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DETERMINATION OF V^{4+}:V^{5+} RATIOS IN THE $[V_{10}O_{28}]^{n-}$ DECAVANADATE POLYANION

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ABSTRACT

The decavanadate anion, $[V_{10}O_{28}]^{6-}$, is a common constituent of vanadate minerals, and both protonated, $[H_xV_{10}O_{28}]^{(6-x)-}$, and mixed-valent, $[(V^{4+}{}_xV^{5+}{}_{10-x})O_{28}]^{(6+x)-}$, derivatives also occur. In addition, other highly charged cations (*e.g.*, As^{5+}) may replace some V^{5+} ions. The V^{5+}–O bond-valence equation of Brown & Altermatt (1985) gives the best calculated valences for V in decavanadates containing only V^{5+}. The V^{4+}–O bond-valence equation of Gagné & Hawthorne (2015) provides the best calculated valences for V^{4+} in non-decavanadate structures containing only V^{4+} in [1+4+1] coordination (*i.e.*, one vanadyl bond, four equatorial bonds, and one longer bond *trans* to the vanadyl bond). Combined application of these two equations to the V–O bond lengths in decavanadates, based on V^{4+}/V^{5+} estimates, provides the most reliable valence assessment. Based on the high level of agreement between valences calculated in this manner and V^{4+}/V^{5+} estimates from the V^{5+}–O bond-valence equation of Brown & Altermatt (1985), V_C, the following equation gives the best estimate of the formal aggregate valence of V in decavanadate minerals: $V_P = 1.538(V_C) - 2.692$. This provides more accurate Lewis basicities for the decavanadate polyanion in analyzing its interaction with the interstitial complex. It should also help in establishing the strengths of donor-hydrogen and hydrogen···acceptor bonding in decavanadate systems relevant to catalysis and bacterial-growth inhibition.

Keywords: decavanadate polyanion, decavanadate minerals, bond-valence.

INTRODUCTION

Secondary vanadium minerals commonly result from oxidation of primary vanadium minerals in ore bodies exposed to near-surface conditions. Evans & Garrels (1958) showed that several V-bearing oxyanions may be present in mineralizing solutions, depending on the Eh and pH of those solutions. At relatively high Eh, the decavanadate anion, $[V_{10}O_{28}]^{6-}$, is stable at mildly acidic conditions, whereas its protonated derivatives, $[H_xV_{10}O_{28}]^{(6-x)-}$, occur at lower pH. At more reducing conditions, conducive to the presence of both V^{4+} and V^{5+}, mixed-valence decavanadate anions, $[(V^{4+}{}_xV^{5+}{}_{10-x})O_{28}]^{(6+x)-}$, may occur. In addition, other highly charged cations (*e.g.*, As^{5+}) may replace some V^{5+} ions (*e.g.*, Kampf *et al.* 2016a). Decavanadates are also important as catalysts (*e.g.*, Villa *et al.* 2001, Csányi *et al.* 2003, Valverde *et al.* 2012) and as inhibitors of bacterial growth (*e.g.*, Gillet *et al.* 2016, Samart *et al.* 2018).

Minerals containing decavanadate polyanions conform well to 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, Schindler *et al.* 2000b). The decavanadate polyanion corresponds to the structural unit, and additional low-acidity cations (Gagné & Hawthorne

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2017a), anions, *e.g.*, $(OH)^-$, and formally neutral species, *e.g.*, $(H_2O)^0$, that link to the decavanadate polyanion by bonds of less than 0.30 *vu* correspond to the interstitial complex. The interaction of the structural unit with the interstitial complex can be evaluated using the principle of correspondence of Lewis acidity-basicity (Hawthorne & Schindler 2008). The recognition and quantitative evaluation of the V^{4+} content in the usually V^{5+}-dominated decavanadate polyanion is important in correctly establishing the net charge and site occupancies of the structural unit, and thereby more accurately evaluating the Lewis acidity of the interstitial unit, which is often less well-constrained chemically and structurally. We plan to address the protonated decavanadate structures rakovanite (Kampf *et al.* 2011a), gunterite (Kampf *et al.* 2011b), and possibly hydropascoite in a subsequent paper.

INCIDENT BOND-VALENCE SUMS AND ION VALENCES

In the bond-valence model (Brown 2016), the incident bond-valence sum for any ion is (approximately) equal to the ion valence, and hence the incident bond-valence sum to an ion should be an accurate measure of the formal valence of that ion. If this were the case, we should be able to calculate the formal valences of V in the polyanion of a decavanadate mineral from the incident bond-valence sums at the constituent V^{n+} cations. However, Gagné & Hawthorne (2015, 2016a) showed that the incident bond-valence sum at an ion is not necessarily an accurate measure of the formal valence of that ion: for example, there is a positive correlation between mean bond-valence sum and coordination number for alkali- and alkaline-earth ions bonded to O^{2-} (*e.g.*, Gagné & Hawthorne 2016a, their Fig. 13). Furthermore, this increase in bond-valence sum is much larger for smaller coordination numbers and tends to level off at larger coordination numbers. In addition, calculation of *a priori* bond-lengths (Gagné & Hawthorne 2016b, Gagné *et al.* 2018) for many ions in different coordination numbers in a single structure-type leads to well-developed linear relations between *a priori* and observed mean-bond-lengths (*e.g.*, Gagné & Hawthorne 2016b). However, calculation of *a priori* bond-lengths (Gagné & Hawthorne 2016a, 2018) for a single ion in one particular coordination number (defined as an ion configuration) in many different structure-types leads to negligible correlation between *a priori* and observed mean-bond-lengths across these different structure types (Gagné & Hawthorne 2017b). Bond-valence parameters best fit the most common configurations (combinations of ions and coordination number) in the structure data used to derive the bond-valence parameters. Thus many structure types will show poorer agreement with the valence-sum rule, and estimation of ion valence-states from incident bond-valence sums in these structures will be correspondingly less accurate. However, the close correlation between *a priori* bond-lengths and observed bond-lengths for many ion configurations in a single structure-type indicates that it should be possible to optimize bond-valence parameters for a specific structure-type such that accurate ion-valences can be obtained. We attempt to do so here for the valences of V in minerals containing the decavanadate polyanion.

The decavanadate polyanion

Schindler *et al.* (2000a) defined the following types of $V^{4+,5+}$–O^{2-} bonds based on their observed populations in $(V^{4+,5+}O_n)$ ($n = 5$, 6) polyhedra: (1a) vanadyl bonds in $(V^{4+}O_n)$ polyhedra, shorter than 1.74 Å; (1b) vanadyl bonds in $(V^{5+}O_5)$ polyhedra, shorter than 1.76 Å; (1c) vanadyl bonds in $(V^{5+}O_6)$ polyhedra, shorter than 1.74 Å; (2a) equatorial bonds in $(V^{4+}O_n)$ polyhedra, in the range 1.90 to 2.12 Å; (2b) equatorial bonds in $(V^{5+}O_5)$ polyhedra, longer than 1.76 Å; (2c) equatorial bonds in $(V^{5+}O_6)$ polyhedra with one vanadyl bond, in the range 1.74 to 2.10 Å; (2d) equatorial bonds in $(V^{5+}O_6)$ polyhedra with two vanadyl bonds, in the range 1.80 to 2.00 Å; (3a) *trans* bonds in $(V^{4+}O_6)$ polyhedra, longer than 2.10 Å; (3b) *trans* bonds in $(V^{5+}O_6)$ polyhedra with one vanadyl bond, longer than 2.15 Å; (3c) *trans* bonds in $(V^{5+}O_6)$ polyhedra with two vanadyl bonds, longer than 2.025 Å. These ranges are illustrated in Figure 1. Schindler *et al.* (2000a) identified two distinct octahedral coordinations: (1) [1+4+1]-coordination in which there is one vanadyl bond, four equatorial bonds, and one *trans* bond (Fig. 1a); (2) [2+2+2]-coordination in which there are two vanadyl bonds, two equatorial bonds, and two *trans* bonds (Fig. 1b).

The decavanadate polyanion $[V_{10}O_{28}]^{6-}$ is a densely packed cluster with edge- and face-sharing between eight (VO_6) octahedra with [1+4+1]-coordination and two (VO_6) octahedra with [2+2+2]-coordination (Fig. 2). Short vanadyl bonds (V–O_V) project outward, opposing long *trans* bonds (V–O_T) that are directed toward the core of the polyanion, and there are two octahedrally coordinated O^{2-} ions at the core of the cluster. Fourteen O^{2-} ions are coordinated by two V^{5+} ions, four O^{2-} ions each involving one equatorial and one vanadyl bond, and ten O atoms each involving two equatorial bonds. In addition, four O^{2-} ions are each involved in three equatorial (V^{5+}–$O^{2-}{}_E$) bonds. The coordination of O^{2-} ions by V^{5+} ions varies from [1] to [6] and the bond valences for individual V^{5+}–O^{2-} bonds vary from ~0.25 to 1.75 *vu* (valence units). Recent high-quality structure-refine-

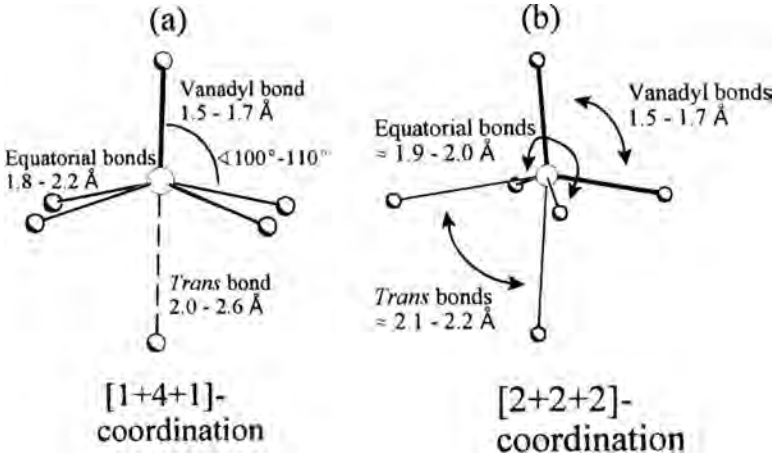

FIG. 1. Coordination geometries in ($V–O_n$) polyhedra: (a) [1+4+1]-coordination with one vanadyl bond and one *trans* bond; (b) [2+2+2]-coordination with two *cis* vanadyl bonds and two *trans* bonds in a *trans* arrangement to each vanadyl bond; after Schindler *et al.* (2000a).

ments have been published for 14 decavanadate minerals (we exclude the lower-quality burroite structure refinement; Kampf *et al.* 2017a); most contain only V^{5+} (*i.e.*, the $[V_{10}O_{28}]^{6-}$ decavanadate cluster), and two (nashite, bluestreakite) are structures that have mixed-valence (*i.e.*, V^{4+},V^{5+}) decavanadate clusters (Kampf *et al.* 2014b). Additionally, green hydropascoite was inferred to contain an unknown amount of V^{4+} (Kampf *et al.* 2017b).

The bond valences of V^{5+} in $[V^{5+}_{10}O_{28}]$ polyanions

The 10 non-protonated decavanadate minerals that contain only V^{5+} in the $[V_{10}O_{28}]$ polyanion (Kampf *et al.* 2014b) contain 48 symmetrically distinct VO_6 octahedra, 10 of which are [2+2+2] coordinated (*i.e.*, have two vanadyl bonds) and 38 of which are [1+4+1] coordinated (*i.e.*, have only one vanadyl bond) (Table 1). The formal valence of a specific V ion can be assessed using bond valences derived from the individual V–O bond-lengths using the bond-valence curves of Brown (1981), Brown & Altermatt (1985), Brese & O'Keeffe (1991), or Gagné & Hawthorne (2015), or calculated directly from the equatorial bond-length $<V–O_E>$ (Schindler *et al.* 2000a) (Table 1). Applying the universal $V^{4+/5+}$ relation of Brown (1981) gives incident bond-valence sums at the 48 *V* sites of 4.57–4.74 *vu*. The V^{5+}–O equation of Brown & Altermatt (1985) (the same equation as given by Brese & O'Keeffe 1991) gives bond-valence sums of 4.95–5.10 *vu*, and the V^{5+}–O equation of Gagné & Hawthorne (2015) gives sums of 4.67–4.80 *vu*. Therefore, only the V^{5+}–O bond-valence equation of Brown & Altermatt (1985) seems to provide bond-valence sums in accord with V^{5+} ions in known $[V^{5+}_{10}O_{28}]^{6-}$ polyanions; the other equations will give valences consistently below 5+, and thereby incorrectly suggest the presence of V^{4+} in the decavanadate polyion. For a decavanadate in which all V is present as V^{5+}, the bond-valence equation of Brown & Altermatt (1985) is expected to produce bond-valence sums near 5.00 *vu* for well-refined decavanadate structures with accurate V–O distances, and a calculated value significantly lower than 5.00 *vu* (*i.e.*, below $\sim$ 4.9 *vu*) should be considered anomalous and suggestive of possible V^{4+} content.

The linear equation of Schindler *et al.* (2000a) for calculating the valence of V for octahedrally coordinated $V^{4–5+}$, $<Z> = 29 - 12.5R$ (where $<Z>$ = mean V valence and $R = <V–O_E>$), gives average bond-valence values of 4.84–5.23 *vu* for the 48 polyhedra involving V^{5+}. Used on its own, this empirical relation may correctly suggest the presence of significant V^{4+}, but the large spread in the results ($\Delta = 0.39$ *vu*) calculated from known V^{5+} decavanadates suggests that it will not reliably detect the presence of minor V^{4+}. However, we were able to improve its agreement using a modified expression, developed by multiple linear-regression analysis, which incorporates additional V–O bond-length criteria. We have found that the magnitude of the departure in the calculated $<Z>$ value from the ideal value of 5 varies based on (1) $V–O_V$/$V–O_T$, (2) $V–O_T - <V–O_E>$, and (3) $<V–O_E> - V–O_V$, where $V–O_V$ is the vanadyl bond (or the average of two vanadyl bonds in [2+2+2] coordination), $V–O_T$ is the *trans* bond (or the average of two

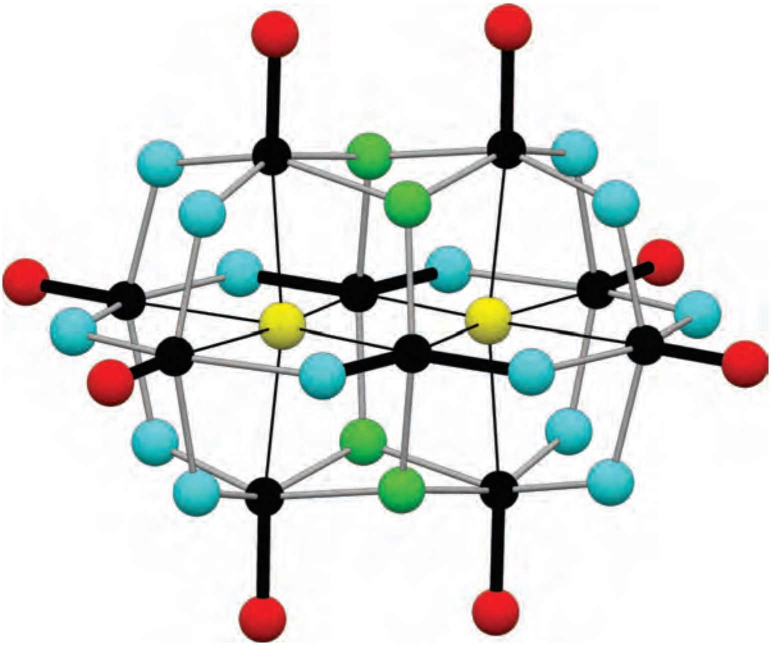

FIG. 2. The $[V_{10}O_{28}]^{n-}$ decavanadate polyanion. V atoms = black circles, [1]-coordinated O atoms = red circles, [2]-coordinated O atoms = blue circles, [3]-coordinated O atoms = green circles, [6]-coordinated O atoms = yellow circles, V–$O_{vanadyl}$ bonds = thick black line, V–O_{trans} bonds = thin black line, V–$O_{equatorial}$ bonds = grey shaded line.

trans bonds in [2+2+2] coordination), and $<V–O_E>$ is the average of the equatorial bonds. The value $(5 - <Z>)_{predicted}$ using the results from multiple regression is shown as a function of $(5 - <Z>)_{observed}$ in Figure 3 for the 48 known $V^{5+}O_6$ polyhedra. The correlation ($r^2 = 0.95$) indicates that the raw $<Z>$ values derived from the Schindler *et al.* (2000a) equation, using only $<V–O_E>$ input, can be significantly improved for decavanadates containing only V^{5+} using the following equation:

$$\begin{aligned}\langle Z\rangle_m = {} & \langle Z\rangle + 39.8(1.9) \times (V{-}O_V/V{-}O_T) \\ & + 11.8(6) \times (V{-}O_T - \langle V{-}O_E\rangle) \\ & + 21.0(1.0) \times (\langle V{-}O_E\rangle - V{-}O_V) \\ & - 38.907(17)\end{aligned}$$

The predicted values of the mean valence, $<Z>_m$, range from 4.96 to 5.05 and the equation is expected to reliably confirm the presence of V^{5+} in a decavanadate. However, it should not be used to quantify the amount of V^{4+} at a given site, as the valence will be significantly overestimated. As there are no known decavanadate structures with fully ordered V^{4+} sites, we cannot empirically develop an analogous method for V^{4+} polyhedra. These results show that accurate prediction of the mean valence of V in decavanadates requires information for all V–O bonds.

Prediction of V^{4+} in decavanadates

Within the decavanadate polyanion, we would expect V^{4+} to occur at one or more of the [1+4+1] coordinated V sites, as V^{4+} does not show [2+2+2] coordination (Schindler *et al.* 2000a). We next carefully selected seven simple stoichiometric (non-decavanadate) structures from the International Crystal Structure Database (Siidra *et al.* 2014, Cooper *et al.* 2003, Cevik *et al.* 2010, Panin *et al.* 2004, Krivovichev *et al.* 2007, Schindler *et al.* 2003, Hawthorne *et al.* 2001) that (1) reliably contain only V^{4+} in [1+4+1] coordination, (2) are recent (> year 2000), (3) are well ordered, and (4) have low R_1 indices ($R_1 < 5\%$). Each structure contains a single symmetrically distinct $V^{4+}O_6$ polyhedron. Bond-valence sums at the *V* sites were calculated using (1) the universal $V^{4+/5+}$–O equation of Brown (1981), (2) the V^{4+}–O equation of Brown & Altermatt (1985), and (3) the V^{4+}–O equation of Gagné & Hawthorne (2015); the following ranges of bond-valence sums for the V sites were obtained: (1) 4.02–4.14 *vu*, (2) 4.11–4.16 *vu*, (3) 3.99–4.06 *vu*, respectively. The results are similar, but the equation of Gagné & Hawthorne (2015) provides sums with the tightest dispersion about the ideal value of 4 *vu*. We also calculated bond-valence sums for all V^{4+}

TABLE 1. BOND LENGTHS AND VALENCES FOR THE 10 ($V^{5+}{}_{10}O_{28}$) DECAVANADATES

	V–O bond lengths (Å)				*V*-site valence sums (*vu*)			
	$V–O_V$	$V–O_T$	$<V–O_E>$	$<Z>$ (S/H,2000)	B/A (1985)	G/H (2015)	B (1981)	Refs.
Huemulite	1.601–1.6901	2.1263–2.3045	1.902–1.923	4.96–5.23	5.00–5.08	4.72–4.78	4.62–4.73	[1]
Hughesite	1.595–1.697	2.111–2.354	1.907–1.933	4.84–5.16	4.95–5.05	4.68–4.76	4.57–4.72	[2]
Hummerite	1.600–1.6931	2.1168–2.3428	1.9061–1.9195	5.01–5.17	5.02–5.07	4.73–4.77	4.62–4.71	[3]
Kokinosite	1.601–1.690	2.129–2.311	1.908–1.924	4.95–5.15	4.98–5.07	4.71–4.77	4.61–4.71	[4]
Lasalite	1.6001–1.6898	2.1124–2.3228	1.9084–1.9215	4.98–5.14	5.03–5.06	4.74–4.77	4.65–4.71	[5]
Magnesiopascoite	1.600–1.689	2.134–2.316	1.908–1.913	5.09–5.15	5.03–5.10	4.74–4.80	4.66–4.73	[6]
Pascoite	1.598–1.687	2.1339–2.312	1.906–1.914	5.08–5.18	5.05–5.09	4.73–4.80	4.68–4.74	[7]
Postite	1.599–1.692	2.120–2.334	1.913–1.925	4.94–5.09	4.96–5.07	4.67–4.78	4.60–4.74	[8]
Schindlerite	1.595–1.695	2.110–2.3608	1.910–1.9204	4.99–5.13	5.00–5.04	4.72–4.75	4.61–4.69	[9, 10]
Wernerbaurite	1.5990–1.6926	2.1182–2.3245	1.9097–1.9183	5.02–5.13	5.01–5.07	4.72–4.77	4.62–4.71	[9, 10]
Δ	1.595–1.697	2.110–2.3608	1.902–1.933	4.84–5.23	4.95–5.10	4.67–4.80	4.57–4.74	

[1]: Colombo *et al.* (2011); [2]: Rakovan *et al.* (2011); [3]: Hughes *et al.* (2002); [4]: Kampf *et al.* (2014a); [5]: Hughes *et al.* (2008); [6]: Kampf & Steele (2008); [7]: Hughes *et al.* (2005); [8]: Kampf *et al.* (2012); [9], [10]: Kampf *et al.* (2013a), Kampf *et al.* (2016b).

sites using the V^{5+}–O equation of Brown & Altermatt (1985) in order to provide a useful baseline value for full V^{4+} occupancy; these sums spanned 4.33–4.38 *vu*. Thus if all *V* sites in all decavanadates are first evaluated using the V^{5+}–O equation of Brown & Altermatt (1985), bond-valence sums at the *V* sites are expected to lie between ~5.00 and 4.35 *vu* for V occupancies spanning $V^{5+}{}_{1.0}$ to $V^{4+}{}_{1.0}$, respectively, following the linear relation $V_C = 0.65V_P + 1.75$ where V_C is the calculated bond-valence and V_P is the actual valence. We may rearrange this expression to give the predicted (actual) valence for V at a given *V* site: $V_P = 1.538(V_C) - 2.692$, where *V*c is the bond-valence sum calculated using the V^{5+}–O equation of Brown & Altermatt (1985). This predicted valence (V_P) can then be further tested against a merged bond-valence calculation (V_{test}), that incorporates the predicted fractional V^{4+} (from the equation of Gagné & Hawthorne 2015) and the fractional V^{5+} character (from the equation of Brown & Altermatt 1985) for each V–O bond using the V_P result.

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

Two decavanadate minerals are known to contain V^{4+} in the decavanadate polyanion: nashite, $Na_3Ca_2[V^{4+}V^{5+}{}_9O_{28}](H_2O)_{24}$ (Kampf *et al.* 2013b), and bluestreakite, $K_4Mg_2[V^{4+}{}_2V^{5+}{}_8O_{28}](H_2O)_{14}$ (Kampf *et al.* 2014b). Notably, such mixed-valence decavanadates are green due to inter-valence charge-transfer, rather than shades of orange that are characteristic of V^{5+} decavanadate minerals.

Nashite. Valence calculations for the five *V* sites in nashite are given in Table 2. Bond-valence sums calculated using the equation of Brown & Altermatt (1985) give values close to 5 (4.99–5.09 *vu*) for *V*1, *V*2, and *V*3, and smaller values (4.76 and 4.88 *vu*) for *V*4 and *V*5. This result was used by Kampf *et al.* (2013b) to indicate the presence of significant V^{4+} at the *V*4 and *V*5 sites. These authors then applied the universal $V^{4+/5+}$ equation of Brown (1981) to the *V*4 and *V*5 sites and reported incident bond-valence values of 4.43 and 4.56 *vu*, respectively. Subsequently, 1.01 atoms of V^{4+} and 0.99 atoms of V^{5+} were jointly assigned to the *V*4 and *V*5 sites, and the decavanadate composition was given as $[V^{4+}V^{5+}{}_9O_{28}]$. However, this formula is not correct, as the assignment of $(V^{4+}{}_{0.99}V^{5+}{}_{1.01})$ to the *V*4 and *V*5 sites would result in a decavanadate composition of $[V^{4+}{}_2V^{5+}{}_8O_{28}]^{8-}$, as the *V*4 and *V*5 sites are both at general positions (4*e*) and jointly contribute 4 *V* (*i.e.*, $V^{4+}{}_2V^{5+}{}_2$) *apfu*. For the 10 decavanadate minerals known to contain only V^{5+}, it was shown above that the universal $V^{4+/5+}$ equation of Brown (1981) gave bond-valence sums at the *V* sites that are significantly below 5 *vu*, and the same is true

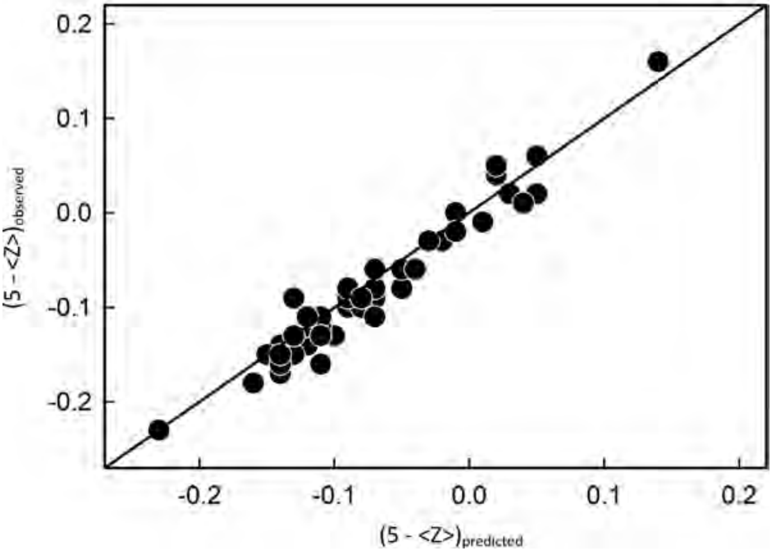

FIG. 3. Predicted (5 – <Z>) values (Schindler *et al.* 2000a) from multiple-regression analysis with dependent variables V–O$_V$/V–O$_T$, V–O$_T$ – <V–O$_E$>, and <V–O$_E$> – V–O$_V$ plotted against the observed (5 – <Z>) values for 48 (VO$_6$) octahedra belonging to decavanadate minerals containing only V^{5+}. The black line is a 1:1 reference line.

for the *V*1, *V*2, and *V*3 sites in nashite (Table 2). We surmise that the values of 4.43 and 4.56 *vu* calculated for the *V*4 and *V*5 sites could also be too low and not accurately reflect the V^{4+} content at these sites. Application of our predictive equation for the valence of V, $V_p = 1.538(V_c) - 2.692$, to the *V*4 and *V*5 sites in nashite gives predicted bond-valences of 4.63 and 4.81 at the *V*4 and *V*5 sites, respectively. We may test these V_p values against similarly partitioned coupled-valence calculations [*i.e.*, 37% V^{4+}–O and 63% V^{5+}–O at *V*4, 19% V^{4+}–O and 81% V^{5+}–O at *V*5 using the V^{4+}–O equation of Gagné & Hawthorne (2015) and the V^{5+}–O equation of Brown & Altermatt (1985)] for each V–O bond; these produce the same valence sums at the *V*4 and *V*5 sites (Table 2). Thus, the inferred *V*4 and *V*5 site occupancies are $^{V4}(V^{4+}_{0.37}V^{5+}_{0.63})$ and $^{V5}(V^{4+}_{0.19}V^{5+}_{0.81})$ and the resulting composition of the decavanadate polyanion is $[V^{4+}_{1.12}V^{5+}_{8.88}O_{28}]$. This expression can be simplified to $[V^{4+}V^{5+}_9O_{28}]^{7-}$ in accord with the formula proposed by Kampf *et al.* (2013b).

Bluestreakite. Valence calculations for the five *V* sites in bluestreakite are given in Table 2. Bond-valence sums using the equation of Brown & Altermatt (1985) show that only the *V*2 site seems to be fully occupied by V^{5+}, with the *V*3 and *V*5 sites most

TABLE 2. BOND-VALENCE SUMS FOR THE *V* SITES IN MIXED (V^{4+}/V^{5+}) DECAVANADATES

	V site	<Z> (S/H, 2000)	B (1981)	B/A (1985) V_C	V_P	*V_{test}
Nashite	V1	5.23	4.61	4.99	5	
	V2	5.05	4.65	5.01	5	
	V3	5.14	4.71	5.09	5	
	V4	4.80	4.43	4.76	4.63	4.63
	V5	4.94	4.56	4.88	4.81	4.82
Bluestreakite	V1	4.98	4.45	4.83	4.74	4.74
	V2	5.00	4.62	4.99	5	
	V3	4.72	4.29	4.63	4.43	4.44
	V4	4.97	4.57	4.91	4.86	4.86
	V5	4.54	4.22	4.56	4.32	4.32

* Partitioned valence calculations using the V_P result, V^{4+}–O equation of Gagné & Hawthorne (2015) and the V^{5+}–O equation of Brown & Altermatt (1985).

strongly occupied by V^{4+}. The $V1$ and $V4$ sites seem to contain only minor V^{4+}. The overall V^{4+} content assigned to the V sites in the decavanadate polyanion by Kampf *et al*. (2014b) is V^{4+}_2 *pfu* based on charge-balance arguments, with nearly fully occupied *Mg* and *K* sites in the interstitial complex. Application of our predictive expression, $V_p = 1.538(V_c) - 2.692$, to the $V1$, $V3$, $V4$, and $V5$ sites in bluestreakite gives predicted bond-valence sums of 4.74, 4.43, 4.86, and 4.32 *vu*, respectively (Table 2). As we saw for nashite, these V_p values are in close agreement (*i.e*., within 0.01 *vu*) with bond-valence sums calculated using the predicted $V^{4+/5+}$ fractional valence character (V_P), the V^{4+}–O equation of Gagné & Hawthorne (2015), and the V^{5+}–O equation of Brown & Altermatt (1985). The resultant V–site compositions for bluestreakite are: $^{V1}(V^{4+}_{0.26}V^{5+}_{0.74})$, $^{V2}(V^{5+})$, $^{V3}(V^{4+}_{0.57}V^{5+}_{0.43})$, $^{V4}(V^{4+}_{0.14}V^{5+}_{0.86})$, and $^{V5}(V^{4+}_{0.68}V^{5+}_{0.32})$, and the resulting decavanadate polyanion composition is $[V^{4+}_{3.30}V^{5+}_{6.70}O_{28}]^{9.3-}$. The V^{4+} content in this expression significantly exceeds that in the simplified expression $[V^{4+}_2V^{5+}_8O_{28}]^{8-}$ given by Kampf *et al*. (2014b) and suggests that, with a fully occupied interstitial component, $\{K_4Mg_2(H_2O)_{14}\}^{8+}$, an additional as yet uncharacterized charge-balancing mechanism is involved.

DISCUSSION

The equation $V_P = 1.538(V_C) - 2.692$, where Vc is the bond-valence sum calculated using the V^{5+}–O equation of Brown & Altermatt (1985), gives the best estimate of the formal aggregate valence, V_P, of V in decavanadate minerals. This accurate valence of V will provide more accurate Lewis basicities for the decavanadate polyanion in analyzing its interaction with the interstitial complex in minerals.

This equation will establish more accurate values of the strengths of donor-hydrogen and hydrogen···acceptor bonds. The latter is of particular importance in decavanadate systems that are of relevance to a wide range of uses (Bošnjaković-Pavlović *et al*. 2011). Vanadium salts are effective anti-diabetic (*e.g*., Crans 2015, Trevino *et al*. 2015, Boulmier *et al*. 2017), anticancer (*e.g*., Lu & Zhu 2011, Leon *et al*. 2017, Crans *et al*. 2018), and immunotherapy (*e.g*., Lu & Zhu 2011, Selman *et al*. 2018) agents. The valence of V is particularly sensitive to redox conditions and V is converted from V^{5+} to lower oxidation states in the body (*e.g*., Thompson *et al*. 2009, Willsky *et al*. 2011). The determination of the valence states of V is of importance here, particularly where decavanadates are involved. Decavanadates are also of relevance to catalysis and bacterial-growth inhibition. In the latter use, some component of a bacterium can catalyze hydrolysis (*i.e*., protonation) of decavanadate (Samart *et al*. 2018), and hence both determination of the valence states of V and the state of protonation of a decavanadate is important in this regard.

SUMMARY

(1) The $V^{4+,5+}$ valence equation of Schindler *et al*. (2000a), $<Z> = 29 - 12.5R$ (where $<Z>$ = mean V valence and R = $<V–O_E>$), predicts the average valence of octahedrally coordinated V in structures using only $<V–O_E>$, but it lacks sufficient accuracy.

(2) Additional accuracy for decavanadates containing only V^{5+} may be obtained by incorporating additional V–O bond-length information into an extended version of this equation:

$$\begin{aligned}\langle Z\rangle_m = \langle Z\rangle &+ 39.8(1.9)\times(V\text{–}O_V/V\text{–}O_T)\\ &+ 11.8(6)\times(V\text{–}O_T - \langle V\text{–}O_E\rangle)\\ &+ 21.0(1.0)\times(\langle V\text{–}O_E\rangle - V\text{–}O_V)\\ &- 38.907(17)\end{aligned}$$

(3) Use of the universal $V^{4+/5+}$ bond-valence equation of Brown (1981) is not recommended for the determination of V^{4+}:V^{5+} ratios in decavanadate minerals, as it generally gives calculated valences significantly below 5 where only V^{5+} is present within the decavanadate.

(4) The V^{5+}–O bond-valence equation of Brown & Altermatt (1985) gives the best calculated valences for V in decavanadates containing only V^{5+}.

(5) The V^{4+}–O bond-valence equation of Gagné & Hawthorne (2015) provides the best calculated valences for V^{4+} in non-decavanadate structures containing only V^{4+} in [1+4+1] coordination.

(6) The combined application of these two equations to the V–O bond lengths, based on a reliable V^{4+}/V^{5+} estimate, is expected to provide the most reliable valence assessment. There is close agreement between valences calculated in this manner, V_C, and V^{4+}/V^{5+} estimates obtained from the V^{5+}–O bond-valence equation of Brown & Altermatt (1985). Extending this relation to an empirically established V^{4+}-only benchmark, the following equation gives the best estimate of the bond-valence sum (and therefore formal valence of V_P): $V_P = 1.538(V_C) - 2.692$.

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