

1 **Revision 1**

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3 **Caseyite, a new mineral containing a variant of the flat-Al<sub>13</sub> polyoxometalate**  
4 **cation**

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**ABSTRACT**

19 Caseyite, [(V<sup>5+</sup>O<sub>2</sub>)Al<sub>10-x</sub>(OH)<sub>20-2x</sub>(H<sub>2</sub>O)<sub>18-2x</sub>]<sub>2</sub>[H<sub>2</sub>V<sup>4+</sup>V<sup>5+</sup><sub>9</sub>O<sub>28</sub>][V<sup>5+</sup><sub>10</sub>O<sub>28</sub>]<sub>2</sub>[(Na,K,Ca)<sub>2-y</sub>(SO<sub>4</sub>)<sub>2-z</sub>  
20 ·(60+8x+y+4z)H<sub>2</sub>O], where  $x = 0 - 2.5$ ,  $y = 0 - 2$ ,  $z = 0 - 2$ , is a new mineral (IMA 2019-002)

21 occurring in low-temperature, post-mining, secondary mineral assemblages at the Burro, Packrat  
22 and West Sunday mines in the Uravan Mineral Belt of Colorado (USA). Crystals of caseyite are  
23 yellow tapering needles or blades, with pale yellow streak, vitreous luster, brittle tenacity, curved  
24 fracture, no cleavage, Mohs hardness between 2 and 3, and 2.151 g/cm<sup>3</sup> calculated density.

25 Caseyite is optically biaxial (+) with  $\alpha = 1.659(3)$ ,  $\beta = 1.670(3)$ ,  $\gamma = 1.720(3)$  (white light),  $2V =$   
26  $52.6(5)^\circ$ , has strong  $r < v$  dispersion, optical orientation  $Z \approx \mathbf{a}$  (elongation of needles), and no

27 pleochroism. Electron-probe microanalysis provided the empirical formula  
28  $[(V^{5+}O_2)Al_{8.94}(OH)_{17.88}(H_2O)_{15.88}]_2[H_2V^{4+}V^{5+}_9O_{28}][V^{5+}_{10}O_{28}]_2[(Na_{0.82}Ca_{0.35}K_{0.27})_{\Sigma 1.44}(SO_4)_{1.33} \cdot 70$   
29  $24H_2O] (+0.94 H)$ . Caseyite is monoclinic,  $P2_1/n$ ,  $a = 14.123(8)$ ,  $b = 30.998(15)$ ,  $c = 21.949(11)$   
30  $\text{\AA}$ ,  $\beta = 97.961(8)^\circ$ ,  $V = 9516(9) \text{\AA}^3$ , and  $Z = 2$ . The crystal structure ( $R_1 = 0.0654$  for  $9162 I_o >$   
31  $2\sigma I$  reflections) contains both normal  $[V_{10}O_{28}]^{6-}$  and doubly protonated mixed-valence  
32  $[H_2V^{4+}_1V^{5+}_9O_{28}]^{5-}$  decavanadate isopolyanions, and a novel vanadoaluminate heteropolycation  
33 (“flat- $Al_{10}V_{10}O_{28}$ ”), ideally  $[(V^{5+}O_2)Al_{10}(OH)_{20}(H_2O)_{18}]^{11+}$ , closely related to the technologically  
34 important flat- $Al_{13}$  polyoxocation.

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36 Keywords: caseyite; new mineral; polyoxometalate; crystal structure; Packrat mine; Burro mine;  
37 West Sunday mine; Colorado

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## INTRODUCTION

40 Millions of synthetic compounds have been prepared in the laboratory, but only about  
41 5,500 minerals have been characterized to date. Nature is much more parsimonious owing to its  
42 more limited combinations of physical conditions and abundant chemical constituents than are  
43 available in a laboratory. However, natural environments sometimes surprise us by duplicating  
44 unusual synthetic phases or by creating entirely new phases unknown from laboratory synthesis.

45 Polyoxometalate anions and, more rarely, polyoxometalate cations have been the subject  
46 of numerous synthesis studies in recent years, largely because of their potential technological  
47 uses. Low-temperature, near-surface environments, particularly those containing highly charged  
48 metal cations, also have the potential to form polyoxometalate ions, some of which have been  
49 proposed to exist in solution as precursors of more extended structural components (chains,

50 sheets, and frameworks) in mineral structures. Only rarely are polyoxometalate ions found as  
51 isolated units in minerals.

52 Deposits in the Uravan Mineral Belt of Colorado and Utah have been a rich source of  
53 uranium and vanadium ores for more than a century. They have also been a rich source of post-  
54 mining secondary vanadium minerals that typically form in mine tunnels. Among the numerous  
55 secondary minerals that have been discovered within the Uravan deposits are various phases  
56 containing polyoxometalate anions. The most common among these are minerals containing the  
57 decavanadate  $[\text{V}_{10}\text{O}_{28}]^{6-}$  isopolyanion, and its protonated and mixed-valence variants (Kampf et  
58 al. 2018). Sherwoodite, from the Peanut mine in Montrose County, Colorado (Thompson et al.  
59 1958) was the first mineral confirmed to contain a heteropolyanion, the  $(\text{AlV}^{4+,5+}_{14}\text{O}_{40})^{n-}$   
60 vanadoaluminate anion (Evans and Konnert 1978), which is structurally similar to the  
61 decavanadate anion. In recent years, new minerals containing variants of the Keggin  
62 heteropolyanion (Kondinski and Parac-Vogt 2018) have also been discovered in mines in the  
63 Uravan Mineral Belt. These include kegginite,  $\text{Pb}_3\text{Ca}_3[\text{AsV}_{12}\text{O}_{40}(\text{VO})] \cdot 20\text{H}_2\text{O}$ , from the Packrat  
64 mine (Mesa County, Colorado) containing a mono-capped Keggin  $\epsilon$ -isomer (Kampf et al. 2017),  
65 and bicapite,  $\text{KNa}_2\text{Mg}_2(\text{H}_2\text{PV}^{5+}_{14}\text{O}_{42}) \cdot 25\text{H}_2\text{O}$ , from the Pickett Corral mine (Montrose County,  
66 Colorado) containing a bi-capped Keggin  $\alpha$ -isomer (Kampf et al. 2019). The Packrat mine has  
67 also yielded several new minerals containing a novel  $[\text{As}^{3+}\text{V}^{4+,5+}_{12}\text{As}^{5+}_6\text{O}_{51}]^{n-}$  heteropolyanion  
68 (Kampf et al. 2016).

69 Caseyite, the new mineral species described here, is the most remarkable polyoxometalate  
70 mineral yet discovered. Besides containing both normal  $[\text{V}_{10}\text{O}_{28}]^{6-}$  and doubly protonated mixed-  
71 valence  $[\text{H}_2\text{V}^{4+}_1\text{V}_9^{5+}\text{O}_{28}]^{5-}$  decavanadate isopolyanions, it contains a novel vanadoaluminate  
72 heteropolycation, ideally  $[(\text{V}^{5+}\text{O}_2)\text{Al}_{10}(\text{OH})_{20}(\text{H}_2\text{O})_{18}]^{11+}$ . This new heteropolycation is a variant

73 of the “flat- $\text{Al}_{13}$ ” polyoxometalate cation  $[\text{Al}_{13}(\text{OH})_{24}(\text{H}_2\text{O})_{24}]^{15+}$  first reported by Seichter et al.  
74 (1998). Although the flat- $\text{Al}_{13}$  cluster has not yet been discovered in Nature, it has been discussed  
75 as a potentially important aluminum hydroxide cluster in natural systems (Casey 2006).  
76 Moreover, metal variants of the flat- $\text{Al}_{13}$  cluster, *e.g.*  $\text{Al}_7\text{In}_6$ , offer new methods of preparation  
77 and enhanced performance in large-area electronics and such devices as flat-panel displays, solar  
78 cells, and LEDs (Kamunde-Devonish et al. 2014). We may write the caseyite vanadoaluminate  
79 cluster as  $\text{Al}_{10}\text{V}\square_2$  ( $\square$  = vacancy) as a metal-vacancy substituted variant of the  $\text{Al}_{13}$  cluster (“flat-  
80  $\text{Al}_{10}\text{V}\square_2$ ”), suggesting new families of  $\text{Al}_{13}$ -type clusters involving both metals of different  
81 valence and vacancies at initial peripheral Al sites with properties that are susceptible to delicate  
82 tuning via modification of redox conditions and composition during synthesis.

83         The name “caseyite” honors American geochemist William H. Casey (born 1955),  
84 Distinguished Professor in the departments of Chemistry and Earth & Planetary Sciences at the  
85 University of California, Davis. Dr. Casey received his Ph.D. degree in mineralogy and  
86 geochemistry from The Pennsylvania State University in 1986. After graduating, he worked as a  
87 research geochemist at Sandia National Laboratories in Albuquerque, New Mexico, for several  
88 years, before joining the faculty of the University of California at Davis in 1991. Dr. Casey was  
89 awarded the Stumm Medal for 2010 from the European Association of Geochemistry for  
90 scientific innovation and the Clair C. Patterson Award for 2016 from the Geochemical Society  
91 for his contributions to geochemical science. He has published more than 250 scientific papers on  
92 subjects relating to aqueous solution chemistry of natural waters, mineral surface chemistry, and  
93 reaction kinetics. Much of Dr. Casey’s research, and that of his research group at UC Davis, has  
94 focused on the interaction of inorganic clusters with water. This research has included studies on  
95 aluminate polyoxometalates. The flat- $\text{Al}_{13}$  polycation, with which the caseyite vanadoaluminate

96 polycation is related, is discussed in his 2006 survey paper on large aqueous aluminum hydroxide  
97 molecules. Prof. Casey has given permission for the mineral to be named in his honor.

98         The holotype and two cotypes from the Packrat mine, one cotype from the West Sunday  
99 mine and two cotypes from the Burro mine are deposited in the collections of the Natural History  
100 Museum of Los Angeles County, Los Angeles, California, USA; catalogue numbers 73526,  
101 73527, 73528, 73529, 73530, and 73531, respectively.

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### OCCURRENCE

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

112         The Burro and West Sunday mines are near the southern end of the Uravan Mineral Belt,  
113 whereas the Packrat mine is near the northern end, about 65 km NNW of the West Sunday mine  
114 and about 70 km NNW of the Burro mine. In the Uravan Mineral Belt, uranium and vanadium  
115 minerals occur together in bedded or roll-front deposits in the sandstone of the Salt Wash  
116 member of the Jurassic Morrison Formation (Carter and Gualtieri 1965; Shawe 2011). The  
117 mineral is rare; however, considering that it was found in mines near opposite ends of the Uravan  
118 Mineral Belt, it may be relatively widespread. Although we have not confirmed the presence of

119 caseyite at any other mines, we have observed similar yellow Al- and V-rich secondary phases at  
120 other mines in the area: the Centennial mine, Uravan district, San Miguel County, Colorado and  
121 the Blue Cap, Black Hat, Pandora, and Vanadium Queen mines, La Sal district, San Juan County,  
122 Utah.

123 At all three type localities, caseyite occurs on sandstone, which is often coated with or  
124 impregnated by montroseite, corvusite, and/or asphaltum. At all three localities, but particularly  
125 at the Packrat and Burro mines, other, yet-uncharacterized, yellow-to-orange, Al- and V-rich  
126 secondary phases occur with caseyite. Gypsum is usually found in close association with caseyite  
127 at all three mines, although its abundance in each association seems to be correlated with the SO<sub>4</sub>  
128 content of caseyite; SO<sub>4</sub>-free caseyite is generally associated with little or no gypsum (see  
129 below). Other minerals found in close association with caseyite are barite (West Sunday mine),  
130 huemulite (Packrat mine), and postite (Burro mine).

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

137

### 138 **PHYSICAL AND OPTICAL PROPERTIES**

139 Crystals of caseyite (Figs. 1, 2, and 3) are yellow tapering needles or blades, elongated on  
140 [100], up to 0.25 mm in length. The streak is pale yellow, the luster is vitreous, and the mineral is  
141 non-fluorescent in long- and short-wave ultraviolet light. The crystals are brittle, with curved

142 fracture, no cleavage, and Mohs hardness estimated to be between 2 and 3. The calculated density  
143 is 2.151 g/cm<sup>3</sup> based on the empirical formula using the single-crystal cell parameters. At room  
144 temperature, the mineral is insoluble in H<sub>2</sub>O, but is easily soluble in dilute HCl. Crystals are  
145 susceptible to dehydration at low relative humidity.

146 Caseyite is optically biaxial (+) with indices of refraction determined in white light:  $\alpha =$   
147 1.659(3),  $\beta = 1.670(3)$ ,  $\gamma = 1.720(3)$ . The  $2V$  based upon extinction data analyzed with  
148 EXCALIBR (Gunter et al. 2004) is 52.6(5)° and that calculated from the indices of refraction is  
149 51.5°. The dispersion is strong,  $r < v$ , the partially determined optical orientation is  $Z \approx \mathbf{a}$   
150 (elongation of needles), and there is no pleochroism. The Gladstone-Dale compatibility  $1 -$   
151 ( $K_p/K_c$ ) is 0.008 for the empirical formula, in the range of superior compatibility (Mandarino  
152 2007).

153

#### 154 CHEMICAL ANALYSIS

155 Analyses (7 points on 2 crystals from the holotype specimen) were performed at the  
156 University of Utah on a Cameca SX-50 electron microprobe with four wavelength dispersive  
157 spectrometers and using Probe for EPMA software. Analytical conditions were 15 kV  
158 accelerating voltage, 10 nA beam current, and a beam diameter of 3  $\mu\text{m}$ . Raw X-ray intensities  
159 were corrected for matrix effects with a  $\phi\rho(z)$  algorithm (Pouchou and Pichoir 1991). Substantial  
160 dehydration of the very water-rich crystals occurs when they are subject to an ultimate vacuum of  
161  $2 \times 10^{-5}$  torr for approximately 5 minutes during vacuum deposition of the conductive carbon coat.  
162 The H<sub>2</sub>O loss results in higher concentrations for the remaining constituents than are to be  
163 expected for the fully hydrated phase. There was also moderate damage from the electron beam,  
164 which likely compounded this problem. Because insufficient material is available for direct

165 determination of H<sub>2</sub>O, it has been calculated based on the structure determination. For this  
166 purpose, we assume that all V sites are fully occupied only by V [32 atoms per formula unit  
167 (apfu)] and all O sites are fully occupied by O or a large cation: Na, K, and/or Ca (234 apfu).  
168 Note that the latter criterion is based on the fact that no O sites in the structure are too close  
169 together to be fully occupied and observations suggest that the structure crystal partly dehydrated  
170 prior to data collection. The analyzed constituents were normalized to provide a total of 100%  
171 when combined with the calculated H<sub>2</sub>O. The chemical data are reported in Table 1.

172 The structurally formatted empirical formula based on 234 O+Na+K+Ca and 32 V apfu is  
173  $[(V^{5+}O_2)Al_{8.94}(OH)_{17.88}(H_2O)_{15.88}]_2$   
174  $[H_2V^{4+}V^{5+}_9O_{28}][V^{5+}_{10}O_{28}]_2[(Na_{0.82}Ca_{0.35}K_{0.27})_{\Sigma 1.44}(SO_4)_{1.33} \cdot 70.24H_2O]$  (+0.94 H). The simplified  
175 formula is  $[(V^{5+}O_2)Al_{10-x}(OH)_{20-2x}(H_2O)_{18-2x}]_2[H_2V^{4+}V^{5+}_9O_{28}][V^{5+}_{10}O_{28}]_2[(Na,K,Ca)_{2-y}(SO_4)_{2-z}$   
176  $\cdot (60+8x+y+4z)H_2O]$ , where  $x = 0 - 2.5$ ,  $y = 0 - 2$ ,  $z = 0 - 2$ . As noted below, interstitial cations  
177 and anions are considered nonessential in caseyite; therefore, the ideal formula (for which  $x =$   
178  $2.5$ ,  $y = 2$ , and  $z = 2$ ) is:  $[(V^{5+}O_2)Al_{7.5}(OH)_{15}(H_2O)_{13}]_2[H_2V^{4+}V^{5+}_9O_{28}][V^{5+}_{10}O_{28}]_2 \cdot 90H_2O$ . The  
179 factors that were considered in the derivation of these formulas are discussed below.

180

## 181 X-RAY CRYSTALLOGRAPHY AND STRUCTURE DETERMINATION

182 The X-ray powder diffraction (PXRD) pattern was recorded with a Rigaku R-Axis Rapid  
183 II curved imaging plate microdiffractometer with monochromatized MoK $\alpha$  radiation. A  
184 Gandolfi-like motion on the  $\phi$  and  $\omega$  axes was used to randomize the sample. The pattern is  
185 dominated by several strong peaks at low angles ( $d$  values  $> 8\text{\AA}$ ). The remainder of the pattern  
186 consists only of very weak and indistinct peaks. Although the PXRD pattern is a good match with  
187 the PXRD calculated from the structure, it is poorly suited for the measurement of most lines and



188 for the refinement of the cell parameters. Consequently, in Table 2, we have opted to report only  
189 the PXRD calculated from the structure refined from the single-crystal X-ray diffraction data.

190 Single-crystal X-ray studies were undertaken on a Bruker D8 three-circle diffractometer  
191 equipped with a rotating-anode generator (MoK $\alpha$ ), multilayer optics, and an APEX-II detector.  
192 Structure data were collected on a single crystal of caseyite from the holotype specimen. The  
193 unit-cell dimensions were obtained by least-squares refinement of 3578 reflections with  $I > 10\sigma I$ .  
194 Systematically absent reflections are consistent with the space group  $P2_1/n$ . Empirical absorption  
195 corrections (SADABS) were applied and equivalent reflections were merged. The structure was  
196 solved by direct methods using SHELXS-2013 and the structure was refined using SHELXL-  
197 2016 (Sheldrick 2015). Most atoms in the structural units and some in the interstitial complex  
198 were located in the initial structure solution. The remaining sites were located using difference  
199 Fourier syntheses. The four peripheral Al sites in the vanadoaluminate unit (Al7, Al8, Al9, and  
200 Al10) refined to less than full occupancies, as did the OW sites coordinated to Al10. Most of the  
201 interstitial OW sites also refined to less than full occupancies. Positional disorder in the  
202 interstitial SO<sub>4</sub> group required the use of soft geometric restraints [S–O: 1.48(2); O–O: 2.40(2)]  
203 and the occupancies of the atom sites in the SO<sub>4</sub> group were refined together, resulting in  
204 approximately half occupancy for the group. Data collection and refinement details are given in  
205 Table 3, atom coordinates and displacement parameters in Table 4, cation-anion bond distances  
206 in Table 5, hydrogen bonds in Table 6, and bond-valence analyses in Table 7.

207

## 208 **DESCRIPTION AND DISCUSSION OF THE STRUCTURE**

209 Hawthorne (1985) first introduced the concept of binary structural representation in which  
210 a structure can be considered a combination of a strongly bonded structural unit (usually anionic)

211 and a weakly bonded interstitial complex; this concept was expanded upon by Schindler and  
212 Hawthorne (2001). This approach is particularly effective in describing structures that contain a  
213 polyoxometalate ion (the structural unit) surrounded by weakly bonded H<sub>2</sub>O groups, with or  
214 without other cations and/or anions (the interstitial complex). The structure of caseyite (Figs. 4  
215 and 5) is unusual in that it contains three different structural units. One is a normal [V<sub>10</sub>O<sub>28</sub>]<sup>6-</sup>  
216 decavanadate isopolyanion, one is a doubly protonated mixed-valence [H<sub>2</sub>V<sup>4+</sup><sub>1</sub>V<sup>5+</sup><sub>9</sub>O<sub>28</sub>]<sup>5-</sup>  
217 decavanadate isopolyanion, and one is a novel vanadoaluminate heteropolycation, ideally  
218 [(V<sup>5+</sup>O<sub>2</sub>)Al<sub>10</sub>(OH)<sub>20</sub>(H<sub>2</sub>O)<sub>18</sub>]<sup>11+</sup> (Fig. 6a). Surrounding these structural units are numerous H<sub>2</sub>O  
219 sites and an SO<sub>4</sub> group. The structural units and the components in the interstitial complex are  
220 linked to one another only by hydrogen bonds.

#### 221 *Decavanadate anionic structural units*

222       There are two different decavanadate anions in the structure of caseyite. The  
223 decavanadate anion, including protonated and mixed-valence variants, is found in numerous other  
224 Uravan-Mineral-Belt minerals. Decavanadate anion #1 [1 per formula unit (pfu)] includes atoms  
225 V1 through V5 and O5 through O18. Based on bond-valence parameters for V<sup>5+</sup>, sites V1, V2,  
226 V3, and V4 have bond-valence sums (BVS) close to 5 valence units (vu), whereas V5 has a very  
227 low BVS of 4.68 vu. Based on our extensive studies of mixed-valence and protonated  
228 decavanadates (Cooper et al. 2019a, b), we have established the formula  $V_p = 1.538(V_c) - 2.692$   
229 for calculating the aggregate valence of V ( $V_p$ ) from the BVS ( $V_c$ ). This yields an aggregate  
230 valence of 4.5+ for the V5 site, corresponding to an occupancy of V<sup>4+</sup><sub>0.5</sub>V<sup>5+</sup><sub>0.5</sub>. It is worth noting  
231 that mixed-valence decavanadates are generally green due to intervalence charge transfer (IVCT)  
232 between V<sup>4+</sup> and V<sup>5+</sup>; however, the occupancy by V<sup>4+</sup> at a single structural site in very large  
233 structure apparently is insufficient to produce any perceptible green color. The O14 site in

234 decavanadate anion #1 has a low BVS of 1.33 vu indicating that it is likely to be occupied by  
235 OH. O14 is only 2.795 Å from O19 in decavanadate anion #2, which is the likely receptor of a  
236 hydrogen bond from O14, especially considering that O19 otherwise has an incident BVS of 1.66  
237 vu. As further support, there is a small electron-density residual (+0.36 e Å<sup>-3</sup>) located 1.04 Å  
238 from O14 and 1.88 Å from O19. Therefore, decavanadate anion #1 is a doubly protonated mixed-  
239 valence decavanadate, [H<sub>2</sub>V<sup>4+</sup>V<sup>5+</sup><sub>9</sub>O<sub>28</sub>]<sup>5-</sup>. Decavanadate anion #2 (2 pfu) includes atoms V6  
240 through V15 and O19 through O46. All V sites have incident BVS close to 5 vu, indicating that  
241 all V is V<sup>5+</sup>.

#### 242 *Vanadoaluminate cationic structural unit*

243 The vanadoaluminate heteropolyocation (flat-Al<sub>10</sub>V□<sub>2</sub>), ideally  
244 [(V<sup>5+</sup>O<sub>2</sub>)Al<sub>10</sub>(OH)<sub>20</sub>(H<sub>2</sub>O)<sub>18</sub>]<sup>11+</sup> (Fig. 6a), is assembled from eleven octahedra, ten centered by  
245 Al1 through Al10 and one centered by V16. All the Al sites have incident BVSs close to 3 vu and  
246 the V site has an incident BVS close to 5 vu. The EPMA provides significantly less than 10 Al  
247 apfu (8.94). The structure refinement also indicates less than 10 Al apfu (9.58), but much closer  
248 to the stoichiometric amount.

249 The central part of the flat-Al<sub>10</sub>V□<sub>2</sub> heteropolyocation consists of a brucite-type-layer  
250 grouping of seven edge-sharing octahedra (Al1 to Al6 and V16). This central unit is topologically  
251 identical to Anderson-type heteropolyoxometalates (Öhman 1989) with one very important  
252 distinction: the hetero cation in an Anderson-type cluster occupies the center octahedron of the  
253 cluster, whereas the V ion in the caseyite vanadoaluminate cluster is in a peripheral octahedron.

254 The other four Al-centered octahedra in the caseyite vanadoaluminate heteropolyocation  
255 (Al7 to Al10) double-link to vertices of Al-centered octahedra around the girdle of the central  
256 unit (Fig. 6a). These four sites all refine to less than full occupancy with the Al10 site in

257 particular exhibiting a deficiency in Al. The 20 O sites that are shared between two or three  
258 cation sites in the cluster have incident BVS values consistent with occupancy by OH groups, and  
259 the 18 O sites that link to a single cation have incident BVS values consistent with occupancy by  
260 H<sub>2</sub>O. It should be noted that the deficient occupancies at the peripheral Al sites, Al7 through  
261 Al10, indicate that locally this polycation is missing one or more of the peripheral Al-centered  
262 octahedra. In those cases, the OH sites to which those Al cations would have been coordinated  
263 are instead occupied by H<sub>2</sub>O and those H<sub>2</sub>O sites to which those Al cations would have been  
264 coordinated remain H<sub>2</sub>O sites, but are instead part of the interstitial complex rather than being  
265 part of the polycation. The compositional “flexibility” of the vanadoaluminate heteropolycation is  
266 formulated as  $[(V^{5+}O_2)Al_{10-x}(OH)_{20-2x}(H_2O)_{18-2x}]^{(11-x)+}$ .

267 The  $[(V^{5+}O_2)Al_{10}(OH)_{20}(H_2O)_{18}]^{11+}$  vanadoaluminate heteropolycation is remarkably  
268 similar to the  $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$  polycation (Fig. 6b) first reported by Seichter et al. (1998)  
269 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  
270 referred to as the “flat-Al<sub>13</sub>” polycation, belongs to a family of large aqueous aluminum  
271 hydroxide clusters whose occurrence in aqueous solution is important in environmental chemistry  
272 (Casey 2006). In the  $[(V^{5+}O_2)Al_{10}(OH)_{20}(H_2O)_{18}]^{11+}$  vanadoaluminate heteropolycation, one of  
273 the Al sites in the girdle of the brucite-like central unit of the flat-Al<sub>13</sub> cluster is replaced by V<sup>5+</sup>  
274 (V16) and, in conjunction with that change, the two peripheral octahedra that corner link with  
275 that girdle Al site in flat-Al<sub>13</sub> are eliminated from the cluster.

#### 276 *(Na,K,Ca)-H<sub>2</sub>O-SO<sub>4</sub> interstitial complex*

277 The interstitial complex includes one SO<sub>4</sub> group (S and O1 to O4) and 31 H<sub>2</sub>O groups  
278 (OW19 to OW49). With the occupancies of the S and O1 to O4 sites refined jointly, the structure  
279 refinement indicated the SO<sub>4</sub> group to be slightly more than half-occupied. The occupancies of

280 many of the interstitial OW sites refined to less than full; however, only three sites had refined  
281 occupancies less than 0.5. The majority of these sites have relatively high displacement  
282 parameters indicative of disorder. The large cations  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  are incompatible with any  
283 sites in the structural units, so it is assumed that they occur in the interstitial complex at one or  
284 more of the interstitial O sites; however, there are no specific sites to which they can be  
285 unambiguously assigned. Our EDS survey of crystals from the Packrat, Burro, and West Sunday  
286 mines indicated the interstitial cation and  $\text{SO}_4$  contents to be quite variable, some crystals having  
287 no interstitial cations and/or  $\text{SO}_4$ . Consequently, we do not consider the large cations (Na, K, and  
288 Ca) and  $\text{SO}_4$  to be essential constituents of the interstitial complex. However, these constituents  
289 must be included in the simplified formula because they can be important to the charge balance.

290 *Formula and charge-balance considerations*

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

- 292 1. The small amounts of Na, K, and Ca, up to a total of about two apfu, provide additional  
293 positive charge. Assuming an upper limit of two ( $\text{Na}+\text{K}+\text{Ca}$ ) apfu, the additional charge can  
294 vary from 0 to 4+.
- 295 2. Although the structure refinement shows the interstitial  $\text{SO}_4$  group to be approximately half-  
296 occupied (1.02  $\text{SO}_4$  pfu) and EPMA provided 1.33  $\text{SO}_4$  pfu, full occupancy of the  $\text{SO}_4$ -group  
297 sites appears possible. Therefore, the  $\text{SO}_4$  content can vary from 0 to 2, and the charge that is  
298 contributed by the  $\text{SO}_4$  can vary from 0 to 4-. It is also worth noting that a  $\text{SO}_4$  group  
299 vacancy is likely to involve a concomitant introduction of additional  $\text{H}_2\text{O}$  into this region of  
300 the structure.
- 301 3. The EPMA provided significantly less than 10 Al apfu (8.94). The structure refinement also  
302 indicated less than 10 Al apfu (9.58), but much closer to the ideal stoichiometric amount. The

303 EDS survey also suggested that an Al deficiency is inherent in the caseyite structure. If the  
304 interstitial complex contributes no charge (i.e. is devoid of large cations and  $\text{SO}_4$ ), a  
305 deficiency of 2.5 Al in the vanadoaluminate heteropolycation is required to charge-balance  
306 the formula, which would then be  $[(\text{V}^{5+}\text{O}_2)\text{Al}_{7.5}(\text{OH})_{15}(\text{H}_2\text{O})_{13}]_2$   
307  $[\text{H}_2\text{V}^{4+}\text{V}^{5+}_9\text{O}_{28}][\text{V}^{5+}_{10}\text{O}_{28}]_2 \cdot 90\text{H}_2\text{O}$ , which can be regarded as the ideal formula.  
308 4. The susceptibility of caseyite crystals to dehydration and the effect that such dehydration has  
309 on the mineral's composition must also be considered. Indeed, our structure studies on two  
310 less hydrated crystals suggest that all crystals are likely to have suffered partial dehydration in  
311 air prior to structure analyses. It is noteworthy that all of the O sites in the interstitial complex  
312 are far enough apart that they could be fully occupied by  $\text{H}_2\text{O}$  groups in a fully hydrated  
313 structure, although some shifting in the interstitial sites would likely be required.

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

317

318

## IMPLICATIONS

319 Aluminum is the third most abundant element (after oxygen and silicon) in the Earth's  
320 crust. Although Al generally has very low solubility in surface waters, its role in environmental  
321 systems is of major importance (Sposito 1996). It is particularly important to understand the role  
322 of aluminum in rock weathering, water and soil chemistry, and toxicity. In water,  $\text{Al}^{3+}$   
323 hydrolyzes, yielding a variety of molecular species, including polycations. Natural aqueous Al  
324 nanoclusters are particularly difficult to isolate and study; they have complex structures that  
325 change readily with changing conditions, especially pH and solution chemistry (Bennett et al.

326 2017; Wang et al. 2011). Although Al nanoclusters are likely precursors of aluminum-hydroxide  
327 minerals, the nanoclusters themselves generally have not been found as isolated entities in  
328 minerals. However, a noteworthy example of an  $\alpha$ -Al<sub>13</sub> Keggin cluster forms part of the  
329 framework structure of zunyite (Louisnathan and Gibbs 1972; Baur and Ohta 1982).

330         Although the flat-Al<sub>13</sub> cluster has not been confirmed to occur in Nature, it has been  
331 discussed as a potentially important aluminum-hydroxide cluster in natural systems (Casey 2006)  
332 because of its structural similarity to aluminum-hydroxide soil minerals. It is one of several  
333 aqueous Al nanoclusters whose interactions with other ions have been investigated in this regard  
334 (Bennett et al. 2017). The discovery of the natural flat-Al<sub>10</sub>V□<sub>2</sub> variant of the flat-Al<sub>13</sub> cluster  
335 lends greater credence to research suggesting that the flat-Al<sub>13</sub> cluster is an important aqueous  
336 ionic species in natural systems.

337         The flat-Al<sub>13</sub> cluster has also proven to have significant utility in technological  
338 applications, in particular as a precursor for deposition of Al<sub>2</sub>O<sub>3</sub> thin films from aqueous solution  
339 (Fulton et al. 2017). Thin films thereby produced are characterized by low-refractive index and  
340 very smooth surfaces, making them extremely useful for optical applications, e.g. anti-reflective  
341 coatings, cell-phone screens, etc. (Perkins et al. 2017). The Al<sub>7</sub>In<sub>6</sub> flat cluster also has significant  
342 potential industrial application as a new route to enhanced performance in large-area electronics  
343 and energy devices such as flat-panel displays, solar cells, and LEDs. The occurrence of the  
344 caseyite flat-Al<sub>10</sub>V□<sub>2</sub> vanadoaluminate cluster suggests that new families of Al<sub>13</sub>-type clusters  
345 involving both metals of different valence and vacancies at initial peripheral Al sites with  
346 properties that are susceptible to delicate tuning via modification of redox conditions and  
347 composition during synthesis.

348         A question that needs to be explored is why the flat-Al<sub>10</sub>V□<sub>2</sub> heteropolycation occurs in a

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

357         The  $\text{V}^{5+}$  ion in the girdle of the central part of the caseyite flat- $\text{Al}_{10}\text{V}\square_2$  heteropolyocation  
358 obviously results in the loss of two of the six peripheral Al-centered octahedra in the flat- $\text{Al}_{13}$   
359 cluster. In place of the two Al octahedra, with their peripheral  $\text{H}_2\text{O}$  vertices, are the two vanadyl  
360 O atoms of the  $\text{V}^{5+}$  octahedron. Two vanadyl O-atoms at the periphery serve to create a ‘relaxed  
361 node’, whereby the entire surface is no longer similarly “H-active” (providing H atoms for  
362 hydrogen bonding); rather, the vanadyl O-atoms are hydrogen-bond acceptors. This offers a  
363 point-of-contact dichotomy at one end of the polyoxocation that may ameliorate hydrogen-bond  
364 connections with nearest neighbours. In effect, the resulting surface is no longer ‘all-key’, and  
365 now has ‘lock & key’ behavior.

366         Based on the different configurations of the peripheral structural elements of the flat- $\text{Al}_{13}$   
367 and flat- $\text{Al}_{10}\text{V}\square_2$  heteropolyocations, we can expect them to exhibit quite different reactivities and  
368 to aggregate in significantly different ways, both in Nature and in the laboratory. Although  
369 transmetalation of the flat- $\text{Al}_{13}$  polycation has been reported and is useful for technological  
370 reasons (Kamunde-Devonish et al. 2014), the caseyite structure shows that heterovalent  
371 substituents are possible, and can involve fewer than the full number of Al octahedra in the  $\text{Al}_{13}$



372 cluster. Indeed, the range of possible valence of vanadium:  $V^{3+}$ ,  $V^{4+}$ , and  $V^{5+}$ , together with the  
373 fact that all these ions can occur in octahedral coordination by  $O^{2-}$  suggests that a range of V-  
374 substituted  $Al_{13}$  clusters may be possible with properties tuned by conditions of synthesis.

375

376

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- 462
- 463

FIGURE CAPTIONS

464

465

466 Figure 1. Caseyite needles with gypsum and orange-yellow balls of another potentially new Al-  
467 V-S-O-bearing mineral; holotype specimen (#73526) from the Packrat mine; FOV 0.68 mm  
468 across.

469

470 Figure 2. Caseyite needles on cotype specimen (#73529) from the West Sunday mine; FOV 0.68  
471 mm across.

472

473 Figure 3. Caseyite blades on cotype specimen (#73530) from the Burro mine; FOV 0.84 mm  
474 across.

475

476 Figure 4. Crystal structure of caseyite viewed along [100]. The interstitial H<sub>2</sub>O groups are white  
477 spheres. The doubly protonated decavanadate anion (#1) includes the V1-V5 octahedra. The  
478 normal decavanadate anion (#2) includes the V6-V15 octahedra. The unit cell is shown by dashed  
479 lines.

480

481 Figure 5. Crystal structure of caseyite viewed along [001]. The interstitial H<sub>2</sub>O groups are white  
482 spheres. The doubly protonated decavanadate anion (#1) includes the V1-V5 octahedra. The  
483 normal decavanadate anion (#2) includes the V6-V15 octahedra. The unit cell is shown by dashed  
484 lines.

485

486 Figure 6. (a) The  $[(V^{5+}O_2)Al_{10}(OH)_{20}(H_2O)_{18}]^{11+}$  vanadoaluminate heteropolyocation in caseyite.  
487 (b) The  $[Al_{13}(OH)_{24}(H_2O)_{24}]^{15+}$  “flat- $Al_{13}$ ” polycation (Seichter *et al.*, 1998).  
488

489 Table 1. Analytical data in wt% for caseyite.  
 490

Constituent	Mean	Range	S.D.	Norm.	Standard
Na <sub>2</sub> O	0.52	0.15–0.87	0.29	0.41	albite
K <sub>2</sub> 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 <sub>2</sub> O <sub>3</sub>	18.74	17.71–19.28	0.69	14.78	sanidine
V <sub>2</sub> O <sub>5</sub>	(59.87)	59.33–61.08	0.58		V metal
VO <sub>2</sub> *	1.71			1.35	
V <sub>2</sub> O <sub>5</sub> *	58.00			45.73	
SO <sub>3</sub>	2.19	2.14–2.21	0.03	1.73	celestine
H <sub>2</sub> O <sup>§</sup>				35.47	
Total				100.00	

491 \* Allotted in accord with the structure.

492 § Based on the structure.

493

494 Table 2. Calculated powder X-ray diffraction data ( $d$  in Å) for caseyite.

495

$I_{\text{calc}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{calc}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{calc}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{calc}}$	$d_{\text{calc}}$	$hkl$
92	17.798	0 1 1	1	5.145	-1 5 2	1	3.185	4 1 2	1	2.412	3 11 0
100	15.499	0 2 0	1	5.117	-2 2 3	3	3.177	2 6 4	1	2.405	0 6 8
26	12.749	1 1 0	1	5.032	-1 2 4	1	3.174	-4 3 3	2	2.395	2 6 7
33	12.620	0 2 1	1	4.801	-2 3 3	1	3.136	-2 6 5	1	2.391	-3 11 2
3	11.085	1 0 1	1	4.711	0 5 3	1	3.132	-1 8 4	1	2.320	4 10 0
16	10.869	0 0 2	1	4.694	-3 0 1	2	3.126	-2 4 6	1	2.312	-4 10 2
2	10.437	1 1 1	1	4.641	-3 1 1	2	3.110	1 4 6	1	2.263	-3 12 1
3	10.384	1 2 0	1	4.610	3 1 0	1	3.090	2 9 0	1	2.255	-2 13 1
7	10.257	0 1 2	2	4.492	-3 2 1	1	3.083	-4 2 4	2	2.253	-3 6 8
11	9.332	0 3 1	1	4.449	0 4 4	1	3.066	-3 6 4	1	2.232	3 12 1
14	9.016	1 2 1	1	4.420	-2 2 4	1	3.034	2 1 6	1	2.230	-2 13 2
43	8.899	0 2 2	3	4.390	3 1 1	2	3.026	1 10 0	1	2.193	-2 8 8
5	8.840	-1 1 2	1	4.274	-3 3 1	1	2.991	-1 3 7	1	2.167	-2 6 9
10	8.311	1 3 0	1	4.177	-1 7 1	1	2.980	3 8 0	1	2.150	-5 4 7
1	7.799	1 1 2	1	4.155	2 6 0	3	2.978	1 5 6	1	2.137	-6 6 2
6	7.750	0 4 0	1	4.145	-2 6 1	1	2.967	1 7 5	1	2.132	3 4 8
1	7.558	1 3 1	1	4.139	-3 3 2	1	2.947	-3 3 6	1	2.130	6 1 3
3	7.489	0 3 2	1	4.108	1 4 4	1	2.938	-1 10 2	1	2.123	3 13 0
3	7.300	0 4 1	2	4.075	3 3 1	1	2.924	2 3 6	1	2.088	-5 10 1
1	7.150	1 2 2	1	4.007	0 3 5	1	2.849	-2 6 6	1	2.083	-2 4 10
2	7.056	0 1 3	2	3.996	2 1 4	1	2.834	2 10 0	1	2.081	4 7 6
3	6.993	2 0 0	1	3.990	-1 3 5	1	2.819	-4 3 5	1	2.054	-5 6 7
2	6.822	2 1 0	2	3.815	0 8 1	1	2.813	-5 1 1	1	2.048	5 10 1
1	6.776	-2 1 1	1	3.780	-3 1 4	1	2.795	-2 4 7	1	2.025	-3 7 9
5	6.598	-1 4 1	2	3.734	-2 7 1	1	2.781	-2 10 2	1	2.012	-3 4 10
3	6.375	2 2 0	2	3.728	1 3 5	1	2.770	3 9 0	1	2.006	4 6 7
1	6.351	1 4 1	1	3.703	-1 8 1	1	2.717	5 1 1	1	1.985	5 11 0
1	6.337	-2 2 1	1	3.572	-1 8 2	1	2.705	2 10 2	1	1.960	5 11 1
1	6.271	2 1 1	1	3.553	1 4 5	1	2.698	-5 2 3	1	1.945	-5 6 8
2	6.251	-1 2 3	1	3.536	-1 2 6	1	2.686	5 2 1	2	1.898	4 8 7
2	6.098	1 0 3	1	3.528	0 2 6	1	2.673	-3 3 7	1	1.876	-5 5 9
3	5.983	1 1 3	1	3.475	4 1 0	1	2.661	1 5 7	1	1.846	-5 8 8
1	5.933	0 3 3	1	3.450	-4 1 2	1	2.637	5 3 1	1	1.840	5 12 2
1	5.919	2 2 1	1	3.388	-4 2 2	1	2.626	2 6 6	1	1.803	0 14 7
3	5.792	2 3 0	1	3.360	1 5 5	1	2.541	3 10 1	1	1.798	-5 7 9
3	5.586	1 4 2	1	3.329	-2 5 5	2	2.527	-3 5 7	1	1.739	4 9 8
1	5.456	2 1 2	1	3.322	-1 9 1	1	2.511	2 7 6	1	1.630	7 11 0
2	5.373	-2 3 2	1	3.315	2 8 1	1	2.484	-4 5 6	1	1.589	-7 12 1
1	5.252	1 3 3	1	3.312	4 3 0	1	2.445	-2 5 8	1	1.539	-7 13 2
1	5.219	2 2 2	2	3.289	1 9 1	1	2.430	-4 3 7	1	1.462	-1 0 15

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498 Table 3. Data collection and structure refinement details for caseyite.  
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500	Diffractometer	Bruker D8 three-circle; multilayer optics; APEX-II CCD
501	X-ray radiation / source	MoK $\alpha$ ( $\lambda = 0.71073$ Å) / rotating anode
502	Temperature	293(2) K
503	Refined cell content	Al <sub>19.16</sub> V <sub>32</sub> S <sub>1.02</sub> O <sub>215.11</sub>
504	Space group	$P2_1/n$
505	Unit cell dimensions	$a = 14.123(8)$ Å
506		$b = 30.998(15)$ Å
507		$c = 21.949(11)$ Å
508		$\beta = 97.961(8)^\circ$
509	$V$	$9516(9)$ Å <sup>3</sup>
510	$Z$	2
511	Absorption coefficient	$1.730$ mm <sup>-1</sup>
512	$F(000)$	5444
513	Crystal size	$120 \times 5 \times 5$ μm
514	$\theta$ range	$2.09$ to $23.64^\circ$
515	Index ranges	$-15 \leq h \leq 15, -34 \leq k \leq 34, -24 \leq l \leq 24$
516	Reflections integrated	183070
517	Reflections collected/unique	56066/14231; $R_{\text{int}} = 0.098$
518	Reflections with $I > 2\sigma I$	9162
519	Completeness to $\theta = 25.02^\circ$	99.4%
520	Refinement method	Full-matrix least-squares on $F^2$
521	Parameter/restraints	1154/10
522	GoF	1.025
523	Final $R$ indices [ $I > 3\sigma I$ ]	$R_1 = 0.0654, wR_2 = 0.1673$
524	$R$ indices (all data)	$R_1 = 0.1102, wR_2 = 0.1932$
525	Extinction coefficient	$0.00052(8)$
526	Largest diff. peak/hole	$+1.43/-0.59$ e Å <sup>-3</sup>
527	* $R_{\text{int}} = \Sigma F_o^2 - F_o^2(\text{mean}) /\Sigma[F_o^2]$ . GoF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ . $R_1 = \Sigma  F_o  -  F_c  /\Sigma F_o $ . $wR_2$	
528	= $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ ; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $a$ is 0.0901, $b$ is 54.2021	
529	and $P$ is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$	

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534 Table 4. Atom coordinates, displacement parameters ( $\text{\AA}^2$ ), and site occupancies for caseyite.  
535

536		$x/a$	$y/b$	$z/c$	$U_{\text{eq}}$	Occupancy
537	V1	0.55617(11)	0.54019(5)	0.03969(7)	0.0286(4)	1
538	V2	0.55449(11)	0.44708(5)	0.09567(7)	0.0331(4)	1
539	V3	0.36501(12)	0.59068(5)	0.02391(7)	0.0357(4)	1
540	V4	0.36858(11)	0.49818(5)	0.07894(7)	0.0312(4)	1
541	V5	0.26195(11)	0.51661(5)	0.94767(8)	0.0375(4)	1
542	V6	0.79315(10)	0.23654(5)	0.23658(6)	0.0257(3)	1
543	V7	0.81269(10)	0.32342(5)	0.32366(7)	0.0287(4)	1
544	V8	0.61516(10)	0.21279(5)	0.29562(7)	0.0301(4)	1
545	V9	0.63145(10)	0.29526(5)	0.37400(7)	0.0326(4)	1
546	V10	0.97098(10)	0.26618(5)	0.18300(7)	0.0329(4)	1
547	V11	0.98922(11)	0.34747(5)	0.26533(8)	0.0360(4)	1
548	V12	0.80120(10)	0.32953(5)	0.17840(7)	0.0332(4)	1
549	V13	0.62361(10)	0.30312(5)	0.23257(7)	0.0268(4)	1
550	V14	0.80250(10)	0.23104(5)	0.38121(7)	0.0309(4)	1
551	V15	0.98233(10)	0.25677(5)	0.32637(7)	0.0298(4)	1
552	V16	0.31130(11)	0.26997(6)	0.43438(7)	0.0358(4)	1
553	Al1	0.30286(17)	0.27887(8)	0.28649(11)	0.0252(6)	1
554	Al2	0.31824(17)	0.35997(9)	0.36242(12)	0.0303(6)	1
555	Al3	0.30960(18)	0.36565(9)	0.22386(11)	0.0281(6)	1
556	Al4	0.29720(17)	0.28602(8)	0.14827(11)	0.0251(6)	1
557	Al5	0.28494(17)	0.19978(8)	0.20493(11)	0.0269(6)	1
558	Al6	0.29279(18)	0.19092(9)	0.34056(12)	0.0297(6)	1
559	Al7	0.1438(2)	0.12036(10)	0.25032(13)	0.0345(12)	0.939(12)
560	Al8	0.4065(2)	0.20425(9)	0.08109(12)	0.0280(11)	0.930(12)
561	Al9	0.18127(18)	0.37486(9)	0.08129(12)	0.0285(11)	0.974(11)
562	Al10	0.4427(3)	0.44105(16)	0.3079(2)	0.053(2)	0.735(13)
563	S	0.1896(5)	0.0331(2)	0.0592(3)	0.069(2)	0.509(8)
564	O1	0.1760(16)	0.0354(7)	0.1222(6)	0.122(8)	0.509(8)
565	O2	0.2893(14)	0.0223(11)	0.0539(16)	0.30(3)	0.509(8)
566	O3	0.125(2)	0.0006(7)	0.0270(12)	0.233(17)	0.509(8)
567	O4	0.1677(13)	0.0751(5)	0.0277(8)	0.093(6)	0.509(8)
568	O5	0.3444(5)	0.4776(2)	0.1422(3)	0.0413(16)	1
569	O6	0.5238(5)	0.4257(2)	0.1563(3)	0.0429(17)	1
570	O7	0.1554(5)	0.5078(2)	-0.0856(3)	0.0550(19)	1
571	O8	0.3436(5)	0.6377(2)	0.0484(3)	0.0493(18)	1
572	O9	0.2592(4)	0.49158(19)	0.0281(3)	0.0336(14)	1
573	O10	0.2553(4)	0.57302(19)	-0.0179(3)	0.0362(15)	1
574	O11	0.3524(4)	0.55635(19)	0.0927(3)	0.0343(15)	1
575	O12	0.6752(4)	0.46054(19)	0.1175(3)	0.0345(15)	1
576	O13	0.5121(4)	0.58757(19)	0.0580(3)	0.0382(15)	1
577	O14	0.5827(4)	0.39518(19)	0.0522(3)	0.0346(15)	1
578	O15	0.6732(4)	0.53962(18)	0.0706(3)	0.0329(14)	1
579	O16	0.5755(4)	0.55302(18)	-0.0430(3)	0.0290(14)	1

580	O17	0.5103(4)	0.50622(18)	0.1027(3)	0.0301(14)	1
581	O18	0.4191(4)	0.52460(17)	-0.0067(3)	0.0276(13)	1
582	O19	0.7365(4)	0.3557(2)	0.1251(3)	0.0434(17)	1
583	O20	0.0450(4)	0.2302(2)	0.3798(3)	0.0404(16)	1
584	O21	0.5617(4)	0.3294(2)	0.1785(3)	0.0353(15)	1
585	O22	0.5450(4)	0.1722(2)	0.2839(3)	0.0394(16)	1
586	O23	0.5751(4)	0.3158(2)	0.4251(3)	0.0451(17)	1
587	O24	0.0598(4)	0.3879(2)	0.2765(3)	0.0459(17)	1
588	O25	0.8685(4)	0.2039(2)	0.4329(3)	0.0458(18)	1
589	O26	0.0277(4)	0.2447(2)	0.1326(3)	0.0440(17)	1
590	O27	0.7384(4)	0.3386(2)	0.3737(3)	0.0341(15)	1
591	O28	0.5764(4)	0.32282(19)	0.3021(3)	0.0322(14)	1
592	O29	0.8663(4)	0.22221(19)	0.1859(3)	0.0315(14)	1
593	O30	0.0436(4)	0.3085(2)	0.3275(3)	0.0339(15)	1
594	O31	0.8949(4)	0.36868(19)	0.2069(3)	0.0385(16)	1
595	O32	0.7105(4)	0.19156(19)	0.3533(3)	0.0338(15)	1
596	O33	0.5606(4)	0.25144(18)	0.2326(2)	0.0267(13)	1
597	O34	0.0421(4)	0.3155(2)	0.2063(3)	0.0355(15)	1
598	O35	0.0283(4)	0.23774(19)	0.2558(3)	0.0314(14)	1
599	O36	0.7064(4)	0.19866(19)	0.2346(3)	0.0309(14)	1
600	O37	0.7253(4)	0.2626(2)	0.4244(3)	0.0351(15)	1
601	O38	0.5640(4)	0.24553(19)	0.3527(3)	0.0307(14)	1
602	O39	0.8978(4)	0.36131(19)	0.3262(3)	0.0351(15)	1
603	O40	0.8789(4)	0.2981(2)	0.1354(3)	0.0356(15)	1
604	O41	0.8858(4)	0.28194(19)	0.3747(3)	0.0299(14)	1
605	O42	0.7199(4)	0.27808(19)	0.1855(2)	0.0279(13)	1
606	O43	0.7348(4)	0.34336(18)	0.2506(3)	0.0290(14)	1
607	O44	0.8708(4)	0.21698(18)	0.3096(3)	0.0284(13)	1
608	O45	0.7234(4)	0.26850(18)	0.3041(2)	0.0251(13)	1
609	O46	0.8815(4)	0.29146(19)	0.2564(3)	0.0294(14)	1
610	O47	0.3950(5)	0.2489(2)	0.4834(3)	0.0455(17)	1
611	O48	0.2311(5)	0.2880(2)	0.4748(3)	0.0517(19)	1
612	OH1	0.3797(4)	0.32845(18)	0.2951(2)	0.0273(13)	1
613	OH2	0.2407(4)	0.30506(18)	0.3474(2)	0.0276(13)	1
614	OH3	0.3708(4)	0.24503(18)	0.3495(2)	0.0260(13)	1
615	OH4	0.2252(4)	0.22927(18)	0.2745(2)	0.0267(13)	1
616	OH5	0.2357(4)	0.31046(17)	0.2195(2)	0.0239(13)	1
617	OH6	0.3631(4)	0.25394(17)	0.2221(2)	0.0246(13)	1
618	OH7	0.4128(5)	0.4006(2)	0.3683(3)	0.0513(18)	1
619	OH8	0.3800(4)	0.3244(2)	0.4235(3)	0.0331(14)	1
620	OH9	0.2538(4)	0.38461(19)	0.2905(3)	0.0323(14)	1
621	OH10	0.4013(4)	0.40693(19)	0.2391(3)	0.0341(15)	1
622	OH11	0.2229(4)	0.38957(19)	0.1633(3)	0.0347(15)	1
623	OH12	0.3692(4)	0.33496(18)	0.1682(2)	0.0255(13)	1
624	OH13	0.2224(4)	0.23733(18)	0.1473(2)	0.0287(14)	1
625	OH14	0.3792(4)	0.26109(19)	0.0997(2)	0.0289(14)	1

626	OH15	0.2124(4)	0.31649(18)	0.0927(2)	0.0274(13)	1
627	OH16	0.3617(4)	0.1802(2)	0.1495(3)	0.0345(15)	1
628	OH17	0.1901(4)	0.15924(19)	0.1978(3)	0.0342(15)	1
629	OH18	0.3499(4)	0.17288(19)	0.2737(3)	0.0314(14)	1
630	OH19	0.2396(4)	0.2184(2)	0.4026(3)	0.0333(15)	1
631	OH20	0.1963(4)	0.1497(2)	0.3229(3)	0.0377(15)	1
632	OW1	0.2381(5)	0.3841(2)	0.4107(3)	0.0469(17)	1
633	OW2	0.3783(4)	0.1597(2)	0.3968(3)	0.0401(16)	1
634	OW3	0.0876(5)	0.0794(2)	0.2990(3)	0.056(2)	1
635	OW4	0.2523(5)	0.0834(2)	0.2507(4)	0.060(2)	1
636	OW5	0.0245(5)	0.1509(2)	0.2462(3)	0.0488(18)	1
637	OW6	0.0861(6)	0.0876(3)	0.1807(3)	0.065(2)	1
638	OW7	0.2867(5)	0.1965(2)	0.0303(3)	0.0491(18)	1
639	OW8	0.5348(4)	0.2085(2)	0.1233(3)	0.0451(17)	1
640	OW9	0.4401(6)	0.1467(2)	0.0569(3)	0.057(2)	1
641	OW10	0.4603(5)	0.2242(2)	0.0083(3)	0.0479(18)	1
642	OW11	0.2990(4)	0.3853(2)	0.0511(3)	0.0375(15)	1
643	OW12	0.1460(4)	0.4331(2)	0.0632(3)	0.0399(16)	1
644	OW13	0.1215(4)	0.3621(2)	-0.0023(3)	0.0393(16)	1
645	OW14	0.0518(4)	0.3660(2)	0.1018(3)	0.0385(16)	1
646	OW15	0.3305(10)	0.4699(4)	0.3032(6)	0.087(6)	0.71(3)
647	OW16	0.4965(9)	0.4777(4)	0.3715(6)	0.071(6)	0.67(2)
648	OW17	0.4825(9)	0.4830(4)	0.2507(6)	0.085(6)	0.75(3)
649	OW18	0.5742(7)	0.4143(3)	0.3113(5)	0.082(5)	0.92(3)
650	OW19	0.9453(5)	0.1681(2)	0.5404(3)	0.0485(18)	1
651	OW20	0.8794(5)	0.3516(2)	0.0237(3)	0.0511(18)	1
652	OW21	0.0880(5)	0.2780(2)	-0.0034(3)	0.0542(19)	1
653	OW22	0.1906(5)	0.3910(2)	-0.1018(3)	0.0565(19)	1
654	OW23	0.9075(6)	0.1299(3)	0.3293(4)	0.073(2)	1
655	OW24	0.1355(8)	0.1542(3)	0.0706(5)	0.095(3)	1
656	OW25	0.1518(8)	0.4661(4)	0.2078(5)	0.107(3)	1
657	OW26	0.4861(10)	0.0917(4)	0.3761(6)	0.135(4)	1
658	OW27	0.5527(8)	0.1621(4)	-0.0499(5)	0.107(5)	0.99(3)
659	OW28	0.7159(7)	0.4330(3)	0.2444(5)	0.083(5)	0.93(3)
660	OW29	0.3935(10)	0.0936(4)	0.1806(6)	0.123(7)	0.95(3)
661	OW30	0.3277(8)	0.0437(4)	0.3573(5)	0.092(5)	0.87(3)
662	OW31	0.9737(9)	0.4541(4)	0.0040(5)	0.094(6)	0.86(3)
663	OW32	0.3214(10)	0.1042(4)	-0.0328(6)	0.085(6)	0.73(3)
664	OW33	0.9480(11)	0.4556(5)	0.1911(7)	0.124(7)	0.85(3)
665	OW34	0.6300(14)	0.2746(6)	0.0429(9)	0.171(11)	0.88(4)
666	OW35	0.9384(13)	0.1696(6)	0.0631(8)	0.150(10)	0.82(3)
667	OW36	0.2017(15)	0.3111(6)	0.5872(9)	0.135(11)	0.65(3)
668	OW37	0.5893(16)	0.5354(7)	0.2221(10)	0.189(13)	0.85(4)
669	OW38	0.1423(16)	0.4546(7)	0.3766(10)	0.123(11)	0.56(3)
670	OW39	0.4719(16)	0.4192(7)	0.4848(10)	0.161(12)	0.73(4)
671	OW40	0.9023(18)	0.0949(8)	0.1304(11)	0.162(14)	0.64(4)

672	OW41	0.6749(18)	0.5053(8)	0.4017(11)	0.097(12)	0.41(3)	
673	OW42	0.598(2)	0.1009(9)	0.0902(13)	0.174(17)	0.58(4)	
674	OW43	0.261(2)	0.3837(9)	0.5304(13)	0.159(16)	0.51(4)	
675	OW44	0.961(3)	0.4424(14)	0.403(2)	0.22(3)	0.47(4)	
676	OW45	0.751(3)	0.1039(13)	0.2245(17)	0.31(3)	0.74(5)	
677	OW46	0.759(4)	0.0416(18)	0.281(3)	0.34(4)	0.56(6)	
678	OW47	0.961(8)	0.486(3)	0.298(5)	0.35(8)	0.32(6)	
679	OW48	0.816(4)	0.4773(16)	0.331(2)	0.29(4)	0.56(5)	
680	OW49	0.570(4)	0.0670(19)	0.238(3)	0.60(3)	1	
681		$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
682	V1	0.0250(8)	0.0285(8)	0.0339(9)	-0.0021(7)	0.0094(7)	-0.0031(6)
683	V2	0.0262(9)	0.0363(9)	0.0388(9)	0.0088(7)	0.0113(7)	0.0045(7)
684	V3	0.0400(10)	0.0313(9)	0.0384(9)	0.0020(7)	0.0148(8)	0.0085(7)
685	V4	0.0268(9)	0.0332(9)	0.0359(9)	0.0024(7)	0.0127(7)	0.0019(7)
686	V5	0.0216(8)	0.0474(10)	0.0436(10)	0.0082(8)	0.0052(7)	0.0019(7)
687	V6	0.0139(7)	0.0378(9)	0.0255(8)	0.0010(6)	0.0035(6)	0.0008(6)
688	V7	0.0141(8)	0.0406(9)	0.0315(8)	-0.0017(7)	0.0038(6)	0.0006(6)
689	V8	0.0146(8)	0.0443(9)	0.0311(8)	0.0059(7)	0.0026(6)	-0.0016(7)
690	V9	0.0137(8)	0.0562(10)	0.0285(8)	-0.0022(7)	0.0052(6)	0.0013(7)
691	V10	0.0162(8)	0.0493(10)	0.0346(9)	0.0061(7)	0.0085(7)	0.0024(7)
692	V11	0.0150(8)	0.0463(10)	0.0476(10)	0.0045(8)	0.0076(7)	-0.0022(7)
693	V12	0.0150(8)	0.0483(10)	0.0368(9)	0.0150(7)	0.0056(7)	0.0032(7)
694	V13	0.0111(7)	0.0406(9)	0.0289(8)	0.0041(7)	0.0032(6)	0.0014(6)
695	V14	0.0142(8)	0.0524(10)	0.0258(8)	0.0067(7)	0.0017(6)	0.0020(7)
696	V15	0.0120(7)	0.0461(9)	0.0313(8)	0.0046(7)	0.0027(6)	0.0020(7)
697	V16	0.0231(9)	0.0575(11)	0.0276(8)	0.0040(7)	0.0062(7)	-0.0001(8)
698	A11	0.0111(12)	0.0408(15)	0.0240(13)	0.0043(11)	0.0030(10)	-0.0002(11)
699	A12	0.0114(13)	0.0428(16)	0.0368(15)	0.0093(12)	0.0038(11)	-0.0007(11)
700	A13	0.0149(13)	0.0439(16)	0.0260(14)	-0.0008(12)	0.0045(11)	0.0001(11)
701	A14	0.0150(13)	0.0372(15)	0.0233(13)	0.0024(11)	0.0037(11)	-0.0003(11)
702	A15	0.0149(13)	0.0398(15)	0.0257(14)	0.0063(11)	0.0019(11)	-0.0004(11)
703	A16	0.0181(14)	0.0467(16)	0.0252(14)	0.0048(12)	0.0061(11)	-0.0046(12)
704	A17	0.0265(19)	0.041(2)	0.0347(19)	0.0082(13)	0.0003(13)	-0.0059(13)
705	A18	0.0247(18)	0.0396(19)	0.0196(17)	-0.0006(12)	0.0025(12)	0.0042(13)
706	A19	0.0185(16)	0.0359(18)	0.0307(17)	0.0039(12)	0.0023(12)	-0.0017(12)
707	A110	0.055(3)	0.066(3)	0.038(3)	-0.005(2)	0.005(2)	-0.027(2)
708	S	0.099(6)	0.061(4)	0.052(4)	0.008(3)	0.028(4)	-0.002(4)
709	O5	0.038(4)	0.048(4)	0.042(4)	0.011(3)	0.019(3)	0.007(3)
710	O6	0.043(4)	0.047(4)	0.043(4)	0.016(3)	0.021(3)	0.008(3)
711	O7	0.033(4)	0.063(5)	0.068(5)	0.007(4)	0.003(4)	-0.003(4)
712	O8	0.062(5)	0.036(4)	0.054(4)	-0.001(3)	0.024(4)	0.012(3)
713	O9	0.020(3)	0.038(4)	0.043(4)	0.007(3)	0.006(3)	0.000(3)
714	O10	0.031(4)	0.036(4)	0.044(4)	0.005(3)	0.013(3)	0.003(3)
715	O11	0.035(4)	0.034(3)	0.035(3)	0.002(3)	0.009(3)	0.003(3)
716	O12	0.025(3)	0.039(4)	0.041(4)	0.003(3)	0.010(3)	0.004(3)
717	O13	0.035(4)	0.038(4)	0.043(4)	-0.005(3)	0.011(3)	-0.005(3)

718	O14	0.025(3)	0.034(3)	0.047(4)	-0.001(3)	0.012(3)	0.001(3)
719	O15	0.023(3)	0.037(4)	0.038(4)	-0.001(3)	0.002(3)	-0.007(3)
720	O16	0.021(3)	0.032(3)	0.036(3)	0.001(3)	0.010(3)	-0.002(3)
721	O17	0.028(3)	0.031(3)	0.033(3)	-0.004(3)	0.012(3)	-0.001(3)
722	O18	0.024(3)	0.024(3)	0.036(3)	-0.002(3)	0.010(3)	-0.002(3)
723	O19	0.025(4)	0.057(4)	0.048(4)	0.024(3)	0.005(3)	0.008(3)
724	O20	0.015(3)	0.066(4)	0.039(4)	0.012(3)	0.001(3)	0.007(3)
725	O21	0.016(3)	0.049(4)	0.041(4)	0.013(3)	0.004(3)	0.003(3)
726	O22	0.022(3)	0.047(4)	0.048(4)	0.005(3)	0.003(3)	-0.007(3)
727	O23	0.025(4)	0.075(5)	0.036(4)	-0.005(3)	0.008(3)	0.009(3)
728	O24	0.018(3)	0.045(4)	0.073(5)	0.001(4)	0.002(3)	-0.004(3)
729	O25	0.021(3)	0.077(5)	0.038(4)	0.016(3)	0.002(3)	0.004(3)
730	O26	0.019(3)	0.068(5)	0.048(4)	0.003(3)	0.013(3)	0.009(3)
731	O27	0.015(3)	0.054(4)	0.033(3)	-0.007(3)	0.003(3)	0.006(3)
732	O28	0.016(3)	0.046(4)	0.034(3)	-0.002(3)	0.004(3)	0.001(3)
733	O29	0.016(3)	0.051(4)	0.028(3)	0.000(3)	0.004(3)	0.002(3)
734	O30	0.014(3)	0.050(4)	0.037(4)	0.002(3)	0.001(3)	0.001(3)
735	O31	0.021(3)	0.040(4)	0.055(4)	0.011(3)	0.006(3)	-0.001(3)
736	O32	0.017(3)	0.046(4)	0.038(4)	0.013(3)	0.001(3)	0.001(3)
737	O33	0.010(3)	0.041(3)	0.028(3)	0.003(3)	0.001(2)	-0.004(3)
738	O34	0.018(3)	0.049(4)	0.041(4)	0.006(3)	0.009(3)	-0.005(3)
739	O35	0.011(3)	0.043(4)	0.041(4)	0.002(3)	0.008(3)	0.001(3)
740	O36	0.019(3)	0.040(4)	0.034(3)	0.004(3)	0.004(3)	0.000(3)
741	O37	0.018(3)	0.065(4)	0.023(3)	0.003(3)	0.004(3)	0.006(3)
742	O38	0.010(3)	0.048(4)	0.035(3)	0.008(3)	0.004(3)	0.001(3)
743	O39	0.017(3)	0.041(4)	0.047(4)	-0.002(3)	0.005(3)	0.001(3)
744	O40	0.016(3)	0.058(4)	0.035(3)	0.014(3)	0.009(3)	0.006(3)
745	O41	0.010(3)	0.049(4)	0.029(3)	-0.001(3)	-0.001(2)	0.001(3)
746	O42	0.013(3)	0.047(4)	0.025(3)	0.004(3)	0.003(2)	0.001(3)
747	O43	0.012(3)	0.039(3)	0.036(3)	0.003(3)	0.000(3)	0.003(3)
748	O44	0.012(3)	0.043(4)	0.031(3)	0.007(3)	0.005(3)	0.001(3)
749	O45	0.013(3)	0.040(3)	0.022(3)	0.005(3)	0.001(2)	0.002(3)
750	O46	0.013(3)	0.042(4)	0.033(3)	0.004(3)	0.005(3)	0.003(3)
751	O47	0.034(4)	0.064(5)	0.036(4)	0.006(3)	-0.005(3)	0.002(3)
752	O48	0.037(4)	0.074(5)	0.048(4)	0.004(4)	0.020(3)	0.007(4)
753	OH1	0.018(3)	0.037(3)	0.027(3)	0.002(3)	0.002(3)	-0.002(3)
754	OH2	0.016(3)	0.042(4)	0.025(3)	0.002(3)	0.004(2)	0.001(3)
755	OH3	0.014(3)	0.044(3)	0.022(3)	0.005(3)	0.008(2)	0.002(3)
756	OH4	0.012(3)	0.038(3)	0.031(3)	0.008(3)	0.005(2)	-0.002(3)
757	OH5	0.013(3)	0.033(3)	0.026(3)	0.003(2)	0.006(2)	0.000(2)
758	OH6	0.015(3)	0.035(3)	0.025(3)	0.006(2)	0.006(2)	-0.001(2)
759	OH7	0.030(4)	0.059(5)	0.064(5)	-0.007(4)	0.002(3)	-0.011(3)
760	OH8	0.021(3)	0.050(4)	0.029(3)	-0.003(3)	0.006(3)	-0.002(3)
761	OH9	0.022(3)	0.043(4)	0.033(3)	0.002(3)	0.008(3)	0.006(3)
762	OH10	0.026(3)	0.043(4)	0.034(3)	-0.001(3)	0.004(3)	-0.007(3)
763	OH11	0.025(3)	0.042(4)	0.035(3)	0.006(3)	0.001(3)	0.001(3)

764	OH12	0.017(3)	0.036(3)	0.024(3)	-0.002(2)	0.005(2)	-0.001(3)
765	OH13	0.022(3)	0.035(3)	0.029(3)	0.009(3)	0.001(3)	-0.001(3)
766	OH14	0.021(3)	0.043(4)	0.024(3)	-0.001(3)	0.008(3)	0.003(3)
767	OH15	0.015(3)	0.038(3)	0.029(3)	0.007(3)	0.000(2)	0.001(3)
768	OH16	0.026(3)	0.046(4)	0.032(3)	0.002(3)	0.006(3)	0.005(3)
769	OH17	0.024(3)	0.042(4)	0.038(4)	0.012(3)	0.005(3)	-0.004(3)
770	OH18	0.017(3)	0.045(4)	0.031(3)	0.009(3)	0.000(3)	0.001(3)
771	OH19	0.020(3)	0.056(4)	0.024(3)	0.011(3)	0.006(3)	0.001(3)
772	OH20	0.024(3)	0.052(4)	0.037(4)	0.008(3)	0.004(3)	-0.008(3)
773	OW1	0.031(4)	0.064(5)	0.048(4)	-0.007(3)	0.013(3)	0.011(3)
774	OW2	0.031(4)	0.057(4)	0.033(4)	0.013(3)	0.005(3)	0.003(3)
775	OW3	0.053(5)	0.048(4)	0.068(5)	0.020(4)	0.009(4)	-0.014(4)
776	OW4	0.052(5)	0.060(5)	0.070(5)	0.012(4)	0.013(4)	0.010(4)
777	OW5	0.028(4)	0.062(5)	0.056(4)	0.013(4)	0.002(3)	-0.001(3)
778	OW6	0.073(6)	0.075(5)	0.043(4)	0.000(4)	-0.008(4)	-0.028(5)
779	OW7	0.045(4)	0.064(5)	0.035(4)	-0.002(3)	-0.007(3)	-0.005(4)
780	OW8	0.026(4)	0.071(5)	0.038(4)	0.001(3)	0.002(3)	0.008(3)
781	OW9	0.078(6)	0.050(4)	0.042(4)	-0.007(3)	0.011(4)	0.009(4)
782	OW10	0.052(5)	0.061(5)	0.033(4)	0.000(3)	0.014(3)	0.003(4)
783	OW11	0.031(4)	0.041(4)	0.041(4)	0.003(3)	0.011(3)	-0.005(3)
784	OW12	0.032(4)	0.040(4)	0.047(4)	0.008(3)	0.003(3)	-0.001(3)
785	OW13	0.028(4)	0.054(4)	0.034(4)	0.005(3)	0.001(3)	-0.002(3)
786	OW14	0.025(3)	0.049(4)	0.043(4)	0.011(3)	0.008(3)	-0.004(3)
787	OW15	0.098(12)	0.071(9)	0.091(11)	-0.035(7)	0.013(8)	-0.004(7)
788	OW16	0.077(10)	0.055(8)	0.081(10)	-0.026(6)	0.010(7)	-0.023(7)
789	OW17	0.095(11)	0.066(8)	0.092(10)	-0.020(7)	0.011(8)	-0.017(7)
790	OW18	0.064(7)	0.085(8)	0.099(9)	-0.009(6)	0.013(6)	-0.007(5)

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793 Table 5. Selected bond distances (Å) for caseyite.  
794

795	V1–O13	1.666(6)	V8–O22	1.599(6)	V15–O20	1.596(6)	Al6–OH19	1.852(6)
796	–O15	1.698(6)	–O38	1.836(6)	–O30	1.822(6)	–OH18	1.856(6)
797	–O16	1.914(6)	–O32	1.837(6)	–O35	1.857(6)	–OH20	1.869(6)
798	–O17	1.921(6)	–O33	1.910(6)	–O44	1.994(6)	–OW2	1.873(7)
799	–O18	2.115(6)	–O36	2.031(6)	–O41	1.998(6)	–OH3	2.001(6)
800	–O18	2.179(5)	–O45	2.297(6)	–O46	2.222(6)	–OH4	2.011(6)
801	<V1–O>	1.916	<V8–O>	1.918	<V15–O>	1.915	<Al6–O>	1.910
802								
803	V2–O6	1.600(6)	V9–O23	1.595(6)	V16–O47	1.622(6)	Al7–OH17	1.850(6)
804	–O12	1.756(6)	–O38	1.838(6)	–O48	1.632(7)	–OH20	1.894(7)
805	–O14	1.940(6)	–O28	1.867(6)	–OH19	1.967(6)	–OW3	1.903(7)
806	–O17	1.949(6)	–O37	1.897(6)	–OH8	1.978(6)	–OW4	1.913(8)
807	–O16	2.030(6)	–O27	2.022(6)	–OH3	2.282(5)	–OW6	1.920(8)
808	–O18	2.218(6)	–O45	2.299(5)	–OH2	2.302(6)	–OW5	1.924(7)
809	<V2–O>	1.916	<V9–O>	1.920	<V16–O>	1.964	<Al7–O>	1.901
810								
811	V3–O8	1.597(6)	V10–O26	1.598(6)	Al1–OH1	1.876(6)	Al8–OH14	1.861(6)
812	–O10	1.775(6)	–O40	1.839(6)	–OH2	1.881(6)	–OH16	1.865(6)
813	–O11	1.876(6)	–O34	1.860(6)	–OH4	1.886(6)	–OW7	1.909(7)
814	–O14	1.967(6)	–O35	1.904(6)	–OH3	1.888(6)	–OW8	1.921(7)
815	–O13	2.110(7)	–O29	2.018(6)	–OH5	1.906(6)	–OW9	1.938(7)
816	–O18	2.318(5)	–O46	2.317(6)	–OH6	1.911(6)	–OW10	1.962(7)
817	<V3–O>	1.941	<V10–O>	1.923	<Al1–O>	1.891	<Al8–O>	1.909
818								
819	V4–O5	1.608(6)	V11–O24	1.598(6)	Al2–OW1	1.815(7)	Al9–OH11	1.870(7)
820	–O9	1.787(6)	–O31	1.837(6)	–OH7	1.827(7)	–OH15	1.871(6)
821	–O11	1.848(6)	–O34	1.868(6)	–OH8	1.857(6)	–OW11	1.900(6)
822	–O16	1.984(6)	–O30	1.903(6)	–OH9	1.873(6)	–OW12	1.901(7)
823	–O17	2.013(6)	–O39	2.029(6)	–OH2	2.026(6)	–OW13	1.952(7)
824	–O18	2.256(6)	–O46	2.299(6)	–OH1	2.060(6)	–OW14	1.961(6)
825	<V4–O>	1.916	<V11–O>	1.922	<Al2–O>	1.910	<Al9–O>	1.909
826								
827	V5–O7	1.603(7)	V12–O19	1.602(6)	Al3–OH10	1.819(6)	Al10–OW15	1.810(15)
828	–O10	1.912(6)	–O40	1.826(6)	–OH11	1.835(6)	–OH10	1.871(7)
829	–O12	1.920(6)	–O31	1.840(6)	–OH12	1.842(6)	–OW16	1.877(12)
830	–O9	1.935(6)	–O42	1.984(6)	–OH9	1.851(6)	–OH7	1.913(8)
831	–O15	2.034(6)	–O43	1.996(6)	–OH5	1.999(6)	–OW17	1.944(13)
832	–O18	2.318(6)	–O46	2.252(6)	–OH1	2.081(6)	–OW18	2.026(11)
833	<V5–O>	1.954	<V12–O>	1.917	<Al3–O>	1.905	<Al10–O>	1.907
834								
835	V6–O29	1.680(6)	V13–O21	1.596(6)	Al4–OH13	1.841(6)	S–O1	1.425(13)
836	–O36	1.693(6)	–O33	1.833(6)	–OH12	1.844(6)	–O2	1.468(15)
837	–O44	1.912(6)	–O28	1.852(6)	–OH15	1.847(6)	–O3	1.474(15)
838	–O42	1.914(6)	–O42	1.976(6)	–OH14	1.848(6)	–O4	1.486(13)
839	–O46	2.120(6)	–O43	2.001(6)	–OH6	2.016(6)	<S–O>	1.463
840	–O45	2.133(6)	–O45	2.233(5)	–OH5	2.037(6)		
841	<V6–O>	1.909	<V13–O>	1.915	<Al4–O>	1.906		
842								
843	V7–O39	1.676(6)	V14–O25	1.603(6)	Al5–OH17	1.827(6)		
844	–O27	1.687(6)	–O37	1.825(6)	–OH16	1.841(6)		
845	–O41	1.912(6)	–O32	1.828(6)	–OH13	1.850(6)		
846	–O43	1.918(6)	–O41	1.986(6)	–OH18	1.853(6)		
847	–O46	2.123(6)	–O44	2.002(6)	–OH6	2.016(6)		
848	–O45	2.126(6)	–O45	2.223(5)	–OH4	2.058(6)		
849	<V7–O>	1.907	<V14–O>	1.911	<Al5–O>	1.908		
850								
851								



852 Table 6. Possible hydrogen bonds ( $O_D \cdots O_A$ ), bond distances (d), and bond strengths\* (v) for  
 853 caseyite. Possible hydrogen bonds to OH and H<sub>2</sub>O groups are not included.  
 854

855	$O_D$	$O_A$	d(Å)	v(vu)	$O_D$	$O_A$	d(Å)	v(vu)
856	O14	O19	2.795(9)	0.19 <sup>§</sup>	OW20	O10	3.004(9)	0.13
857	OH1	O28	2.766(8)	0.20	OW20	O40	2.963(9)	0.14
858	OH2	O30	2.759(8)	0.20	OW21	O47	2.827(14)	0.17
859	OH3	O38	2.721(7)	0.22	OW22	O15	2.903(15)	0.15
860	OH4	O35	2.767(8)	0.20	OW22	O32	2.771(14)	0.19
861	OH5	O34	2.714(8)	0.22	OW23	O13	2.890(11)	0.16
862	OH6	O33	2.768(7)	0.20	OW23	O44	2.771(10)	0.19
863	OH8	O23	2.763(8)	0.20	OW24	O4	2.688(19)	0.23
864	OH9	O24	2.715(8)	0.22	OW27	O30	2.825(16)	0.17
865	OH10	O6	2.739(8)	0.21	OW27	O48	2.942(17)	0.14
866	OH12	O21	2.703(8)	0.22	OW28	O12	2.893(11)	0.15
867	OH13	O26	2.733(8)	0.21	OW28	O43	2.792(11)	0.19
868	OH18	O22	2.732(8)	0.21	OW32	O4	2.85(2)	0.17
869	OH19	O20	2.750(8)	0.20	OW32	O27	2.839(17)	0.17
870	OH20	O8	2.979(9)	0.13	OW33	O7	2.803(16)	0.17
871	OW3	O11	2.514(9)	0.36	OW33	O31	2.830(16)	0.18
872	OW5	O35	2.700(9)	0.23	OW34	O48	2.94(2)	0.14
873	OW6	O1	2.52(2)	0.35	OW35	O47	3.087(19)	0.12
874	OW7	O37	2.684(9)	0.23	OW36	O29	3.12(2)	0.11
875	OW8	O33	2.723(9)	0.22	OW36	O48	2.65(2)	0.26
876	OW10	O41	2.981(9)	0.13	OW37	O17	2.85(2)	0.17
877	OW11	O16	2.630(8)	0.27	OW38	O2	2.69(4)	0.23
878	OW12	O9	2.602(8)	0.29	OW39	O3	2.86(3)	0.16
879	OW14	O34	2.797(8)	0.18	OW39	O4	2.80(3)	0.18
880	OW15	O1	2.62(2)	0.28	OW41	O3	2.94(4)	0.14
881	OW17	O5	2.866(14)	0.16	OW44	O39	3.09(4)	0.12
882	OW18	O28	2.843(12)	0.17	OW45	O36	3.02(4)	0.13
883	OW19	O25	2.695(9)	0.23				

884 \* Hydrogen-bond strengths are based on O–O bond lengths from Ferraris and Ivaldi (1988).  
 885  
 886

887 Table 7. Bond-valence analyses for the structural components in caseyite. Values are expressed in  
 888 valence units.\*

890 *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		

891 Note that the O sites are partially disordered, requiring soft restraints on the distances. This probably  
 892 accounts for the anomalously high and low BVS values for O1, O2, and O3.

893  
 894 *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				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		

895 Note that O14 is considered an OH.

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897  
898

*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		0.55							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		

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901 *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		

902 \* All bond strengths are based on full occupancies by the indicated cations and anions. The bond strengths  
903 due to a possible H atom shared between O14 and O19 are not included. V<sup>5+</sup>-O bond-valence parameters  
904 are from Brown and Altermatt (1985). Al<sup>3+</sup>-O and S<sup>6+</sup>-O bond-valence parameters are from Gagné &  
905 Hawthorne (2015). Hydrogen-bond strengths (also listed in Table S4) are based on O-O bond lengths as  
906 provided by Ferraris and Ivaldi (1988).

907

Figure 1



Figure 2



Figure 3

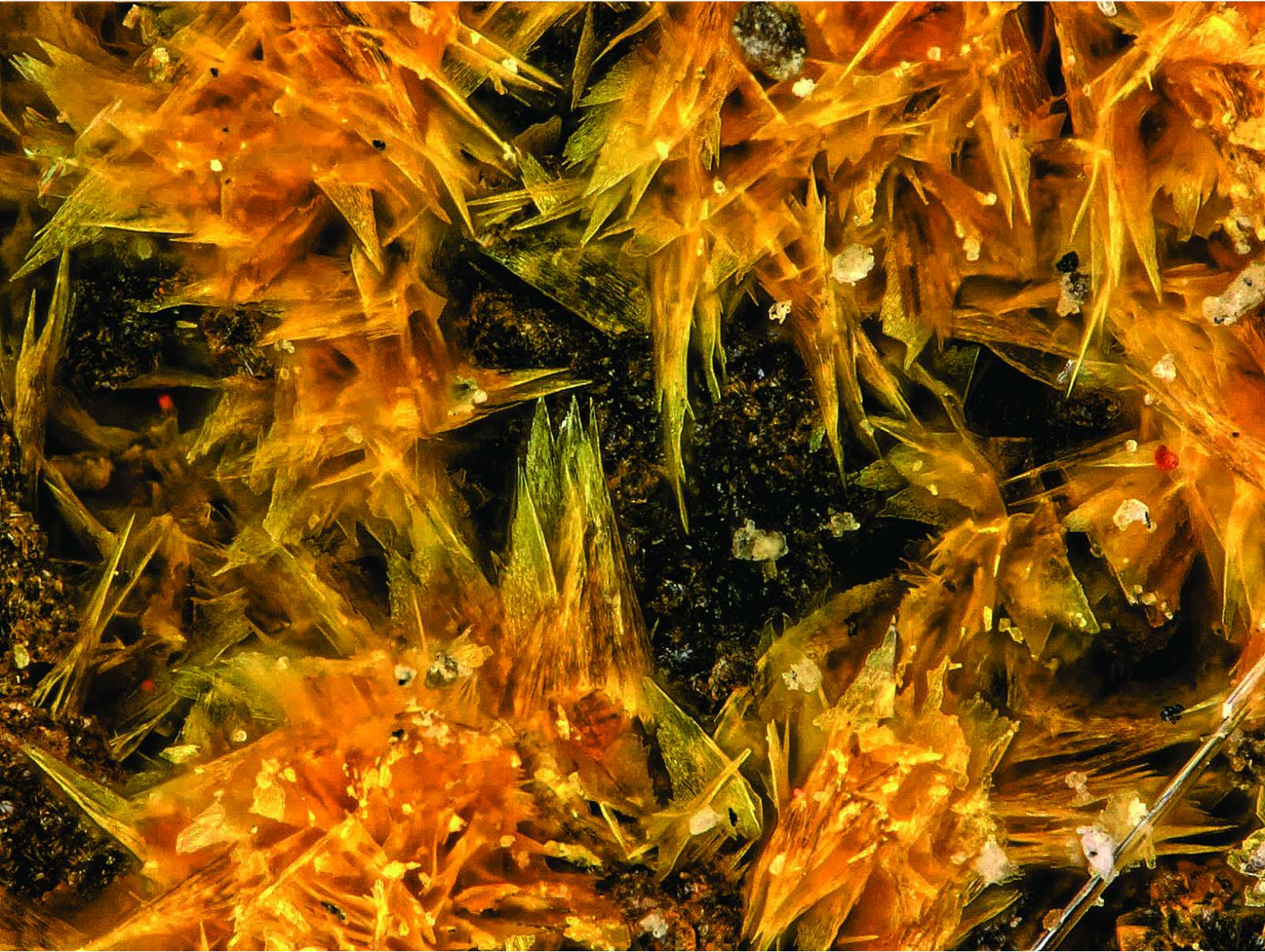


Figure 4

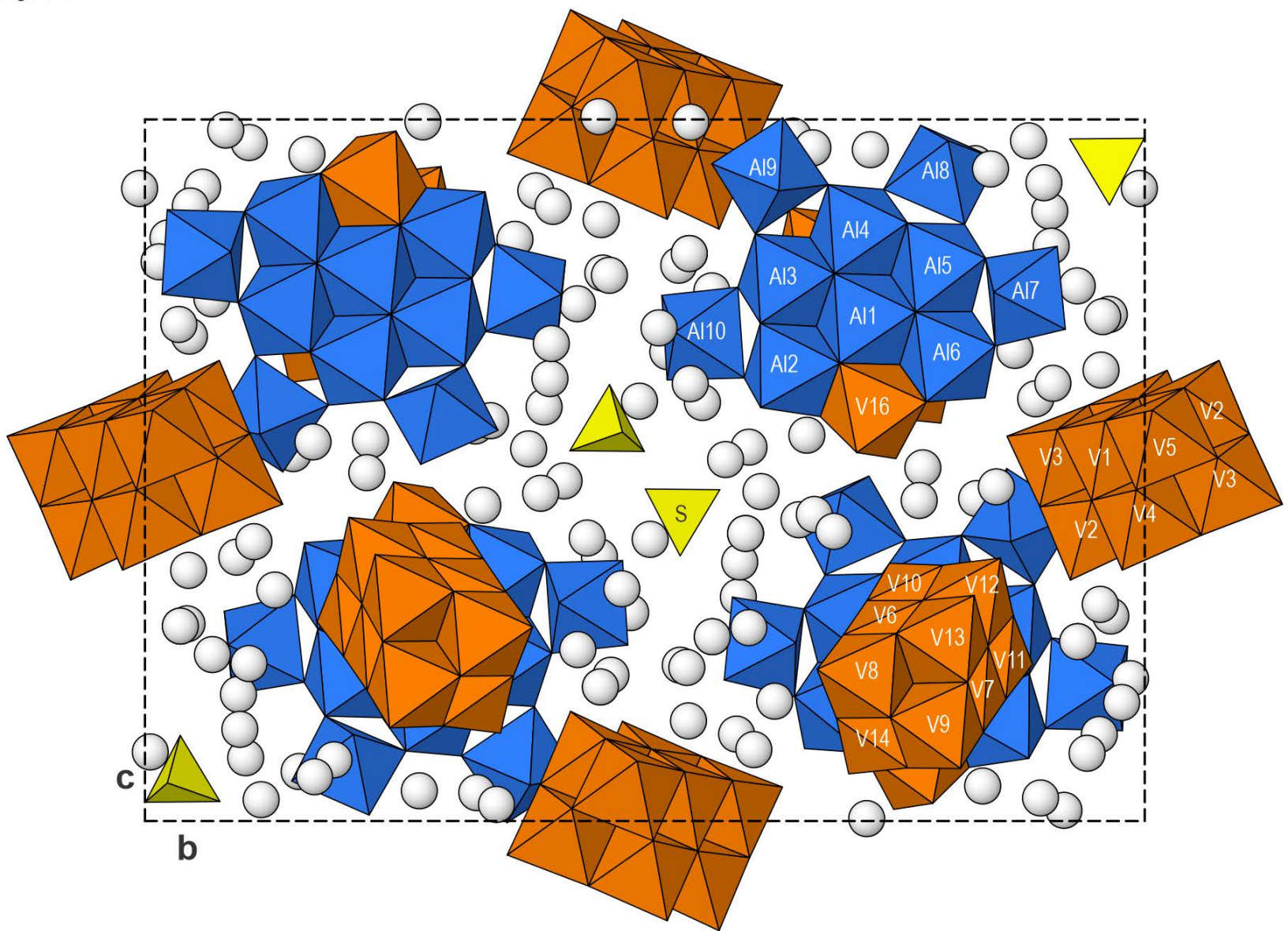




Figure 5

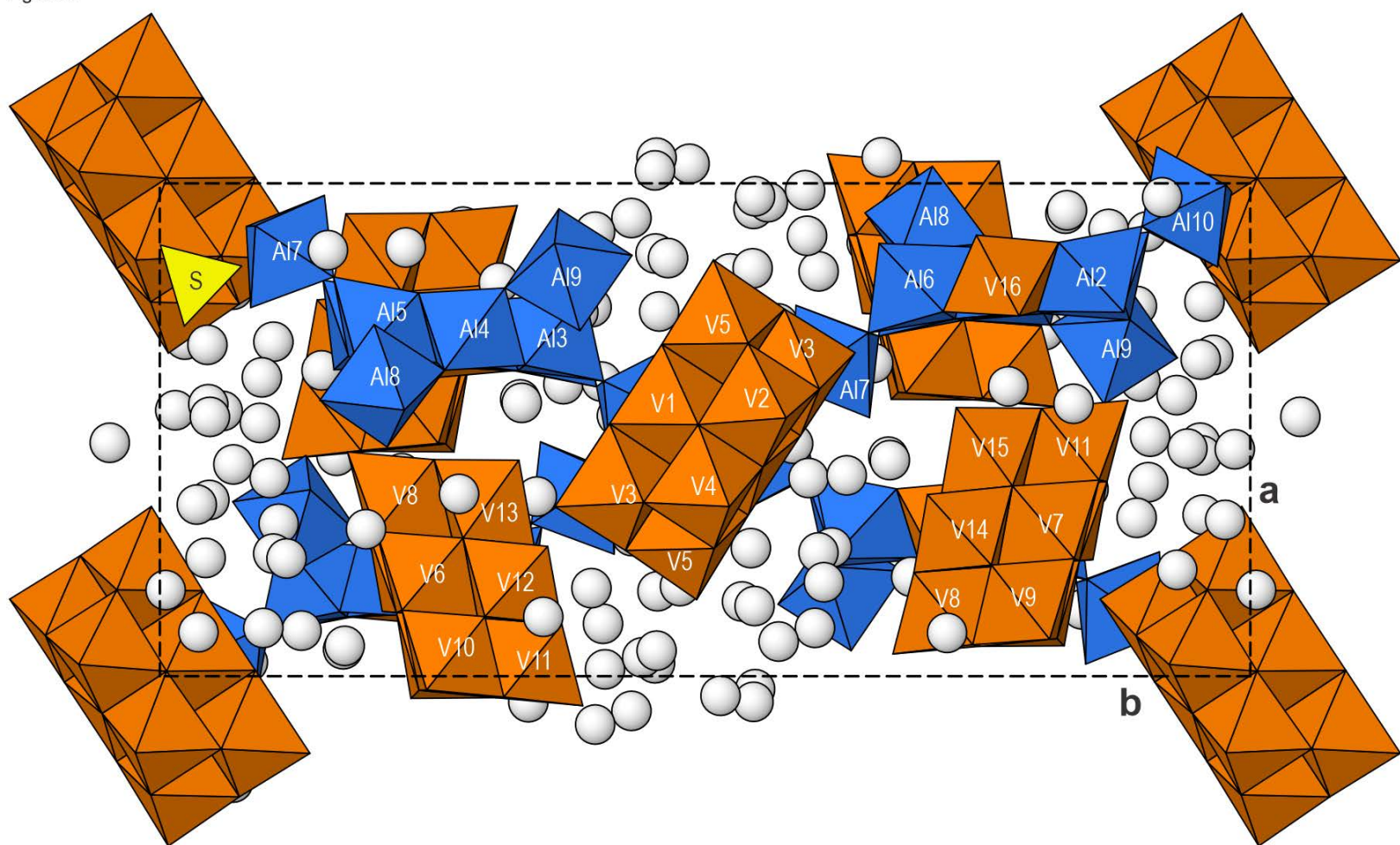
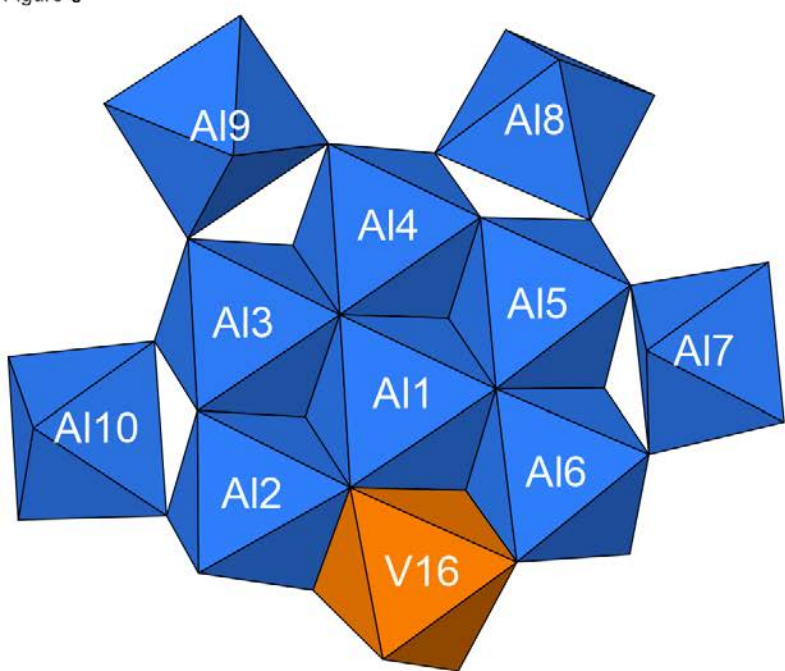
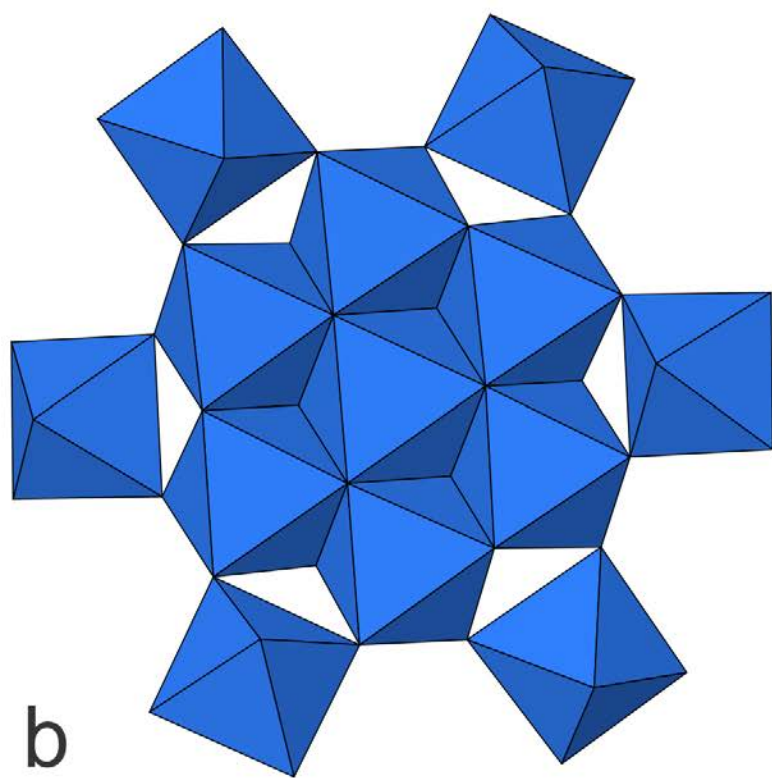


Figure 6



a



b