

Phosphovanadylite-Ca, $\text{Ca}[\text{V}_4^{4+}\text{P}_2\text{O}_8(\text{OH})_8]\cdot 12\text{H}_2\text{O}$, the Ca analogue of phosphovanadylite-Ba

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ABSTRACT

Phosphovanadylite-Ca, $\text{Ca}[\text{V}_4^{4+}\text{P}_2\text{O}_8(\text{OH})_8]\cdot 12\text{H}_2\text{O}$, is a new mineral from the South Rasmussen (or South Rasmussen Ridge) phosphate mine, Soda Springs, Caribou County, Idaho. It is named as the Ca analog of phosphovanadylite, which is now renamed as phosphovanadylite-Ba. The new mineral grows on matrix containing fine-grained quartz, massive, porous fluorapatite and hydroxylapatite, framboidal pyrite, and tiny, euhedral sphalerite crystals. Other minerals directly associated with the new mineral are sincosite and native Se. Phosphovanadylite-Ca crystallized at ambient temperatures from late-stage aqueous solutions of near neutral pH under relatively reducing conditions. The mineral is cubic, space group $\bar{I}43m$, $a = 15.441(11) \text{ \AA}$, $V = 3682(5) \text{ \AA}^3$, and $Z = 6$. Crystals occur as small, greenish-blue simple cubes (to 0.1 mm on edge) intergrown to form thin crusts. Penetration twinning on $\{111\}$ is common. The color is bright greenish blue, the streak is very pale greenish blue, and the luster is vitreous. The Mohs hardness is estimated at 2. The new mineral is brittle with irregular fracture and no cleavage. The measured density is $2.02(3) \text{ g/cm}^3$ and the calculated density based on the empirical formula is 2.038 g/cm^3 . Phosphovanadylite-Ca is isotropic with $n = 1.559(2)$. The normalized electron microprobe analysis based upon sufficient H for charge balance and 12 molecules of zeolitic H_2O is: Na_2O 0.22, K_2O 0.55, CaO 5.58, SrO 0.10, BaO 0.21, Al_2O_3 3.27, VO_2 35.85, P_2O_5 18.78, H_2O 35.44, Total 100.00. The empirical formula (based on 2 P and 28 O apfu) is: $(\text{Ca}_{0.75}\text{K}_{0.09}\text{Na}_{0.05}\text{Ba}_{0.01}\text{Sr}_{0.01})_{\Sigma 0.91}[(\text{V}_{3.27}\text{Al}_{0.49})_{\Sigma 3.76}\text{P}_{2.00}\text{O}_{10.23}(\text{OH})_{5.77}]\cdot 12\text{H}_2\text{O}$. The eight strongest powder X-ray diffraction lines are [d_{obs} in Å (hkl) I]: 11.04 (110) 97, 7.7881 (200) 100, 4.487 (222) 14, 3.1706 (422) 46, 2.749 (440) 32, 2.4576 (620) 14, 2.3426 (622) 15, and 1.8295 (822) 16. The crystal structure of phosphovanadylite-Ca ($R_1 = 0.027$ for 171 reflections with $F_o > 4\sigma F$) contains $\text{V}_4^{4+}\text{O}_{16}$ polyvanadate clusters of four edge-sharing V^{4+}O_6 octahedra. The polyvanadate clusters are linked into a three-dimensional zeolite-like framework by sharing corners with PO_4 tetrahedra. The open space in the framework is dominated by H_2O with the equivalent of one large cation pfu sharing one of the H_2O sites. The framework is identical to that in phosphovanadylite-Ba; however, in phosphovanadylite-Ba, the dominant extra-framework cation is Ba, while in phosphovanadylite-Ca, it is Ca.

Keywords: Phosphovanadylite-Ca, new mineral, crystal structure, zeolite-type structure, phosphovanadylite-Ba, South Rasmussen phosphate mine, Idaho

INTRODUCTION

Phosphovanadylite, $\text{Ba}[\text{V}_4^{4+}\text{P}_2\text{O}_8(\text{OH})_8]\cdot 12\text{H}_2\text{O}$, was described in 1998 by Medrano et al. from the Enoch Valley phosphate mine, Soda Springs, Caribou County, Idaho. This mine was operated by the Monsanto Company from 1986 to 2004 and is now reclaimed. The mining of phosphates in southeastern Idaho has come under intensive scrutiny in recent years because of contamination of the water system, especially by Se. Nevertheless, mines continue to be operated by several companies, including Monsanto (through its wholly owned subsidiary, P4 Production LLC). Development of the South Rasmussen (or South Rasmussen Ridge) mine began with the issuance of a lease to Monsanto in 2001 by the Bureau of Land Management (BLM). Specimen collecting at the South

Rasmussen mine in 2010 by then mine geologist John Keefner and one of the authors (T.A.L.) yielded crystals of the new mineral Phosphovanadylite-Ca, described herein. Interestingly, the new mineral occurs in association with native Se.

Phosphovanadylite-Ca is named as the Ca-dominant analog of phosphovanadylite. The new mineral and name has been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA 2011-101). The description of the mineral is based upon material from five co-type specimens now deposited in the collections of the Natural History Museum of Los Angeles County, California, U.S.A., catalog numbers 63578, 63579, 63580, 63581, and 63582. The CNMNC has also approved the name change for the original phosphovanadylite to phosphovanadylite-Ba.

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OCCURRENCE

Phosphovanadylite-Ca occurs at the South Rasmussen (or South Rasmussen Ridge) phosphate mine, Soda Springs, Caribou County, Idaho, U.S.A. (42°51'N, 111°21'W). The mineral was found on surfaces and in thin seams in a black mudstone rich in phosphate and organic material on the 6740 foot bench of the open pit, about 300 feet (90 m) below the original topography. Sincosite, native Se, and an unidentified Ca-Fe vanadate occur in direct association with the new mineral. The matrix contains fine-grained quartz, massive, porous fluorapatite and hydroxylapatite, framboidal pyrite (10 μm), and tiny, euhedral sphalerite crystals (Bart Cannon, personal communication). Other minerals noted in the same horizon are cacoxenite, fluellite, hawleyite, minyulite, and wavellite.

The mineral occurs in the Mead Peak Phosphatic Shale Member of the Permian Phosphoria Formation, which is notable for abundant and widespread beds that are enriched in vanadium, including one, the vanadiferous zone, that contains up to 1 wt% V_2O_5 (Love 1961; McKelvey et al. 1986). Piper and Medrano (1994) describe in detail the stratigraphy and geochemistry of the Phosphoria Formation, and Medrano et al. (1998) in their description of phosphovanadylite provide a summary of the stratigraphy and areal distribution of the Mead Peak Phosphatic Shale Member and its secondary vanadium minerals, including sincosite, hewettite, and pascoite. The occurrence of phosphovanadylite-Ca is essentially identical to that described by Medrano et al. (1998) for phosphovanadylite from the nearby and now-reclaimed Enoch Valley phosphate mine. Phosphovanadylite, in close association with sincosite, was collected from a vanadium-rich bed stratigraphically well below the vanadiferous zone, as is the case for phosphovanadylite-Ca.

Regarding the stability conditions for phosphovanadylite formation, under acidic conditions, such as in the presence of abundant pyrite, vanadium would be expected to be +5. Medrano et al. (1998) however concluded that the presence of carbonate and organic matter in the dark-colored matrix rock was, with pyrite absent and under near neutral acidic conditions, sufficient to reduce V to the +4 state (see also Wanty and Goldhaber 1992). In spite of the presence of very minor pyrite in the matrix hosting phosphovanadylite-Ca, we believe its environment of formation to be generally consistent with that of phosphovanadylite, except for the presence of significant Ba in the latter case. Phosphovanadylite-Ca crystallized at ambient temperatures from late-stage aqueous solutions of near neutral pH under relatively reducing conditions.

PHYSICAL AND OPTICAL PROPERTIES

Phosphovanadylite-Ca occurs as small, greenish-blue cubes (to 0.1 mm on edge) intergrown to form thin crusts (Fig. 1). The cube, $\{100\}$, is always prominent; it is rarely modified by a small and less-well-formed octahedron, $\{111\}$. Penetration twinning on $\{111\}$ is common. The color is bright greenish blue. On long-term (about one year) exposure to sunlight, the mineral gradually turns from greenish blue to green and then black. The color change is probably due to the partial oxidation of V^{4+} to V^{5+} , with the blackening being due to V^{4+} - V^{5+} charge transfer. The streak is very pale greenish blue and the luster is vitreous.

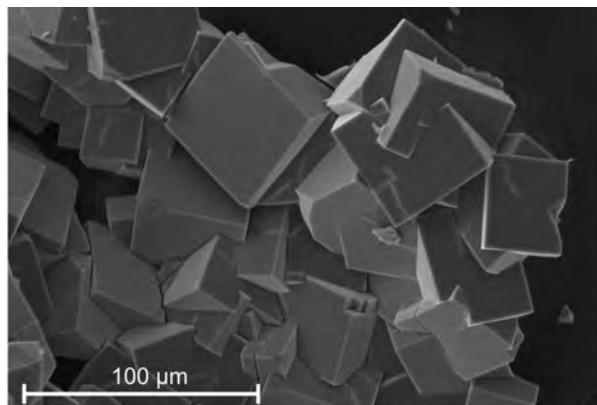


FIGURE 1. SEM image of phosphovanadylite-Ca.

The Mohs hardness is about 2. The new mineral is brittle with irregular fracture and no cleavage. The density measured by sink-float in an aqueous solution of sodium polytungstate is 2.02(3) g/cm^3 . The calculated density based on the empirical formula is 2.038 g/cm^3 . The mineral is isotropic with the index of refraction $n = 1.559(2)$ determined in white light; it is greenish blue in plane-polarized light. Phosphovanadylite-Ca dissolves slowly in cold, concentrated acids (HCl, H_2SO_4 , and HNO_3). In HNO_3 , it quickly turns from greenish blue to orangish yellow, presumably due to the oxidation of V^{4+} to V^{5+} .

CHEMICAL COMPOSITION

Analyses (18 from 12 crystals) were performed at the University of Utah on a Cameca SX-50 electron microprobe with four wavelength-dispersive spectrometers. Analytical conditions were 15 kV accelerating voltage, 10 nA beam current, and a nominal beam diameter of 10–15 μm . Counting times were 10 s for each element. Raw X-ray intensities were corrected for matrix effects with a ϕ -rho-z algorithm (Pouchou and Pichoir 1991). The grains exhibit only minor visible damage from the electron beam. A single determination on a 1.1 mg sample using a CEC 440HA CHN analyzer in the Marine Science Institute, University of California, Santa Barbara, provided 27.57 wt% H_2O . The small CHN sample size and minor sample impurities from attached matrix suggest that this measurement is of relatively low reliability.

Several factors contributed to problems in unambiguously establishing the H_2O content of phosphovanadylite-Ca:

(1) Highly hydrated phases with loosely held water often provide high EMPA totals, due to partial dehydration under vacuum, and we believe this to be true in this case.

(2) The water from CHN, even when combined with an EMPA normalized to 100%, yields only 7.42 molecules of zeolitic H_2O pfu, much less than the 12 molecules reported for phosphovanadylite (Medrano et al. 1998).

(3) The structure determination is consistent with 14.2 molecules of zeolitic H_2O ; however, because the H_2O molecules are located at numerous disordered sites (with high displacement parameters), this value could very well be too high.

We ultimately decided that the best compromise was to calculate H_2O based upon the same content of zeolitic water as

was reported for phosphovanadylite and to the normalize EMPA to 100% accordingly. The relatively close match between the measured and calculated densities further supports this approach. Analytical data are given in Table 1.

The empirical formula (based on 2 P and 28 O apfu) is, with rounding errors, $(\text{Ca}_{0.75}\text{K}_{0.09}\text{Na}_{0.05}\text{Ba}_{0.01}\text{Sr}_{0.01})_{\Sigma 0.91}[(\text{V}_{3.27}\text{Al}_{0.49})_{\Sigma 3.76}\text{P}_{2.00}\text{O}_{10.23}(\text{OH})_{5.77}]\cdot 12\text{H}_2\text{O}$. The simplified formula is $\text{Ca}[\text{V}_{3.44}\text{P}_{2.00}\text{O}_8(\text{OH})_8]\cdot 12\text{H}_2\text{O}$, which requires CaO 6.86, VO_2 40.56, P_2O_5 17.35, H_2O 35.24, total 100.00 wt%. The Gladstone-Dale compatibility index $1 - (\text{K}_p/\text{K}_c)$ is -0.028 for the empirical formula, indicating excellent compatibility (Mandarino 1981). For comparison, the empirical formula of phosphovanadylite-Ba reported by Medrano et al. (1998) is $(\text{Ba}_{0.38}\text{Ca}_{0.20}\text{K}_{0.06}\text{Na}_{0.02})_{\Sigma 0.66}[(\text{V}_{3.44}\text{Al}_{0.46})_{\Sigma 3.90}\text{P}_{2.00}\text{O}_{10.34}(\text{OH})_{5.66}]\cdot 12\text{H}_2\text{O}$.

X-RAY CRYSTALLOGRAPHY AND STRUCTURE DETERMINATIONS

All powder and single-crystal X-ray diffraction data were obtained on a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer utilizing monochromatized $\text{MoK}\alpha$ radiation. Observed powder d -values (with standard deviations) and intensities were derived by profile fitting using JADE 9.3 software. Data (in angstroms) are given in Table 2. Unit-cell parameters refined from the powder data using JADE 9.3 with whole pattern fitting are: $a = 15.457(3)$ Å and $V = 3693(1)$ Å³. The observed powder data fit well with those calculated from the structure, also using JADE 9.3.

The Rigaku CrystalClear software package was used for processing of the diffraction data, including the application of an empirical multi-scan absorption correction using ABSCOR (Higashi 2001). We used the atom coordinates for the framework atoms (V, P, O1, O2, and O3) reported for phosphovanadylite-Ba (Medrano et al. 1998) as a starting point. SHELXL-97 software (Sheldrick 2008) was used for the refinement of the structure. The channel sites were located in difference Fourier maps. Unfortunately, the small crystal size and low diffracting power of phosphovanadylite-Ca provided useful data only to 15.92° θ . Thus, with only 188 unique reflections and 68 refined parameters, the reflection to parameter ratio (2.76) is considered poor.

In the final refinement, all framework sites were assigned full occupancy with the V/Al site assigned occupancy by 0.83 V and 0.13 Al, in keeping with the relative amounts of these cations indicated by the chemical analyses. Coincidentally, this is the same occupancy used for this site by Medrano et al. (1998). Initially, all of the channel sites were assumed to be O atoms and their occupancies were refined. The OW1 site refined to 1.21(5)

TABLE 1. Chemical analytical data for phosphovanadylite-Ca

Constituent	wt%	Range	St.dev.	Standard	Norm. wt%
Na_2O	0.26	0.04–0.52	0.13	allbite	0.22
K_2O	0.66	0.38–0.99	0.14	sanidine	0.55
CaO	6.67	5.44–8.05	0.73	diopside	5.58
SrO	0.12	0.04–0.28	0.06	syn. SrTiO_3	0.10
BaO	0.25	0.15–0.40	0.08	barite	0.21
Al_2O_3	3.91	3.21–4.73	0.41	sanidine	3.27
VO_2	42.84	40.63–46.28	1.47	syn. YVO ₄	35.85
P_2O_5	22.44	20.98–24.00	0.81	fluorapatite	18.78
H_2O	27.57			from CHN	35.44*
Total	104.73				100.00

Note: MgO was sought, but found to be below the limit of detection, 0.03 wt%. * Calculated based upon sufficient H for charge balance and 12 molecules of zeolitic H_2O .

occupancy by O and was the only channel site that refined to greater than full occupancy. Consequently, we assigned both Ca and O to the site with Ca occupancy held at 0.25 (corresponding to one Ca apfu) and refined the O occupancy to 0.61(5) O.

Details concerning data collection and structure refinement are provided in Table 3. Site occupancies, fractional coordinates, and atom displacement parameters are provided in Table 4, selected interatomic distances in Table 5, and bond valences in Table 6. CIF available on deposit¹.

¹ Deposit item AM-13-015, Data set and CIF. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for pricing information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 2. X-ray powder diffraction data for phosphovanadylite-Ca

l_{obs}	d_{obs}	d_{calc}	l_{calc}	hkl	l_{obs}	d_{obs}	d_{calc}	l_{calc}	hkl
97	11.04(3)	10.9184	100	110	10	1.8897(7)	1.8725	5	8 2 0
100	7.7881(12)	7.7205	85	200			1.8456	1	6 5 3
6	6.373(8)	6.3038	5	211	16	1.8295(13)	1.8197	8	8 2 2
7	5.498(5)	5.4592	7	220			1.7950	2	7 4 3
11	4.922(3)	4.8829	9	310			1.7712	1	6 6 2
14	4.487(2)	4.4574	12	222	4	1.730(3)	1.7264	3	8 4 0
8	4.154(3)	4.1268	7	321	4	1.6895(6)	1.6848	3	8 4 2
9	3.662(3)	3.6395	5	411			1.6650	1	6 5 5
5	3.327(5)	3.2920	4	332	2	1.6436(15)	1.6460	1	6 6 4
46	3.1706(5)	3.1519	38	422			1.6276	2	8 5 1
13	3.0413(15)	3.0282	11	431			1.5926	1	7 6 3
10	2.8378(12)	2.8191	10	521			1.5759	1	8 4 4
32	2.749(2)	2.7296	8	440			1.5598	1	7 7 0
		2.6481	2	530	7	1.5579(7)	1.5441	5	8 6 0
11	2.590(4)	2.5735	9	600			1.5141	1	8 6 2
10	2.5202(19)	2.5049	7	611	9	1.4972(9)	1.4998	2	9 4 3
14	2.4576(3)	2.4414	11	620			1.4858	2	10 2 2
15	2.3426(11)	2.3278	4	622			1.4722	1	10 3 1
6	2.2080(13)	2.2287	3	444			1.4462	2	8 7 1
		2.1837	3	710			1.4337	1	8 6 4
10	2.1081(9)	2.1013	6	721	2	1.4199(8)	1.4096	2	10 4 2
		2.0634	2	642			1.3980	1	9 5 4
13	1.9403(6)	1.9301	6	800			1.3756	1	9 6 3
		1.9007	2	811	10	1.3672(7)	1.3648	4	8 8 0

TABLE 3. Data collection and structure refinement details for phosphovanadylite-Ca

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation/power	$\text{MoK}\alpha$ ($\lambda = 0.71075$ Å)
Temperature	298(2) K
Structural formula	$\text{Ca}[(\text{V}_{3.33}\text{Al}_{0.67})_4\text{P}_2\text{O}_{11.33}(\text{OH})_{4.67}]\cdot 14.21\text{H}_2\text{O}$
Space group	<i>I</i> 43m
Unit-cell dimension	$a = 15.441(11)$ Å
V	$3682(5)$ Å ³
Z	6
Density (for above formula)	2.183 g/cm ³
Absorption coefficient	1.726 mm ⁻¹
$F(000)$	2460.4
Crystal size	70 × 70 × 40 μm
θ range	3.23 to 15.92°
Index ranges	$-11 \leq h \leq 11, -11 \leq k \leq 11, -11 \leq l \leq 11$
Reflections collected/unique	1215/188 [$R_{\text{int}} = 0.068$]
Reflections with $F_o > 4\sigma F$	171
Completeness to $\theta = 15.92^\circ$	98.2%
Max. and min. transmission	0.934 and 0.889
Refinement method	Full-matrix least-squares on F^2
Parameters refined	68
GoF	1.174
Final R indices [$F_o > 4\sigma(F)$]	$R_1 = 0.0272, wR_2 = 0.0534$
R indices (all data)	$R_1 = 0.0331, wR_2 = 0.0560$
Absolute structure parameter	0.05(13)
Largest diff. peak, hole	+0.16, -0.13 e Å ⁻³

Notes: $R_{\text{int}} = \sum[F_o^2 - F_o^2(\text{mean})]/\sum[F_o^2]$. $\text{GoF} = S = [\sum[w(F_o^2 - F_o^2)/(n - p)]]^{1/2}$. $R_1 = \sum[|F_o| - |F_c|]/\sum[F_o]$. $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where a is 0.024, b is 0, and P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

TABLE 4. Site occupancies, fractional coordinates, and atomic displacement parameters for phosphovanadylite-Ca

	Occ.*	x/a	y/b	z/c	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V/Al	0.87/0.13	0.42846(14)	0.42846(14)	0.0814(2)	0.0426(14)	0.0410(16)	0.0410(16)	0.046(3)	-0.0005(15)	-0.0005(15)	0.007(3)
P	1	0.2500	0.5000	0.0000	0.049(3)	0.051(6)	0.048(4)	0.048(4)	0.000	0.000	0.000
O1	1	0.4357(5)	0.3059(5)	0.0515(4)	0.042(2)	0.035(6)	0.038(5)	0.053(6)	-0.003(5)	0.016(5)	-0.001(5)
O2	1	0.4214(5)	0.4214(5)	0.1866(7)	0.050(3)	0.046(5)	0.046(5)	0.059(10)	-0.008(6)	-0.008(6)	-0.007(10)
O3	1	0.5561(5)	-0.5561(5)	0.0664(6)	0.043(3)	0.044(5)	0.044(5)	0.041(8)	-0.005(5)	0.005(5)	0.005(7)
Ca/OW1	0.25/0.61(5)	0.6590(12)	-0.6590(12)	0.1605(19)	0.272(15)	0.255(19)	0.255(19)	0.31(3)	0.128(14)	-0.128(14)	0.01(2)
OW2	1	0.2938(19)	0.2938(19)	0.2938(19)	0.194(17)	0.194(17)	0.194(17)	0.05(2)	0.05(2)	0.05(2)	0.05(2)
OW3	0.56(6)	0.3361(19)	0.452(2)	0.3361(19)	0.13(2)	0.11(2)	0.19(4)	0.11(2)	-0.020(15)	0.06(2)	-0.020(15)
OW4	1	0.2451(9)	0.490(3)	0.2451(9)	0.221(14)	0.134(13)	0.40(4)	0.134(13)	0.009(16)	0.001(14)	0.009(16)
OW5	0.67(13)	0.345(5)	0.542(6)	-0.542(6)	0.43(10)	0.15(5)	0.56(15)	0.56(15)	0.13(14)	0.11(5)	-0.11(5)
OW6	0.54(13)	0.309(3)	0.691(3)	-0.691(3)	0.44(15)	0.44(15)	0.44(15)	0.44(15)	0.21(7)	-0.21(7)	0.21(7)
OW7	0.20(9)	0.295(11)	0.596(6)	-0.596(6)	0.15(6)						

*The occupancies of V, Al, and Ca were fixed to the values given.

TABLE 5. Selected bond lengths (Å) in phosphovanadylite-Ca

V-O2	1.631(11)	Ca-OW6	2.40(3)
V-O1(x2)	1.951(8)	Ca-OW7	2.50(18)
V-O3(x2)	1.998(8)	Ca-O3	2.676(18)
V-O3	2.307(10)	Ca-OW4	2.99(4)
<V-O>	1.973	Ca-OW2	3.03(4)
P-O1(x4)	1.537(7)		

TABLE 6. Bond valence sums for the framework atoms in the structure of phosphovanadylite-Ca

	O1	O2	O3	Σ
V/Al	$0.61 \times 2 \rightarrow$	1.44	$0.53 \times 2 \rightarrow \downarrow$	3.95
P	$1.24 \times 4 \rightarrow$		0.23	4.96
Σ	1.85	1.44	1.29	

Notes: Values are expressed in valence units. Multiplicity is indicated by $\times \rightarrow \downarrow$. V^{4+} -O, Al^{3+} -O, and P^{5+} -O bond strengths from Brown and Altermatt (1985). V/Al values are based upon occupancy by 0.83 V^{4+} and 0.13 Al^{3+} .

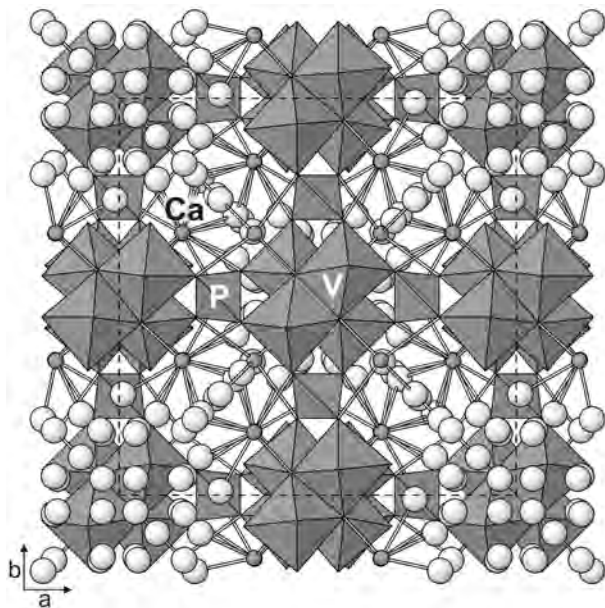


FIGURE 2. The crystal structure of phosphovanadylite-Ca viewed down [001]. The $V^{4+}O_6$ octahedra and PO_4 tetrahedra are dark gray. The Ca atoms are small dark gray spheres and O atoms of H_2O molecules are large white spheres. The radii of the atomic spheres in the drawing does not reflect the positional displacement parameters of the atoms but were chosen to allow the atomic linkages to be clearly seen. Note that the Ca site is occupied by both Ca and H_2O , and that most O sites are partially occupied. The Ca-O bonds are shown and the unit cell is outlined by dashed lines.

DESCRIPTION OF THE STRUCTURE

The structure of phosphovanadylite-Ca (Fig. 2) contains $V_4^{4+}O_{16}$ polyvanadate clusters of four edge-sharing $V^{4+}O_6$ octahedra. The polyvanadate clusters are linked into a three-dimensional zeolite-type framework by sharing corners with PO_4 tetrahedra. The open space in the framework is dominated

by H_2O with the equivalent of one large cation pfu sharing the OW1 site. The $V_4^{4+}P_2O_{16}$ framework is essentially identical to that in phosphovanadylite-Ba (Medrano et al. 1998); however, in phosphovanadylite-Ba the dominant extra-framework cation is Ba, while in phosphovanadylite-Ca, it is Ca.

The V-O and P-O bond lengths are consistent with those in phosphovanadylite-Ba. As noted for phosphovanadylite-Ba, the V coordination is characteristic of octahedral V^{4+} and the bond-valence sum of 3.95 v.u. is further confirmation of its 4+ valence state. The bond-valence analysis, only considering the framework atoms, indicates that all of the framework O atoms have bond-valence sums (BVS) significantly less than 2 v.u. The BVS for O1 of 1.85 v.u. is consistent with it being an O atom and it probably receives at least one hydrogen bond from OW4 at distances of 3.05 and 3.24 Å. The BVS for O2 is 1.44 and that for O3 is 1.29 v.u. Several channel H_2O sites (OW2, OW3, OW4, OW5, and OW7) are close enough to the O2 site to contribute hydrogen bonds, but it is unlikely that bond-valence balance can be achieved through hydrogen bonding alone, so it is likely that O2 has some OH character. The Ca/OW1 certainly provides additional bond-valence to O3, both as a Ca-O bond and a hydrogen bond; nevertheless, it is clear that O3 must have significant OH character. The ideal formula, $Ca[V_4^{4+}P_2O_8(OH)_8] \cdot 12H_2O$, requires that half of the O atoms in the framework are OH and, as noted above, these must be accommodated at the O2 and O3 sites.

Finally, considering that the large cations in the structure (Ca, Ba, Sr, and Na) are extra-framework (zeolitic), it seems safe to assume that the differing compositions of phosphovanadylite-Ca and phosphovanadylite-Ba principally reflect differing chemistries in their environments of formation.

ACKNOWLEDGMENTS

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MANUSCRIPT RECEIVED AUGUST 8, 2012

MANUSCRIPT ACCEPTED OCTOBER 14, 2012

MANUSCRIPT HANDLED BY ANDREW McDONALD

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