

**DICKTHOMSSSENITE, $\text{Mg}(\text{V}_2\text{O}_6)\cdot 7\text{H}_2\text{O}$, A NEW MINERAL SPECIES
FROM THE FIREFLY-PIGMAY MINE, UTAH:
DESCRIPTIVE MINERALOGY AND ARRANGEMENT OF ATOMS**

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ABSTRACT

Dickthomssenite, $\text{Mg}(\text{V}_2\text{O}_6)\cdot 7\text{H}_2\text{O}$, is a new mineral species from the Firefly-Pigmay uranium-vanadium mine, San Juan County, Utah. The phase crystallizes as platy light golden brown crystals up to 1.5 mm in length, with white streak and vitreous luster. Its Mohs hardness is $2\frac{1}{2}$, its calculated density, 2.037(1), and its observed density, between 1.96 and 2.09 g/cm³. Dickthomssenite displays a perfect {100} cleavage. In 589.3 nm light, the mineral is translucent, α 1.6124(3), β 1.6740, and γ 1.7104(4), $2V_{\text{meas}}$ 74(1)°, $2V_{\text{calc}}$ 73°, $b = Z$, $c \wedge Y = 17^\circ$. Electron-microprobe analyses yielded (in wt.%) MgO 15.38%, FeO 0.46%, V₂O₅ 73.92%, H₂O (difference) 10.24%, yielding $(\text{Mg}_{0.94}\text{Fe}_{0.02})\text{V}_2\text{O}_6\cdot 1.4\text{H}_2\text{O}$. Dickthomssenite dehydrates rapidly under the electron beam; the crystal-structure determination reveals that there are seven H₂O groups, giving the ideal formula $\text{Mg}(\text{V}_2\text{O}_6)\cdot 7\text{H}_2\text{O}$. Dickthomssenite is monoclinic, $C2/c$, a 38.954(2), b 7.2010(4), c 16.3465(9) Å, β 97.602(1)°, V 4544.0(4) Å³, $Z = 16$. The strongest three measured X-ray lines [d in Å(hkl)] are: 9.704(100)(400), 5.843(100)(402), and 3.139(90)($\bar{1}20$).

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The phase is formed of (100) planes of chains of V_2O_6 divanadate edge-sharing polyhedra containing [2 + 3]-coordinated vanadium atoms, linked in (100) by corner-sharing with Mg octahedra. These (100) planes are linked along [100] by layers of $Mg(H_2O)_6$ octahedra and non-bonded H_2O molecules. Dickthomssenite is named after Richard W. Thomssen (b. 1933), consulting geologist from Dayton, Nevada, U.S.A.

Keywords: dickthomssenite, new mineral species, vanadate, Utah.

SOMMAIRE

Nous décrivons la dickthomssenite, $Mg(V_2O_6) \cdot 7H_2O$, nouvelle espèce minérale provenant de la mine d'uranium et de vanadium de Firefly–Pigmy, comté de San Juan, au Utah. Elle forme des plaquettes de cristaux dorés pâles atteignant une longueur de 1.5 mm; sa rayure est blanche, et son éclat, vitreux. Sa dureté de Mohs est $2\frac{1}{2}$, sa densité calculée, 2.037(1), et sa densité observée, entre 1.96 et 2.09 g/cm³. Elle possède un clivage {100} parfait. En lumière de 589.3 nm, la dickthomssenite est translucide, α 1.6124(3), β 1.6740, et γ 1.7104(4), $2V_{mes}$ 74(1)°, $2V_{calc}$ 73°, $b = Z$, $c \wedge Y = 17^\circ$. Les analyses à la microsonde électronique ont donné (en %, poids): MgO 15.38%, FeO 0.46%, V_2O_5 73.92%, H_2O (par différence) 10.24%, menant à la formule $(Mg_{0.94}Fe_{0.02})V_2O_6 \cdot 1.4H_2O$. Elle se déshydrate rapidement sous le faisceau d'électrons; l'ébauche de la structure révèle qu'il y a sept groupes H_2O , de sorte que la formule idéale serait $Mg(V_2O_6) \cdot 7H_2O$. La dickthomssenite est monoclinique, $C2/c$, a 38.954(2), b 7.2010(4), c 16.3465(9) Å, β 97.602(1)°, V 4544.0(4) Å³, $Z = 16$. Les trois raies les plus intenses du spectre de diffraction X [d en Å(1)(hkl)] sont: 9.704(100)(400), 5.843(100)(402), et 3.139(90)($\bar{1}202$). La structure est faite de plans (100) de chaînes de divanadate, V_2O_6 , contenant des atomes de vanadium à coordination cinq [2 + 3] liés le long de (100) par partage de coins avec des octaédres à Mg. Ces plans (100) sont liés le long de [100] par des niveaux d'octaédres $Mg(H_2O)_6$ et des molécules de H_2O non liées. La dickthomssenite honore Richard W. Thomssen (né en 1933), géologue consultant de Dayton, Nevada, U.S.A.

(Traduit par la Rédaction)

Mots-clés: dickthomssenite, nouvelle espèce minérale, vanadate, Utah.

INTRODUCTION

The Firefly–Pigmy uranium–vanadium deposit was discovered in 1952 during the U.S. Geological Survey exploration program. The resulting Firefly–Pigmy mine, located in southeastern San Juan County, Utah, produced ore that yielded 2.04% V_2O_5 and 0.35% U_3O_8 through 1956.

Recent collecting at the mine yielded several unknown mineral species. Among these is a phase that crystallizes as light golden brown crystals up to 1.5 mm in length. The mineral has been approved as a new species by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. We are pleased to name the mineral dickthomssenite to honor Richard W. Thomssen (b. 1933), consulting geologist from Dayton, Nevada, U.S.A. Mr. Thomssen has had a long and distinguished career in mineral exploration and ore deposit geology, and has served as Associate Editor of *The Mineralogical Record* (1978–1988), as President and Executive Director of The Mineralogical Record, Inc. (1983–1988), and as Editor of *International Micromounter's Journal* (1994 to the present).

OCCURRENCE

The mineral was discovered by J. Marty at the Firefly–Pigmy mine, Sec. 30, T. 28 S., R 26 E., 16 km east of La Sal, San Juan County, Utah. The mineral occurs in a small area as coatings on a sandstone wall slightly west of the main tunnel, approximately 300 m from the

main portal, close to an area that was mined for vanadium and uranium. Locally, the sandstone contains organic material, including log fragments, some of which contain uranium and vanadium mineralization. Mineral deposition is believed to have occurred since the mining activities ceased, from circulating groundwater, under conditions similar to those that led to pascoite. In addition to pascoite, minor amounts of sherwoodite and native selenium are present in close proximity. Other newly identified minerals at the mine include bariandite, devilline, rossite and hewetitite. Previously identified minerals at the site included carnotite, clausthalite, coffinite, tyuyamunite, uraninite, corvusite, montroseite, roscoelite, galena, pyrite, and tennantite (Carter & Gualtieri 1965).

Uranium–vanadium minerals in the La Sal area are stratigraphically restricted to specific layers in the sandstone (paleochannels) of the Salt Wash Member and near the base of the Brushy Basin Member of the Morrison Formation. Orebodies are mostly associated with carbonaceous material that probably provided a reducing environment for vanadyl and uranyl ions carried in solution. There is little evidence of any hydrothermal alteration in the mine.

Both oxidized and partially oxidized uranium–vanadium minerals occur. In the upper workings, principally carnotite and tyuyamunite are present. In the lower levels of the mine, groundwater prevailed, and the unoxidized minerals were present, including uraninite, coffinite, corvusite, and montroseite. Presently, the mine is closed, with water running out of the portal.

PHYSICAL PROPERTIES

Dickthomssenite occurs as crystals ranging from 0.25-mm needle-like to 0.5×1.5 mm platy, prismatic crystals with basal terminations. The crystals occur in fibroradial groups to a length of 5 mm, creating solid coverage to 1.5×2.5 cm (Fig. 1).

Dickthomssenite is light golden brown (RHS Chart #164A to #164B) with a white streak and vitreous luster. The phase is translucent, does not fluoresce in short- or long-wave ultraviolet radiation, and has a Mohs hardness of $2\frac{1}{2}$. Dickthomssenite has a perfect {100} cleavage, brittle tenacity, and hackly fracture. The calculated density is $2.037(1) \text{ g/cm}^3$, and density was constrained to be greater than that of ulexite (1.96 g/cm^3) and less than that of sulfur (2.09 g/cm^3) by heavy-liquid sink-float comparisons.

OPTICAL PROPERTIES

The measured and calculated optical values for dickthomssenite are given in Table 1. These properties were determined by use of the spindle stage as described in Bloss (1981). A crystal was mounted on the spindle stage, and with the aid of the computer program EXCALIBUR (Bloss 1981, Bartelmehs *et al.* 1992), $2V$ and orientation of the optical indicatrix were determined

at 486, 589, and 656 nm. The crystal's three principal indices of refraction were measured using the double-variation method (Bloss 1981) and the computer programs described in Su *et al.* (1987) and Gunter *et al.* (1989). The optical orientation of the mineral was determined by orienting the crystal on a single-crystal diffractometer (Gunter & Twamley 2001).

Dickthomssenite is optically negative, with $2V_x = 74^\circ(1)$ at 589, $79^\circ(1)$ at 486, and $73^\circ(2)$ at 656 nm. Thus, $r < v$ applies on the basis of measured $2V$ values for these three wavelengths. The sets of extinction data used to obtain these values also yield orientation of the optical indicatrix at three separate wavelengths. EXCALIBUR contains an algorithm to determine if the indicatrix moves between wavelengths (Bloss 1981); there is no movement for this sample, and the indicatrix does not exhibit dispersion.

Dickthomssenite exhibits rather unique characteristics of its indices of refraction, including a large birefringence, which can be related to the crystal structure, and differing dispersions of the indices of refraction. Both properties warrant explanation. The principal indices of refraction for dickthomssenite are α 1.6124(3), β 1.6740, and γ 1.7104(4) at 589 nm, with a very high birefringence, $(\gamma - \alpha) = 0.0980$, one of the highest values of birefringence observed for a biaxial mineral. On the basis of the optical orientation ($b = Z$), the direction



FIG. 1. A cluster of dickthomssenite crystals. Cluster is 1 mm in largest dimension.

TABLE 1. OBSERVED AND CALCULATED OPTICAL PROPERTIES OF DICKTHOMSSENITE

	n_{589}	n_{486}	n_{656}	$n_{486}-n_{656}$
α	1.6124(3)	1.6276(5)	1.6088(4)	0.0188
β^*	1.6740	1.6989	1.6648	0.0341
γ	1.7104(4)	1.752(1)	1.6985(5)	0.0535
$\gamma - \alpha$	0.098	0.1244	0.0897	
$2V_{\text{obs}}$	74°(1)	79°(1)	73°(2)	
$2V_{\text{calc}}$	72.7°	78.5°	73.4°	

Mean $n_{\text{obs}} = 1.6656$. Compatibility index = -0.0003 (superior). Gladstone–Dale values of Mandarino (1981). Optical orientation: $b = Z, c \wedge Y = 17^\circ$.
 * β values are those for the 1.674 index of refraction liquid.

of the large index of refraction corresponds to the direction of the V_2O_6 chains.

Structural control of the optical properties can be understood by recalling that increased electron density causes increases in indices of refraction. In dickthomssenite, the V_2O_6 chains are parallel to b , which corresponds to Z of the indicatrix. Light vibrating along Z thus encounters a very high density of electrons. From structural projections, it is also clear that the electron density is less for light vibrating in the X direction than in the Y direction.

Some background in the double-variation method used to determine dispersion is appropriate. This method is one of the most precise methods to determine the index of refraction of minerals and is based on varying the index of an immersion liquid by slightly changing the temperature to obtain a match with a mineral's index of refraction. The colored Becke lines observed in polychromatic light become light and dark lines in monochromatic light. The match between liquid and index of refraction of a crystal occurs where the dispersion curves for the liquid and the mineral intersect. Thus, monochromatic light is used, and a wavelength of match found. (The double-variation method gains its name from variations in two physical parameters, the temperature of the liquid and the wavelength of light.) The dispersion curve of the liquid is greater than that of the mineral, and as the liquid is heated, its index of refraction decreases and the match moves to lower wavelengths. By collecting a series of matches, the dispersion curve for the mineral can be determined on the basis of the known dispersion curve for the liquid. Bloss (1981) provided an excellent discussion of this method.

As stated above, the assumption in the use of the double-variation method is that the dispersion of the liquid is greater than that of the mineral. For dickthomssenite, this is only the case for α . For β , the dispersion of the mineral is the same as that of the index of refraction of the liquid, and the dispersion of γ is *greater* than that of the liquid. Table 1 lists values of $n_{486} - n_{656}$ for each of the principal indices of refraction, and they clearly differ from each other. These differences pose problems in measurement of indices of refraction by the double-

variation method. For instance, no colored Becke lines appear for β ; colored Becke lines are a result of the intersection of the dispersion curves of the liquid and mineral in the visible. For β , these two curves have the same slope, and the match was obtained by disappearance of the light- and dark-colored Becke lines in polychromatic light. To our knowledge, this phenomenon has never been observed in minerals, although it was observed, but not reported, for α in Cu-exchanged heulandite in Palmer & Gunter (2000).

In the process of measuring γ for the mineral, a confusing phenomenon occurred in which upon heating the liquid, the wavelength of match moved to *higher*, and not lower, wavelengths. This led to the conclusion that γ had a *higher* dispersion than that of the liquid, a phenomenon essentially unknown in the mineral world. In the most comprehensive review of the dispersion data of minerals and synthetic compounds, McCrone & Delay (1973) noted that the only mineral in which this phenomenon occurs is ice. It does occur in several synthetic compounds, but none of these synthetic anisotropic compounds showed such a large difference in the dispersion of the three principal indices of refraction.

To confirm the observed values of $2V$, values can be calculated using the indices of refraction at three separate wavelengths. Recall that $2V$ was measured independently on the basis of the calculations provided by EXCALIBR (Table 1). Also presented in Table 1 are $2V$ values calculated from the measured indices of refraction at each of the three wavelengths. The excellent agreement between observed and calculated values confirms the data on indices of refraction.

The Gladstone–Dale constants of Mandarino (1981) provide confirmation of the optical data and chemical data. The observed mean index of refraction for dickthomssenite is 1.6656, and its calculated value is 1.6655 using the 0.255 value for MgO (Mandarino 1981). For dickthomssenite, the compatibility index equals -0.0003 , which is in the superior range (Mandarino 1981). The excellent agreement between the calculated and observed indices of refraction further confirms the validity of the measured chemical composition and density of the mineral.

INFRARED SPECTROSCOPY

Figure 2 records the infrared spectrum of dickthomssenite; the spectrum was collected using a Perkin Elmer Spectrum 2000 FTIR outfitted with a Harrick Split-pea micro attenuated total internal reflectance (ATR) accessory and a deuterium triglycine sulfate detector. A small crystal of the sample was placed on the internal reflection element of the accessory and held in place with an infrared-transparent potassium chloride window. The spectrum was collected at 4 cm^{-1} resolution and represents the average of 32 individual scans. In conducting an ATR measurement, the length of the optical path increases at lower wavenumbers. As such, absorptions in

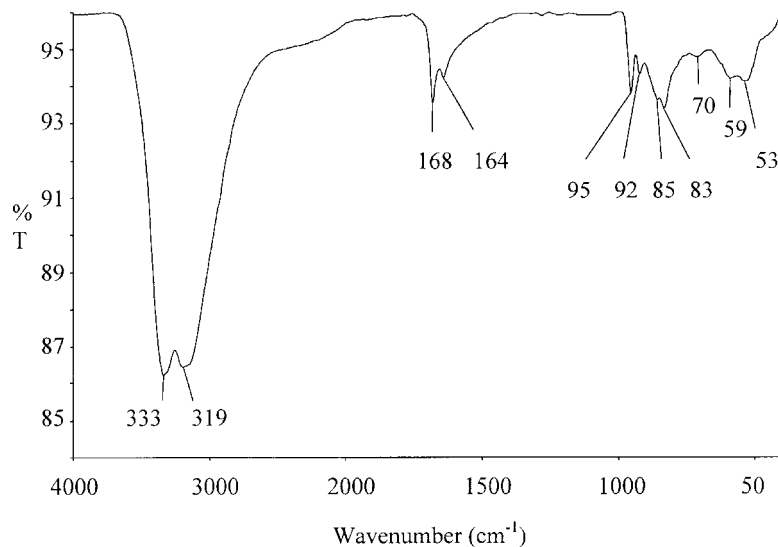


FIG. 2. Infrared spectrum of dickthomssenite. Wavenumber labels on spectrum $\times 10^{-1}$.

the low-wavenumber region are enhanced with respect to a transmission spectrum, in which the length of the optical path is independent of wavenumber. The spectrum has been normalized for length of the optical path using an algorithm that calculates the optical path length at different wavelengths using the index of refraction of the sample.

Vibrational assignments for absorptions observed in the spectrum include asymmetric and symmetric stretching modes of O–H (at 3338 and 3191 cm^{-1}), H–O–H bending mode (at 1681 and 1638 cm^{-1}), and librational modes of H_2O or vibrations associated with metal aquo complexes (at 591 and 537 cm^{-1}). In addition, various vibrations associated with vanadate groups are found between wavenumbers 953 and 832 cm^{-1} , including the characteristically sharp, very strong V=O stretching

band at 954 cm^{-1} (Schindler *et al.* 2000b) denoting vanadyl bonds within the compound.

The infrared analysis was used to address one question: does any free hydroxyl exist in the crystal? The characteristic feature for such a moiety is an extremely sharp band located near 3570 cm^{-1} . The absence of such a band indicates that no free hydroxyl exists. Finally, the splitting of the H–O–H absorption indicates that there are two types of bound H_2O in the system.

CHEMICAL COMPOSITION

Chemical analyses were performed in wavelength-dispersion mode on a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. Data reduction was undertaken with a PAP routine in XMAQNT (pers. commun., C. Davidson, CSIRO). The operating voltage was 15 kV, and the beam current was 20 nA. Data for all elements in the samples were collected for 25 s or 0.50% precision, whichever was attained first. A 100 s energy-dispersion scan indicated no elements with Z greater than 8 other than those reported here. In addition, Mn, Ti, Pb, Ca and S were sought but not detected. Data for the three elements Mg, Fe and V were collected simultaneously on three separate wavelength-dispersion spectrometers.

Dickthomssenite decomposes rapidly under the electron beam. Normally, defocusing the beam will solve this problem. However, because of the small size of the crystals, a defocused beam could not be employed. This resulted in extensive loss of H_2O and resultant elevated sums of oxides when H_2O is calculated by difference.

TABLE 2. CHEMICAL ANALYTICAL DATA FOR DICKTHOMSSSENITE

Constituent	Observed	Ideal composition	Range	Standard
MgO wt. %	15.38	11.57	15.09 – 15.82	diopside
FeO	0.46	---	0.44 – 0.49	almandine
V_2O_5	73.92	52.22	72.61 – 76.09	synthetic VP_2O_7
H_2O	10.24*	36.21		
TOTAL	100.00	100.00		

* Calculated by difference from 100%.

Empirical formula from analysis: $(\text{Mg}_{0.94}\text{Fe}_{0.02})_{20.96}\text{V}_2\text{O}_6 \cdot 1.4\text{H}_2\text{O}$, on basis of $V = 2$.
Empirical formula on the basis of 13 anions, as confirmed by structure analysis:
 $(\text{Mg}_{0.95}\text{Fe}_{0.02})_{20.97}\text{V}_{2.01}\text{O}_6 \cdot 7\text{H}_2\text{O}$ (see text).

TABLE 3. CRYSTAL DATA AND RESULTS OF STRUCTURE REFINEMENT FOR DICKTHOMSSSENITE

Unit Cell:			
a 38.954(2)Å	b 7.2010(4)Å	c 16.3465(9)Å	β 97.602(1)°
V 4544.0(4) Å ³	[Refinement of positions of 4,208 reflections, $I > 20\sigma(I)$]		
$C2/c$	Z 16	μ_{Mo} 1.759 mm ⁻¹	
Data Collection:			
Frames: 1800	0.30°, 30 s/frame	$2\theta_{\text{max}}$ 65.0°	28,531 data
8,037 unique	Redundancy 3.55	Completeness 97.9%	R_{int} 4.22%
3,090 > 4 $\sigma(F)$		$-56 \leq h \leq 58$; $-10 \leq k \leq 10$; $-24 \leq l \leq 23$	
Refinement Results:			
Absorption Correction: SADABS			
Refinement on F^2 , 2 σ data, 293 parameters:			
$R1$ 0.0645	w $R2$ 0.1390	GOOF 1.351	
$\Delta \rho$ max, min:	+3.304	-0.688 eÅ ³	

TABLE 4. INDEXED POWDER-DIFFRACTION PATTERN OF DICKTHOMSSSENITE

l	d_{meas}	d_{calc}	h	k	l
100	9.704 Å	9.653 Å	4	0	0
60	8.117	8.101	0	0	2
100	5.843	5.837	4	0	2
40	4.828	4.826	8	0	0
50	4.061	4.051	0	0	4
20	3.586	3.570	4	0	4
20	3.470	3.476	$\frac{2}{2}$	2	1
90	3.139	3.136	$\frac{12}{2}$	0	2
60	2.920	2.918	8	0	4
50	2.707	2.700	0	0	6
		2.699	$\frac{12}{2}$	0	4
10	1.969	1.963	$\frac{8}{8}$	0	8
10	1.778	1.785	8	0	8
10	1.689	1.692	16	0	6
		1.679	$\frac{20}{2}$	0	6
		1.687	8	4	0
20b	1.629	1.634	4	0	10

Conditions: 114.6mm Gandolfi camera, Ni-filtered Cu radiation, air. Indexed with aid of single-crystal data.

The relative numbers of cations determined in the electron-probe analysis were confirmed by the crystal-structure analysis and, together with the determination of H₂O by structure analysis, the correct ideal chemical formula, Mg(V₂O₆)•7H₂O, was established. Table 2 contains the results of the chemical analysis.

CRYSTALLOGRAPHY

A single crystal of dickthomsssenite was mounted on a conventional diffractometer with a scintillation detector. Orientation routines correctly identified a subcell of the correct unit-cell, with $a = a/2$ and $b = b/2$ of the correct cell. The crystal was subsequently mounted on a CCD-based X-ray diffractometer; the increased sensitivity of the CCD detector allowed us to elucidate the superstructures along a and b , and gave the unit cell given in Table 3. On the basis of systematic extinctions in the dataset, space group $C2/c$ was indicated, and shown to be correct in the subsequent crystal-structure solution and refinement.

Gandolfi photographs were taken of a multiple-grain mount of dickthomsssenite. The indexed powder pattern and conditions of data collection are given in Table 4.

CRYSTAL STRUCTURE

Experimental

A single-crystal of dickthomsssenite (0.030 × 0.080 × 0.20 mm) was mounted on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube operated at 2000 watts. The detector was placed at a distance of 5.60 cm from the crystal.

Frames (0.30° scan width) were collected with the parameters listed in Table 3; the frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The structure was solved and refinement undertaken using the Bruker SHELXTL (Version 5.1) software package. Full-matrix least-squares refinement was undertaken on F^2 . Hydrogen atom positions and isotropic displacement parameters were calculated; anisotropic displacement parameters were refined for all atoms except hydrogen.

Table 3 contains data-collection parameters and refinement results for dickthomsssenite, and Table 5 lists the atom coordinates and equivalent isotropic displacement parameters for all atoms in the arrangement. Table 6 gives selected interatomic distances in the mineral, and Table 7 lists bond-valence sums for atoms in the phase. A table of structure factors is available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

Description of the structure

Evans & Hughes (1990) summarized the crystal chemistry of the vanadium oxide bronze minerals, and noted several structural elements that are characteristic of the arrangements of atoms in those phases. Interest in vanadium oxide compounds, both synthetic and natural, has recently been rekindled in part because of their potential use as secondary cathode materials for advanced lithium batteries and their important role in oxidative catalysis (Zavalij & Whittingham 1999). Zavalij & Whittingham provided a detailed summary and classification of vanadium oxides with open frameworks, including synthetic and natural phases. They noted that compounds containing trigonal bipyramids (such as in dickthomsssenite) were not included in their study "because they exist only in such compounds as monomeric metal-inorganic compounds and clusters, mixed-metal frameworks, and vanadate chains", which were beyond the scope of their work. Schindler *et al.* (2000b) gave an excellent summary of the crystal-chemical aspects of vanadium derived from examination of the structural chemistry of natural and synthetic phases. We adopt their polyhedron-based classification here. Schindler *et*

TABLE 5. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS FOR DICKTHOMSSSENITE

Atom	x	y	z	U_{eq}
V1	0.1506(1)	0.1163(2)	0.2101(1)	0.008(1)
V2	0.0991(1)	0.3673(2)	0.2912(1)	0.009(1)
V3	0.1518(1)	0.6170(2)	0.2117(1)	0.009(1)
V4	0.0987(1)	0.8661(2)	0.2904(1)	0.009(1)
Mg1	0.1255(1)	0.6238(3)	0.0018(1)	0.019(1)
Mg2	0	½	0	0.021(1)
Mg3	¾	¾	½	0.022(1)
O1	0.1132(1)	0.1176(8)	0.2833(2)	0.020(1)
O2	0.1364(1)	0.3688(8)	0.2184(2)	0.019(1)
O3	0.1157(1)	0.6180(8)	0.2906(2)	0.016(1)
O4	0.1346(1)	0.8663(8)	0.2117(2)	0.016(1)
O5	0.1895(1)	0.1120(9)	0.2605(2)	0.023(1)
O6	0.1547(1)	0.1253(8)	0.1095(2)	0.018(1)
O7	0.0607(1)	0.3744(9)	0.2388(2)	0.022(1)
O8	0.0930(1)	0.6350(8)	-0.1086(2)	0.015(1)
O9	0.1896(1)	0.6249(10)	0.2653(2)	0.023(1)
O10	0.1581(1)	0.6154(8)	0.1119(2)	0.015(1)
O11	0.0604(1)	0.8582(9)	0.2377(2)	0.024(1)
O12	0.0937(1)	0.8754(9)	0.3903(2)	0.022(1)
Ow13	0.1435(1)	0.8942(5)	-0.0206(2)	0.026(1)
H13A	0.1250	0.9576	-0.0237	0.031
H13B	0.1553	0.9412	0.0218	0.031
Ow14	0.0900(1)	0.7474(6)	0.0675(2)	0.036(1)
H14A	0.0964	0.7313	0.1188	0.044
H14B	0.0847	0.8543	0.0477	0.044
Ow15	0.1062(1)	0.3563(5)	0.0191(2)	0.025(1)
H15A	0.1113	0.2898	-0.0205	0.029
H15B	0.0954	0.2869	0.0492	0.029
Ow16	0.1607(1)	0.4948(6)	-0.0646(2)	0.038(1)
H16A	0.1621	0.5505	-0.1098	0.045
H16B	0.1807	0.4920	-0.0367	0.045
Ow17	-0.0264(1)	0.5035(7)	0.0997(2)	0.025(1)
H17A	-0.0332	0.6136	0.1072	0.030
H17B	-0.0131	0.4663	0.1420	0.030
Ow18	0.0416(1)	0.3922(6)	0.0715(2)	0.040(1)
H18A	0.0352	0.2958	0.0953	0.048
H18B	0.0572	0.3634	0.0421	0.048
Ow19	-0.0188(1)	0.2306(5)	-0.0267(2)	0.030(1)
H19A	-0.0056	0.1600	0.0052	0.036
H19B	-0.0332	0.1581	-0.0542	0.036
Ow20	0.7762(1)	0.7523(7)	0.4015(2)	0.028(1)
H20A	0.7723	0.6677	0.3652	0.034
H20B	0.7803	0.8633	0.3878	0.034
Ow21	0.7918(1)	0.8566(6)	0.5734(2)	0.039(1)
H21A	0.7966	0.9656	0.5586	0.046
H21B	0.8097	0.7911	0.5697	0.046
Ow22	0.7680(1)	0.4802(5)	0.5271(2)	0.030(1)
H22A	0.7561	0.4064	0.4941	0.036
H22B	0.7829	0.4102	0.5546	0.036
Ow23	0.7503(1)	0.4161(9)	0.2475(2)	0.024(2)
H23A	0.7684	0.4801	0.2440	0.029
H23B	0.7425	0.3657	0.2018	0.029
Ow24	0.7748(1)	0.2516(7)	0.3974(2)	0.030(1)
H24A	0.7614	0.1811	0.4204	0.036
H24B	0.7956	0.2169	0.3965	0.036
Ow25	0.9755(1)	0.0019(7)	0.6015(2)	0.028(1)
H25A	0.9547	0.0393	0.6005	0.034
H25B	0.9887	0.0726	0.5782	0.034
Ow26	1.0	0.3382(10)	¾	0.026(2)
H26	0.9814	0.3070	0.7682	0.031
Ow27	1.0	0.8307(10)	¾	0.030(2)
H27	0.9926	0.8833	0.7045	0.036

U_{eq} = 1/3 of the trace of the orthogonalized U_i tensor.

TABLE 6. SELECTED INTERATOMIC DISTANCES IN DICKTHOMSSSENITE (Å)

V1		V2		V3		V4		
-05	1.624(4)*	-07	1.621(4)*	-09	1.610(4)*	-011	1.622(4)*	
-04	1.908(6)	-08	1.686(3)*	-010	1.682(3)*	-012	1.672(3)*	
-01	2.005(4)	-01	1.889(6)	-02	1.894(6)	-01	1.906(6)	
-06	1.673(3)*	-03	1.919(6)	-04	1.917(6)	-03	1.906(6)	
-02	1.911(6)	-02	1.994(4)	-03	2.028(4)	-04	2.021(4)	
Mean	1.824	Mean	1.822	Mean	1.826	Mean	1.825	
Mg1	-Ow14	2.060(4)	Mg2	-Ow18(x2)	2.022(4)	O6	H13B	1.97(1)
-Ow16	2.076(4)	-Ow17(x2)	2.038(4)	O6	H24B	2.06(1)		
-Ow15	2.100(4)	-Ow19(x2)	2.099(4)	O9	H23A	1.95(1)		
-Ow13	2.118(4)	Mean	2.053	O11	H26	2.01(1)		
-08	2.064(4)			O12	H15A	1.94(1)		
-010	2.061(4)			O12	H25A	2.01(1)		
Mean	2.080							
Mg3	-Ow20(x2)	2.018(4)						
-Ow21(x2)	2.039(3)							
-Ow22(x2)	2.093(4)							
Mean	2.050							

*Vanadyl bond.

TABLE 7. BOND-VALENCE SUMS FOR ATOMS IN DICKTHOMSSSENITE

	V1	V2	V3	V4	Mg1	Mg2	Mg3	Total	*H Total
O1	0.56	0.79	-	0.75	-	-	-	2.10	2.10
O2	0.74	0.58	0.78	-	-	-	-	2.10	2.10
O3	-	0.73	0.53	0.75	-	-	-	2.01	2.01
O4	0.75	-	0.73	0.54	-	-	-	2.02	2.02
O5	1.73	-	-	-	-	-	-	1.73	1.73
O6	1.50	-	-	-	-	-	-	1.50	1.82
O7	-	1.74	-	-	-	-	-	1.74	1.74
O8	-	1.44	-	-	0.36	-	-	1.80	1.80
O9	-	-	1.80	-	-	-	-	1.80	1.97
O10	-	-	1.46	-	0.36	-	-	1.82	1.82
O11	-	-	-	1.74	-	-	-	1.74	1.90
O12	-	-	-	1.50	-	-	-	1.50	1.83
Ow13	-	-	-	-	0.32	-	-	0.32	
Ow14	-	-	-	-	0.36	-	-	0.36	
Ow15	-	-	-	-	0.33	-	-	0.33	
Ow16	-	-	-	-	0.35	-	-	0.35	
Ow17	-	-	-	-	-	0.38(×21)	-	0.38	
Ow18	-	-	-	-	-	0.40(×21)	-	0.40	
Ow19	-	-	-	-	-	0.33(×21)	-	0.33	
Ow20	-	-	-	-	-	-	0.40(×21)	0.40	
Ow21	-	-	-	-	-	-	0.38(×21)	0.38	
Ow22	-	-	-	-	-	-	0.34(×21)	0.34	
Ow23	-	-	-	-	-	-	-	-	
Ow24	-	-	-	-	-	-	-	-	
Ow25	-	-	-	-	-	-	-	-	
Ow26	-	-	-	-	-	-	-	-	
Ow27	-	-	-	-	-	-	-	-	
Total	5.28	5.28	5.30	5.28	2.08	2.22	2.24		

* For oxygen atoms exclusive of H₂O, H Total = bond-valence sum calculated with addition of hydrogen bonds contributed by calculated H atoms <2.20 Å distant. Bond-valence parameters from Brown (1981).

al. (2000b) evaluated bonding in numerous vanadium polyhedra, and defined three types of vanadium-oxygen bonds on the basis of distinct populations of V-O bond lengths separated by ranges in which no bonds

occur. They defined several types of V⁵⁺O_n polyhedra, including [2 + 3]-coordination in which two vanadyl bonds (defined by those authors as a V⁵⁺-O bond shorter

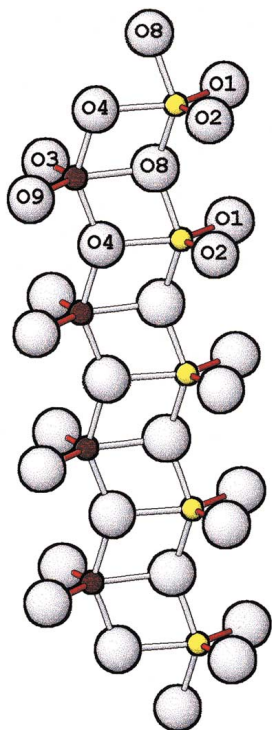


FIG. 3. $[2 + 3] (V_2O_6)_\infty$ chains parallel to $[010]$; vanadyl bonds are red, V1 Atoms are yellow, V2 atoms are maroon.

than 1.74 \AA) and three equatorial bonds (defined as $V^{5+}-O$ bonds longer than 1.74 \AA) occur. In dickthomssenite, the four distinct vanadium polyhedra are $[2 + 3]$ -coordinated (Table 6).

Figure 3 depicts the atom arrangement of the $[010]$ vanadate chains in dickthomssenite. These chains are formed of edge-shared $[2 + 3]$ polyhedra. Figure 4 illustrates the atom arrangement of the phase. As shown in Figure 3, the $[2 + 3]$ polyhedra link to form $(V_2O_6)_\infty$ chains of edge-sharing polyhedra. The $[010]$ chains are linked in (100) by $Mg1[O_2(H_2O)_4]$ octahedra (Fig. 4); the central Mg atom bonds to oxygen atoms of the divanadate chains, and the four non-shared vertices of octahedra bond to oxygen of H_2O . We subsequently refer to as “vanadate – Mg octahedron” planes the (100) planes formed of the linked vanadate groups and Mg octahedra.

Dickthomssenite possesses a perfect $\{100\}$ cleavage; the cleavage plane separates successive vanadate – Mg octahedron layers. The intervening layers consist of H_2O molecules and $Mg_2(H_2O)_6$ and $Mg_3(H_2O)_6$ octahedra, with neither Mg octahedron being linked to other polyhedra except by hydrogen bonding.

Schindler *et al.* (2000a, b) proffered a crystal-chemical approach to the composition and occurrence of vanadium minerals that is suited to the description of the arrangement of atoms in dickthomssenite. Those authors described vanadium minerals by their two component parts: the structural unit, which is the anionic portion of the structure that consists of polyhedra of higher bond-valences, and the interstitial complex, which is the cationic portion of the structure that contains alkaline and alkaline-earth cations and H_2O or OH groups (or both). They also described the role of H_2O groups in vanadium minerals, predicted the range in Lewis basicity for different structural units, and demonstrated the efficacy of the valence-matching principle in complex vanadium hydrate minerals.

In dickthomssenite, the structural unit is formed of the two $[V_2O_6]$ dimers, and the interstitial unit is $[^{6}Mg_2(H_2O)_{10}(H_2O)_0]^{4+}$, with the four unbonded H_2O molecules completing the unit-cell contents. The value of the Lewis acidity calculated for this interstitial unit (0.18 valence units, *vu*) is within the range of Lewis basicity (0.14–0.22) predicted for $[V_2O_6]$ structural units; thus the valence-matching principle is satisfied, and dickthomssenite is a stable structure.

As indicated in diffraction experiments, a strong substructure with $a = a/2$, $b = b/2$ was observed. Indeed, the true structure was not detected in orientation routines using a diffractometer equipped with a scintillation detector, but only revealed with the weak reflections that were detected using the CCD detector. Inspection of the atom coordinates and Figure 4 illustrates that the cause of the substructure is the atomic arrangement of the $(V_2O_6)_\infty$ chains, the chains being the structural element that contains the majority of the scatterers within the unit cell. Merged into the subcell, each unique V atom in the true cell is superimposed on another V atom ($V1 \approx V3$, $V2 \approx V4$), within 0.05 \AA . Each oxygen atom of the $(V_2O_6)_\infty$ chains also projects onto another atom in the subcell, all within 0.14 \AA . Such a substructure is manifested by non-equivalent atoms in the true cell being superimposed by translations of $(\sim 2x, \sim y, \sim z)$ or $(\sim x, \sim 2y, \sim z)$, in addition to the lattice centering. The atoms of the vanadate chains exhibit such a relationship in dickthomssenite, leading to the observed superstructure. The Mg atoms and H_2O molecules are not so related, thus leading to the true cell and the weaker h and $k = 2n + 1$ reflections.

Similar species

Dickthomssenite is the first known vanadate mineral structure with Mg as a major interstitial cation. The atom arrangement in synthetic anhydrous $Mg(V_2O_6)$ is described by Ng & Calvo (1972) in space group $C2/m$; the structural unit of that phase is also formed of $[V_2O_6]$ divanadate groups, connected by octahedrally coordinated Mg atoms. Although structural relationships

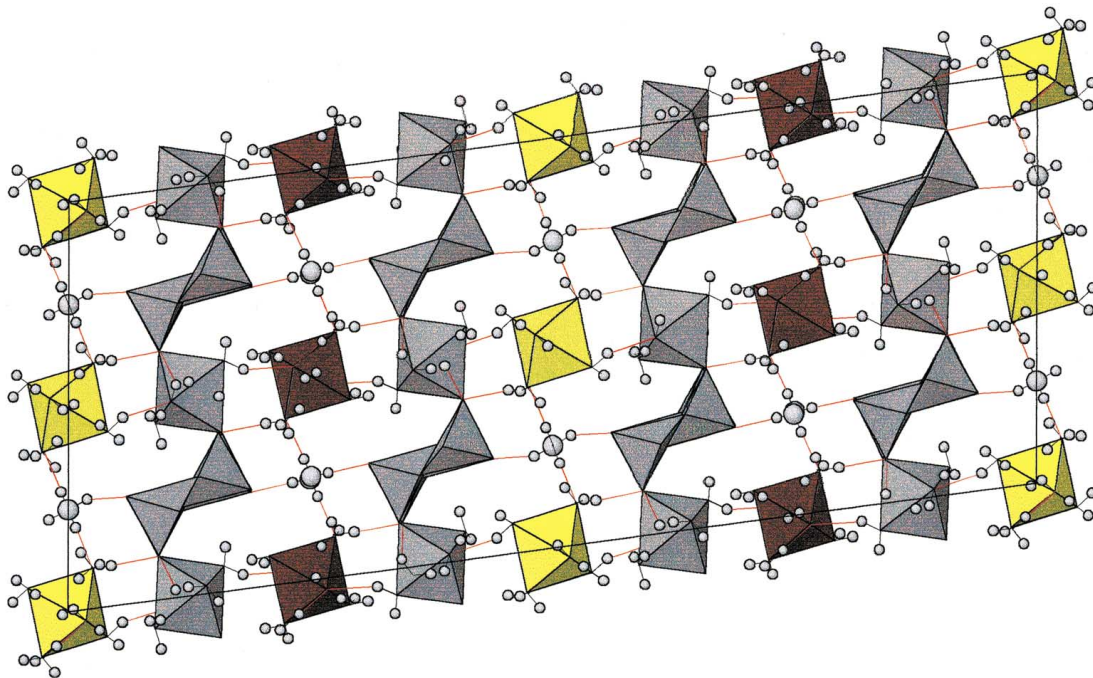


FIG. 4. Atomic arrangement of dickthomssenite projected on (010), with c vertical. Vanadate–Mg1 octahedron planes in gray, Mg2 octahedron is yellow, and Mg3 octahedron is maroon. Red lines indicate hydrogen bonds between 1.0 and 2.1 Å and define a network of hydrogen bonds.

between the anhydrous phase and dickthomssenite are not obvious, the effect of H_2O in the atom arrangement on the vanadate polyhedron is of interest. The general topology of the divanadate groups in both phases is similar, but the individual V–O bonds respond to the interstitial unit. In the anhydrous phase, both vanadyl-bonded oxygen atoms also bond to Mg atoms to complete their bond-valence requirements. In dickthomssenite, the shortest vanadyl-bonded oxygen atom only receives additional bonding from weaker hydrogen bonds in both VO_5 polyhedra. The shortest vanadyl bond is thus ~ 0.06 Å shorter in dickthomssenite, as the vanadyl oxygen atom attains its requisite bond-valence from the shortened V–O bond.

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