

Caseyite, a new mineral containing a variant of the flat-Al₁₃ polyoxometalate cation

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ABSTRACT

Caseyite, [(V⁵⁺O₂)Al_{10-x}(OH)_{20-2x}(H₂O)_{18-2x}]₂[H₂V⁴⁺V⁵⁺O₂₈][V⁵⁺O₂₈]₂[(Na,K,Ca)_{2-z}(SO₄)_{2-z}(60+8x+y+4z)H₂O], where $x = 0-2.5$, $y = 0-2$, $z = 0-2$, is a new mineral (IMA 2019-002) occurring in low-temperature, post-mining, secondary mineral assemblages at the Burro, Packrat, and West Sunday mines in the Uravan Mineral Belt of Colorado, U.S.A. Crystals of caseyite are yellow tapering needles or blades, with a pale yellow streak, vitreous luster, brittle tenacity, curved fracture, no cleavage, Mohs hardness between 2 and 3, and 2.151 g/cm³ calculated density. Caseyite is optically biaxial (+) with $\alpha = 1.659(3)$, $\beta = 1.670(3)$, $\gamma = 1.720(3)$ (white light), $2V = 52.6(5)^\circ$, has strong $r < v$ dispersion, optical orientation $Z \approx a$ (elongation of needles), and no pleochroism. Electron-probe microanalysis provided the empirical formula [(V⁵⁺O₂)Al_{8.94}(OH)_{17.88}(H₂O)_{15.88}]₂[H₂V⁴⁺V⁵⁺O₂₈][V⁵⁺O₂₈]₂[(Na_{0.82}Ca_{0.35}K_{0.27})_{Σ1.44}(SO₄)_{1.33}·70.24H₂O] (+0.94 H). Caseyite is monoclinic, $P2_1/n$, $a = 14.123(8)$, $b = 30.998(15)$, $c = 21.949(11)$ Å, $\beta = 97.961(8)^\circ$, $V = 9516(9)$ Å³, and $Z = 2$. The crystal structure ($R_1 = 0.0654$ for 9162 $I_0 > 2\sigma I$ reflections) contains both normal [V₁₀O₂₈]⁶⁻ and doubly protonated mixed-valence [H₂V⁴⁺V⁵⁺O₂₈]⁵⁻ decavanadate isopolyanions, and a novel vanadoaluminate heteropolyocation (“flat-Al₁₀V□₂”), ideally [(V⁵⁺O₂)Al₁₀(OH)₂₀(H₂O)₁₈]¹¹⁺, closely related to the technologically important flat-Al₁₃ polyoxocation.

Keywords: Caseyite, new mineral, polyoxometalate, flat-Al₁₃ polyoxocation, crystal structure, Packrat mine, Burro mine, West Sunday mine, Colorado

INTRODUCTION

Millions of synthetic compounds have been prepared in the laboratory, but only about 5500 minerals have been characterized to date. Nature is much more parsimonious owing to its more limited combinations of physical conditions and abundant chemical constituents than are available in a laboratory. However, natural environments sometimes surprise us by duplicating unusual synthetic phases or by creating entirely new phases unknown from laboratory synthesis.

Polyoxometalate anions and, more rarely, polyoxometalate cations have been the subject of numerous synthesis studies in recent years, largely because of their potential technological uses. Low-temperature, near-surface environments, particularly those containing highly charged metal cations, also have the potential to form polyoxometalate ions, some of which have been proposed to exist in solution as precursors of more extended structural components (chains, sheets, and frameworks) in mineral structures. Only rarely are polyoxometalate ions found as isolated units in minerals.

Deposits in the Uravan Mineral Belt of Colorado and Utah have been a rich source of uranium and vanadium ores for more than a century. They have also been a rich source of post-mining secondary vanadium minerals that typically form in mine tunnels. Among

the numerous secondary minerals that have been discovered within the Uravan deposits are various phases containing polyoxometalate anions. The most common among these are minerals containing the decavanadate [V₁₀O₂₈]⁶⁻ isopolyanion, and its protonated and mixed-valence variants (Kampf et al. 2018). Sherwoodite, from the Peanut mine in Montrose County, Colorado (Thompson et al. 1958), was the first mineral confirmed to contain a heteropolyanion, the (AlV₁₄^{4+,5+}O₄₀)ⁿ⁻ vanadoaluminate anion (Evans and Konner 1978), which is structurally similar to the decavanadate anion. In recent years, new minerals containing variants of the Keggin heteropolyanion (Kondinski and Parac-Vogt 2018) have also been discovered in mines in the Uravan Mineral Belt. These include kegginite, Pb₃Ca₃[AsV₁₂O₄₀(VO)]·20H₂O, from the Packrat mine (Mesa County, Colorado) containing a mono-capped Keggin ε-isomer (Kampf et al. 2017), and bicapite, KNa₂Mg₂(H₂PV₄O₄₂)·25H₂O, from the Pickett Corral mine (Montrose County, Colorado) containing a bi-capped Keggin α-isomer (Kampf et al. 2019). The Packrat mine has also yielded several new minerals containing a novel [As³⁺V₁₂^{4+,5+}As₆⁵⁺O₅₁]ⁿ⁻ heteropolyanion (Kampf et al. 2016).

Caseyite, the new mineral species described here, is the most remarkable polyoxometalate mineral yet discovered. Besides containing both normal [V₁₀O₂₈]⁶⁻ and doubly protonated mixed-valence [H₂V⁴⁺V⁵⁺O₂₈]⁵⁻ decavanadate isopolyanions, it contains a novel vanadoaluminate heteropolyocation, ideally [(V⁵⁺O₂)Al₁₀(OH)₂₀(H₂O)₁₈]¹¹⁺. This new heteropolyocation is a variant of

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the “flat- Al_{13} ” polyoxometalate cation $[\text{Al}_{13}(\text{OH})_{24}(\text{H}_2\text{O})_{24}]^{15+}$ first reported by Seichter et al. (1998). Although the flat- Al_{13} cluster has not yet been discovered in Nature, it has been discussed as a potentially important aluminum hydroxide cluster in natural systems (Casey 2006). Moreover, metal variants of the flat- Al_{13} cluster, e.g., Al_7In_6 , offer new methods of preparation and enhanced performance in large-area electronics and such devices as flat-panel displays, solar cells, and LEDs (Kamunde-Devonish et al. 2014). We may write the caseyite vanadoaluminate cluster as $\text{Al}_{10}\text{V}\square_2$ (\square = vacancy) as a metal-vacancy substituted variant of the Al_{13} cluster (“flat- $\text{Al}_{10}\text{V}\square_2$ ”), suggesting new families of Al_{13} -type clusters involving both metals of different valences and vacancies at initial peripheral Al sites with properties that are susceptible to delicate tuning via modification of redox conditions and composition during synthesis.

The name “caseyite” honors American geochemist William H. Casey (born 1955), Distinguished Professor in the Departments of Chemistry and Earth & Planetary Sciences at the University of California, Davis. Dr. Casey received his Ph.D. degree in mineralogy and geochemistry from The Pennsylvania State University in 1986. After graduating, he worked as a research geochemist at Sandia National Laboratories in Albuquerque, New Mexico, for several years, before joining the faculty of the University of California at Davis in 1991. Dr. Casey was awarded the Stumm Medal in 2010 from the European Association of Geochemistry for scientific innovation and the Clair C. Patterson Award in 2016 from the Geochemical Society for his contributions to geochemical science. He has published more than 250 scientific papers on subjects relating to aqueous solution chemistry of natural waters, mineral surface chemistry, and reaction kinetics. Much of Dr. Casey’s research, and that of his research group at UC Davis, has focused on the interaction of inorganic clusters with water. This research has included studies on aluminate polyoxometalates. The flat- Al_{13} polycation, with which the caseyite vanadoaluminate polycation is related, is discussed in his 2006 survey paper on large aqueous aluminum hydroxide molecules. Dr. Casey has given permission for the mineral to be named in his honor.

The holotype and two cotypes from the Packrat mine, one co-type from the West Sunday mine and two cotypes from the Burro mine are deposited in the collections of the Natural History Museum of Los Angeles County, Los Angeles, California, U.S.A.; catalog numbers 73526, 73527, 73528, 73529, 73530, and 73531, respectively.

OCCURRENCE

Caseyite was first collected in 2009 underground at the West Sunday mine, Slick Rock district, San Miguel County, Colorado, U.S.A. ($38^\circ 04' 48.03''\text{N}$, $108^\circ 49' 18.07''\text{W}$). Better crystals were found in 2011 in the main tunnel level of the Packrat mine, near Gateway, Mesa County, Colorado, U.S.A. ($38^\circ 38' 51.28''\text{N}$, $109^\circ 02' 49.77''\text{W}$). In 2014, samples of the mineral were collected in the lower adit of the Burro mine in the Slick Rock district ($38^\circ 2' 42''\text{N}$, $108^\circ 53' 23''\text{W}$). The largest and best crystals are on the specimen collected in 2011 at the Packrat. The description of the species is principally based on crystals from this specimen, which is designated as the holotype. All three mines are considered type localities for the mineral.

The Burro and West Sunday mines are near the southern end

of the Uravan Mineral Belt, whereas the Packrat mine is near the northern end, about 65 km NNW of the West Sunday mine and about 70 km NNW of the Burro mine. In the Uravan Mineral Belt, uranium and vanadium minerals occur together in bedded or roll-front deposits in the sandstone of the Salt Wash member of the Jurassic Morrison Formation (Carter and Gualtieri 1965; Shawe 2011). The mineral is rare; however, considering that it was found in mines near opposite ends of the Uravan Mineral Belt, it may be relatively widespread. Although we have not confirmed the presence of caseyite at any other mines, we have observed similar yellow Al- and V-rich secondary phases at other mines in the area: the Centennial mine, Uravan district, San Miguel County, Colorado, and the Blue Cap, Black Hat, Pandora, and Vanadium Queen mines, La Sal district, San Juan County, Utah.

At all three type localities, caseyite occurs on sandstone, which is often coated with or impregnated by montroseite, corvusite, and/or asphaltum. At all three localities, but particularly at the Packrat and Burro mines, other, yet-uncharacterized, yellow-to-orange, Al- and V-rich secondary phases occur with caseyite. Gypsum is usually found in close association with caseyite at all three mines, although its abundance in each association seems to be correlated with the SO_4 content of caseyite; SO_4 -free caseyite is generally associated with little or no gypsum (see below). Other minerals found in close association with caseyite are barite (West Sunday mine), huemulite (Packrat mine), and postite (Burro mine).

Caseyite forms by oxidation of montroseite-corvusite assemblages in a moist environment. Under ambient temperatures and generally oxidizing near-surface conditions, water reacts with pyrite and other sulfides to form aqueous solutions of relatively low pH. The secondary vanadate phases that form depend upon prevailing Eh-pH conditions and the presence of other cations (e.g., Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} , Pb^{2+} , and Al^{3+}). The formation of caseyite clearly requires the presence of high concentrations of Al^{3+} in solution.

PHYSICAL AND OPTICAL PROPERTIES

Crystals of caseyite (Figs. 1, 2, and 3) are yellow tapering needles or blades, elongated on [100], up to 0.25 mm in length. The streak is pale yellow, the luster is vitreous, and the mineral is non-fluorescent in long- and short-wave ultraviolet light. The crystals are brittle, with curved fracture, no cleavage, and Mohs hardness estimated to be between 2 and 3. The calculated density is 2.151 g/cm³ based on the empirical formula using the cell parameters determined by single-crystal X-ray diffraction. At room temperature, the mineral is insoluble in H_2O , but is easily soluble in dilute HCl. Crystals are susceptible to dehydration at low relative humidity.

Caseyite is optically biaxial (+) with indices of refraction determined in white light: $\alpha = 1.659(3)$, $\beta = 1.670(3)$, $\gamma = 1.720(3)$. The $2V$ based upon extinction data analyzed with EXCALIBUR (Gunter et al. 2004) is $52.6(5)^\circ$ and that calculated from the indices of refraction is 51.5° . The dispersion is strong, $r < v$, the partially determined optical orientation is $Z \approx a$ (elongation of needles), and there is no pleochroism. The Gladstone-Dale compatibility $1 - (K_p/K_c)$ is 0.008 for the empirical formula, in the range of superior compatibility (Mandarino 2007).

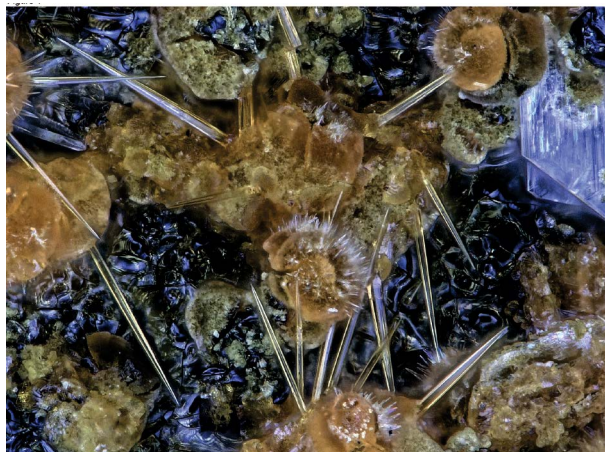


FIGURE 1. Caseyite needles with gypsum and orange-yellow balls of another potentially new Al-V-S-O-bearing mineral; holotype specimen (no. 73526) from the Packrat mine; FOV 0.68 mm across. (Color online.)



FIGURE 2. Caseyite needles on cotype specimen (no. 73529) from the West Sunday mine; FOV 0.68 mm across. (Color online.)

CHEMICAL ANALYSIS

Analyses (7 points on 2 crystals from the holotype specimen) were performed at the University of Utah on a Cameca SX-50 electron microprobe with four wavelength-dispersive spectrometers and using Probe for EPMA software. Analytical conditions were 15 kV accelerating voltage, 10 nA beam current, and a beam diameter of 3 μm . Raw X-ray intensities were corrected for matrix effects with a $\phi\rho(z)$ algorithm (Pouchou and Pichoir 1991). Substantial dehydration of the very water-rich crystals occurs when they are subject to an ultimate vacuum of 2×10^{-5} torr for approximately 5 min during vacuum deposition of the conductive carbon coat. The H_2O loss results in higher concentrations for the remaining constituents than are to be expected for the fully hydrated phase. There was also moderate damage from the electron beam, which likely compounded this problem. Because insufficient material is available for direct determination of H_2O , it has been calculated based on the structure determination. For this purpose, we assume that all V sites are fully occupied only



FIGURE 3. Caseyite blades on cotype specimen (no. 73530) from the Burro mine; FOV 0.84 mm across. (Color online.)

by V [32 atoms per formula unit (apfu)] and all O sites (234 pfu) are fully occupied by O or a large cation: Na, K, and/or Ca. Note that the latter criterion is based on the fact that no O sites in the structure are too close together to be fully occupied and observations suggest that the structure crystal partly dehydrated prior to data collection. The analyzed constituents were normalized to provide a total of 100% when combined with the calculated H_2O . The chemical data are reported in Table 1.

The structurally formatted empirical formula based on 234 O+Na+K+Ca and 32 V apfu is $[(\text{V}^{5+}\text{O}_2)\text{Al}_{8.94}(\text{OH})_{17.88}(\text{H}_2\text{O})_{15.88}]_2[\text{H}_2\text{V}^{4+}\text{V}_9^{5+}\text{O}_{28}][\text{V}_{10}^{5+}\text{O}_{28}]_2[(\text{Na}_{0.82}\text{Ca}_{0.35}\text{K}_{0.27})_{\Sigma 1.44}(\text{SO}_4)_{1.33} \cdot 70.24\text{H}_2\text{O}] (+0.94\text{H})$. The simplified formula is $[(\text{V}^{5+}\text{O}_2)\text{Al}_{10-x}(\text{OH})_{20-2x}(\text{H}_2\text{O})_{18-2x}]_2[\text{H}_2\text{V}^{4+}\text{V}_9^{5+}\text{O}_{28}][\text{V}_{10}^{5+}\text{O}_{28}]_2[(\text{Na,K,Ca})_{2-y}(\text{SO}_4)_{2-z} \cdot (60+8x+y+4z)\text{H}_2\text{O}]$, where $x = 0-2.5$, $y = 0-2$, $z = 0-2$. As noted below, interstitial cations and anions are considered nonessential in caseyite; therefore, the ideal formula (for which $x = 2.5$, $y = 2$, and $z = 2$) is: $[(\text{V}^{5+}\text{O}_2)\text{Al}_{7.5}(\text{OH})_{15}(\text{H}_2\text{O})_{13}]_2[\text{H}_2\text{V}^{4+}\text{V}_9^{5+}\text{O}_{28}][\text{V}_{10}^{5+}\text{O}_{28}]_2 \cdot 90\text{H}_2\text{O}$. The factors that were considered in the derivation of these formulas are discussed below.

X-RAY CRYSTALLOGRAPHY AND STRUCTURE DETERMINATION

The powder X-ray diffraction (PXRD) pattern was recorded with a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer with monochromatized $\text{MoK}\alpha$ radiation. A Gandolfi-like motion on the φ and ω axes was used to randomize the sample. The pattern is dominated by several strong peaks at low angles (d values $> 8 \text{ \AA}$). The remainder of the pattern consists only of very weak and indistinct peaks. Although the PXRD pattern is a good match with the PXRD calculated from the structure, it is poorly suited for the measurement of most lines and for the refinement of the cell parameters. Consequently, in Supplemental¹ Table S1, we have opted to report only the PXRD calculated from the structure refined from the single-crystal X-ray diffraction data.

Single-crystal X-ray studies were undertaken on a Bruker D8 three-circle diffractometer equipped with a rotating-anode generator ($\text{MoK}\alpha$), multilayer optics, and an APEX-II detector.

TABLE 1. Chemical compositions in wt% for caseyite

Constituent	Mean	Range	S.D.	Norm.	Standard
Na ₂ O	0.52	0.15–0.87	0.29	0.41	albite
K ₂ O	0.27	0.23–0.34	0.04	0.21	sanidine
CaO	0.41	0.36–0.49	0.04	0.32	diopside
Al ₂ O ₃	18.74	17.71–19.28	0.69	14.78	sanidine
V ₂ O ₅	(59.87)	59.33–61.08	0.58		V metal
VO ₂ ^a	1.71			1.35	
V ₂ O ₅ ^a	58.00			45.73	
SO ₃	2.19	2.14–2.21	0.03	1.73	celestine
H ₂ O ^b				35.47	
Total				100.00	

^a Allotted in accord with the structure.^b Based on the structure.

Structure data were collected on a single crystal of caseyite from the holotype specimen. The unit-cell dimensions were obtained by least-squares refinement of 3578 reflections with $I > 10\sigma I$. Systematically absent reflections are consistent with the space group $P2_1/n$. Empirical absorption corrections (SADABS) were applied and equivalent reflections were merged. The structure was solved by direct methods using SHELXS-2013 and the structure was refined using SHELXL-2016 (Sheldrick 2015). Most atoms in the structural units and some in the interstitial complex were located in the initial structure solution. The remaining sites were located using difference Fourier syntheses. The four peripheral Al sites in the vanadoaluminate unit (Al7, Al8, Al9, and Al10) refined to less than full occupancies, as did the OW sites coordinated to Al10. Most of the interstitial OW sites also refined to less than full occupancies. Positional disorder in the interstitial SO₄ group required the use of soft geometric restraints [S–O: 1.48(2); O–O: 2.40(2)] and the occupancies of the atom sites in the SO₄ group were refined together, resulting in approximately half occupancy for the group. Data collection and refinement details are given in Table 2, atom coordinates and displacement parameters in Supplemental¹ Table S2, cation-anion bond distances in Table 3, hydrogen bonds in Table 4, and bond-valence analyses in Table 5.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Hawthorne (1985) first introduced the concept of binary structural representation in which a structure can be considered a combination of a strongly bonded structural unit (usually anionic) and a weakly bonded interstitial complex; this concept was expanded upon by Schindler and Hawthorne (2001). This approach is particularly effective in describing structures that contain a polyoxometalate ion (the structural unit) surrounded by weakly bonded H₂O groups, with or without other cations and/or anions (the interstitial complex). The structure of caseyite (Figs. 4 and 5) is unusual in that it contains three different structural units. One is a normal [V₁₀O₂₈]⁶⁻ decavanadate isopolyanion, one is a doubly protonated mixed-valence [H₂V⁴⁺V⁵⁺O₂₈]⁵⁻ decavanadate isopolyanion, and one is a novel vanadoaluminate heteropolycation, ideally [(V⁵⁺O₂)Al₁₀(OH)₂₀(H₂O)₁₈]¹¹⁺ (Fig. 6a). Surrounding these structural units are numerous H₂O sites and an SO₄ group. The structural units and the components in the interstitial complex are linked to one another only by hydrogen bonds.

DECAVANADATE ANIONIC STRUCTURAL UNITS

There are two different decavanadate anions in the structure of caseyite. The decavanadate anion, including protonated and

TABLE 2. Data collection and structure refinement details for caseyite

Diffractionmeter	Bruker D8 three-circle; multilayer optics; APEX-II CCD
X-ray radiation/source	MoK α ($\lambda = 0.71073$ Å)/rotating anode
Temperature	293(2) K
Refined cell content	Al _{19.16} V ₃₂ S _{1.02} O _{215.11}
Space group	$P2_1/n$
Unit cell dimensions	$a = 14.123(8)$ Å $b = 30.998(15)$ Å $c = 21.949(11)$ Å $\beta = 97.961(8)^\circ$
V	9516(9) Å ³
Z	2
Absorption coefficient	1.730 mm ⁻¹
F(000)	5444
Crystal size	120 × 5 × 5 μ m
θ range	2.09 to 23.64°
Index ranges	$-15 \leq h \leq 15, -34 \leq k \leq 34, -24 \leq l \leq 24$
Reflections integrated	183070
Reflections collected/unique	56066/14231; $R_{int} = 0.098$
Reflections with $I > 2\sigma I$	9162
Completeness to $\theta = 23.64^\circ$	99.4%
Refinement method	Full-matrix least-squares on F^2
Parameter/restraints	1154/10
GoF	1.025
Final R indices [$I > 3\sigma I$]	$R_1 = 0.0654, wR_2 = 0.1673$
R indices (all data)	$R_1 = 0.1102, wR_2 = 0.1932$
Extinction coefficient	0.00052(8)
Largest diff. peak/hole	+1.43/−0.59 e/Å ³

Notes: $R_{int} = \sum |F_o^2 - F_c^2(\text{mean})| / \sum F_o^2$. GoF = $S = \{ \sum [w(F_o^2 - F_c^2)]^2 / (n - p) \}^{1/2}$. $R_1 = \sum |F_o - |F_c|| / \sum |F_o|$. $wR_2 = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2 \}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where a is 0.0901, b is 54.2021, and P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

mixed-valence variants, is found in numerous other Uravan-Mineral-Belt minerals. Decavanadate anion #1 [1 per formula unit (pfu)] includes atoms V1 through V5 and O5 through O18. Based on bond-valence parameters for V⁵⁺, sites V1, V2, V3, and V4 have bond-valence sums (BVS) close to 5 valence units (v.u.), whereas V5 has a very low BVS of 4.68 v.u. Based on our extensive studies of mixed-valence and protonated decavanadates (Cooper et al. 2019a, 2019b), we have established the formula $V_p = 1.538(V_c) - 2.692$ for calculating the aggregate valence of V (V_p) from the BVS (V_c). This yields an aggregate valence of 4.5+ for the V5 site, corresponding to an occupancy of V_{0.5}⁴⁺V_{0.5}⁵⁺. It is worth noting that mixed-valence decavanadates are generally green due to intervalence charge transfer (IVCT) between V⁴⁺ and V⁵⁺; however, the occupancy by V⁴⁺ at a single structural site in a very large structure apparently is insufficient to produce any perceptible green color. The O14 site in decavanadate anion #1 has a low BVS of 1.33 v.u. indicating that it is likely to be occupied by OH. O14 is only 2.795 Å from O19 in decavanadate anion #2, which is the likely receptor of a hydrogen bond from O14, especially considering that O19 otherwise has an incident BVS of 1.66 v.u. As further support, there is a small electron-density residual (+0.36 e Å⁻³) located 1.04 Å from O14 and 1.88 Å from O19. Therefore, decavanadate anion #1 is a doubly protonated mixed-valence decavanadate, [H₂V⁴⁺V⁵⁺O₂₈]⁵⁻. Decavanadate anion #2 (2 pfu) includes atoms V6 through V15 and O19 through O46. All V sites have incident BVS close to 5 v.u., indicating that all V is V⁵⁺.

VANADOALUMINATE CATIONIC STRUCTURAL UNIT

The vanadoaluminate heteropolycation (flat-Al₁₀V□₂), ideally [(V⁵⁺O₂)Al₁₀(OH)₂₀(H₂O)₁₈]¹¹⁺ (Fig. 6a), is assembled from eleven octahedra, ten centered by Al1 through Al10 and one centered by V16. All the Al sites have incident BVSs close to 3

TABLE 3. Selected bond distances (Å) for caseyite

V1-O13	1.666(6)	V8-O22	1.599(6)	V15-O20	1.596(6)	Al6-OH19	1.852(6)
-O15	1.698(6)	-O38	1.836(6)	-O30	1.822(6)	-OH18	1.856(6)
-O16	1.914(6)	-O32	1.837(6)	-O35	1.857(6)	-OH20	1.869(6)
-O17	1.921(6)	-O33	1.910(6)	-O44	1.994(6)	-OW2	1.873(7)
-O18	2.115(6)	-O36	2.031(6)	-O41	1.998(6)	-OH3	2.001(6)
-O18	2.179(5)	-O45	2.297(6)	-O46	2.222(6)	-OH4	2.011(6)
<V1-O>	1.916	<V8-O>	1.918	<V15-O>	1.915	<Al6-O>	1.910
V2-O6	1.600(6)	V9-O23	1.595(6)	V16-O47	1.622(6)	Al7-OH17	1.850(6)
-O12	1.756(6)	-O38	1.838(6)	-O48	1.632(7)	-OH20	1.894(7)
-O14	1.940(6)	-O28	1.867(6)	-OH19	1.967(6)	-OW3	1.903(7)
-O17	1.949(6)	-O37	1.897(6)	-OH8	1.978(6)	-OW4	1.913(8)
-O16	2.030(6)	-O27	2.022(6)	-OH3	2.282(5)	-OW6	1.920(8)
-O18	2.218(6)	-O45	2.299(5)	-OH2	2.302(6)	-OW5	1.924(7)
<V2-O>	1.916	<V9-O>	1.920	<V16-O>	1.964	<Al7-O>	1.901
V3-O8	1.597(6)	V10-O26	1.598(6)	Al1-OH1	1.876(6)	Al8-OH14	1.861(6)
-O10	1.775(6)	-O40	1.839(6)	-OH2	1.881(6)	-OH16	1.865(6)
-O11	1.876(6)	-O34	1.860(6)	-OH4	1.886(6)	-OW7	1.909(7)
-O14	1.967(6)	-O35	1.904(6)	-OH3	1.888(6)	-OW8	1.921(7)
-O13	2.110(7)	-O29	2.018(6)	-OH5	1.906(6)	-OW9	1.938(7)
-O18	2.318(5)	-O46	2.317(6)	-OH6	1.911(6)	-OW10	1.962(7)
<V3-O>	1.941	<V10-O>	1.923	<Al1-O>	1.891	<Al8-O>	1.909
V4-O5	1.608(6)	V11-O24	1.598(6)	Al2-OW1	1.815(7)	Al9-OH11	1.870(7)
-O9	1.787(6)	-O31	1.837(6)	-OH7	1.827(7)	-OH15	1.871(6)
-O11	1.848(6)	-O34	1.868(6)	-OH8	1.857(6)	-OW11	1.900(6)
-O16	1.984(6)	-O30	1.903(6)	-OH9	1.873(6)	-OW12	1.901(7)
-O17	2.013(6)	-O39	2.029(6)	-OH2	2.026(6)	-OW13	1.952(7)
-O18	2.256(6)	-O46	2.299(6)	-OH1	2.060(6)	-OW14	1.961(6)
<V4-O>	1.916	<V11-O>	1.922	<Al2-O>	1.910	<Al9-O>	1.909
V5-O7	1.603(7)	V12-O19	1.602(6)	Al3-OH10	1.819(6)	Al10-OW15	1.810(15)
-O10	1.912(6)	-O40	1.826(6)	-OH11	1.835(6)	-OH10	1.871(7)
-O12	1.920(6)	-O31	1.840(6)	-OH12	1.842(6)	-OW16	1.877(12)
-O9	1.935(6)	-O42	1.984(6)	-OH9	1.851(6)	-OH7	1.913(8)
-O15	2.034(6)	-O43	1.996(6)	-OH5	1.999(6)	-OW17	1.944(13)
-O18	2.318(6)	-O46	2.252(6)	-OH1	2.081(6)	-OW18	2.026(11)
<V5-O>	1.954	<V12-O>	1.917	<Al3-O>	1.905	<Al10-O>	1.907
V6-O29	1.680(6)	V13-O21	1.596(6)	Al4-OH13	1.841(6)	S-O1	1.425(13)
-O36	1.693(6)	-O33	1.833(6)	-OH12	1.844(6)	-O2	1.468(15)
-O44	1.912(6)	-O28	1.852(6)	-OH15	1.847(6)	-O3	1.474(15)
-O42	1.914(6)	-O42	1.976(6)	-OH14	1.848(6)	-O4	1.486(13)
-O46	1.120(6)	-O43	2.001(6)	-OH6	2.016(6)	<S-O>	1.463
-O45	2.133(6)	-O45	2.233(5)	-OH5	2.037(6)		
<V6-O>	1.909	<V13-O>	1.915	<Al4-O>	1.906		
V7-O39	1.676(6)	V14-O25	1.603(6)	Al5-OH17	1.827(6)		
-O27	1.687(6)	-O37	1.825(6)	-OH16	1.841(6)		
-O41	1.912(6)	-O32	1.828(6)	-OH13	1.850(6)		
-O43	1.918(6)	-O41	1.986(6)	-OH18	1.853(6)		
-O46	2.123(6)	-O44	2.002(6)	-OH6	2.016(6)		
-O45	2.126(6)	-O45	2.223(5)	-OH4	2.058(6)		
<V7-O>	1.907	<V14-O>	1.911	<Al5-O>	1.908		

v.u. and the V site has an incident BVS close to 5 v.u. The EPMA provides significantly less than 10 Al apfu (8.94). The structure refinement also indicates less than 10 Al apfu (9.58), but much closer to the stoichiometric amount.

The central part of the flat-Al₁₀V□₂ heteropolycation consists of a brucite-type-layer grouping of seven edge-sharing octahedra (Al1 to Al6 and V16). This central unit is topologically identical to Anderson-type heteropolyoxometalates (Öhman 1989) with one very important distinction: the hetero cation in an Anderson-type cluster occupies the center octahedron of the cluster, whereas the V ion in the caseyite vanadoaluminat cluster is in a peripheral octahedron.

The other four Al-centered octahedra in the caseyite vanadoaluminat heteropolycation (Al7 to Al10) double-link to vertices of Al-centered octahedra around the girdle of the central unit (Fig. 6a). These four sites all refine to less than full occupancy

TABLE 4. Possible hydrogen bonds (O_D...O_A), bond distances (d), and bond strengths (v) for caseyite

O _D	O _A	d (Å)	v (v.u.)	O _D	O _A	d (Å)	v (v.u.)
O14	O19	2.795(9)	0.19 ^s	OW20	O10	3.004(9)	0.13
OH1	O28	2.766(8)	0.20	OW20	O40	2.963(9)	0.14
OH2	O30	2.759(8)	0.20	OW21	O47	2.827(14)	0.17
OH3	O38	2.721(7)	0.22	OW22	O15	2.903(15)	0.15
OH4	O35	2.767(8)	0.20	OW22	O32	2.771(14)	0.19
OH5	O34	2.714(8)	0.22	OW23	O13	2.890(11)	0.16
OH6	O33	2.768(7)	0.20	OW23	O44	2.771(10)	0.19
OH8	O23	2.763(8)	0.20	OW24	O4	2.688(19)	0.23
OH9	O24	2.715(8)	0.22	OW27	O30	2.825(16)	0.17
OH10	O6	2.739(8)	0.21	OW27	O48	2.942(17)	0.14
OH12	O21	2.703(8)	0.22	OW28	O12	2.893(11)	0.15
OH13	O26	2.733(8)	0.21	OW28	O43	2.792(11)	0.19
OH18	O22	2.732(8)	0.21	OW32	O4	2.85(2)	0.17
OH19	O20	2.750(8)	0.20	OW32	O27	2.839(17)	0.17
OH20	O8	2.979(9)	0.13	OW33	O7	2.803(16)	0.17
OW3	O11	2.514(9)	0.36	OW33	O31	2.830(16)	0.18
OW5	O35	2.700(9)	0.23	OW34	O48	2.94(2)	0.14
OW6	O1	2.52(2)	0.35	OW35	O47	3.087(19)	0.12
OW7	O37	2.684(9)	0.23	OW36	O29	3.12(2)	0.11
OW8	O33	2.723(9)	0.22	OW36	O48	2.65(2)	0.26
OW10	O41	2.981(9)	0.13	OW37	O17	2.85(2)	0.17
OW11	O16	2.630(8)	0.27	OW38	O2	2.69(4)	0.23
OW12	O9	2.602(8)	0.29	OW39	O3	2.86(3)	0.16
OW14	O34	2.797(8)	0.18	OW39	O4	2.80(3)	0.18
OW15	O1	2.62(2)	0.28	OW41	O3	2.94(4)	0.14
OW17	O5	2.866(14)	0.16	OW44	O39	3.09(4)	0.12
OW18	O28	2.843(12)	0.17	OW45	O36	3.02(4)	0.13
OW19	O25	2.695(9)	0.23				

Notes: Possible hydrogen bonds to OH and H₂O groups are not included. Hydrogen-bond strengths are based on O-O bond lengths from Ferraris and Ivaldi (1988).

TABLE 5a. Bond-valence analyses for the structural components in caseyite: Sulfate group

	S	H bonds	sum
O1	1.69	0.35, 0.27	2.31
O2	1.52	0.23	1.75
O3	1.49	0.16, 0.14	1.79
O4	1.45	0.23, 0.18, 0.17	2.03
sum	6.15		

Notes: The O sites are partially disordered, requiring soft restraints on the distances. This probably accounts for the anomalously high and low BVS values for O1, O2, and O3. Values are expressed in valence units.

TABLE 5b. Bond-valence analyses for the structural components in caseyite: Decavanadate anion #1

	V1	V2	V3	V4	V5	H bonds	sum
O5				1.69		0.16	1.85
O6		1.73				0.21	1.94
O7					1.72	0.18	1.90
O8			1.75			0.13	1.88
O9				1.04	0.70	0.29	2.03
O10			1.08		0.74	0.13	1.95
O11			0.82	0.89		0.36	2.07
O12		1.14			0.73	0.15	2.02
O13	1.45		0.44			0.16	2.05
O14		0.69	0.64			0.15	1.33
O15	1.33				0.54	0.15	2.02
O16	0.74	0.54		0.61		0.27	2.16
O17	0.73	0.67		0.57		0.17	2.14
O18	0.43, 0.36	0.33	0.25	0.29	0.25		1.91
sum	5.04	5.10	4.98	5.09	4.68		

Note: O14 is considered an OH.

with the Al10 site in particular exhibiting a deficiency in Al. The 20 O sites that are shared between two or three cation sites in the cluster have incident BVS values consistent with occupancy by OH groups, and the 18 O sites that link to a single cation have incident BVS values consistent with occupancy by H₂O. It should

TABLE 5c. Bond-valence analyses for the structural components in caseyite: Decavanadate anion #2

	V6	V7	V8	V9	V10	V11	V12	V13	V14	V15	H bonds	sum
O19							1.66				0.19	1.85
O20										1.69	0.20	1.89
O21								1.69			0.23	1.92
O22			1.74								0.21	1.95
O23				1.75							0.20	1.95
O24						1.68					0.22	1.90
O25									1.66		0.23	1.89
O26					1.74						0.21	1.95
O27		1.37									0.17	2.09
O28				0.84				0.87			0.20, 0.17	2.08
O29	1.39				0.56						0.11	2.06
O30						0.76				0.94	0.20, 0.17	2.07
O31						0.91	0.90				0.17	1.98
O32			0.91						0.93		0.19	2.03
O33			0.75					0.92			0.20, 0.22	2.09
O34					0.86	0.84					0.22, 0.18	2.10
O35					0.76					0.86	0.20, 0.23	2.05
O36	1.35		0.54								0.13	2.02
O37				0.78					0.94		0.23	1.95
O38			0.91	0.78							0.22	1.91
O39		1.41				0.55					0.12	2.08
O40					0.91		0.93				0.14	1.98
O41		0.74							0.62	0.60	0.13	2.09
O42	0.74						0.62	0.63				1.99
O43		0.73					0.60	0.59			0.19	2.11
O44	0.74								0.59	0.60	0.19	2.12
O45	0.41	0.42	0.26	0.26				0.33	0.34			2.02
O46	0.42	0.42			0.25	0.28	0.31			0.34		2.02
sum	5.05	5.09	5.12	4.96	5.08	5.02	5.02	5.03	5.08	5.03		

TABLE 5d. Bond-valence analyses for the structural components in caseyite: Vanadoaluminate cation

	V16	Al1	Al2	Al3	Al4	Al5	Al6	Al7	Al8	Al9	Al10	H bonds	sum
O47	1.63											0.17, 0.12	1.92
O48	1.59											0.14, 0.14, 0.26	2.13
OH1		0.54	0.34	0.32									1.20
OH2	0.26	0.53	0.37										1.16
OH3	0.27	0.52					0.39						1.18
OH4		0.52					0.34	0.38					1.24
OH5		0.50		0.39	0.36								1.25
OH6		0.49			0.38	0.38							1.25
OH7			0.61								0.49		1.10
OH8	0.62		0.56										1.18
OH9			0.54	0.57									1.12
OH10				0.62							0.54		1.16
OH11				0.60						0.55			1.15
OH12				0.59	0.58								1.17
OH13					0.59	0.57							1.16
OH14					0.58				0.56				1.14
OH15					0.58					0.54			1.12
OH16						0.59			0.55				1.14
OH17						0.61		0.57					1.18
OH18						0.57	0.57						1.14
OH19	0.64						0.57						1.21
OH20							0.55	0.51					1.06
OW1			0.63										0.63
OW2							0.54						0.54
OW3								0.50					0.50
OW4								0.49					0.49
OW5								0.48					0.48
OW6								0.48					0.48
OW7									0.49				0.49
OW8									0.48				0.48
OW9									0.46				0.46
OW10									0.43				0.43
OW11										0.51			0.51
OW12										0.50			0.50
OW13										0.44			0.44
OW14										0.43			0.43
OW15											0.64		0.64
OW16											0.54		0.54
OW17											0.45		0.45
OW18											0.37		0.37
sum	5.01	3.10	3.05	3.09	3.07	3.06	3.00	3.03	2.97	2.97	3.03		

Notes: All bond strengths are based on full occupancies by the indicated cations and anions. The bond strengths due to a possible H atom shared between O14 and O19 are not included. V^{5+} -O bond-valence parameters are from Brown and Altermatt (1985). Al^{3+} -O and S^{6+} -O bond-valence parameters are from Gagné and Hawthorne (2015). Hydrogen-bond strengths (also listed in Table 4) are based on O-O bond lengths from Ferraris and Ivaldi (1988).

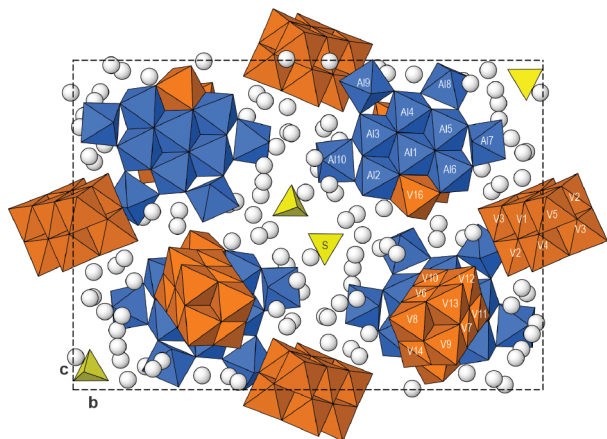


FIGURE 4. Crystal structure of caseyite viewed along [100]. The interstitial H₂O groups are white spheres. The doubly protonated decavanadate anion #1 includes the V1–V5 octahedra. The normal decavanadate anion #2 includes the V6–V15 octahedra. The unit cell is shown by dashed lines. (Color online.)

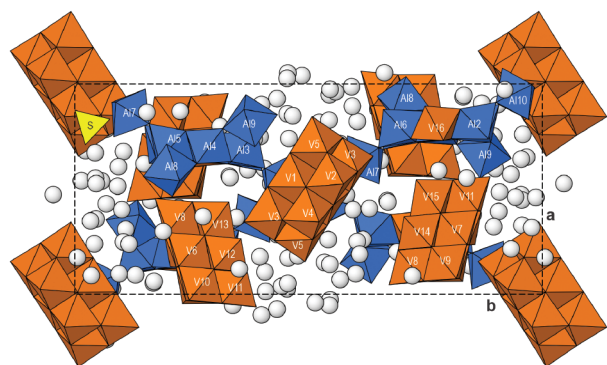


FIGURE 5. Crystal structure of caseyite viewed along [001]. Labeling as in Figure 4. (Color online.)

be noted that the deficient occupancies at the peripheral Al sites, Al7 through Al10, indicate that locally this polycation is missing one or more of the peripheral Al-centered octahedra. In those cases, the OH sites to which those Al cations would have been coordinated are instead occupied by H₂O and those H₂O sites to which those Al cations would have been coordinated remain H₂O sites, but are instead part of the interstitial complex rather than being part of the polycation. The compositional “flexibility” of the vanadoaluminate heteropolycation is formulated as $[(V^{5+}O_2)Al_{10-x}(OH)_{20-2x}(H_2O)_{18-2x}]^{(11-x)+}$.

The $[(V^{5+}O_2)Al_{10}(OH)_{20}(H_2O)_{18}]^{11+}$ vanadoaluminate heteropolycation is remarkably similar to the $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$ polycation (Fig. 6b) first reported by Seichter et al. (1998) in synthetic $[Al_{13}(OH)_{24}(H_2O)_{24}]Cl_{15} \cdot 13H_2O$. The $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$ polycation, now referred to as the “flat- Al_{13} ” polycation, belongs to a family of large aqueous aluminum hydroxide clusters whose occurrence in aqueous solution is important in environmental chemistry (Casey 2006). In the $[(V^{5+}O_2)Al_{10}(OH)_{20}(H_2O)_{18}]^{11+}$ vanadoaluminate heteropolycation, one

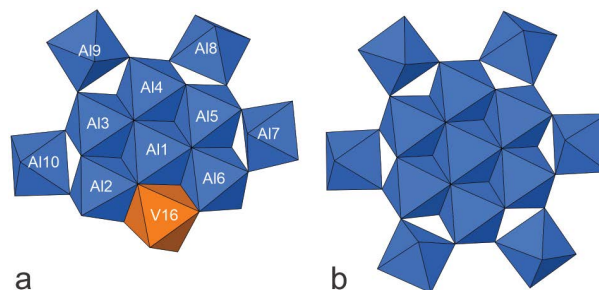


FIGURE 6. (a) The $[(V^{5+}O_2)Al_{10}(OH)_{20}(H_2O)_{18}]^{11+}$ vanadoaluminate heteropolycation in caseyite. (b) The $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$ “flat- Al_{13} ” polycation (Seichter et al. 1998). (Color online.)

of the Al sites in the girdle of the brucite-like central unit of the flat- Al_{13} cluster is replaced by V^{5+} (V16) and, in conjunction with that change, the two peripheral octahedra that corner-link with that girdle Al site in flat- Al_{13} are eliminated from the cluster.

(Na,K,Ca)-H₂O-SO₄ interstitial complex

The interstitial complex includes one SO₄ group (S and O1 to O4) and 31 H₂O groups (OW19 to OW49). With the occupancies of the S and O1 to O4 sites refined jointly, the structure refinement indicated the SO₄ group to be slightly more than half-occupied. The occupancies of many of the interstitial OW sites refined to less than full; however, only three sites had refined occupancies less than 0.5. The majority of these sites have relatively high displacement parameters indicative of disorder. The large cations Na⁺, K⁺, and Ca²⁺ are incompatible with any sites in the structural units, so it is assumed that they occur in the interstitial complex at one or more of the interstitial O sites; however, there are no specific sites to which they can be unambiguously assigned. Our EDS survey of crystals from the Packrat, Burro, and West Sunday mines indicated the interstitial cation and SO₄ contents to be quite variable, some crystals having no interstitial cations and/or SO₄. Consequently, we do not consider the large cations (Na, K, and Ca) and SO₄ to be essential constituents of the interstitial complex. However, these constituents must be included in the simplified formula because they can be important to the charge balance.

Formula and charge-balance considerations

Devising a simplified formula for caseyite requires the consideration of several factors:

(1) The small amounts of Na, K, and Ca, up to a total of about two apfu, provide additional positive charge. Assuming an upper limit of two (Na+K+Ca) apfu, the additional charge can vary from 0 to 4+.

(2) Although the structure refinement shows the interstitial SO₄ group to be approximately half-occupied (1.02 SO₄ pfu) and EPMA provides 1.33 SO₄ pfu, full occupancy of the SO₄-group sites appears possible. Therefore, the SO₄ content can vary from 0 to 2, and the charge that is contributed by the SO₄ can vary from 0 to 4-. It is also worth noting that a SO₄ group vacancy is likely to involve a concomitant introduction of additional H₂O into this region of the structure.

(3) The EPMA provided significantly less than 10 Al apfu (8.94). The structure refinement also indicated less than 10 Al apfu (9.58), but much closer to the ideal stoichiometric amount. The EDS survey also suggested that an Al deficiency is inherent in the caseyite structure. If the interstitial complex contributes no charge (i.e., is devoid of large cations and SO_4), a deficiency of 2.5 Al in the vanadoaluminate heteropolyocation is required to charge-balance the formula, which would then be $[(\text{V}^{5+}\text{O}_2)\text{Al}_{7.5}(\text{OH})_{15}(\text{H}_2\text{O})_{13}]_2[\text{H}_2\text{V}^4\text{V}_9^5\text{O}_{28}][\text{V}_{10}^5\text{O}_{28}]_2 \cdot 90\text{H}_2\text{O}$, which can be regarded as the ideal formula.

(4) The susceptibility of caseyite crystals to dehydration and the effect that such dehydration has on the mineral's composition must also be considered. Indeed, our structure studies on two less hydrated crystals suggest that all crystals are likely to have suffered partial dehydration in air prior to structure analyses. It is noteworthy that all of the O sites in the interstitial complex are far enough apart that they could be fully occupied by H_2O groups in a fully hydrated structure, although some shifting in the interstitial sites would likely be required.

The foregoing considerations are the basis for our proposing of the simplified formula $[(\text{V}^{5+}\text{O}_2)\text{Al}_{10-x}(\text{OH})_{20-2x}(\text{H}_2\text{O})_{18-2x}]_2[\text{H}_2\text{V}^4\text{V}_9^5\text{O}_{28}][\text{V}_{10}^5\text{O}_{28}]_2(\text{Na,K,Ca})_{2-z}(\text{SO}_4)_{2-z} \cdot (60+8x+y+4z)\text{H}_2\text{O}$, where $x = 0-2.5$, $y = 0-2$, $z = 0-2$.

IMPLICATIONS

Aluminum is the third most abundant element (after oxygen and silicon) in the Earth's crust. Although Al generally has very low solubility in surface waters, its role in environmental systems is of major importance (Sposito 1996). It is particularly important to understand the role of aluminum in rock weathering, water and soil chemistry, and toxicity. In water, Al^{3+} hydrolyzes, yielding various molecular species, including polycations. Natural aqueous Al nanoclusters are particularly difficult to isolate and study; they have complex structures that change readily with changing conditions, especially pH and solution chemistry (Wang et al. 2011; Bennett et al. 2017). Although Al nanoclusters are likely precursors of aluminum-hydroxide minerals, the nanoclusters themselves generally have not been found as isolated entities in minerals. However, a noteworthy example of an $\alpha\text{-Al}_{13}$ Keggin cluster forms part of the framework structure of zuniyite (Louisnathan and Gibbs 1972; Baur and Ohta 1982).

Although the flat- Al_{13} cluster has not been confirmed to occur in nature, it has been discussed as a potentially important aluminum-hydroxide cluster in natural systems (Casey 2006) because of its structural similarity to aluminum-hydroxide soil minerals. It is one of several aqueous Al nanoclusters whose interactions with other ions have been investigated in this regard (Bennett et al. 2017). The discovery of the natural flat- $\text{Al}_{10}\text{V}\square_2$ variant of the flat- Al_{13} cluster lends greater credence to research suggesting that the flat- Al_{13} cluster is an important aqueous ionic species in natural systems.

The flat- Al_{13} cluster has also proven to have significant utility in technological applications, in particular as a precursor for deposition of Al_2O_3 thin films from aqueous solution (Fulton et al. 2017). Thin films thereby produced are characterized by low-refractive index and very smooth surfaces, making them extremely useful for optical applications, e.g., anti-reflective coatings and cell-phone screens. (Perkins et al. 2017). The Al_7In_6

flat cluster also has significant potential industrial application as a new route to enhanced performance in large-area electronics and energy devices such as flat-panel displays, solar cells, and LEDs. The occurrence of the caseyite flat- $\text{Al}_{10}\text{V}\square_2$ vanadoaluminate cluster suggests that new families of Al_{13} -type clusters involving both metals of different valences and vacancies at initial peripheral Al sites with properties that are susceptible to delicate tuning via modification of redox conditions and composition during synthesis.

A question that needs to be explored is why the flat- $\text{Al}_{10}\text{V}\square_2$ heteropolyocation occurs in a structure also containing decavanadate polyanions. The answer certainly involves the role of hydrogen bonding in linking the structural units. The surface of the flat- $\text{Al}_{10}\text{V}\square_2$ heteropolyocation is draped in H, and the surfaces of the two different decavanadate anions (except for the protonated peripheral O sites) are ripe for hydrogen-bond receivership. All three structural units are "bulky" and complex; they presumably can only assemble in limited geometrical ways to achieve satisfactory hydrogen-bond coupling to one another (i.e., free energy tendency away from disorder). It seems crystallographically reasonable to expect ordered Al-nanoclusters to be more likely to occur among larger highly charged polyanions in general.

The V^{5+} ion in the girdle of the central part of the caseyite flat- $\text{Al}_{10}\text{V}\square_2$ heteropolyocation obviously results in the loss of two of the six peripheral Al-centered octahedra in the flat- Al_{13} cluster. In place of the two Al octahedra, with their peripheral H_2O vertices, are the two vanadyl O atoms of the V^{5+} octahedron. Two vanadyl O-atoms at the periphery serve to create a "relaxed node," whereby the entire surface is no longer similarly "H-active" (providing H atoms for hydrogen bonding); rather, the vanadyl O-atoms are hydrogen-bond acceptors. This offers a point-of-contact dichotomy at one end of the polyoxocation that may ameliorate hydrogen-bond connections with nearest neighbors. In effect, the resulting surface is no longer "all-key," and now has "lock & key" behavior.

Based on the different configurations of the peripheral structural elements of the flat- Al_{13} and flat- $\text{Al}_{10}\text{V}\square_2$ heteropolyocations, we can expect them to exhibit quite different reactivities and to aggregate in significantly different ways, both in Nature and in the laboratory. Although transmetalation of the flat- Al_{13} polycation has been reported and is useful for technological reasons (Kamunde-Devonish et al. 2014), the caseyite structure shows that heterovalent substituents are possible, and can involve fewer than the full number of Al octahedra in the Al_{13} cluster. Indeed, the range of possible valence of vanadium: V^{3+} , V^{4+} , and V^{5+} , together with the fact that all these ions can occur in octahedral coordination by O^{2-} suggests that a range of V-substituted Al_{13} clusters may be possible with properties tuned by conditions of synthesis.

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Endnote:

¹Deposit item AM-20-17181, CIF and Supplemental Tables. Deposit items are free to all readers and found on the MSA website, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2020/Jan2020_data/Jan2020_data.html).