) ×2	1.94(3)	O(1)-O(1) ×2	2.51(5)
V-O(2)	1.58(4)	O(1)-O(1)′	2.52(5)
V-O(3) ×2	2.01(3)	O(1)-O(2)	2.71(5)
V-O(3)	2.32(5)	O(1)-O(3)	2.81(4)
		O(1)-O(3)′	2.75(5)
P-O(3) ×4	1.54(3)	O(2)-O(3) ×2	2.82(5)
		O(3)-O(3) ×2	2.72(6)
Water molecules			
O(4)-O(1) ×2	3.10(8)	O(5)-O(2) ×3	2.97(9)
O(4)-O(1) ×2	3.18(8)	O(5)-O(4) ×3	2.94(10)
O(4)-O(2) ×2	3.00(8)		
O(6)-O(1) ×2	3.47(6)		
O(6)-O(3)	2.69(9)		
O(6)-O(4) ×2	3.30(9)		
O(6)-O(4)′	3.21(10)		

where the number of H_2O molecules varies depending on ambient humidity.

The crystal structure we find for phosphovanadylite is based on a zeolitic framework of V_4O_{16} groups, which consist of four condensed VO_6 octahedra joined to each other by phosphate groups (Fig. 2). These groups lie at the edge centers and face centers of the unit cell, thus forming a three-dimensional framework containing large open cavities at the origin and body center of the cell (Figs. 3 and 4). These cavities, about 7 Å in diameter, are occupied by H_2O molecules plus a small number of cations in zeolitic fashion. The passages along the body diagonal of the cell connecting the cavities are about 5.5 Å in diameter.

The zeolitic structure found for phosphovanadylite is unprecedented for vanadium. Much work has been done on vanadophosphate chemistry in connection with catalyst research (see review by Beltran-Porter et al. 1991) All phases reported until now have P/V ratios of one or greater. Among the phases known for the phosphates of the early transition elements (V, Ti, Nb, Mo, W; see review by Borel et al. 1991), a close analog to our structure is found in the dark red-brown cubic compound $[(CH_3)_4N]_{1.3}(H_3O)_{0.7}[Mo_4O_8(PO_4)_2]\cdot 2H_2O$ (Haushalter et al. 1989). It consists of a network of Mo_4O_{16} groups of the type shown in Figure 2 linked by phosphate groups in a cubic arrangement (a = 15.05 Å, $I\bar{4}3m$) enclosing an open cavity occupied by large tetramethylammonium groups and oxonium ions. The framework is identical with that of the vanadophosphate structure found here. In this molybdenum compound, the Mo-Mo distance in the Mo_4O_{16} group is 2.61 Å, short enough to lead Haushalter et al. (1989) to propose that there is considerable Mo-Mo bonding present. In the corresponding V_4O_{16} cluster in phosphovanadylite, the V-V distance is 3.09 Å, too large for V-V bonding. The molybdenum compound was prepared hydrothermally at 200 °C, but phosphovanadylite was clearly formed under much milder conditions. A simpler analog was found earlier by Haushalter (1987) for the compound $Cs_3Mo_4P_3O_{16}$, which is cubic, space group $P\bar{4}3m$, a = 7.728 Å. The framework is the same, but without the large cavity at the origin in the doubled body-centered structure described above. This structure was first proposed by Zemann (1948) for pharmacosiderite $K[Fe_4(OH)_4(ASO_4)_3]\cdot 6H_2O$, and refined by Buerger et al. (1967) (space group $P\bar{4}3m$, a = 7.98 Å.) The mineral compound is zeolitic with varying water and cation content.

Sodium enneagermanate ($Na_4Ge_9O_{20}$) also has a similar structure (Ingri and Ludgren 1963; Fleet 1990). This tetragonal compound consists of Ge_4O_{16} groups identical in geometry to the V_4O_{16} groups in phosphovanadylite, joined into a framework by tetrahedral GeO_4 groups. The framework linkage is different and more compact, but the analogy is striking. The Ge-Ge distances in the Ge_4O_{16} groups are 2.92 and 3.03 Å, thus showing no tendency for cation-cation bonding, as is not expected. The stability of this type of structure with M_4O_{16} groups joined by XO_4 groups is evidently not only related to the chemical nature of its components, but also some more general lattice principle.

Phosphate mine companies only mine where the phosphate has been concentrated and made friable by weathering out of both organic matter and carbonates. By comparison, a completely unweathered section of the Phosphoria Formation contains abundant pyrite, organic matter, and carbonates. Phosphovanadylite was found in the bottom of an open pit mine where mining had ceased. It is assumed that the mineral was found in an intermediate zone between unweathered and weathered rock.

Vanadium is profoundly sensitive to two environmental conditions; acidity and oxidation (Evans and White 1987). Vanadium can be reduced to V^{4+} under near neutral pH conditions by the presence of organic matter, whereas V^{3+} is stable under acidic conditions caused by the presence of pyrite (Wanty and Goldhaber 1992). Pyrite probably was weathered out, but there was still ample organic matter and carbonate, as evidenced by the black-colored and indurated matrix rocks. Under these conditions, the pH was probably near neutral, yet the organic matter was sufficient to reduce the V to a +4 state. According to theoretical equilibrium phase diagrams relating pH and Eh, V^{4+} minerals are stable at Ehs of −0.1 to 0.5 volts (Evans and Garrels 1958).

ACKNOWLEDGMENTS

Our appreciation goes to Roscoe Bolton and other members of the Monsanto Corporation for allowing us access to trenches at the Enoch Valley Mine and sharing their invaluable knowledge of the mine's geology. Thanks also go to John Donovan at U.C. Berkeley for the electron microprobe analyses and Robert Oscars on of the U.S. Geological Survey for the SEM micrographs. We are grateful to Jeffrey E. Post of the Division of Mineral Sciences, Smithsonian Institution, for arranging the use of the CAD4 Automatic Diffractometer for this study. All available sample material has been deposited with this Institution.

The mineral's name is descriptive, chosen because the mineral is primarily composed of vanadium and phosphorus. Vanadyl is the term used for the VO^{2+} group with vanadium in the +4 oxidation state. Both the mineral and mineral name have been approved by the IMA Commission on New Minerals and Mineral Names (96-037).

REFERENCES CITED

Brown, I.D. and Altermatt, D. (1985) Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure data base. Acta Crystallographica, B41, 244–247.

Beltran-Porter, D., Beltran-Porter, A., Amoros, P., Ibañez, R., Martinez, E., Le Bail, A., Ferey, G., and Villeneuve, G. (1991) Recent advances in the chemistry and properties of oxovanadium phosphates. European Journal of Solid State Chemistry, 28, 131–161.

Borel, M.M., Goreaud, M., Grandin, A., Labbé, P., Leclaire, A., and Ravaau, B. (1991) Phosphates of mixed valent transition elements. European Journal of Solid State Chemistry, 28, 93–129.

Buerger, M.J., Dollase, W.A., and Garaycochea-Wittke, I. (1967) The structure and composition of the mineral pharmacosiderite. Zeitschrift für Kristallographie 125, 92–108.

Burnham, C.W. (1962) Lattice constant refinement. Yearbook Carnegie Institute, Washington, 61, 132–135.

Donovan, J.J., Rivers, M.L., and Armstrong, J.T. (1992) PRSUPR: Automation and analysis software for wavelength dispersive electron-beam microanalysis on a PC. American Mineralogist, 77, 444–445.

Evans, H.T. and Garrels, R.M. (1958) Thermodynamic equilibria of vanadium in aqueous systems as applied to the interpretation of the Colorado Plateau ore deposits. Geochimica et Cosmochimica Acta, 15, 131–149.

Evans, H.T. and White, J.S. (1987) The colorful vanadium minerals: A brief review and a new classification. The Mineralogical Record, 18, 333–340.

Fleet, M.E. (1990) Refinement of the crystal structure of sodium enneagermanate $Na_4Ge_9O_{20}$. Acta Crystallographica, C46, 1202–1204.

Hall, S.R. and Stewart, J.M., Eds. (1988) XTAL system of crystallographic programs. Universities of Western Australia and Maryland.

Haushalter, R.C. (1987) $Mo_4O_4^{6+}$ cubes in $Cs_3Mo_4P_3O_{16}$. Journal of the Chemical Society Chemical Communications, 1566–1568.

Haushalter, R.C., Strohmaier, K.G., and Lai, F.W. (1989) Structure of a three-dimensional microporous molybdenum phosphate with large cavities. Science, 246, 1289–1291.

Ingri, N. (1963) The crystal structure of $Na_4Ge_9O_{20}$. Acta Chemica Scandinavica, 17, 617–633.

Love, J.D. (1961) Vanadium and associated elements in the Phosphoria Formation in the Afton area, western Wyoming. In Geological Survey Research, Chapter C, U.S. Geological Survey Professional Paper, 424-C, C279–C282.

McKelvey, V.E., Williams, J.S., Sheldon, R.P., Cressman, E.R., Cheney, T.M., and Swanson, R.W. (1959) The Phosphoria, Park City and Shedhorn Formations in the western phosphate field. U.S. Geological Survey Professional Paper, 313A, 1–47.

McKelvey, V.E., Strobell, J.D., and Slaughter, A.L. (1986) The vanadiferous zone of the Phosphoria Formation in Western Wyoming and Southeastern Idaho. U.S. Geological Survey Professional Paper, 1465.

Medrano, M.D. and Piper, D.Z. (1992) A normative-calculation procedure used to determine mineral abundances in rocks from the Montpelier Canyon Section of the Phosphoria Formation, Idaho: A tool in deciphering the minor-element geochemistry of sedimentary rocks. U.S. Geological Survey Bulletin, 2023-A, 1–23.

——— (1995) Partitioning of minor elements and major-element oxides between rock components and calculation of the marine derived fraction of the minor elements in rocks of the Phosphoria Formation, Idaho and Wyoming. U.S. Geological Survey Open-File Report, 95-270, 1–79.

Piper, D.Z. and Medrano, M.D. (1994) Geochemistry of the Phosphoria Formation at Montpelier Canyon, Idaho: Environment of Deposition. U.S. Geological Survey Bulletin, 2023-B, 1–28.

Wanty, R.B. and Goldhaber, M.B. (1992) Thermodynamics and kinetics of reactions involving vanadium in natural systems: Accumulation of vanadium in sedimentary rocks. Geochimica et Cosmochimica Acta, 56, 1471–1483.

Zemann, J. (1948) Formel und Strukturtyp des Pharmacosiderite. Tschermaks mineralogische und petrologische Mitteilungen series 3, 1, 1–13.

MANUSCRIPT RECEIVED MAY 28, 1997
MANUSCRIPT ACCEPTED FEBRUARY 19, 1998
PAPER HANDLED BY GILBERTO ARTIOLI