The Canadian Mineralogist
Vol. 57, pp. 245-253 (2019)
DOI: 10.3749/canmin.1800069

IDENTIFYING PROTONATED DECAVANADATE POLYANIONS

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ABSTRACT

The decavanadate anion, $[V_{10}O_{28}]^{6-}$, is a common constituent in vanadate minerals and synthetic materials, and both protonated, $[H_xV_{10}O_{28}]^{(6-x)-}$, and mixed-valent, $[(V^{4+}{}_xV^{5+}{}_{10-x})O_{28}]^{(6+x)-}$, varieties also occur. Here we examine recent structure refinements containing protonated decavanadates in order to develop simple criteria to help identify specific O_D atom(s) belonging to (OH) groups of the decavanadate polyanion. Non-protonated O atoms on the surface of the decavanadate polyanion (*i.e.*, [1]-, [2]-, and [3]-coordinated O atoms) have incident bond-valence sums from V atoms in the range ~1.7–2.0 *vu*. Protonated O atoms on the exterior have incident bond-valence sums from V atoms in the range ~1.2–1.5 *vu* and are either [3]-coordinated or [2]-coordinated by V atoms. All hydrogen bonds are directed toward a neighboring decavanadate polyanion in which the O_A (acceptor) anions are 2.61–3.08 Å from their respective O_D (donor) anions on the adjacent polyanion, and there is a linear relation between the $O_D...O_A$ distance and the incident bond-valence received by O_D from the bonded V atoms. For well-refined structures, the incident bond-valence sums from V atoms and the associated $O_D...O_A$ distances suffice to identify protonation of the decavanadate polyanion and the specific anion(s) that is (are) protonated. These criteria show that one structure reported as protonated is not protonated, and one structure reported as containing a mixed $V^{4+/5+}$ protonated decavanadate polyanion contains only V^{5+} and is not protonated, and another structure also reported as containing a mixed $V^{4+/5+}$ protonated decavanadate polyanion contains both V^{4+} and V^{5+} but is not protonated.

Keywords: decavanadate polyanion, vanadate minerals, mixed-valence $V^{4+/5+}$, protonation, bond valence.

INTRODUCTION

The $[V_{10}O_{28}]^{6-}$ decavanadate polyanion is a cluster of eight (VO_6) octahedra with [1+4+1] coordination and two (VO_6) octahedra with [2+2+2] coordination, in which the O atoms are coordinated by 1, 2, 3 or 6 V atoms (Fig. 1). It is a common constituent of secondary vanadium minerals that form from oxidation of primary vanadium minerals in ore bodies exposed to near-surface conditions. Decavanadates are also important as catalysts (*e.g.*, Csányi *et al*. 2003, Valverde *et al*. 2012) and as inhibitors of bacterial growth (*e.g.*, Gillet *et al*. 2016, Samart *et al*. 2018). The decavanadate anion, $[V_{10}O_{28}]^{6-}$, is stable at mildly acidic conditions and relatively high Eh. At lower pH, protonated derivatives occur: $[H_xV_{10}O_{28}]^{(6-x)-}$; at more reducing conditions, mixed-valence decavanadate anions, $[(V^{4+}{}_xV^{5+}{}_{10-x})O_{28}]^{(6+x)-}$, are common. In the last 16 years, the atomic arrangements of 18 decavanadate minerals have been determined and refined (Table 1). The structures consist of negatively charged decavanadate clusters, the structural unit, linked by weakly bonded interstitial complexes consisting of monovalent and divalent (simple or

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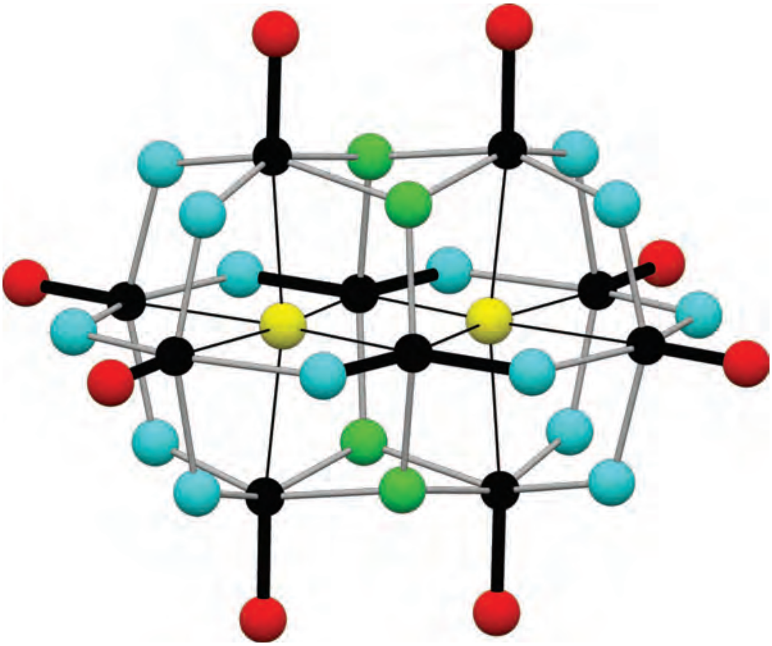

FIG. 1. The $[V_{10}O_{28}]^{n-}$ decavanadate polyanion. V atoms = black circles, [1]-coordinated O atoms = red circles, [2]-coordinated O_C atoms = blue circles, [3]-coordinated O_B atoms = green circles, [6]-coordinated O atoms = yellow circles, V–$O_{vanadyl}$ bonds = thick black line, V–O_{trans} bonds = thin black line, V–$O_{equatorial}$ bonds = grey shaded line. Known O_D sites: $^{[2]}$C- and $^{[3]}$B-type anions (Day *et al.* 1987).

complex) cations and (H_2O) groups, and are consistent with the idea of binary representation of structure whereby a complicated structure is considered as two parts, a strongly bonded structural unit and a weakly bonded interstitial complex (Hawthorne 1983, Hawthorne & Schindler 2008, Schindler *et al.* 2000). In order to examine the interaction of these two constituents, we need to derive the Lewis basicity of the decavanadate polyanion, which is a function of the net charge of the polyanion, which in turn depends on (1) the amounts of V^{4+} and V^{5+}, and (2) the presence of any protonated anions in the polyanion. Cooper *et al.* (2019) addressed the issue of calculating the site occupancies of V^{4+} and V^{5+} in non-protonated decavanadates. The interstitial complexes of decavanadate minerals are commonly disordered and more poorly characterized relative to the more robust decavanadate polyanion. The final charge balance between the decavanadate polyanion and the interstitial complex is sometimes achieved *via* speculative assignment of protons to exterior anions of the decavanadate group. Here we address the issue of deriving the number of H^+ ions in protonated decavanadates *via* a more quantitative assessment of prospective O_D (*i.e.*, O_{DONOR}) and O_A ($O_{ACCEPTOR}$) anions. Issues involving O_D and O_A in synthetic decavanadates have been examined previously: Ferreira da Silva *et al.* (2003) and Correia *et al.* (2004) examined the effect of protonation and hydrogen bond donor-acceptor relations on the polymerization of decavanadate polyanions; and Bošnjaković-Pavlović *et al.* (2011) showed that the strengths of hydrogen bonds are strongly dependent on the connectivity of the anions to V, and suggest that this could be a key to understanding the physiological functions of decavanadates.

GENERAL APPROACH

Here we examine recent structure refinements containing known protonated decavanadates with the intent of developing simple criteria to help identify specific O_D and O_A atom(s) belonging to the decavanadate polyanion. Direct detection of a H atom belonging to an (OH) group from residual electron-density in a difference-Fourier map at the final stages of structure refinement is often not possible in these structures, particularly in minerals, because of disorder in the structure, and a more general crystal-chemical approach is required.

Using bond-valence sums for decavanadate O atoms, Evans & Popev (1984) showed that long V–O

TABLE 1. RECENTLY CHARACTERIZED DECAVANADATE MINERALS

Mineral species	Ideal formula*	First reference, best structure reference
	Decavanadates: $[V_{10}O_{28}]^{6-}$	
Ammoniolasalite	$\{(NH_4)_2Mg_2(H_2O)_{20}\}\ [V_{10}O_{28}]$	Kampf *et al.* 2018a
Burroite	$\{(NH_4)_2Ca_2(H_2O)_{15}\}[V_{10}O_{28}]$	Kampf *et al.* 2017a
Huemulite	$\{Na_4Mg(H_2O)_{24}\}\ [V_{10}O_{28}]$	Gordillo *et al.* 1966, Colombo *et al.* 2011
Hughesite	$\{Na_3Al(H_2O)_{22}\}\ [V_{10}O_{28}]$	Rakovan *et al.* 2011
Hummerite	$\{[K_2Mg_2(H_2O)_{16}\}\ [V_{10}O_{28}]$	Weeks *et al.* 1951, Hughes *et al.* 2002
Hydropascoite**	$\{Ca_3(H_2O)_{24}\}\ [V_{10}O_{28}]$	Kampf *et al.* 2017b
Kokinosite	$\{Na_2Ca_2(H_2O)_{24}\}\ [V_{10}O_{28}]$	Kampf *et al.* 2014a
Lasalite	$\{Na_2Mg_2(H_2O)_{20}\}\ [V_{10}O_{28}]$	Hughes *et al.* 2008
Magnesiopascoite	$\{Ca_2Mg(H_2O)_{16}\}\ [V_{10}O_{28}]$	Kampf & Steele 2008
Okieite	$\{Mg_3(H_2O)_{27}\}\ [V_{10}O_{28}]$	Kampf *et al.* 2018b
Pascoite	$\{Ca_3(H_2O)_{17}\}\ [V_{10}O_{28}]$	Hillebrand *et al.* 1914, Hughes *et al.* 2005
Postite	$\{MgAl_2(OH)_2(H_2O)_{27}\}\ [V_{10}O_{28}]$	Kampf *et al.* 2012
Schindlerite	$\{(NH_4)_4Na_2(H_2O)_{10}\}\ [V_{10}O_{28}]$	Kampf *et al.* 2013a, Kampf *et al.* 2016
Wernerbaurite	$\{(NH_4)_2Ca_2(H_2O)_{16}\}\ [V_{10}O_{28}]$	Kampf *et al.* 2013a, Kampf *et al.* 2016
	Protonated Decavanadates: $[H_xV_{10}O_{28}]^{(6-x)-}$	
Gunterite	$\{Na_4(H_2O)_{22}\}\ [H_2V_{10}O_{28}]$	Kampf *et al.* 2011a
Rakovanite***	$\{Na_3(H_2O)_{15}\}\ [H_3V_{10}O_{28}]$	Kampf *et al.* 2011b
	Mixed-Valence Decavanadates: $[(V^{4+}{}_xV^{5+}{}_{10-x})O_{28}]^{(6+x)-}$	
Bluestreakite	$\{K_4Mg_2(H_2O)_{14}\}\ [V^{4+}{}_2V^{5+}{}_8O_{28}]$	Kampf *et al.* 2014b
Nashite	$\{Na_3Ca_2(H_2O)_{24}\}\ [(V^{4+}V^{5+}{}_9)O_{28}]$	Kampf *et al.* 2013b

* Expressed as the interstitial complex and the structural unit.

** Kampf *et al.* (2017b) proposed that, in hydropascoite, a small amount of V is tetravalent and there is some protonation to balance the charge; however, the ideal formula is written with all V^{5+} and no protonation.

*** The formula for rakovanite is probably $[(NH_4)_3Na_3(H_2O)_{12}]\ [V_{10}O_{28}]$.

bonds are associated with O_D atoms. A recent analysis of bond valence in the structures of many decavanadate minerals showed that the bond-valence equation of Brown & Altermatt (1985) for V^{5+}–O interactions is accurate in validating the formal valence of V only in decavanadates containing only V^{5+}. Cooper *et al.* (2019) developed a bond-valence equation that predicts site-specific V^{4+} content; this equation may also be used to calculate accurate sums of the bond valence incident at the decavanadate O atoms for high-quality structure-refinements, as these have accurate V–O bond-lengths.

PROTONATED DECAVANADATES

Seventeen well-characterized protonated decavanadate structures that contain either inorganic or organic interstitial components were used in this work (Table 2). The structures are well ordered, recent (1987–2015), have low *R* values ($R < 10\%$), and contain only V^{5+}. For many of these decavanadates, the H atoms belonging to the decavanadate (OH) group were located experimentally. The protonated decavanadate polyanions contain from one to four H atoms that form ordered (OH) groups on the exterior of the decavanadate groups at specific O sites.

Bond-valence sums at the decavanadate anions

We calculated partial bond-valence sums at the decavanadate anions resulting from the V–O interactions alone ($s\ \Sigma_{OV}$) using the V^{5+}–O equation of Brown & Altermatt (1985). Non-protonated O atoms on the surface of the decavanadate polyanion (*i.e.*, bonded to one, two, or three V atoms) have $s\ \Sigma_{OV}$ values from ~1.7–2.0 *vu* (Table 2), and the remaining bond-valence received by these anions to satisfy the valence-sum rule comes from interstitial constituents or from hydrogen bonds from a neighboring decavanadate (OH) group. Protonated O atoms on the exterior of the polyanion have significantly lower $s\ \Sigma_{OV}$ values, from ~1.2–1.5 *vu*, and occur for two specific types of O atoms: (1) [3]-coordinated O atoms [denoted here as O_B] and (2) [2]-coordinated O atoms [denoted here as O_C] (nomenclature of Day *et al.* 1987) (Fig. 1, Table 1).

TABLE 2. MISCELLANEOUS INFORMATION FOR 17 PROTONATED DECAVANADATES

[POV]	Interstitial component	$s\ \Sigma_{OV}$* (*vu*)	O_D type**	$O_D...O_A$ (Å)	Ref.
$[HV_{10}O_{28}]$	$K_4Na(H_2O)_{10}$	1.49	C	3.03	[1]
$[HV_{10}O_{28}]$	$Rb_4Na(H_2O)_{10}$	1.52	C	3.08	[2]
$[HV_{10}O_{28}]$	$[NH_2(CH_2)_4]_5$	1.36	C	2.65	[3]
$[H_2V_{10}O_{28}]$	$(C_7H_{14}N)_4$	1.15	C	2.88	[4]
$[H_2V_{10}O_{28}]$	$[(CH_3)_3CNH_3]_4$	1.23	C	2.77	[5]
$[H_2V_{10}O_{28}]$	$Cs_4(H_2O)_4$	1.28	C	2.61	[6]
$[H_2V_{10}O_{28}]$	$[N(CH_3)_4]_4(CH_3COOH)(H_2O)_{2.8}$	1.26	C	2.75	[7]
		1.31	B	2.75	
$[H_2V_{10}O_{28}]$	$[CH_3(CH_2)_{11}N(CH_3)_3]_4(H_2O)_8$	1.22	C	2.76	[8]
$[H_2V_{10}O_{28}]$	$[(CH_3)_4N]_4(H_2O)_{3.8}$	1.29	C	2.76	[9]
		1.34	B	2.77	
$[H_3V_{10}O_{28}]$	$(C_6H_8N)_3(H_2O)$	1.29	C	2.74	[10]
		1.32	B	2.80	
		1.29	C	2.75	
$[H_3V_{10}O_{28}]$	$(C_7H_{10}N)_3(H_2O)$	1.30	B	2.81	[11]
		1.27	C	2.74	
		1.24	C	2.73	
$[H_3V_{10}O_{28}]$	$[(C_6H_5)_4P]_3(CH_3CN)_4$	1.27	B	2.76	[12]
		1.29	C	2.76	
		1.25	C	2.78	
$[H_3V_{10}O_{28}]$	$[(C_2H_5)_4N]_3(H_2O)_2$	1.24	C	2.76	[9]
		1.26	B	2.76	
		1.24	C	2.76	
$[H_3V_{10}O_{28}]$	$[(n\text{–}C_3H_7)_4N]_3$	1.26	C	2.79	[9]
		1.29	B	2.89	
		1.23	C	2.96	
$[H_3V_{10}O_{28}]$	$[(n\text{–}C_4H_9)_4N]_3$	1.26	C	2.76	[9]
		1.31	B	2.81	
		1.31	C	2.78	
$[H_4V_{10}O_{28}]$	$[(n\text{–}C_3H_7)_4N]_2$	1.38	B	2.70	[9]
		1.37	C	2.72	
$[H_4V_{10}O_{28}]$	$[(n\text{–}C_4H_9)_4N]_2$	1.36	B	2.72	[9]
		1.36	C	2.74	

References: [1] Lee & Joo (2004); [2] Yakubovich *et al.* (2015); [3] Jouffret *et al.* (2010); [4] Riou *et al.* (1998); [5] Wery *et al.* (1996); [6] Tatyanina *et al.* (1987); [7] Pecquenard *et al.* (1998); [8] Janauer *et al.* (1997); [9] Nakamura & Ozeki (2001); [10] Santiago *et al.* (1988); [11] Arrieta *et al.* (1988); [12] Day *et al.* (1987).

* Bond valence from V–O_D contributions using Brown & Altermatt (1985); ** Day *et al.* (1987).

Hydrogen-bond-acceptor anions for decavanadate (OH) groups

For the seventeen protonated decavanadate structures examined, there are 33 individual (OH) groups associated with either $^{[3]}O_B$ or $^{[2]}O_C$ anions of the decavanadate polyanion (Table 2). All hydrogen bonds are directed toward a neighboring decavanadate polyanion in which the O_A anions are 2.61–3.08 Å from their respective O_D anions on the adjacent polyanion. Figure 2 shows the variation in $O_D...O_A$ distance as a function of $s\ \Sigma_{OV}$ values for the respective O_D anions. The line through the data in the lower part of Figure 2 has a negative slope that is consistent with longer $O_D...O_A$ distances (and weaker hydrogen bonds) coupled to lower incident bond-valence received by the O_D from the bonded V atoms. This relation is in good agreement with the valence-sum rule (Brown 2016). Strong V–O bonds provide ~1.4 *vu* to O_D and the H atom provides ~0.6 *vu* to O_D to satisfy the valence-sum rule at O_D. In turn, the valence-sum rule at the H atom requires a relatively strong hydrogen bond (~0.4 *vu*) to a close O_A anion (*i.e.*, $O_D...O_A \approx 2.6$ Å) of a neighboring decavanadate polyanion. Weak V–O bonds provide ~1.2 *vu* to O_D and the H atom provides ~0.8 *vu* to O_D to satisfy the valence-sum rule at O_D. The valence-sum rule at the H atom requires a weaker hydrogen bond (~0.2 *vu*) to an O_A anion (*i.e.*, $O_D...O_A \approx 2.9$ Å) of a neighboring

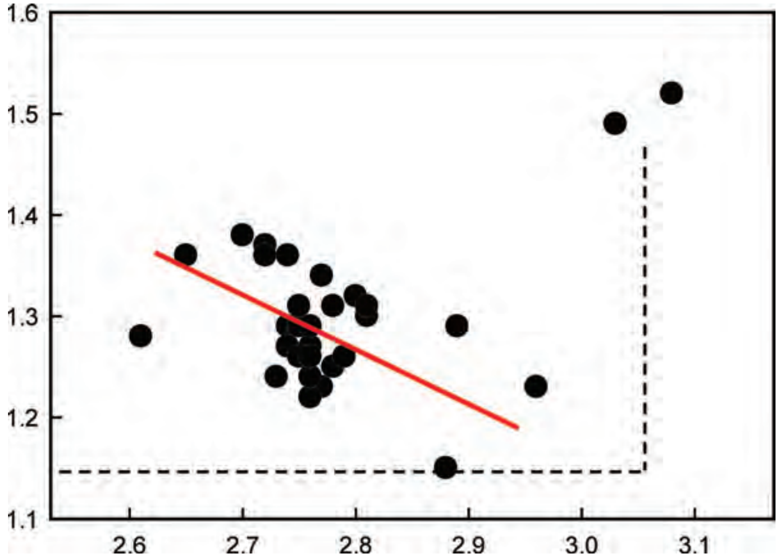

FIG. 2. $O_D...O_A$ distances for the 33 (OH) groups as a function of the bond valence incident at O_D from the V–O bonds alone. Solid red line: hand drawn through the ordered (OH) data; dashed lines: disordered (OH) groups extrapolated to main trend.

decavanadate polyanion. Thus, accurate assessment of the incident bond-valence to an O_D atom of a potential (OH) group on a decavanadate polyanion, coupled with its distance to a prospective O_A on a neighboring decavanadate polyanion, can provide powerful confirmation of protonation without the requirement that the H atom itself be located during structure refinement.

Two data points fall off the trend in Figure 2; these belong to two isostructural decavanadates, $K_4Na(H_2O)_{10}[HV_{10}O_{28}]$ and $Rb_4Na(H_2O)_{10}[HV_{10}O_{28}]$ (Lee & Joo 2004, Yakubovich *et al*. 2015). For this structure type, the hydrogen atom is disordered between symmetrically equivalent O_C anions on adjacent decavanadate groups (Fig. 3); whether this disorder is static or dynamic is not known. The net effect is that two local arrangements (Fig. 3a, b) occur with equal frequency. In each local arrangement, the observed $O_D...O_A$ distance of ~3.05 Å indicates that O_D will receive ~1.15 *vu* from its two bonds with V (dashed lines on Fig. 2). The remaining bond-valence (*i.e*., 2 – 1.15 = 0.85 *vu*) required to satisfy the valence-sum rule will come from the H atom, and the ensuing hydrogen-bond-valence is 0.15 *vu*. If we then average the two different bond-valences incident from the V atoms for the two arrangements [*i.e*., (1.15 + 1.85) / 2 = 1.5 *vu*], the predicted long-range value of ~1.5 *vu* is in close agreement with the value calculated from the experimental (long-range-averaged) bond lengths (Table 2, Fig. 2).

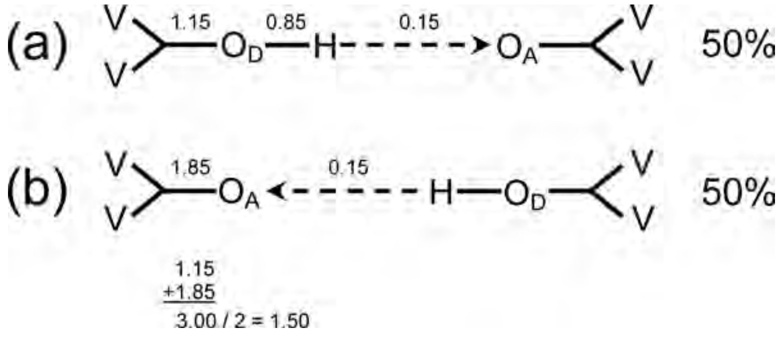

FIG. 3. The two local hydrogen-bond arrangements associated with the disordered (OH) group in $K_4Na(H_2O)_{10}[HV_{10}O_{28}]$ and $Rb_4Na(H_2O)_{10}[HV_{10}O_{28}]$, resulting in an average bond-valence contribution of 1.50 *vu* to $O_{A/D}$ from the V atoms.

Protonated decavanadate minerals

The structures reported for rakovanite and gunterite contain protonated decavanadate polyanions with the formulae $Na_3\{H_3[V_{10}O_{28}]\}(H_2O)_{15}$ and $Na_4(H_2O)_{16}(H_2V_{10}O_{28})(H_2O)_6$, respectively (Kampf *et al.* 2011a, b). For rakovanite, the orange color and bond-valence sums at the V atoms (5.00–5.11 *vu*) indicate that all V is V^{5+}. The decavanadate O atoms have $s\ \Sigma_{OV}$ sums from 1.66 to 1.98 *vu* and 1.73 to 1.92 *vu* for O_B and O_C anions specifically. The lowest $s\ \Sigma_{OV}$ value is for a vanadyl O atom that also receives additional bond-valence from interstitial Na. Thus, all decavanadate O_B and O_C atoms belonging to the rakovanite polyanion contain $s\ \Sigma_{OV}$ sums within the range ~1.7–2.0 *vu* and are expected to be unprotonated by analogy with known protonated decavanadate structures (Table 2, Fig. 2). In addition, the closest anion approach between polyanions involving at least one O_B or O_C anion is 3.41 Å, which lies well outside the range of data in Figure 2. However, we note that even though all the known protonated decavanadates investigated thus far have hydrogen bonds from (OH) groups to O_A anions on a neighboring polyanion (and thus closer $O_D\ldots O_A$ approaches; Fig. 2), there is no crystal-chemical rationale that excludes an interstitial constituent [*e.g.*, the O atom of an (H_2O) group] as a possible hydrogen-bond acceptor. The strong indication of an unprotonated decavanadate polyanion in rakovanite has led us to initiate a re-evaluation of rakovanite both chemically and structurally in terms of the interstitial components. An FTIR examination of rakovanite indicates that it contains significant NH_4^+ (Paul M. Adams, *pers. commun.*). As a result, a reinvestigation of rakovanite has been initiated, which is likely to lead to a revision of its formula. For gunterite, poor crystal quality and uncertainty in the refined structure does not allow conclusive evaluation of possible decavanadate protonation using the above crystal-chemical criteria; a better-quality refinement is needed, but FTIR examination of gunterite indicates that it does not contain significant NH_4^+ (Paul M. Adams, *pers. commun.*).

Mixed $V^{4+/5+}$ protonated decavanadates

The occurrence of V^{4+} in a decavanadate increases the net charge of the polyanion, whereas protonation decreases the net charge of the polyanion. If attainment of electroneutrality were the only constraint on polyanion charge, one would not expect mixed V^{4+}/V^{5+} protonated decavanadates to occur. On the other hand, one expects the V^{4+}/V^{5+} ratio to be sensitive to oxygen fugacity, and hence low fO_2 and a need for a high polyanion charge to attain electroneutrality might lead to mixed V^{4+}/V^{5+} protonated decavanadates. Protonation of a decavanadate polyanion requires an abnormally low value of $s\ \Sigma_{OV}$ at a potential O_D anion. This can occur *via* two mechanisms: (1) V^{5+}–O bond elongation in typical decavanadates containing only V^{5+}, or (2) incorporation of a lower-valence cation (*i.e.*, V^{4+}).

In this regard, the well-refined structure of $(H_3O)_2[M(H_2O)_6]_2[H_6V_{10}O_{28}]\cdot 4H_2O$ (M = Co,Ni) piqued our interest as the polyanion was inferred to have the composition $[H_6V^{4+}{}_6V^{5+}{}_4O_{28}]^{6-}$ (Khan *et al.* 2000). The Co and Ni variants are isostructural and we evaluated the slightly better refined (R = 5.0%) Ni structure. Application of the V^{5+}–O bond-valence parameters to $^{[6]}$V–O distances would result in an incident bond-valence sum at the V atom significantly below 5 if significant V^{4+} is ordered at the *V* site; a *V* site occupied completely by V^{4+} is expected to have an incident bond-valence sum of ~4.35 *vu* (Cooper *et al.* 2019). Bond-valence calculations for the M = Ni decavanadate of Khan *et al.* (2000) using the V^{5+}–O relation of Brown & Altermatt (1985) gives bond-valence sums from 4.99 to 5.07 *vu* for the *V* sites and from 1.70 to 1.97 *vu* for the O sites of the polyanion. We therefore conclude that the polyanion contains only V^{5+} and is unprotonated.

Hydropascoite, ideally $Ca_3(V_{10}O_{28})(H_2O)_{24}$, is yellow-green and contains minor V^{4+} at the *V*4 and *V*5 sites (Kampf *et al.* 2017b). Bond-valence calculations using the V^{5+}–O relation of Brown & Altermatt (1985) give bond-valence sums of 4.85 and 4.73 *vu*, respectively, for the *V*4 and *V*5 sites in hydropascoite. Cooper *et al.* (2019) derived an equation to predict the actual bond-valence, V_P, incident at a given *V* site: $V_P = 1.538(V_C) - 2.692$ *vu*, where V_C is the incident bond-valence sum calculated using the V^{5+}–O equation of Brown & Altermatt (1985). Application of this equation gives a composition of $(V^{5+}{}_{0.77}V^{4+}{}_{0.23})$ for the *V*4 site and $(V^{5+}{}_{0.58}V^{4+}{}_{0.42})$ for the *V*5 site. The resultant polyanion composition is $(V^{5+}{}_{9.35}V^{4+}{}_{0.65}O_{28})^{-6.65}$, and charge balance was inferred to occur *via* protonation of the decavanadate polyanion (Kampf *et al.* 2017b). The bond-valence sums for the O sites of the polyanion from V span 1.60–1.96 *vu*, with the incident bond-valences at the O_B and O_C anions spanning 1.72–1.87 *vu*. The atom displacement parameters for all V and O atoms of the two symmetrically distinct polyanions are reasonably uniform and do not suggest any significant local V–O bond elongation that might be coupled to a V–O bond arrangement (possibly involving V^{4+}) that would result in a significant reduction in bond valence at the anion. Thus, all decavanadate O_B and O_C atoms belonging to the hydropascoite polyanion contain $s\ \Sigma_{OV}$ sums in the range ~1.7–2.0 *vu* and are expected to be unprotonated by analogy with known protonated decavanadate structures (Table 1, Fig. 2). Additionally, the hydropascoite structure does not contain close anion–anion approaches between neighboring polyanions. Charge balance involving $V^{4+/5+}$ may possibly involve an unknown positively charged interstitial constituent in the vicinity of the OW24 position: the atom-displacement parameters associated with the OW24 site are extreme, and there is a minor peak in the difference-Fourier map ~1.5 Å from OW24. In this context, it should be noted that FTIR examination of hydropascoite indicates that it does not contain significant NH_4^+ (Paul M. Adams, *pers. commun.*).

CONCLUSIONS

The following criteria are key indicators of decavanadate protonation:

(1) Incident bond-valence sums ($s\ \Sigma_{OV}$) at the O_C or O_B decavanadate exterior anions that are in the range 1.2–1.5 *vu*, indicative of O_D anions;
(2) $O_D...O_A$ distances between neighboring decavanadate polyanions that are <3.1 Å;
(3) An obvious lack of proximal interstitial constituents capable of providing substantial bond valence to the low-valence O_B or O_C anions in (1) above.

Moreover, we have found no evidence so far for mixed $V^{4+/5+}$ protonated decavanadates.

ACKNOWLEDGMENTS

We thank reviewers Fernando Cámara and Michael Schindler for their useful comments. Paul M. Adams is thanked for providing the results of his FTIR studies on rakovanite, gunterite, and hydropascoite. Financial support was provided by a Discovery Grant from the Natural Sciences and Engineering Research Council of Canada to FCH and by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County to ARK.

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Received November 28, 2018. Revised manuscript accepted January 30, 2019.