

## GUNTERITE, $\text{Na}_4(\text{H}_2\text{O})_{16}(\text{H}_2\text{V}_{10}\text{O}_{28})\cdot 6\text{H}_2\text{O}$ , A NEW MINERAL SPECIES WITH A DOUBLY-PROTONATED DECAVANADATE POLYANION: CRYSTAL STRUCTURE AND DESCRIPTIVE MINERALOGY

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### ABSTRACT

Gunterite,  $\text{Na}_4(\text{H}_2\text{O})_{16}(\text{H}_2\text{V}_{10}\text{O}_{28})\cdot 6\text{H}_2\text{O}$ , is a new mineral species from the West Sunday mine, Slick Rock district, San Miguel County, Colorado, U.S.A. Crystals of gunterite are tabular on {001} and generally stacked into elongate curved multiple crystals up to 0.5 mm in maximum dimension; the crystals are orange-yellow, with a yellow streak. The mineral displays a subadamantine luster, and is transparent; it does not fluoresce in short- or long-range ultraviolet radiation. Gunterite has a hardness of about 1, a brittle tenacity, and an irregular fracture; no cleavage or parting was observed. The density calculated from the empirical formula using the single-crystal cell data is  $2.398 \text{ g cm}^{-3}$ . Gunterite is biaxial (+), with  $\alpha$  1.735(5),  $\beta$  1.770(5) and  $\gamma$  1.825(5);  $2V$  is equal to  $78^\circ$  (white light). The dispersion  $v < r$  is strong and parallel. Optical orientation;  $X = \mathbf{b}$ ,  $Y \approx \mathbf{c}$ ; pleochroism:  $X$  yellow,  $Y$  orange,  $Z$  yellow;  $Y > X > Z$ . Gunterite is soluble in water at room temperature. Electron-probe microanalysis and the crystal-structure solution provided the empirical formula ( $V + \text{Al} = 10 \text{ apfu}$ ):  $(\text{Na}_{3.20}\text{K}_{0.02}\text{Ca}_{0.87})_{\Sigma 4.09}[\text{H}_{1.06}(\text{V}_{9.99}\text{Al}_{0.01})_{\Sigma 10}\text{O}_{28}]\cdot 22\text{H}_2\text{O}$ . The simplified formula of gunterite is  $\text{Na}_4(\text{H}_2\text{O})_{16}(\text{H}_2\text{V}_{10}\text{O}_{28})\cdot 6\text{H}_2\text{O}$ . There is extensive substitution of Ca for Na in gunterite, yielding a structural formula of  $(\text{Na}_{4-x}\text{Ca}_x)_{\Sigma 4.00}(\text{H}_2\text{O})_{16}(\text{H}_{2-x}\text{V}_{10}\text{O}_{28})\cdot 6\text{H}_2\text{O}$ ; the average value of  $x$  from the chemical analyses is 0.85. Gunterite is monoclinic,  $C2/m$ , with  $a$  19.848(2),  $b$  10.1889(11),  $c$  13.1184(15) Å,  $\beta$  130.187(9)°,  $V$  2026.6(4) Å<sup>3</sup>, and  $Z = 2$ . The strongest four lines in the diffraction pattern [ $d$  in Å( $hkl$ )] are: 10.01(100) $\bar{2}$ 01, 001, 8.44(72)110, 8.09(46) $\bar{1}$ 11, and 2.997(29) $\bar{3}$ 31,401. The atomic arrangement of gunterite was refined to  $R_1 = 0.0632$ . The structural unit is a doubly-protonated decavanadate polyanion,  $\{\text{H}_2[\text{V}_{10}\text{O}_{28}]\}$ . The interstitial units linking the structural units contain two Na polyhedra; the Na<sub>2</sub> polyhedron is split into two partially occupied sites that are 0.76 Å apart, and significant Ca occupies that site. Several of the H<sub>2</sub>O molecules in the interstitial complex are disordered. The mineral is named in honor of Mickey E. Gunter, Professor of Mineralogy at the University of Idaho.

*Keywords:* gunterite, new mineral species, decavanadate, crystal structure, West Sunday mine, Slick Rock district, Colorado.

### SOMMAIRE

La gunterite,  $\text{Na}_4(\text{H}_2\text{O})_{16}(\text{H}_2\text{V}_{10}\text{O}_{28})\cdot 6\text{H}_2\text{O}$ , est une nouvelle espèce minérale provenant de la mine West Sunday mine, district de Slick Rock, comté de San Miguel, au Colorado. Les cristaux sont tabulaires sur {001} et généralement empilés en amas de cristaux courbes allongés atteignant 0.5 mm en dimension maximale; les cristaux sont orange-jaunes, avec une rayure jaune. Il s'agit d'un minéral transparent ayant un éclat subadamantin, qui ne montre aucune fluorescence en lumière ultraviolette, en longueur d'onde courte ou longue. La gunterite possède une dureté d'environ 1, une ténacité cassante, et une

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fracture irrégulière; aucun clivage ou plan de séparation n'a été observé. La densité calculée à partir de la formule empirique en utilisant les données acquises sur la maille élémentaire est  $2.398 \text{ g cm}^{-3}$ . La gunterite est biaxe (+), avec  $\alpha$  1.735(5),  $\beta$  1.770(5) et  $\gamma$  1.825(5);  $2V$  est égal à  $78^\circ$  (lumière blanche). La dispersion  $v < r$  est forte et parallèle. L'orientation optique serait  $X = \mathbf{b}$ ,  $Y \approx \mathbf{c}$ ; pléochroïsme: X jaune, Y orange, Z jaune;  $Y > X > Z$ . La gunterite est soluble dans l'eau à température ambiante. Une analyse effectuée avec une microsonde électronique et la solution de la structure cristalline ont fourni la formule empirique:  $(\text{Na}_{3.20}\text{K}_{0.02}\text{Ca}_{0.87})_{\Sigma 4.09}[\text{H}_{1.06}(\text{V}_{9.99}\text{Al}_{0.01})_{\Sigma 10}\text{O}_{28}] \cdot 22\text{H}_2\text{O}$ . La formule simplifiée de la gunterite est  $\text{Na}_4(\text{H}_2\text{O})_{16}(\text{H}_2\text{V}_{10}\text{O}_{28}) \cdot 6\text{H}_2\text{O}$ . La substitution du Ca pour Na est importante, ce qui mène à la formule structurale  $(\text{Na}_{4-x}\text{Ca}_x)_{\Sigma 4.00}(\text{H}_2\text{O})_{16}(\text{H}_{2-x}\text{V}_{10}\text{O}_{28}) \cdot 6\text{H}_2\text{O}$ ; d'après les résultats d'analyses, la valeur moyenne de  $x$  est 0.85. La gunterite est monoclinique,  $C2/m$ , avec  $a$  19.848(2),  $b$  10.1889(11),  $c$  13.1184(15) Å,  $\beta$  130.187(9)°,  $V$  2026.6(4) Å<sup>3</sup>, et  $Z = 2$ . Les quatre raies les plus intenses du spectre de diffraction [ $d$  en Å( $hkl$ )] sont: 10.01(100)201,001, 8.44(72)110, 8.09(46)111, et 2.997(29)331,401. L'agencement des atomes a été affiné jusqu'à un résidu  $R_1$  égal à 0.0632. L'unité structurale est le polyanion décavanadate doublement protoné,  $\{\text{H}_2[\text{V}_{10}\text{O}_{28}]\}$ . Les unités interstitielles connectées aux unités structurales contiennent deux polyèdres Na; le polyèdre Na2 est réparti sur deux sites partiellement occupés à une distance de 0.76 Å l'un de l'autre; une proportion importante de Ca occupe ce site. Plusieurs des molécules de H<sub>2</sub>O du complexe interstitiel sont désordonnées. Le minéral honore Mickey E. Gunter, professeur de minéralogie à l'Université de l'Idaho.

(Traduit par la Rédaction)

**Mots-clés:** gunterite, nouvelle espèce minérale, décavanadate, structure cristalline, mine West Sunday, district de Slick Rock, Colorado.

## INTRODUCTION

The West Sunday mine, located in the Slick Rock district, San Miguel County, Colorado, USA ( $38^\circ 04'48.03''\text{N}$ ,  $108^\circ 49' 18.07''\text{W}$ ), forms part of the Colorado Plateau Uravan Mineral Belt, and produces uranium and vanadium ore with an approximate yield of  $\text{U}_3\text{O}_8:\text{V}_2\text{O}_5$  of 1:4 by weight. The mines of the Uravan Mineral Belt and the nearby Uravan Mining District (Shawe 2011) have been a rich source of new vanadium minerals, including rossite ( $\text{CaV}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ ) and metarossite ( $\text{CaV}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ ) (Foshag & Hess 1927) from O'Neill's claim, metamunirite ( $\text{NaVO}_3$ ; Evans 1991) from the Burro mine, lasalite ( $\text{Na}_2\text{Mg}_2[\text{V}_{10}\text{O}_{28}] \cdot 20\text{H}_2\text{O}$ ; Hughes *et al.* 2008) from the Vanadium Queen mine, magnesiospascoite ( $\text{Ca}_2\text{Mg}[\text{V}_{10}\text{O}_{28}] \cdot 16\text{H}_2\text{O}$ ; Kampf & Steele 2008a) and martyrite ( $\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ ; Kampf & Steele 2008b) from the Blue Cap mine, hughesite ( $\text{Na}_3\text{Al}[\text{V}_{10}\text{O}_{28}] \cdot 22\text{H}_2\text{O}$ ; Schmidt *et al.* 2009, Rakovan *et al.* 2011) from the Sunday mine, and rakovanite ( $\text{Na}_3\{\text{H}_3[\text{V}_{10}\text{O}_{28}]\} \cdot 15\text{H}_2\text{O}$ ; Kampf *et al.* 2011) from the West Sunday mine. Several of these minerals (lasalite, magnesiospascoite, hughesite and rakovanite) contain the  $[\text{V}_{10}\text{O}_{28}]$  decavanadate group, and in rakovanite, that polyanion is triply protonated, existing as the  $\{\text{H}_3[\text{V}_{10}\text{O}_{28}]\}^{3-}$  polyanion. Herein, we describe the physical attributes and atomic arrangement of another new vanadium mineral from the West Sunday mine, a mineral with a doubly protonated decavanadate polyanion,  $\{\text{H}_2[\text{V}_{10}\text{O}_{28}]\}^{4-}$ .

The name honors Dr. Mickey Eugene Gunter (b. 1953), Professor of Mineralogy at the University of Idaho. Professor Gunter is particularly well known for his studies in optical mineralogy and the mineralogy of asbestos minerals, and served from 1999 to 2006 as Associate Editor of this journal. Professor Gunter has also served the Mineralogical Society of America with

distinction in several roles, recently as Secretary of the organization. The new mineral and name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2011–001). The two cotype specimens used in the description of the mineral are housed in the mineral collection of the Natural History Museum of Los Angeles County under catalogue numbers 63506 and 63507.

## OCCURRENCE

Gunterite was found on several specimens from the West Sunday mine, Slick Rock district, San Miguel County, Colorado, U.S.A. The Sunday, St. Jude, and West Sunday mines are interconnected, and it is likely that this is not an isolated occurrence. Gunterite occurs in efflorescences on the sandstone walls of the mine workings and in fractures in the sandstone.

This new species is a rare vanadium mineral. The crystals grow both as crystalline crusts on an amorphous dehydrated vanadium phase and as crystals tightly adhered to a corvusite  $[(\text{Na},\text{Ca},\text{K})\text{V}_8\text{O}_{20} \cdot 4\text{H}_2\text{O}]$  – montroseite  $[(\text{V}^{3+},\text{Fe}^{3+})\text{O}(\text{OH})]$  matrix. On one of the cotype specimens, crystals of gunterite occur on and with well-formed huemulite crystals  $[\text{Na}_4\text{Mg}(\text{V}_{10}\text{O}_{28}) \cdot 24\text{H}_2\text{O}]$ ; Colombo *et al.* 2011]. On the other cotype specimen, well-formed crystals of rossite occur on the gunterite crystals. Other minerals found nearby include calcite, hewettite ( $\text{CaV}_6\text{O}_{16} \cdot 9\text{H}_2\text{O}$ ), hughesite, munirite ( $\text{NaVO}_3 \cdot 1.9\text{H}_2\text{O}$ ), paramontroseite ( $\text{VO}_2$ ), pascoite ( $\text{Ca}_3[\text{V}_{10}\text{O}_{28}] \cdot 17\text{H}_2\text{O}$ ), sherwoodite ( $\text{Ca}_{4.5}[\text{AlV}^{5+}_{12}\text{V}^{4+}_2\text{O}_{40}] \cdot 28\text{H}_2\text{O}$ ), and rakovanite.

The mineral is interpreted as forming from the oxidation of montroseite–corvusite assemblages. Mining operations have exposed unoxidized and oxidized phases. Under ambient temperatures and

generally oxidizing near-surface environments, water reacts with pyrite in the deposit to form aqueous solutions with relatively low pH. The various secondary vanadate phases that form depend upon the Eh–pH conditions and the presence of other cations (*e.g.*, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>). Mine ventilation to reduce radon levels appears to destroy many of the hydrated vanadium phases.

#### APPEARANCE AND PHYSICAL PROPERTIES

Crystals of gunterite are tabular on {001} and generally stacked into elongate curved multiple crystals up to 0.5 mm in maximum dimension. The crystals typically exhibit warping and, in some cases, skeletal growth features. Figure 1 depicts an idealized crystal drawing of gunterite.

Gunterite is orange-yellow, with a yellow streak. The mineral displays a subadamantine luster, and is transparent to translucent; it does not fluoresce in short- or long-wave ultraviolet radiation. Gunterite has a hardness of about 1, a brittle tenacity, and an irregular fracture; no cleavage or parting was observed. The density could not be measured because the mineral dissolves in available aqueous density liquids, and there is insufficient material for direct measurement. The density calculated from the empirical formula using the single-crystal cell data is 2.398 g cm<sup>-3</sup>, and that calculated from the structural formula is 2.400 g cm<sup>-3</sup>. Gunterite is soluble in water at room temperature.

#### OPTICAL PROPERTIES

Gunterite is biaxial (+). The value of 2*V* was measured using conoscopy, which yielded 77(2)°, and determined using extinction data with EXCALIBUR (Gunter *et al.* 2004, 2005), which yielded 79(2)°. The indices of refraction  $\alpha$  and  $\beta$ , determined in white light, are 1.735(5) and 1.770(5), respectively. Because gunterite decomposes slowly in index of refraction oils with an index greater than 1.8, the value of  $\gamma$  could not be measured directly. Instead, it was calculated on the basis of  $\alpha$ ,  $\beta$ , and 2*V* (78°), which yields 1.825(5). The

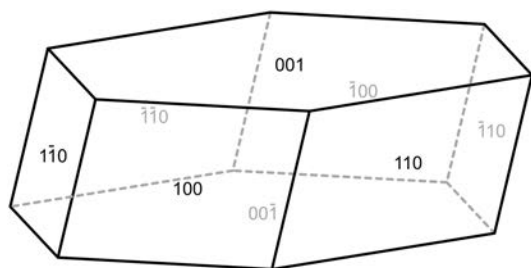


FIG. 1. Crystal drawing of gunterite obtained on the basis of reflecting goniometer measurements.

dispersion is  $v < r$ , strong, parallel. The optical orientation is  $X = \mathbf{b}$ ,  $Y \approx \mathbf{c}$ . The mineral is pleochroic:  $X$  yellow,  $Y$  orange,  $Z$  yellow;  $Y > X > Z$ .

#### THE COMPOSITION OF GUNTERITE

Analyses were performed at the University of Utah on a Cameca SX–50 electron microprobe with four wavelength-dispersive spectrometers. Analytical conditions were: 15 keV accelerating voltage, 10 nA beam current, and a nominal beam diameter of 10  $\mu\text{m}$ , although a larger diameter, 15  $\mu\text{m}$ , was occasionally used on larger fragments. Counting times were 10 seconds for each element. Raw X-ray intensities were corrected for matrix effects with a phi-rho-z algorithm (Pouchou & Pichoir 1991).

Gunterite dehydrates rapidly under vacuum and in the electron beam of the microprobe. Table 1 presents the average result of nine analyses obtained from four crystals of partially dehydrated gunterite. The fully hydrated composition, as indicated by the structure determination, contains 22 H<sub>2</sub>O. The cation ratios are in excellent agreement with the results of the crystal-structure analysis. The empirical formula for gunterite is, therefore, (Na<sub>4-x</sub>Ca<sub>x</sub>) $\Sigma$ 4.00(H<sub>2</sub>O)<sub>16</sub>(H<sub>2-x</sub>V<sub>10</sub>O<sub>28</sub>)•6H<sub>2</sub>O; the average value of  $x$  established in the chemical analyses is 0.85, and the value of  $x$  for the crystal studied structurally is 1.10. The simplified formula of gunterite is Na<sub>4</sub>(H<sub>2</sub>O)<sub>16</sub>(H<sub>2</sub>V<sub>10</sub>O<sub>28</sub>)•6H<sub>2</sub>O. Magnesium is below the detection limit (0.03%). The excess charge from the heterovalent Ca  $\leftrightarrow$  Na substitution is presumably balanced by deprotonation of the decavanadate group, leading to the formula (Na<sub>4-x</sub>Ca<sub>x</sub>) $\Sigma$ 4.00(H<sub>2</sub>O)<sub>16</sub>(H<sub>2-x</sub>V<sub>10</sub>O<sub>28</sub>)•6H<sub>2</sub>O.

Analytical data are given in Table 1. In the fourth column of that table, the H<sub>2</sub>O content is provided on the basis of the structure determination, with additional H added for charge balance, and the analytical data are normalized to provide a total of 100 wt%.

TABLE 1. CHEMICAL COMPOSITION OF GUNTERITE

Constituent	% wt <sup>§</sup>	St. dev.	Normalized wt%	Microprobe standard
Na <sub>2</sub> O	8.76	1.89	6.77	albite
K <sub>2</sub> O	0.07	0.03	0.05	sanidine
CaO	4.32	0.36	3.34	diopside
Al <sub>2</sub> O <sub>3</sub>	0.02	0.03	0.02	sanidine
V <sub>2</sub> O <sub>5</sub>	80.4	3.8	62.1	V metal
H <sub>2</sub> O (diff.)	6.44		27.73	structure and charge balance
Total	100.0		100.0	

<sup>§</sup> Column 1 represents the average result of nine analyses of dehydrated gunterite.

The empirical formula, based on 10 [V + Al] *apfu* and the H<sub>2</sub>O value derived from the crystal-structure analysis (shown in column 4), is (Na<sub>3.20</sub>K<sub>0.02</sub>Ca<sub>0.87</sub>Zr<sub>0.06</sub>H<sub>1.06</sub>(V<sub>9.99</sub>Al<sub>0.01</sub>) $\Sigma$ 10O<sub>28</sub>)•22H<sub>2</sub>O. The simplified formula is Na<sub>4</sub>(H<sub>2</sub>O)<sub>16</sub>(H<sub>2</sub>V<sub>10</sub>O<sub>28</sub>)•6H<sub>2</sub>O, which requires Na<sub>2</sub>O 8.56, V<sub>2</sub>O<sub>5</sub> 62.83, H<sub>2</sub>O 28.61, total 100.00 wt%.

TABLE 2. POWDER X-RAY DATA FOR GUNTERITE

$l_{\text{obs}}$	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	$l_{\text{calc}}$	$h$	$k$	$l$	$l_{\text{obs}}$	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	$l_{\text{calc}}$	$h$	$k$	$l$
100	10.01(2)	10.0217	29	0	0	1	8	2.535(2)	2.5403	3	5	1	5
		9.8205	71	2	0	1			2.5386	2	7	1	3
72	8.44(8)	8.4569	76	1	1	0	4	2.474(4)	2.4682	3	8	0	3
46	8.09(17)	8.0462	55	1	1	1	1	2.333(8)	2.3362	3	3	3	4
4	5.50(2)	5.4836	6	3	1	1	3	2.258(6)	2.2559	1	2	2	3
10	5.09(1)	5.0945	8	0	2	0	4	2.2007(23)	2.2026	6	1	3	3
		5.0109	3	0	0	2			2.1541	3	9	1	4
5	4.54(4)	4.5414	2	0	2	1	18	2.1443(33)	2.1498	7	7	3	4
		4.5222	2	2	2	1			2.1212	6	9	1	3
3	4.18(2)	4.2285	2	2	2	0	15	2.0244(11)	2.0256	9	0	4	3
		4.1780	1	4	0	3			2.0106	3	3	3	5
3	3.78(22)	3.7907	2	4	0	0	18	1.9707(24)	1.9821	9	10	0	4
1	3.69(16)	3.6944	5	5	1	2			1.9504	6	2	4	4
7	3.51(7)	3.5354	7	4	2	2	2	1.8243(8)	1.8263	1	7	3	0
		3.5226	2	5	1	3	6	1.7839(8)	1.7862	3	0	4	4
10	3.45(10)	3.4481	9	4	2	1	6	1.7095(36)	1.7180	2	9	3	6
		3.3114	3	2	0	2			1.6982	3	0	6	0
14	3.297(6)	3.2789	3	4	0	4			1.6510	1	10	2	7
		3.2531	4	6	0	2	8	1.6428(12)	1.6457	2	7	3	1
		3.0690	6	3	1	4			1.6429	1	7	5	4
29	2.997(3)	3.0108	15	3	3	1			1.6423	1	3	5	2
		2.9680	4	4	0	1			1.6088	1	2	0	7
21	2.795(2)	2.7936	16	0	2	3	4	1.5957(48)	1.5975	2	9	3	7
		2.7764	3	2	2	2			1.5841	1	10	2	1
		2.7418	5	6	2	2			1.5839	1	11	3	4
		2.7316	3	7	1	3			1.5206	1	8	4	0
3	2.674(2)	2.6768	4	3	1	2	8	1.5111(8)	1.5093	2	9	3	0
									1.5034	1	1	1	7

## CRYSTAL STRUCTURE: EXPERIMENTAL

Powder and single-crystal X-ray diffraction data were obtained on a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer using monochromatized MoK $\alpha$  radiation. The powder data presented in Table 2 are in good agreement with those calculated from the structure data. Observed  $d$  values and intensities were derived by profile fitting using JADE 9.1 software.

The Rigaku CrystalClear software package was used for reducing X-ray intensity data to structure factors, including corrections for Lorentz and polarization effects; the structure was solved by direct methods using SIR92 (Altomare *et al.* 1994). The SHELXL-97 software (Sheldrick 2008) was used for the structure refinement; we employed neutral-atom scattering factors. Details of the data collection and structure refinement are provided in Table 3, and the atomic coordinates and equivalent displacement parameters are in Table 4. Table 5 lists the anisotropic displacement parameters for gunterite, and selected interatomic distances and bond valences are listed in Table 6. A table of structure factors and a cif file are available from the Depository of Unpublished Data on the MAC website [document Gunterite CM49\_1243].

TABLE 3. GUNTERITE: DATA COLLECTION AND STRUCTURE-REFINEMENT DETAILS

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation / power	MoK $\alpha$ ( $\lambda = 0.71075$ Å) / 50 kV, 40 mA
Temperature	298(2) K
Structural formula	(Na $_{4-x}$ Ca $_x$ ) $_{2x,00}$ (H $_2$ O) $_{16}$ (H $_{2-x}$ V $_{10}$ O $_{28}$ ) $\cdot$ 6H $_2$ O, $x = 1.10$
Space group	C2/m
Unit-cell dimensions	
$a, b$	19.848(2) Å, 10.1889(11) Å
$c, \beta$	13.1184(15) Å, 130.187(9) $^\circ$
$Z$	2
$V$	2026.7(4) Å $^3$
Density (for above formula)	2.400 g/cm $^3$
Absorption coefficient	2.501 mm $^{-1}$
$F(000)$	1457
Crystal size	250 $\times$ 150 $\times$ 30 $\mu$ m
$\theta$ range	3.11 to 20.82 $^\circ$
Index ranges	$-19 \leq h \leq 19, -10 \leq k \leq 10, -13 \leq l \leq 13$
Reflections collected / unique	8220 / 1128 [ $R_{\text{int}} = 0.0902$ ]
Reflections with $F_o > 4\sigma F$	929
Max. and min. transmission	0.9287 and 0.5736
Refinement method	Full-matrix least-squares on $F^2$
Parameters refined	186
GoF	1.081
Final $R$ indices [ $F_o > 4\sigma F$ ]	$R_1 = 0.0632, wR_2 = 0.1781$
$R$ indices (all data)	$R_1 = 0.0726, wR_2 = 0.1916$
Largest diff. peak / hole	+0.957 / -0.882 e/Å $^3$

$$R_{\text{int}} = \Sigma |F_o^2 - F_c^2(\text{mean})| / \Sigma F_o^2, \quad \text{GoF} = S = \{ \Sigma [w(F_o^2 - F_c^2)^2] / (n-p) \}^{1/2}$$

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, \quad wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}, \quad w = 1 / [ \sigma^2(F_o^2) + (aP)^2 + bP ], \quad \text{where } a \text{ is } 0.1412, b \text{ is } 0.0000, \text{ and } P \text{ is } [2F_c^2 + \text{Max}(F_o^2, 0)] / 3.$$

TABLE 4. ATOMIC COORDINATES AND EQUIVALENT DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ ) FOR GUNTERITE

Atom	x/a	y/b	z/c	$U_{eq}$
V1	0	0.3386(2)	1/2	0.0337(11)
V2	0.93435(17)	1/2	0.6285(3)	0.0368(11)
V3	0.82092(17)	1/2	0.3223(3)	0.0367(11)
V4	0.88655(12)	0.34890(17)	0.1951(2)	0.0392(10)
Na1	0.3134(5)	1/2	0.0401(8)	0.066(2)
Na2	0.623(3)	1/2	0.344(5)	0.056(7)
Ca2	0.6693(14)	1/2	0.413(2)	0.052(5)
O1	0.7338(7)	1/2	0.3092(12)	0.045(3)
O2	0.8454(7)	1/2	0.6088(12)	0.046(3)
O3	0.9494(4)	0.2369(7)	0.3644(7)	0.037(2)
O4	0.8477(7)	1/2	0.0940(11)	0.039(3)
O5	1.0504(6)	1/2	0.6337(10)	0.033(3)
O6	0.8977(5)	0.6222(7)	0.4811(7)	0.032(2)
O7	0.9995(5)	0.6317(7)	0.7489(8)	0.041(2)
O8	0.8491(5)	0.2304(7)	0.0891(8)	0.048(2)
O9	0.7991(5)	0.3685(7)	0.2102(8)	0.037(2)
OW1	0.4161(9)	1/2	0.0050(15)	0.073(4)
H1A	0.3985	0.4392	0.0275	2(3)
OW2	0.3211(11)	1/2	0.2369(17)	0.099(5)
H2A	0.3833	1/2	0.2530	0.119
H2B	0.3724	1/2	0.3286	0.119
OW3	0.5651(8)	0.6650(9)	0.2031(15)	0.108(5)
H3A	0.6107	0.6836	0.2763	0.129
H3B	0.5409	0.7302	0.2024	0.129
OW4	0.7011(7)	0.6773(9)	0.5326(13)	0.084(3)
H4A	0.7065	0.6472	0.6003	0.04(4)
H4B	0.6634	0.7269	0.5318	0.13(7)
OW5	0.5270(19)	1/2	0.376(4)	0.223(19)
H5	0.5069	0.4289	0.3773	0.4(3)
OW6	0.6693(9)	0.1947(11)	0.1683(12)	0.089(3)
H6A	0.6433	0.2706	0.1287	0.13(8)
H6B	0.7230	0.2130	0.1952	0.27(17)
OW7	0.583(2)	0	0.026(2)	0.183(12)
H7A	0.5582	0	-0.0597	0.01(3)
H7B	0.5259	0	-0.0078	0.07(9)
OW8	0.7600(15)	1/2	0.684(2)	0.134(7)
H8A	0.80(4)	1/2	0.67(9)	2(5)
H8B	0.71(2)	1/2	0.60(4)	2(5)

## ATOMIC ARRANGEMENT OF GUNTERITE

Minerals containing the decavanadate group can be considered members of the pascoite family, pascoite ( $\text{Ca}_3\text{V}_{10}\text{O}_{28}\cdot 17\text{H}_2\text{O}$ ; Hughes *et al.* 2005) being the decavanadate mineral first described. All minerals of the pascoite family possess bipartite structures consisting of a structural unit and an interstitial unit, as elucidated by Hawthorne (1983). The  $[\text{V}_{10}\text{O}_{28}]^{6-}$  polyanion defines the *structural unit*, the anhydrous anionic portion of the structure. The structural units are linked by the *interstitial unit*, the cationic portion of the structure, with bonds of lower bond-valence linking alkalis, alkaline earths, and Al to O atoms of the structural unit and interstitial  $\text{H}_2\text{O}$  groups (Hughes *et al.* 2008). The minerals of the pascoite family differ in the composition and structure of the interstitial unit, the +6 charge of which balances the charge of the decavanadate polyanions. The members of the pascoite family are listed in Kampf *et al.* (2011).

Prior to the discovery of rakovanite, no minerals with protonated decavanadate polyanions were known. There is, however, an extensive literature on synthetic protonated decavanadate polyanions; numerous compounds with protonated decavanadate groups have been synthesized, and solids with  $[\text{V}_{10}\text{O}_{28}]^{6-}$ ,  $[\text{HV}_{10}\text{O}_{28}]^{5-}$ ,  $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$ ,  $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$ , and  $[\text{H}_4\text{V}_{10}\text{O}_{28}]^{2-}$  are well characterized (Duraismy *et al.* 2000). Rakovanite is the naturally occurring equivalent of one of the phases synthesized by Duraismy *et al.* (2000).

Gunterite,  $(\text{Na})_4(\text{H}_2\text{V}_{10}\text{O}_{28})\cdot 22\text{H}_2\text{O}$ , also possesses a protonated decavanadate polyanion, and thus the

TABLE 5. ANISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ ) FOR NON-HYDROGEN ATOMS IN GUNTERITE

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
V1	0.0303(19)	0.0280(17)	0.049(2)	0.000	0.0284(17)	0.000
V2	0.0310(18)	0.0355(18)	0.051(2)	0.000	0.0297(17)	0.000
V3	0.0289(18)	0.0355(19)	0.051(2)	0.000	0.0280(17)	0.000
V4	0.0361(16)	0.0339(15)	0.0504(17)	-0.0023(9)	0.0291(13)	-0.0010(8)
Na1	0.059(5)	0.047(4)	0.098(6)	0.000	0.053(5)	0.000
Na2	0.045(17)	0.044(10)	0.09(2)	0.000	0.046(18)	0.000
Ca2	0.045(10)	0.044(5)	0.083(12)	0.000	0.048(10)	0.000
O1	0.033(6)	0.047(7)	0.055(8)	0.000	0.029(6)	0.000
O2	0.042(7)	0.049(7)	0.061(8)	0.000	0.040(7)	0.000
O3	0.035(5)	0.033(4)	0.050(5)	-0.003(3)	0.030(4)	-0.003(3)
O4	0.041(7)	0.027(6)	0.049(7)	0.000	0.029(6)	0.000
O5	0.031(7)	0.029(7)	0.049(7)	0.000	0.030(6)	0.000
O6	0.029(4)	0.027(4)	0.050(5)	-0.001(3)	0.028(4)	0.001(3)
O7	0.038(5)	0.033(4)	0.057(6)	-0.004(4)	0.033(5)	-0.001(3)
O8	0.048(5)	0.036(5)	0.061(6)	-0.009(4)	0.035(5)	-0.004(4)
O9	0.033(4)	0.036(4)	0.049(5)	-0.004(3)	0.029(4)	-0.002(3)
OW1	0.062(9)	0.065(8)	0.092(11)	0.000	0.050(9)	0.000
OW2	0.107(13)	0.102(12)	0.100(13)	0.000	0.072(11)	0.000
OW3	0.133(11)	0.049(6)	0.215(14)	-0.025(7)	0.146(12)	-0.006(5)
OW4	0.082(8)	0.070(7)	0.126(10)	0.014(7)	0.079(8)	0.025(6)
OW5	0.32(4)	0.056(11)	0.56(6)	0.000	0.41(5)	0.000
OW6	0.091(8)	0.085(8)	0.109(10)	0.015(7)	0.074(8)	0.009(7)
OW7	0.37(4)	0.093(15)	0.140(19)	0.000	0.19(2)	0.000
OW8	0.166(19)	0.104(14)	0.19(2)	0.000	0.140(18)	0.000

TABLE 6. SELECTED BOND-DISTANCES (*d*, Å)  
AND BOND-VALENCE VALUES (BV, *vu*) IN GUNTERITE

		<i>d</i>	BV			<i>d</i>	BV Na	BV Ca
V1	– O3	(×2) 1.715(8)	1.27	Na2	– OW5	2.203(33)	0.34	0.53
	O6	(×2) 1.923(7)	0.72		OW3	(×2) 2.195(37)	0.34	0.54
	O5	(×2) 2.125(7)	0.42		O1	2.512(30)	0.15	0.23
<V1	– O>	1.921	Σ 4.82		OW4	(×2) 2.616(38)	0.11	0.17
					<Na2	–O>	2.38	1.39 2.18
V2	– O2	1.611(11)	1.68			<i>d</i>	BV Ca	BV Na
	O7	(×2) 1.825(8)	0.94	Ca2	– OW4	(×2) 2.198(14)	0.54	0.34
	O6	(×2) 2.000(8)	0.59		O1	2.402(16)	0.31	0.20
	O5	2.260(9)	0.29		OW5	2.533(25)	0.22	0.14
<V2	– O>	1.920	Σ 5.03		O2	2.688(25)	0.14	0.09
					OW3	(×2) 2.712(24)	0.13	0.09
V3	– O1	1.623(11)	1.63		OW8	2.757(32)	0.12	0.08
	O9	(×2) 1.823(7)	0.95	<Ca2	–O>	2.516	2.13	1.37
	O6	(×2) 2.029(8)	0.54					
	O5	2.226(9)	0.32					
<V3	– O>	1.927	Σ 4.93					
V4	– O8	1.615(8)	1.66					
	O4	1.845(6)	0.89					
	O9	1.880(7)	0.81					
	O7	1.883(7)	0.81					
	O3	2.054(8)	0.51					
	O5	2.314(8)	0.25					
<V4	– O>	1.930	Σ 4.93					
Na1	– OW1	2.361(15)	0.22					
	O8	(×2) 2.416(7)	0.19					
	O4	2.462(13)	0.17					
	OW2	2.486(18)	0.16					
	O9	(×2) 2.846(11)	0.06					
<Na1	–O>	2.543	Σ 1.05					
				Oxygen atoms		H <sub>2</sub> O molecules		
				Atom	BV	Atom	BV	
				O1	1.87	OW1	0.22	
				O2	1.76	OW2	0.16	
				O3	1.78	OW3	0.22	
				O4	1.95	OW4	0.35	
				O5	1.95	OW5	0.27	
				O6	1.85	OW6	–	
				O7	1.75	OW7	–	
				O8	1.85	OW8	0.07	
				O9	1.82			

interstitial unit must balance the remaining +4 charges from the doubly-protonated decavanadate polyanion, (H<sub>2</sub>V<sub>10</sub>O<sub>28</sub>)<sup>4-</sup>; although the doubly-protonated decavanadate group is well known in synthetic phases, gunterite is the first known mineral with that polyanion. Below, we provide details of the structural unit and the interstitial unit in gunterite.

#### The structural unit in gunterite

The structural unit in gunterite consists of the decavanadate polyanion similar to that found in structurally related minerals (Fig. 2). The decavanadate polyanion consists of ten distorted, edge-sharing octahedra. In the V2, V3, and V4 octahedra in gunterite, each octahedron contains one vanadyl bond, defined as a V<sup>5+</sup>–O bond less than 1.74 Å in length (Schindler *et al.* 2000). The V1 octahedron has two vanadyl bonds. In all cases, the vanadyl bond is *trans* to the longest V–O bond(s) of the octahedron, which is typical of the disposition of bonds in the octahedra of the decavanadate polyanion.

In rakovanite and gunterite, as in most protonated decavanadates (Duraismy *et al.* 2000), the hydrogen atoms of the decavanadate polyanion are difficult to locate. Day *et al.* (1987) undertook an examination of H<sub>3</sub>V<sub>10</sub>O<sub>28</sub>[(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P]<sub>3</sub>•4CH<sub>3</sub>CN to attempt to locate the

H atoms in the triply-protonated decavanadate polyanion. In their study, they utilized <sup>17</sup>O NMR spectroscopy to locate three oxygen atoms of the decavanadate polyanion as the likely sites for protonation in CH<sub>3</sub>CN/H<sub>2</sub>O solutions of H<sub>3</sub>V<sub>10</sub>O<sub>28</sub>[(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>3</sub>. In gunterite, bond-valence sums of the decavanadate oxygen atoms demonstrate that all decavanadate oxygen atoms would be overbonded if bonded to a hydrogen atom, but are permissive of the two hydrogen atoms being disordered over the oxygen atoms of the decavanadate polyanion. We thus conclude that the protonation sites in the decavanadate polyanion are disordered and cannot be conclusively located.

#### The interstitial unit in gunterite

To balance the residual charge of the doubly-protonated decavanadate polyanion, the interstitial group contains two Na polyhedra, Na1 and Na2; the Na2 polyhedron is split into two partially occupied sites that are 0.76 Å apart.

Figure 3 displays the NaO<sub>5</sub>(H<sub>2</sub>O)<sub>2</sub> group centered on the Na1 site; that site is occupied only by Na. The NaO<sub>5</sub>(H<sub>2</sub>O)<sub>2</sub> group shares five oxygen atoms with the decavanadate polyanions (O4, 2 × O8, 2 × O9) and also bonds to two H<sub>2</sub>O molecules of the interstitial



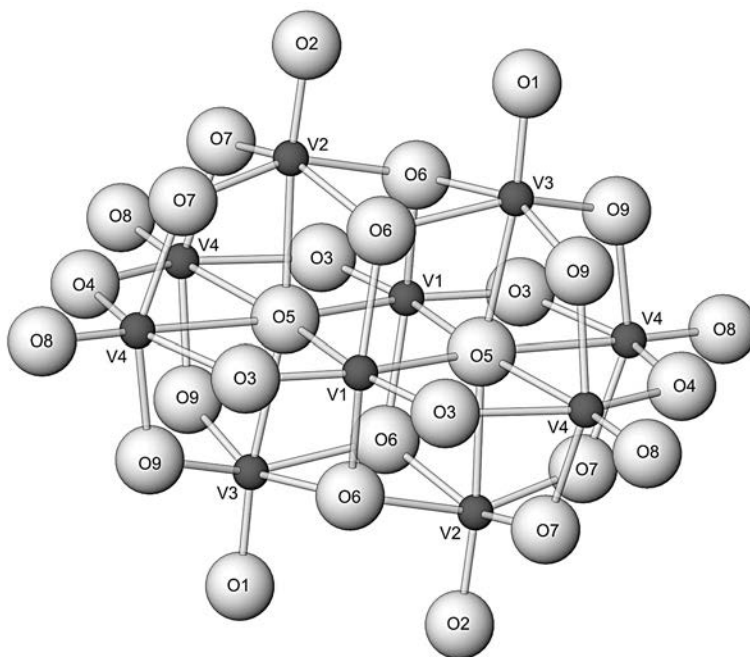


FIG. 2. The decavanadate polyanion in gunterite.

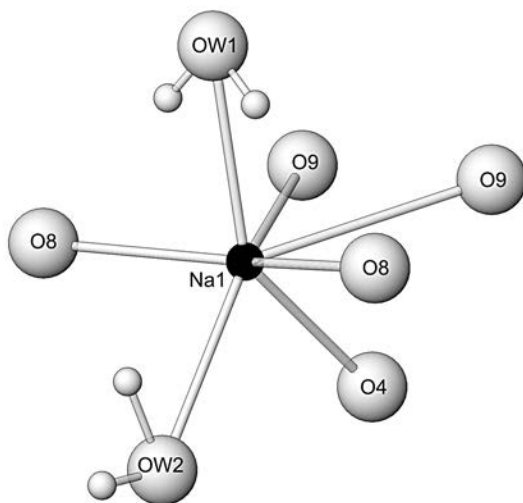


FIG. 3. The  $\text{NaO}_5(\text{H}_2\text{O})_2$  interstitial group in gunterite.

group (OW1, OW2). The Na1 polyhedron does not share any oxygen atoms with the Na2(Ca)2 polyhedron, but is linked through hydrogen bonding.

Figure 4 displays the Na2(Ca2) polyhedron in gunterite. It was clear throughout the solution procedure

and refinement of the atomic arrangement that the Na2 site is split into two partially occupied sites 0.76 Å apart, presumably to accommodate the Na and substituent Ca in gunterite. The presence of significant Ca was confirmed in the electron-microprobe analyses. The excess charge contributed by the Ca substituting for Na is presumably balanced by reducing the protonation of the decavanadate group, leading to the structural formula  $(\text{Na}_{4-x}\text{Ca}_x)_{\Sigma 4.00}(\text{H}_{2-x}\text{V}_{10}\text{O}_{28}) \cdot 22\text{H}_2\text{O}$ ,  $x = 1.10$  for the crystal characterized structurally.

It is tempting to assign one of the sites to Na and the other to Ca occupancy. We have done that in the following analysis, assigning Na to the site labeled Na2 and Ca to that labeled Ca2, as refinement with that scheme of order gives a better  $R$  value than reversing the Na and Ca occupants. However, bond-valence sums for Na and Ca in both sites are permissive of occupancy of both sites by either cation, suggesting that there may be disorder of both cations over both sites. It may be that the site splitting is not a result of substituent Ca, but rather disordering of  $\text{H}_2\text{O}$  molecules in the interstitial group, described subsequently. However, below we describe the split sites as Na2 and Ca2, and in the calculation of bond-valence sums, we use the values of 45% occupancy of the Na2 site by Na and 55% occupancy of the Ca2 site by Ca, as determined in the structure refinement, *i.e.*, there is a disordered distribution of Na and Ca.

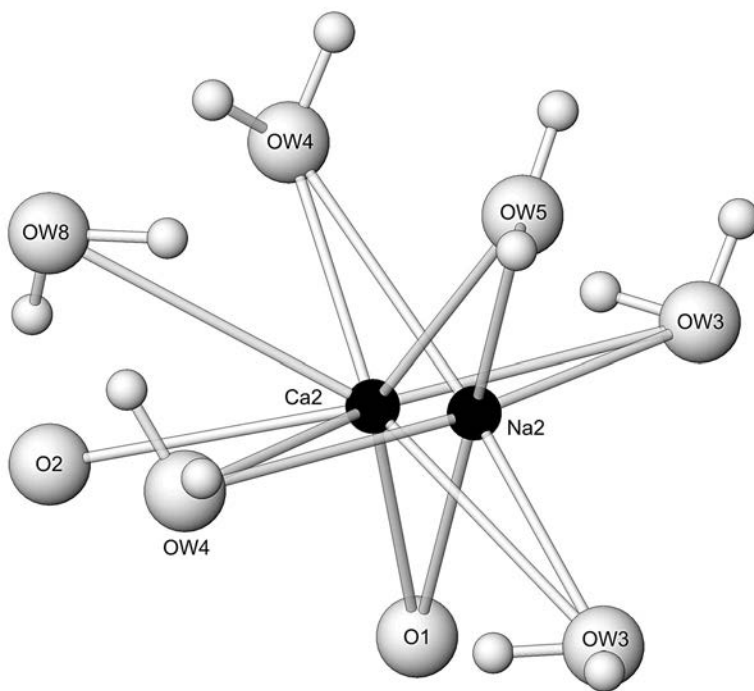


FIG. 4. The split Na<sub>2</sub>Ca<sub>2</sub> site in the interstitial unit of gunterite.

The Na<sub>2</sub> site in the split Na<sub>2</sub>(Ca<sub>2</sub>) polyhedron bonds to one oxygen atom of the decavanadate polyanion and five H<sub>2</sub>O molecules of the interstitial group, forming a distorted octahedron. Atom Ca<sub>2</sub> bonds to the same oxygen atoms as Na<sub>2</sub>, and also to an additional atom of oxygen of the decavanadate group as well as an additional H<sub>2</sub>O molecule from the the interstitial group.

In gunterite, the oxygen atoms of H<sub>2</sub>O molecules OW6 and OW7 are not bonded to any of the cations in the interstitial unit. In addition, several H<sub>2</sub>O molecules were found to be disordered. The refinement results suggest that OW3, OW5, and OW7 could each be split into two partially occupied sites, although that splitting was not modeled in the final refinement because it was deemed that the data were not of sufficient quality to allow such a detailed refinement. In the case of OW3 and OW5, the site-splitting is most likely a result of the bonding of both H<sub>2</sub>O molecules to the Na<sub>2</sub>(Ca<sub>2</sub>) split site, with the H<sub>2</sub>O molecules in question splitting their sites to accommodate bonding to both of the cation sites.

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- (H<sub>2</sub>O)<sub>10</sub>] [H<sub>3</sub>V<sub>10</sub>O<sub>28</sub>{Na(H<sub>2</sub>O)<sub>2</sub>}]•3H<sub>2</sub>O. *Crystal Engineering* **3**, 237-250.
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