

1 **Revision 1**

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3 **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**  
4 **phosphovanadylite-Ba.**

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16 **ABSTRACT**

17 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  
18 Rasmussen (or South Rasmussen Ridge) phosphate mine, Soda Springs, Caribou County,  
19 Idaho. It is named as the Ca analogue of phosphovanadylite, which is now renamed as  
20 phosphovanadylite-Ba. The new mineral grows on matrix containing fine-grained quartz,  
21 massive, porous fluorapatite and hydroxylapatite, framboidal pyrite, and tiny, euhedral  
22 sphalerite crystals. Other minerals directly associated with the new mineral are sincosite and  
23 native Se. Phosphovanadylite-Ca crystallized at ambient temperatures from late-stage aqueous  
24 solutions of near neutral pH under relatively reducing conditions. The mineral is cubic, space  
25 group  $I-43m$ ,  $a = 15.441(11)$ ,  $V = 3682(5) \text{ \AA}^3$ , and  $Z = 6$ . Crystals occur as small, greenish-

26 blue simple cubes (to 0.1 mm on edge) intergrown to form thin crusts. Penetration twinning  
27 on {111} is common. The color is bright greenish blue, the streak is very pale greenish blue,  
28 and the luster is vitreous. The Mohs hardness is estimated at 2. The new mineral is brittle with  
29 irregular fracture and no cleavage. The measured density is 2.02(3) g/cm<sup>3</sup> and the calculated  
30 density based on the empirical formula is 2.038 g/cm<sup>3</sup>. Phosphovanadylite-Ca is isotropic  
31 with  $n = 1.559(2)$ . The normalized electron microprobe analysis based upon sufficient H for  
32 charge balance and 12 molecules of zeolitic H<sub>2</sub>O is: CaO 5.58, SrO 0.10, BaO 0.21, Al<sub>2</sub>O<sub>3</sub>  
33 3.27, VO<sub>2</sub> 35.85, P<sub>2</sub>O<sub>5</sub> 18.78, H<sub>2</sub>O 35.44, Total 100.00. The empirical formula (based on 2 P  
34 and 28 O apfu) is:  
35  $(\text{Ca}_{0.75}\text{K}_{0.09}\text{Na}_{0.05}\text{Ba}_{0.01}\text{Sr}_{0.01})_{\Sigma 0.91}[(\text{V}^{4+}_{3.27}\text{Al}_{0.49})_{\Sigma 3.76}\text{P}_{2.00}\text{O}_{10.23}(\text{OH})_{5.77}] \cdot 12\text{H}_2\text{O}$ . The eight  
36 strongest powder X-ray diffraction lines are [ $d_{\text{obs}}$  in Å ( $hkl$ )  $I$ ]: 11.04 (110) 97, 7.7881 (200)  
37 100, 4.487 (222) 14, 3.1706 (422) 46, 2.749 (440) 32, 2.4576 (620) 14, 2.3426 (622) 15, and  
38 1.8295 (822) 16. The crystal structure of phosphovanadylite-Ca ( $R_1 = 0.027$  for 171  
39 reflections with  $F_o > 4\sigma F$ ) contains V<sup>4+</sup><sub>4</sub>O<sub>16</sub> polyvanadate clusters of four edge-sharing V<sup>4+</sup>O<sub>6</sub>  
40 octahedra. The polyvanadate clusters are linked into a three-dimensional zeolite-like  
41 framework by sharing corners with PO<sub>4</sub> tetrahedra. The open space in the framework is  
42 dominated by H<sub>2</sub>O with the equivalent of one large cation pfu sharing one of the H<sub>2</sub>O sites.  
43 The framework is identical to that in phosphovanadylite; however, in phosphovanadylite the  
44 dominant extra-framework cation is Ba, while in phosphovanadylite-Ca, it is Ca.  
45 Phosphovanadylite is renamed phosphovanadylite-Ba.

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47 Keywords: phosphovanadylite-Ca; new mineral; crystal structure; zeolite-type structure;  
48 phosphovanadylite-Ba; South Rasmussen phosphate mine, Idaho.

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## INTRODUCTION

51 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  
52 al. from the Enoch Valley phosphate mine, Soda Springs, Caribou County, Idaho. This mine  
53 was operated by the Monsanto Company from 1986 to 2004 and is now reclaimed. The  
54 mining of phosphates in southeastern Idaho has come under intensive scrutiny in recent years  
55 because of contamination of the water system, especially by Se. Nevertheless, mines continue  
56 to be operated by several companies, including Monsanto (through its wholly-owned  
57 subsidiary, P4 Production LLC). Development of the South Rasmussen (or South Rasmussen  
58 Ridge) mine began with the issuance of a lease to Monsanto in 2001 by the Bureau of Land  
59 Management (BLM). Specimen collecting at the South Rasmussen mine in 2010 by then mine  
60 geologist John Keefner and one of the authors (TAL) yielded crystals of the new mineral  
61 Phosphovanadylite-Ca, described herein. Interestingly, the new mineral occurs in association  
62 with native Se.

63 Phosphovanadylite-Ca is named as the Ca-dominant analogue of phosphovanadylite.  
64 The new mineral and name has been approved by the Commission on New Minerals,  
65 Nomenclature, and Classification (CNMNC) of the International Mineralogical Association  
66 (IMA 2011–101). The description of the mineral is based upon material from five cotype  
67 specimens now deposited in the collections of the Natural History Museum of Los Angeles  
68 County, 900 Exposition Boulevard, Los Angeles, CA 90007, U.S.A., catalogue numbers  
69 63578, 63579, 63580, 63581, and 63582. The CNMNC has also approved the name change  
70 for the original phosphovanadylite to phosphovanadylite-Ba.

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## OCCURRENCE

73 Phosphovanadylite-Ca occurs at the South Rasmussen (or South Rasmussen Ridge)  
74 phosphate mine, Soda Springs, Caribou County, Idaho, U.S.A. ( $42^\circ 51' \text{N}$ ,  $111^\circ 21' \text{W}$ ). The  
75 mineral was found on surfaces and in thin seams in a black mudstone rich in phosphate and

76 organic material on the 6740 foot bench of the open pit, about 300 feet (90 m) below the  
77 original topography. Sincosite, native Se, and an unidentified Ca-Fe vanadate occur in direct  
78 association with the new mineral. The matrix contains fine-grained quartz, massive, porous  
79 fluorapatite and hydroxylapatite, framboidal pyrite (10  $\mu\text{m}$ ), and tiny, euhedral sphalerite  
80 crystals (Bart Cannon, personal communication). Other minerals noted in the same horizon  
81 are cacoxenite, fluellite, hawleyite, minyulite, and wavellite.

82         The mineral occurs in the Mead Peak Member of the Permian Phosphoria Formation,  
83 which is notable for abundant and widespread beds that are enriched in vanadium, including  
84 one, the vanadiferous zone, that contains up to 1 wt%  $\text{V}_2\text{O}_5$  (Love, 1961; McKelvey et al.,  
85 1986). Piper and Medrano (1994) describe in detail the stratigraphy and geochemistry of the  
86 Phosphoria Formation, and Medrano et al. (1998) in their description of phosphovanadylite  
87 provide a summary of the stratigraphy and areal distribution of the Mead Peak Member and  
88 its secondary vanadium minerals, including sincosite, hewettite, and pascoite. The occurrence  
89 of phosphovanadylite-Ca is essentially identical to that described by Medrano et al. (1998) for  
90 phosphovanadylite from the nearby and now-reclaimed Enoch Valley phosphate mine.  
91 Phosphovanadylite, in close association with sincosite, was collected from a vanadium-rich  
92 bed stratigraphically well below the vanadiferous zone, as is the case for phosphovanadylite-  
93 Ca.

94         Regarding the stability conditions for phosphovanadylite formation, under acidic  
95 conditions, such as in the presence of abundant pyrite, vanadium would be expected to be +5.  
96 Medrano et al. (1998) however concluded that the presence of carbonate and organic matter in  
97 the dark-colored matrix rock was, with pyrite absent and under near neutral acidic conditions,  
98 sufficient to reduce V to the +4 state. In spite of the presence of very minor pyrite in the  
99 matrix hosting phosphovanadylite-Ca, we believe its environment of formation to be  
100 generally consistent with that of phosphovanadylite, except for the presence of significant Ba

101 in the latter case. Phosphovanadylite-Ca crystallized at ambient temperatures from late-stage  
102 aqueous solutions of near neutral pH under relatively reducing conditions.

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#### PHYSICAL AND OPTICAL PROPERTIES

105 Phosphovanadylite-Ca occurs as small, greenish-blue cubes (to 0.1 mm on edge)  
106 intergrown to form thin crusts (Fig. 1). The cube, {100}, is always prominent; it is rarely  
107 modified by a small and less-well-formed octahedron, {111}. Penetration twinning on {111}  
108 is common. The color is bright greenish blue. On long-term (about one year) exposure to  
109 sunlight, the mineral gradually turns from greenish blue to green and then black. The colour  
110 change is probably due to the partial oxidation of  $V^{4+}$  to  $V^{5+}$ , with the blackening being due to  
111  $V^{4+}$ - $V^{5+}$  charge transfer. The streak is very pale greenish blue and the luster is vitreous. The  
112 Mohs hardness is about 2. The new mineral is brittle with irregular fracture and no cleavage.  
113 The density measured by sink-float in an aqueous solution of sodium polytungstate is 2.02(3)  
114  $g/cm^3$ . The calculated density based on the empirical formula is 2.038  $g/cm^3$ . The mineral is  
115 isotropic with the index of refraction  $n = 1.559(2)$  determined in white light; it is greenish  
116 blue in plane-polarized light. Phosphovanadylite-Ca dissolves slowly in cold, concentrated  
117 acids (HCl,  $H_2SO_4$ , and  $HNO_3$ ). In  $HNO_3$ , it quickly turns from greenish blue to orangish  
118 yellow, presumably due to the oxidation of  $V^{4+}$  to  $V^{5+}$ .

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#### CHEMICAL COMPOSITION

121 Analyses (18 from 12 crystals) were performed at the University of Utah on a Cameca  
122 SX-50 electron microprobe with four wavelength-dispersive spectrometers. Analytical  
123 conditions were 15 kV accelerating voltage, 10 nA beam current and a nominal beam  
124 diameter of 10-15  $\mu m$ . Counting times were 10 seconds for each element. Raw X-ray  
125 intensities were corrected for matrix effects with a phi-rho-z algorithm (Pouchou and Pichoir,

126 1991). The grains exhibit only minor visible damage from the electron beam. A single  
127 determination on a 1.1 mg sample using a CEC 440HA CHN analyzer in the Marine Science  
128 Institute, University of California, Santa Barbara provided 27.57 wt% H<sub>2</sub>O. The small CHN  
129 sample size and minor sample impurities from attached matrix suggest that this measurement  
130 is of relatively low reliability.

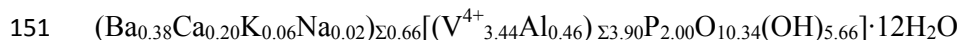
131 Several factors contributed to problems in unambiguously establishing the H<sub>2</sub>O  
132 content of phosphovanadylite-Ca:

- 133 (1) Highly hydrated phases with loosely held water often provide high EMPA totals, due to  
134 partial dehydration under vacuum, and we believe this to be true in this case.
- 135 (2) The water from CHN, even when combined with an EMPA normalized to 100%, yields  
136 only 7.42 molecules of zeolitic H<sub>2</sub>O pfu, much less than the 12 molecules reported for  
137 phosphovanadylite (Medrano et al., 1998).
- 138 (3) The structure determination is consistent with 14.2 molecules of zeolitic H<sub>2</sub>O; however,  
139 because the H<sub>2</sub>O molecules are located at numerous disordered sites (with high  
140 displacement parameters), this value could very well be too high.

141 We ultimately decided that the best compromise was to calculate H<sub>2</sub>O based upon the same  
142 content of zeolitic water as was reported for phosphovanadylite and to the normalize the  
143 EMPA to 100% accordingly. The relatively close match between the measured and calculated  
144 densities further supports this approach. Analytical data are given in Table 1.

145 The empirical formula (based on 2 P and 28 O apfu) is, with rounding errors,  
146  $(\text{Ca}_{0.75}\text{K}_{0.09}\text{Na}_{0.05}\text{Ba}_{0.01}\text{Sr}_{0.01})_{\Sigma 0.91}[(\text{V}^{4+}_{3.27}\text{Al}_{0.49})_{\Sigma 3.76}\text{P}_{2.00}\text{O}_{10.23}(\text{OH})_{5.77}] \cdot 12\text{H}_2\text{O}$ . The simplified  
147 formula is  $\text{Ca}[\text{V}^{4+}_4\text{P}_2\text{O}_8(\text{OH})_8] \cdot 12\text{H}_2\text{O}$ , which requires CaO 6.86, VO<sub>2</sub> 40.56, P<sub>2</sub>O<sub>5</sub> 17.35, H<sub>2</sub>O  
148 35.24, total 100.00 wt%. The Gladstone-Dale compatibility index  $1 - (K_p/K_c)$  is -0.028 for  
149 the empirical formula, indicating excellent compatibility (Mandarino, 1981). For comparison,

150 the empirical formula of phosphovanadylite-Ba reported by Medrano et al. (1998) is



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154 **X-RAY CRYSTALLOGRAPHY AND STRUCTURE DETERMINATIONS**

155 All powder and single-crystal X-ray diffraction data were obtained on a Rigaku R-Axis Rapid

156 II curved imaging plate microdiffractometer utilizing monochromatized  $\text{MoK}\alpha$  radiation.

157 Observed powder  $d$ -values (with standard deviations) and intensities were derived by profile

158 fitting using JADE 9.3 software. Data (in Å) are given in Table 2. Unit cell parameters refined

159 from the powder data using JADE 9.3 with whole pattern fitting are:  $a = 15.457(3)$  Å and  $V =$

160  $3693(1)$  Å<sup>3</sup>. The observed powder data fit well with those calculated from the structure, also

161 using JADE 9.3.

162 The Rigaku CrystalClear software package was used for processing of the diffraction

163 data, including the application of an empirical multi-scan absorption correction using

164 ABSCOR (Higashi 2001). We used the atom coordinates for the framework atoms (V, P, O1,

165 O2, and O3) reported for phosphovanadylite-Ba (Medrano et al., 1998) as a starting point.

166 SHELXL-97 software (Sheldrick 2008) was used for the refinement of the structure. The

167 channel sites were located in difference Fourier maps. Unfortunately, the small crystal size

168 and low diffracting power of phosphovanadylite-Ca provided useful data only to  $15.92^\circ \theta$ .

169 Thus, with only 188 unique reflections and 68 refined parameters, the reflection to parameter

170 ration (2.76) is considered poor.

171 In the final refinement, all framework sites were assigned full occupancy with the

172 V/Al site assigned occupancy by 0.83 V and 0.13 Al, in keeping with the relative amounts of

173 these cations indicated by the chemical analyses. Coincidentally, this is the same occupancy

174 used for this site by Medrano et al. (1998). Initially, all of the channel sites were assumed to

175 be O atoms and their occupancies were refined. The OW1 site refined to 1.21(5) occupancy  
176 by O and was the only channel site that refined to greater than full occupancy. Consequently,  
177 we assigned both Ca and O to the site with Ca occupancy held at 0.25 (corresponding to one  
178 Ca apfu) and refined the O occupancy to 0.61(5) O.

179 Details concerning data collection and structure refinement are provided in Table 3.  
180 Site occupancies, fractional coordinates, and atom displacement parameters are provided in  
181 Table 4, and selected interatomic distances in Table 5.

182

### 183 DESCRIPTION OF THE STRUCTURE

184 The structure of phosphovanadylite-Ca (Fig. 2) contains  $V^{4+}_4O_{16}$  polyvanadate clusters  
185 of four edge-sharing  $V^{4+}O_6$  octahedra. The polyvanadate clusters are linked into a three-  
186 dimensional zeolite-type framework by sharing corners with  $PO_4$  tetrahedra. The open space  
187 in the framework is dominated by  $H_2O$  with the equivalent of one large cation pfu sharing the  
188 OW1 site. The  $V^{4+}_4P_2O_{16}$  framework is essentially identical to that in phosphovanadylite-Ba  
189 (Medrano et al., 1998); however, in phosphovanadylite-Ba the dominant extra-framework  
190 cation is Ba, while in phosphovanadylite-Ca, it is Ca.

191 The V–O and P–O bond lengths are consistent with those in phosphovanadylite-Ba.  
192 As noted for phosphovanadylite-Ba, the V coordination is characteristic of octahedral  $V^{4+}$  and  
193 the bond-valence sum of 3.95 *vu* is further confirmation of its 4+ valence state. The bond-  
194 valence analysis, only considering the framework atoms, indicates that all of the framework O  
195 atoms have bond-valence sums (BVS) significantly less than 2 *vu*. The BVS for O1 of 1.85 *vu*  
196 is consistent with it being an O atom and it probably receives at least one hydrogen bond from  
197 OW4 at distances of 3.05 and 3.24 Å. The BVS for O2 is 1.44 and that for O3 is 1.29 *vu*.  
198 Several channel  $H_2O$  sites (OW2, OW3, OW4, OW5, and OW7) are close enough to the O2  
199 site to contribute hydrogen bonds, but it is unlikely that bond-valence balance can be achieved



200 through hydrogen bonding alone, so it is likely that O2 has some OH character. The Ca/OW1  
201 certainly provides additional bond-valence to O3, both as a Ca–O bond and a hydrogen bond;  
202 nevertheless, it is clear that O3 must have significant OH character. The ideal formula,  
203  $\text{Ca}[\text{V}^{4+}_4\text{P}_2\text{O}_8(\text{OH})_8]\cdot 12\text{H}_2\text{O}$ , requires that half of the O atoms in the framework are OH and, as  
204 noted above, these must be accommodated at the O2 and O3 sites.

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

209

#### 210 ACKNOWLEDGEMENTS

211 The paper benefited from comments by associate editor Andrew M. McDonald. This  
212 study was funded by the John Jago Trelawney Endowment to the Mineral Sciences  
213 Department of the Natural History Museum of Los Angeles County.

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241

## FIGURE CAPTIONS

242

243 Figure 1. SEM image of phosphovanadylite-Ca.

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245 Figure 2. The crystal structure of phosphovanadylite-Ca viewed down [001]. The  $V^{4+}O_6$   
246 octahedra and  $PO_4$  tetrahedra are dark gray. The Ca atoms are small dark gray spheres and O  
247 atoms of  $H_2O$  molecules are large white spheres. Note that the Ca site is occupied by both Ca  
248 and  $H_2O$ , and that most O sites are partially occupied. The Ca–O bonds are shown and the  
249 unit cell is outlined by dashed lines.

250

251

252 Table 1. Chemical analytical data for phosphovanadylite-Ca.

Constituent	wt%	Range	SD	Standard	Norm. wt. %
Na <sub>2</sub> O	0.26	0.04–0.52	0.13	albite	0.22
K <sub>2</sub> O	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 <sub>3</sub>	0.10
BaO	0.25	0.15–0.40	0.08	barite	0.21
Al <sub>2</sub> O <sub>3</sub>	3.91	3.21–4.73	0.41	sanidine	3.27
VO <sub>2</sub>	42.84	40.63–46.28	1.47	syn. YVO <sub>4</sub>	35.85
P <sub>2</sub> O <sub>5</sub>	22.44	20.98–24.00	0.81	fluorapatite	18.78
H <sub>2</sub> O	27.57			from CHN	35.44*
Total	104.73				100.00

253 \*Calculated based upon sufficient H for charge balance and 12 molecules of zeolitic H<sub>2</sub>O.  
 254 *Note:* MgO was sought, but found to be below the limit of detection, 0.03 wt.%.  
 255

256

257 Table 2. X-ray powder diffraction data for phosphovanadylite-Ca.

258

$I_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{calc}}$	$hkl$	$I_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{calc}}$	$hkl$
97	11.04(3)	10.9184	100	110	10	1.8897(7)	1.8725	5	820
100	7.7881(12)	7.7205	85	200			1.8456	1	653
6	6.373(8)	6.3038	5	211	16	1.8295(13)	1.8197	8	822
7	5.498(5)	5.4592	7	220			1.7950	2	743
11	4.922(3)	4.8829	9	310			1.7712	1	662
14	4.487(2)	4.4574	12	222	4	1.730(3)	1.7264	3	840
8	4.154(3)	4.1268	7	321	4	1.6895(6)	1.6848	3	842
9	3.662(3)	3.6395	5	411			1.6650	1	655
5	3.327(5)	3.2920	4	332	2	1.6436(15)	1.6460	1	664
46	3.1706(5)	3.1519	38	422			1.6276	2	851
13	3.0413(15)	3.0282	11	431			1.5926	1	763
10	2.8378(12)	2.8191	10	521			1.5759	1	844
32	2.749(2)	2.7296	8	440			1.5598	1	770
		2.6481	2	530	7	1.5579(7)	1.5441	5	860
11	2.590(4)	2.5735	9	600			1.5141	1	862
10	2.5202(19)	2.5049	7	611	9	1.4972(9)	1.4998	2	943
14	2.4576(3)	2.4414	11	620			1.4858	2	1022
15	2.3426(11)	2.3278	4	622			1.4722	1	1031
6	2.2080(13)	2.2287	3	444			1.4462	2	871
		2.1837	3	710			1.4337	1	864
10	2.1081(9)	2.1013	6	721	2	1.4199(8)	1.4096	2	1042
		2.0634	2	642			1.3980	1	954
13	1.9403(6)	1.9301	6	800			1.3756	1	963
		1.9007	2	811	10	1.3672(7)	1.3648	4	880

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260

261 Table 3. Data collection and structure refinement details for phosphovanadylite-Ca.  
 262

263	Diffractometer	Rigaku R-Axis Rapid II
264	X-ray radiation / power	MoK $\alpha$ ( $\lambda = 0.71075 \text{ \AA}$ )
265	Temperature	298(2) K
266	Structural Formula	Ca[(V <sup>4+</sup> <sub>3.33</sub> Al <sup>3+</sup> <sub>0.67</sub> ) <sub>4</sub> P <sub>2</sub> O <sub>11.33</sub> (OH) <sub>4.67</sub> ] $\cdot$ 14.21H <sub>2</sub> O
267	Space group	<i>I</i> -43 <i>m</i>
268	Unit cell dimension	<i>a</i> = 15.441(11) $\text{\AA}$
269	<i>V</i>	3682(5) $\text{\AA}^3$
270	<i>Z</i>	6
271	Density (for above formula)	2.106 g cm <sup>-3</sup>
272	Absorption coefficient	1.716 mm <sup>-1</sup>
273	<i>F</i> (000)	2396
274	Crystal size	70 $\times$ 70 $\times$ 40 $\mu\text{m}$
275	$\theta$ range	3.23 to 15.92 $^\circ$
276	Index ranges	$-11 \leq h \leq 11, -11 \leq k \leq 11, -11 \leq l \leq 11$
277	Reflections collected/unique	1215/188 [ <i>R</i> <sub>int</sub> = 0.068]
278	Reflections with <i>F</i> <sub>o</sub> > 4 $\sigma$ <i>F</i>	171
279	Completeness to $\theta = 15.92^\circ$	98.2%
280	Max. and min. transmission	0.935 and 0.889
281	Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
282	Parameters refined	68
283	GoF	1.174
284	Final <i>R</i> indices [ <i>F</i> <sub>o</sub> > 4 $\sigma$ ( <i>F</i> )]	<i>R</i> <sub>1</sub> = 0.0272, w <i>R</i> <sub>2</sub> = 0.0534
285	<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0331, w <i>R</i> <sub>2</sub> = 0.0560
286	Absolute structure parameter	0.05(13)
287	Largest diff. peak, hole	+0.16, -0.13 e $\text{\AA}^{-3}$
288	<i>Notes:</i> <i>R</i> <sub>int</sub> = $\Sigma F_o^2 - F_o^2(\text{mean}) /\Sigma[F_o^2]$ . GoF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ . <i>R</i> <sub>1</sub> = $\Sigma F_o  -$	
289	$ F_c /\Sigma F_o $ . w <i>R</i> <sub>2</sub> = $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ . $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where <i>a</i> is	
290	0.024, <i>b</i> is 0 and <i>P</i> is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$ .	

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

292

293		occ.*	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>
294	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)
295	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
296	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)
297	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)
298	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)
299	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)
300	OW2	1	0.2938(19)	0.2938(19)	0.2938(19)	0.194(17)	0.194(17)	0.194(17)	0.194(17)	0.05(2)	0.05(2)	0.05(2)
301	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)
302	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)
303	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)
304	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)
305	OW7	0.20(9)	0.295(11)	0.596(6)	-0.596(6)	0.15(6)						

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

307

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

309	V–O2	1.631(11)	Ca–OW6	2.40(3)
310	V–O1(×2)	1.951(8)	Ca–OW7	2.50(18)
311	V–O3(×2)	1.998(8)	Ca–O3	2.676(18)
312	V–O3	2.307(10)	Ca–OW4	2.99(4)
313	<V–O>	1.973	Ca–OW2	3.03(4)
314				
315	P–O1(×4)	1.537(7)		

316

317 Table 6. Bond valence sums for the framework atoms in the structure of phosphovanadylite-Ca.  
318 Values are expressed in valence units.

319

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

320

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

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323



