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# ORTHOMINASRAGRITE, $V^{4+}O (SO_4) (H_2O)_5$, A NEW MINERAL SPECIES FROM TEMPLE MOUNTAIN, EMERY COUNTY, UTAH, U.S.A.

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## ABSTRACT

Orthominasragrite, $V^{4+}O (SO_4) (H_2O)_5$, is a new mineral species from Temple Mountain, Emery County, Utah. It occurs as rounded aggregates (up to ~200 μm across) of irregular grains that are pale blue to bright blue, depending on size. Orthominasragrite has a pale blue streak, a vitreous luster, and no observable fluorescence under ultraviolet light. It has no cleavage or parting. The Mohs hardness is ~1, and the calculated density is 2.00 g/cm$^3$. Orthominasragrite is biaxial negative (pseudo-uniaxial) with $\alpha$ 1.529(2), $\beta$ 1.534(2), $\gamma$ 1.534(2), $2V_{obs}$ = 2(4)°, $2V_{calc}$ = 0°, non-pleochroic, $X = b$, $Y = c$, $Z = a$. Orthominasragrite is orthorhombic, space group $Pmn2_1$, $a$ 7.246(4), $b$ 9.333(6), $c$ 6.210(4) Å, $V$ 420.0(3) Å$^3$, $Z$ = 2. The strongest seven lines in the X-ray powder-diffraction pattern [$d$ in Å($I$)($hkl$)] are as follows: 4.699(10)(101,020), 3.322(5)(121), 2.865(4)(220), 2.602(3)(221,131,022), 3.734(2)(021), 3.622(2)(200), and 3.108(2)(002). Chemical analysis by electron microprobe gave $VO_2$ 33.88, $SO_3$ 31.97, $H_2O$ (calc.) 36.30, sum 102.15 wt.%; the proportion of $H_2O$ was determined by crystal-structure analysis. The resulting empirical formula on the basis of 10 anions (including 5 $H_2O$) is $V_{1.014} S_{0.991} O_5 (H_2O)_5$; the end-member formula is $VO (SO_4) (H_2O)_5$. Orthominasragrite is the orthorhombic form of (monoclinic) minasragrite. The crystal structure was solved by direct methods and refined to an $R$ index of 4.4% for 1007 observed ($|F_o| > 5\sigma F$) reflections measured with an automated four-circle X-ray diffractometer using Mo$K\alpha$ X-radiation. There is one $V$ site occupied by $V^{4+}$ and surrounded by one O atom and 5 ($H_2O$) groups in an octahedral arrangement, with one short apical vanadyl bond (1.580 Å), four similar equatorial bonds (<2.026 Å>), and one longer V–O bond (2.231 Å) *trans* to the vanadyl bond. The structure consists of isolated ($V^{4+}\phi_6$) octahedra ($\phi$: unspecified anion) and ($SO_4$) tetrahedra linked by hydrogen bonds.

*Keywords*: orthominasragrite, new mineral species, crystal structure, minasragrite, vanadate, Temple Mountain, Utah.

## SOMMAIRE

Nous décrivons ici l'orthominasragrite, $V^{4+}O (SO_4) (H_2O)_5$, nouvelle espèce minérale provenant du mont Temple, comté d'Emery, au Utah. On la trouve en amas arrondis atteignant ~200 μm faits de cristaux irréguliers qui sont bleu pâle ou bleu brillant, selon la taille des grains. L'orthominasragrite a une rayure bleu pâle, un éclat vitreux, et semble sans fluorescence sous lumière ultra-violette et sans clivage ou plan de séparation. La dureté de Mohs est environ 1, et la densité calculée est 2.00 g/cm$^3$. Elle est biaxe négative (pseudo-uniaxe), avec $\alpha$ 1.529(2), $\beta$ 1.534(2), $\gamma$ 1.534(2), $2V_{obs}$ = 2(4)°, $2V_{calc}$ = 0°, non-pléochroïque, $X = b$, $Y = c$, $Z = a$. Elle est orthorhombique, groupe spatial $Pmn2_1$, $a$ 7.246(4), $b$ 9.333(6), $c$ 6.210(4) Å, $V$ 420.0(3) Å$^3$, $Z$ = 2. Les sept raies les plus intenses du spectre de diffraction, méthode des poudres [$d$ en Å($I$)($hkl$)] sont: 4.699(10)(101,020), 3.322(5)(121), 2.865(4)(220), 2.602(3)(221,131,022), 3.734(2)(021), 3.622( 2)(200), et 3.108(2)(002). Une analyse chimique effectuée avec une microsonde électronique a donné $VO_2$ 33.88, $SO_3$ 31.97, $H_2O$ (calc.) 36.30, somme 102.15% (poids); la proportion de $H_2O$ a été déterminée par ébauche de la structure cristalline. La formule empirique qui en résulte, calculée sur une base de 10 anions (y inclus 5 $H_2O$), est $V_{1.014} S_{0.991} O_5 (H_2O)_5$; la formule idéale est $VO (SO_4) (H_2O)_5$. L'orthominasragrite est la forme orthorhombique de la minasragrite. Nous en avons résolu la structure cristalline par méthodes directes, avec affinement jusqu'à un résidu $R$ de 4.4% pour 1007 réflexions observées ($|F_o| > 5\sigma F$), mesurées avec un diffractomètre automatisé à quatre cercles et rayonnement

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Mo*K*α. Il y a un site *V* où loge le $V^{4+}$, entouré par un atome d'oxygène et cinq groupes ($H_2O$) définissant un agencement octaédrique, avec une liaison apicale de type vanadyle (1.580 Å), quatre liaisons équatoriales semblables (<2.026 Å>), et une liaison V–O plus longue (2.231 Å) disposée *trans* par rapport à la liaison vanadyle. La structure est faite d'octaèdres isolés ($V^{4+}\phi_6$) (ϕ: anion non spécifié) et de tétraèdres ($SO_4$) liés par des liaisons hydrogène.

(Traduit par la Rédaction)

*Mots-clés*: orthominasragrite, nouvelle espèce minérale, structure cristalline, minasragrite, vanadate, mont Temple, Utah.

## INTRODUCTION

Mining and mineral-collecting activity in the Temple Mountain region of Utah has revealed the occurrence of some novel and rare vanadium sulfate minerals associated with fossil trees of Triassic age. The late Howard Evans, Jr. first recognized that these vanadium sulfates could be new minerals, but further work was hindered by the small size and hygroscopic nature of the crystals. As a result of the successful solution and refinement of the crystal structure, we identified orthominasragrite as a new mineral species. The new mineral and mineral name were approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association. The mineral's name denotes its relation to minasragrite: it is the orthorhombic polymorph. The holotype specimen of orthominasragrite is stored in the collection of the Canadian Museum of Nature, Ottawa, Ontario (catalogue number CMNMC 83269), with the X-ray powder mount in the X-ray powder-mount reference collection at the X-ray-diffraction laboratory at the Geological Survey of Canada.

## PARAGENESIS

Orthominasragrite was found (by PH) at the North Mesa mine group, Temple Mountain mining district, Emery County, Utah. The mine group is located in the west ½, southwest ¼ of section 35, Township 24 South, Range 11 East. The host rock is the Shinarump conglomerate member of the late Triassic Chinle Formation. Orthominasragrite occurs in a silicified tree, approximately 46 cm wide by 30 cm high by an undetermined length; there is a rim of coal 6–25 mm thick around the tree. Pyrite has replaced part of the tree, and groundwater has reacted with the pyrite to produce various colorless, white and yellow iron sulfate minerals, accompanied by microscopic yellow crystals and yellow to green fine-grained aggregates of native sulfur. The iron sulfates generally occur in the outer rim of coal and in the adjacent conglomerate. There is dense submetallic to somewhat earthy, dull grey, radiating material in the silicified tree, the probable source of the V that occurs in blue and green secondary vanadium sulfate minerals, including orthominasragrite, minasragrite, and an as-yet undescribed sulfate of vanadium, all of which are subtly different shades of blue.

Specimens of these vanadium sulfate minerals leave a sticky resinous material on the fingers. Droplets of an Fe–V-rich liquid are, in some cases, present on fractures in freshly exposed tree fragments. This liquid is acidic, destroying paper containers, and seeps from fractures to evaporate and form vanadium sulfate minerals, including orthominasragrite.

## PHYSICAL PROPERTIES

Orthominasragrite consists of rounded aggregates (up to 200 μm across) of irregular grains. The aggregates occur as blue-green crusts and efflorescences; individual grains are pale blue to bright blue, depending on grain size. The streak is pale blue, the luster vitreous. No cleavage or parting was observed. The Mohs hardness is difficult to measure accurately because of the minute size of individual crystals, but it is approximately 1. The density could not be measured because of the intimate association with other minerals identical in appearance; the calculated density is 2.001 g/cm$^3$.

Optical properties were measured with a Bloss spindle stage for the wavelength 590 nm using a gel filter. The indices of refraction are α 1.529(2), β 1.534(2), γ 1.534(2), the calculated birefringence γ–α is 0.005, (+)2*V*(meas.) 2°, 2*V*(calc.) 0°; orientation X = *b*, Y = *c*, Z = *a*; there is no pleochroism.

## CHEMICAL COMPOSITION

Crystals were analyzed with a Cameca SX–50 electron microprobe operating in wavelength-dispersion mode, with an accelerating voltage of 15 kV, a specimen current of 20 nA, and a beam diameter of 5 μm. The following standards were used: $VP_2O_7$ (V) and anhydrite (Ca). The crystals broke down almost immediately under the electron beam, presumably losing $H_2O$, and only single analyses could be made at any point; subsequent analyses had totals (including calculated $H_2O$) exceeding 116 wt%. The data were reduced and corrected by the *PAP* method of Pouchou & Pichoir (1984, 1985). The presence and quantity of $H_2O$ groups were established by crystal-structure solution and refinement (Hawthorne & Grice 1990). The resultant chemical composition is given in Table 1, together with the formula unit based on 10 anions (including 5 $H_2O$ groups) *pfu* (per formula unit). The excess in wt.% total

TABLE 1. CRYSTAL COMPOSITION (wt.%) AND UNIT FORMULA* (*apfu*) FOR ORTHOMINASRAGRITE

| | | | |
|---|---|---|---|
| $VO_2$ | 33.88 | V | 1.01 |
| $SO_3$ | 31.97 | | |
| $H_2O$ | (36.30) | S | 0.99 |
| Sum | 102.15 | | |
| | | O | 5 |
| | | $H_2O$ | 5 |

* calculated on the basis of 5 oxygen atoms and 5 ($H_2O$) groups

TABLE 2. X-RAY POWDER-DIFFRACTION PATTERN FOR ORTHOMINASRAGRITE

| $I_{obs}$ | $d_{obs}$ (Å) | $d_{calc}$ (Å) | *h* | *k* | *l* |
|---|---|---|---|---|---|
| 100 B | 4.699 | 4.715 | 1 | 0 | 1 |
| | | 4.667 | 0 | 2 | 0 |
| 20 | 3.734 | 3.731 | 0 | 2 | 1 |
| 20 | 3.622 | 3.623 | 2 | 0 | 0 |
| 50 | 3.322 | 3.317 | 1 | 2 | 1 |
| 20 | 3.108 | 3.105 | 0 | 0 | 2 |
| 15 | 2.952 | 2.946 | 0 | 1 | 2 |
| 40 | 2.865 | 2.862 | 2 | 2 | 0 |
| 30 | * 2.602 | 2.599 | 2 | 2 | 1 |
| | | 2.597 | 1 | 3 | 1 |
| | | 2.585 | 0 | 2 | 2 |
| 15 | 2.436 | 2.435 | 1 | 2 | 2 |
| 20 | 2.363 | 2.360 | 2 | 3 | 0 |
| | | 2.358 | 2 | 0 | 2 |
| 15 B | * 2.194 | 2.206 | 2 | 3 | 1 |
| | | 2.198 | 0 | 3 | 2 |
| | | 2.188 | 3 | 1 | 1 |
| | | 2.184 | 0 | 4 | 1 |
| 5 | 2.103 | 2.104 | 2 | 2 | 2 |
| 20 | 2.030 | 2.027 | 3 | 2 | 1 |
| 5 | 1.988 | 1.990 | 1 | 0 | 3 |
| 5 | 1.960 | 1.962 | 2 | 4 | 0 |
| 5 | 1.891 | 1.892 | 0 | 2 | 3 |
| 5 | 1.868 | 1.871 | 2 | 4 | 1 |
| 15 | * 1.828 | 1.831 | 1 | 2 | 3 |
| | | 1.824 | 3 | 3 | 1 |
| 10 | 1.811 | 1.812 | 4 | 0 | 0 |
| 5 | 1.766 | 1.765 | 3 | 2 | 2 |
| | | 1.765 | 2 | 1 | 3 |
| 5 | 1.734 | 1.736 | 1 | 5 | 1 |
| 5 | 1.687 | 1.689 | 4 | 2 | 0 |
| 10 | 1.660 | 1.658 | 2 | 4 | 2 |
| 10 | 1.622 | 1.620 | 3 | 4 | 1 |

114.6 Debye-Scherrer camera with Gandolfi attachment; Cu*K*α (Ni-filtered) λ= 1.5406 Å; observed intensities visually estimated; calculated powder pattern from single-crystal structure refinement used to aid indexing; no correction for shrinkage; no internal standard; indices marked with an asterisk were not used for cell refinement; B: broad line; a = 7.246(4), b = 9.333(6), c = 6.210(4) Å, V = 420.0(3) $Å^3$

over 100 is caused by incipient dehydration of the mineral during electron-microprobe analysis, which increases the weight percentages of non-$H_2O$ components.

## X-RAY POWDER DIFFRACTION

The powder-diffraction pattern was recorded with a Gandolfi camera using Ni-filtered Cu*K*α X-radiation. Table 2 shows the X-ray powder-diffraction data for orthominasragrite, together with the refined unit-cell dimensions. Unit-cell dimensions were also determined on a Nicolet *P*4 automated 4-circle diffractometer with a CCD detector (Table 2).

## SINGLE-CRYSTAL DIFFRACTION

A small crystal was attached to a glass fiber and mounted on a Siemens *P*4 automated four-circle diffractometer equipped with a CCD detector and Mo*K*α X-radiation. Intensity data were collected according to the procedure described by Cooper & Hawthorne (2001). Data were corrected for Lorentz, polarization and background effects, and reduced to structure factors. The final unit-cell parameters (Table 3) are based on least-squares refinement of 1615 reflections (>10 σ*F*). A total of 4897 reflections was measured out to 60°2θ, with index ranges $8 \leq h \leq 8$, $10 \leq k \leq 9$, $13 \leq l \leq 12$. Of the 1307 unique reflections, 1007 reflections were considered as observed [$|F_o| \geq 5\,\sigma F$].

TABLE 3. EXPERIMENTAL DATA FOR ORTHOMINASRAGRITE

| | | | |
|---|---|---|---|
| Crystal system | orthorhombic | Crystal size (μm) | 30 x 50 x 50 |
| Space group | $Pmn2_1$ | Wavelength (Å) | Mo*K*α |
| *a* (Å) | 7.242(1) | μm ($mm^{-1}$) | 1.47 |
| *b* | 9.319(2) | No. of *I* | 4897 |
| *c* | 6.192(1) | No. of unique $\|F\|$ | 1307 |
| *V* ($Å^3$) | 417.9(1) | No. of $\|Fo\| > 5\sigma F$ | 1007 |
| *Z* | 2 | $R_{int}$ (%) | 2.6 |
| *R* (%) | 4.4 | $R = \Sigma(\|Fo\|-\|Fc\|) / \Sigma\|Fo\|$ | |
| *wR (%)* | 5.0 | $wR = \Sigma w(\|Fo\|-\|Fc\|)^2 / \Sigma Fo^2)^{1/2}$, $w = 1$ | |

## STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms were taken from the International Tables for Crystallography (Ibers & Hamilton 1992). *R* indices are of the form given in Table 1, and are expressed as percentages. The Siemens SHELXTL PLUS (PC version) system of programs was used for this work.

The structure was solved by direct methods. Two cation sites were identified by a combination of site-scattering values and local stereochemistry. All anions were assumed to be oxygen ($Z = 8$), and the cation scattering indicated that the two cation sites are occupied by V ($Z = 23$) and S ($Z = 16$), and the local stereochemistry is in accord with this. The structure refined rapidly to an *R* index of ~5% for a model with anisotropic-displacement factors at all non-hydrogen atoms. At this stage, a difference-Fourier map allowed identification of the H-atom sites. These were added to the refinement with the soft constraint that O–H ≈ 0.98 Å. Full-matrix least-squares refinement of all atoms (with fixed isotropic-displacement factors on all the H atoms) converged to an *R*-index of 4.4%. Positional and displacement parameters for the constrained refinement are given in Table 4, and selected interatomic distances are listed in Table 5. Observed and calculated structure-factors are available from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

## DESCRIPTION OF THE STRUCTURE

The structure of synthetic V O $SO_4$ $(H_2O)_5$ was described by Tachez & Théobald (1980) in space group $Pmn2_1$, with *a* 7.234, *b* 9.304 and *c* 6.184 Å. The struc-

TABLE 4. POSITIONAL COORDINATES AND ANISOTROPIC-DISPLACEMENT PARAMETERS FOR ORTHOMINASRAGRITE

| Atom | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|---|---|---|
| V | 0 | 0.2867(1) | 0 | 0.0188(5) | 0.0165(5) | 0.0173(6) | −0.0035(7) | 0 | 0 |
| S | 0 | 0.7647(2) | −0.0238(4) | 0.0181(7) | 0.0164(7) | 0.0188(9) | 0.0011(8) | 0 | 0 |
| O(1) | 0 | 0.3468(7) | 0.239(1) | 0.0447(38) | 0.0285(33) | 0.0249(26) | −0.0098(26) | 0 | 0 |
| O(2) | 0 | 0.1708(7) | 0.6848(9) | 0.0302(30) | 0.0308(31) | 0.0152(24) | 0.0000(22) | 0 | 0 |
| O(3) | 0.2030(6) | 0.1390(4) | 0.0459(7) | 0.0297(20) | 0.0187(16) | 0.0282(22) | −0.0021(16) | −0.0090(16) | 0.0034(16) |
| O(4) | 0.1938(6) | 0.4154(4) | 0.8681(8) | 0.0208(20) | 0.0240(19) | 0.0494(25) | 0.0024(20) | 0.0102(20) | −0.0012(18) |
| O(5) | 0.1653(5) | 0.8563(4) | −0.0429(6) | 0.0174(16) | 0.0244(16) | 0.0259(22) | 0.0032(16) | 0.0028(15) | −0.0036(14) |
| O(6) | 0 | 0.6608(8) | 0.7997(12) | 0.0367(39) | 0.0184(31) | 0.0391(38) | −0.0007(28) | 0 | 0 |
| O(7) | 0 | 0.6911(8) | 0.1881(11) | 0.0245(31) | 0.0367(43) | 0.0238(29) | 0.0111(27) | 0 | 0 |
| H(1) | 0 | 0.157(9) | 0.528(2) | 0.0300* | | | | | |
| H(2) | 0 | 0.256(6) | 0.592(12) | 0.0300* | | | | | |
| H(3) | 0.164(7) | 0.045(3) | −0.007(13) | 0.0300* | | | | | |
| H(4) | 0.274(7) | 0.131(7) | 0.180(5) | 0.0300* | | | | | |
| H(5) | 0.306(5) | 0.370(6) | 0.812(9) | 0.0300* | | | | | |
| H(6) | 0.189(9) | 0.517(2) | 0.829(9) | 0.0300* | | | | | |

*The displacement factors of the hydrogen atoms H(1)–H(6) are isotropic and were fixed during refinement.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR ORTHOMINASRAGRITE

| | | | |
|---|---|---|---|
| V–O(1) | 1.580(6) | S–O(5) | 1.475(4) |
| V–O(2)a | 2.231(6) | S–O(5)a | 1.475(4) |
| V–O(3) | 2.033(4) | S–O(6)a | 1.460(8) |
| V–O(3)a | 2.033(4) | S–O(7) | 1.481(7) |
| V–O(4)a | 2.019(5) | <S–O> | 1.473 |
| V–O(4)b | 2.019(5) | | |
| | | O(3)–H(3) | 0.98(4) |
| O(2)–H(1) | 0.98(2) | O(3)–H(4) | 0.98(4) |
| O(2)–H(2) | 0.98(7) | H(3)–O(5)a | 1.77(3) |
| O(2)–O(1) | 3.214(8) | H(4)–O(5)c | 1.77(4) |
| | | | |
| O(4)–H(5) | 0.98(4) | H(4)–O(3)–H(3) | 111(5) |
| O(4)–H(6) | 0.98(3) | O(3)–H(3)–O(5)a | 158(6) |
| H(5)–O(7)b | 1.70(4) | O(3)–H(4)–O(5)c | 161(5) |
| H(6)–O(6) | 1.93(5) | | |
| | | H(5)–O(4)–H(6) | 111(5) |
| | | O(4)–H(5)–O(7) | 172(5) |
| | | O(4)–H(6)–O(6) | 136(5) |

a: $x, y, z+1$; b: $-x+1/2, -y, z+1/2$, c: $x-1/2, -y, z-1/2$.

The O(2)–H(1), O(2)–H(2), O(3)–H(3), O(3)–H(4), O(4)–H(5) and O(4)–H(6) bondlengths were softly constrained to the value 0.98 Å.

TABLE 6. BOND-VALENCE* (*vu*) TABLE FOR ORTHOMINASRAGRITE

| | V | *S* | H(1) | H(2) | H(3) | H(4) | H(5) | H(6) | Σ |
|---|---|---|---|---|---|---|---|---|---|
| O(1) | 1.74 | | 0.10 | 0.10 | | | | | 1.94 |
| O(2) | 0.30 | | 0.90 | 0.90 | | | | | 2.10 |
| O(3) | $0.51\downarrow^{\times2}$ | | | | 0.75 | 0.75 | | | 2.01 |
| O(4) | $0.53\downarrow^{\times2}$ | | | | | | 0.75 | 0.80 | 2.08 |
| O(5) | | $1.50\downarrow^{\times2}$ | | | 0.25 | 0.25 | | | 2.00 |
| O(6) | | 1.56 | | | | | | $0.20\rightarrow^{\times2}$ | 1.96 |
| O(7) | | 1.47 | | | | | $0.25\rightarrow^{\times2}$ | | 1.97 |
| Σ | 4.12 | 6.03 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | |

*The bond-valence curves are from Brown & Altermatt (1985)

ture is identical to that of the newly proposed mineral. The experimental data relevant to our structure refinement are listed in Table 3, and the bond-valence summations are presented in Table 6.

### *Coordination of the cations*

There is one *S* site, occupied by S and surrounded by four O atoms in a tetrahedral arrangement with a <S–O> distance of 1.473 Å, equal to the grand <S–O> distance of 1.473 Å reported for sulfate minerals by Hawthorne *et al.* (2000). There is one *V* site, occupied by V and surrounded by six O atoms in an octahedral arrangement. There is one very short V–O distance of 1.580 Å, four intermediate-length V–O bonds in the range 2.019–2.033 Å and approximately orthogonal to the short V–O bond, and one long bond of 2.231 Å *trans* to the short V–O bond. The short V–O bond is a *vanadyl bond*, the intermediate-length bonds are *equatorial bonds*, and the long bond is a *trans* bond. This geometry is characteristic of $^{[6]}V^{4+}$, as discussed by Schindler *et al.* (2000).

### *Hydrogen bonding*

All H atoms were located at the final stages of refinement of orthominasragrite, and all are attached to O atoms (bonded to V) to form ($H_2O$) groups. The formula of orthominasragrite indicates five ($H_2O$) groups per $V^{4+}$ cation; the O(1) atom receives 1.74 *vu* (valence units) from the central V atom, and hence the anion must be an O atom, whereas the other ligands associated with V receive ≤0.5 *vu*, and hence are ($H_2O$) groups.

Details of the hydrogen-bonding scheme are given in Tables 5 and 6, and Figure 1. The H(3) and H(4) atoms are linked to the O(3) atom, and each hydrogen atom bonds to the O(5) anions, with H-acceptor distances of 1.76 and 1.73 Å, respectively, and O–H...O angles of 160°. The H(5) and H(6) atoms are linked to the O(4) atoms, and hydrogen bond to the O(6) and O(7) anions, with H-acceptor distances of 1.91 and 1.69 Å, respectively, and O–H...O angles of 160 and 173°. These values are typical for normal hydrogen bonds.

### *Structure topology*

V O $SO_4$( $H_2O$)$_5$ is built of isolated ($V\phi_6$) ($\phi$: O, $H_2O$) octahedra and ($SO_4$) tetrahedra. Hydrogen bonds of the four equatorial ($H_2O$) groups link the ($V\phi_6$) octahedron to six $(SO_4)^{2-}$ tetrahedra (Fig. 1), and each $(SO_4)^{2-}$ tetrahedron is linked *via* hydrogen bonds to six ($V\phi_6$) octahedra (Table 4). The bond-valence sum incident at O(2) requires that this site is also occupied by an ($H_2O$) group, but the refined H sites show an unreasonably small H(1)–O(2)–H(2) angle of 62(6)°. However, geometrical and bond-valence considerations show that the hydrogen atoms associated with O(2) must bond to O(1), the O-atom of the vanadyl bond. It seems prob-

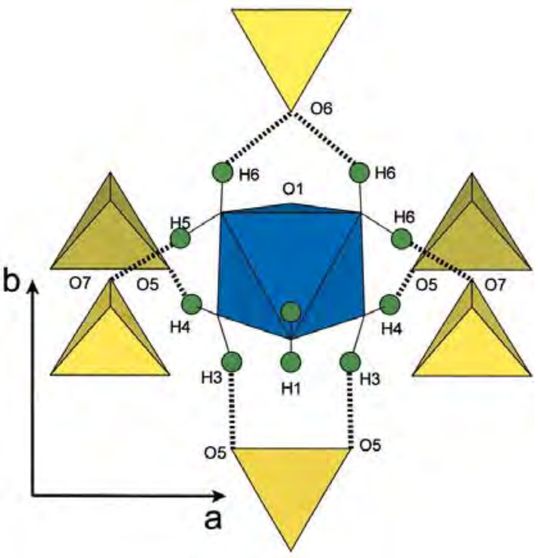

FIG. 1. Coordination polyhedra and hydrogen bonding in orthominasragrite; ($V\phi_6$) octahedron: blue; ($SO_4$) tetrahedron: yellow; H atoms: green circles; hydrogen bonds: broken lines. The variation in yellow shading denotes height relative to the plane of the diagram.

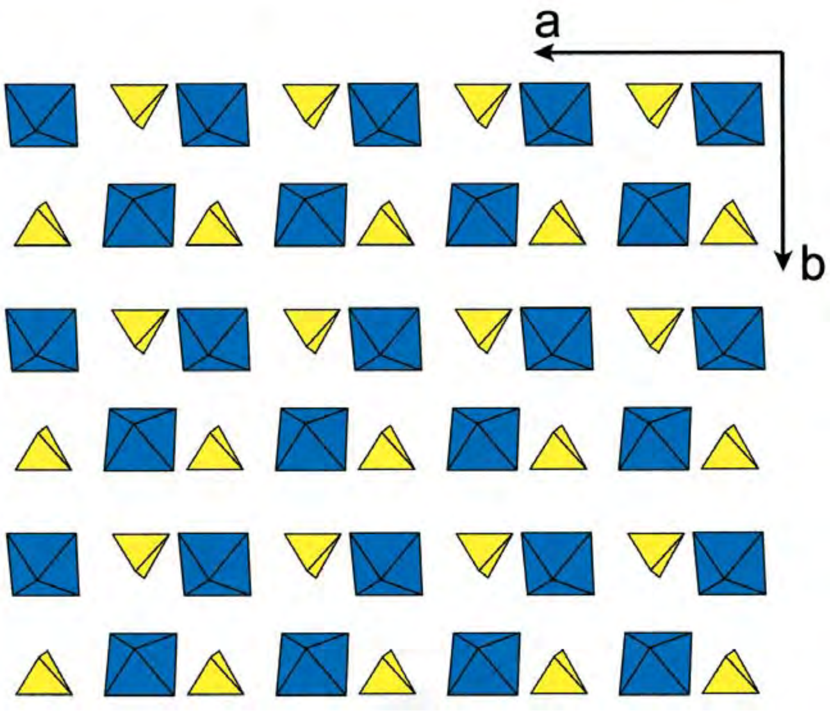

FIG. 2. The ($V\phi_6$) and ($SO_4$) polyhedra in orthominasragrite viewed down the *c* axis; legend as in Figure 1.

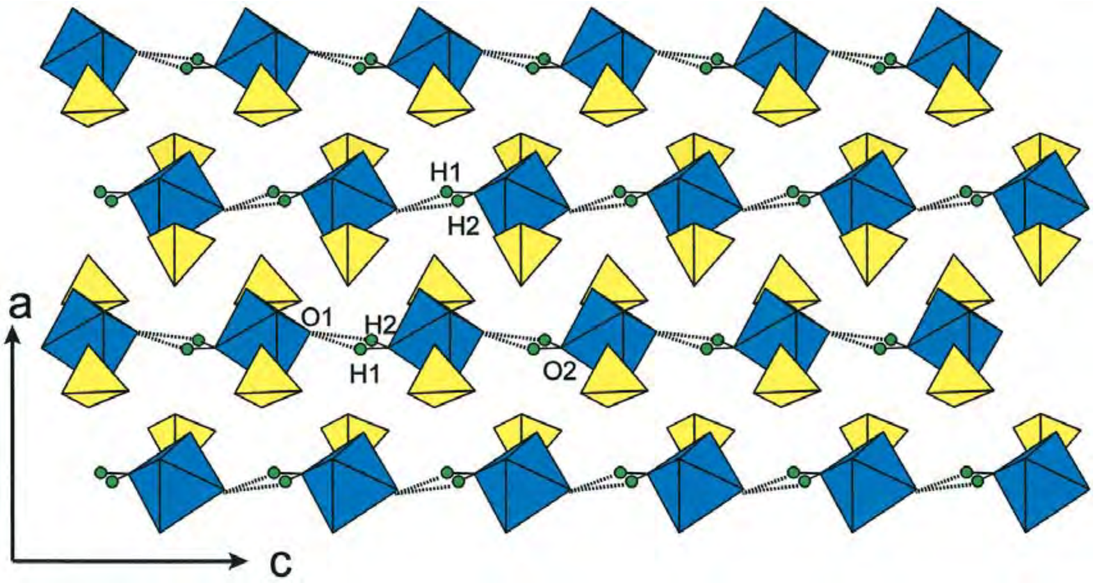

FIG. 3. The crystal structure of orthominasragrite viewed down the *b* axis; legend as in Figure 1.

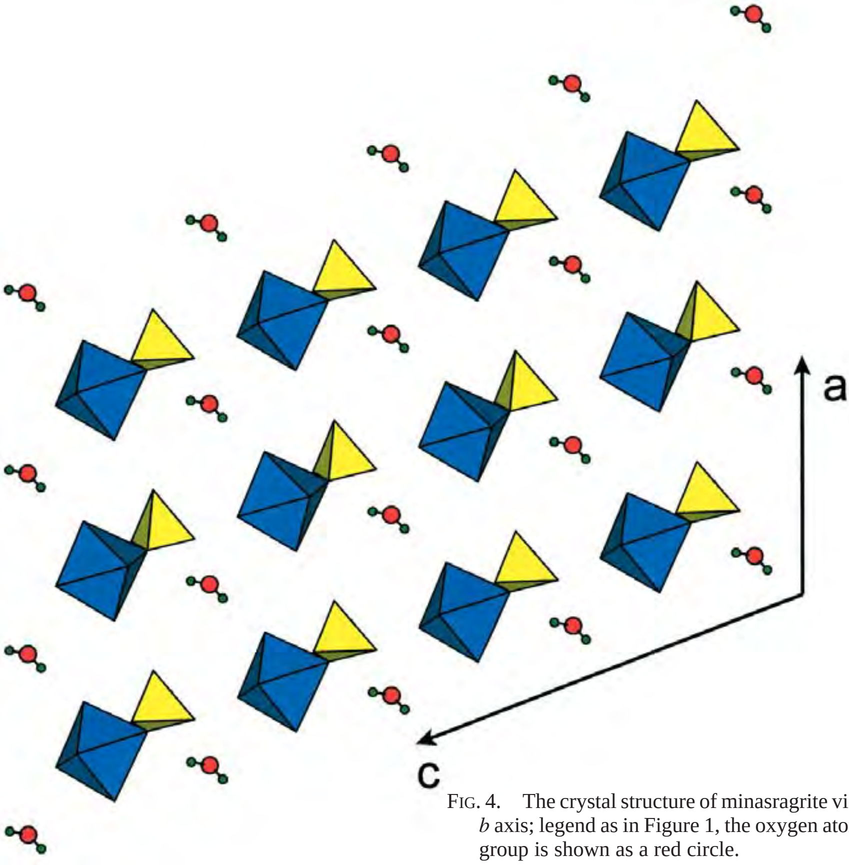

FIG. 4. The crystal structure of minasragrite viewed along the *b* axis; legend as in Figure 1, the oxygen atom of the $(H_2O)$ group is shown as a red circle.

able that the H atoms attached to O(2) are positionally disordered such that, for any one local configuration, one H atom occupies either the H(1) or H(2) site and hydrogen bonds to O(1), and the other H-atom does not hydrogen bond to any anion.

The octahedra and tetrahedra occur in different layers parallel to {110} (Fig. 2); it is also apparent from Figure 2 that the octahedra and tetrahedra are not linked directly in orthominasragrite. The structure of $VOSO_4(H_2O)_5$ can thus be described as chains of $(V\phi_6)$ octahedra linked by hydrogen bonds parallel to c (Fig. 3), which are linked by hydrogen bonds to sulfate tetrahedra in the *ab* plane (Fig. 1).

### *Related structures*

Orthominasragrite and minasragrite (Schaller 1917, Smith & Marinenko 1973) are polymorphs, and hence two of the three known polymorphs of $VO(SO_4)(H_2O)_5$ (Ballhausen *et al.* 1968, Tachez & Théobald 1980, Tachez *et al.* 1979) are now known as minerals. Minasragrite is monoclinic, but the difference between the two structures is not one of stacking sequence. Inspection of the structure of minasragrite (Fig. 4) shows that the $(V\phi_6)$ octahedron and the $(SO_4)$ tetrahedron share a corner to form a $[VO(SO_4)(H_2O)_4]$ group, and there is one $(H_2O)$ group (shaded red in Fig. 4) that does not link directly to a cation, but is held in the structure solely by hydrogen bonding. If we write the formula of each mineral in terms of their structural unit and interstitial species (Hawthorne 1985, 1990, 1997), this difference becomes apparent: orthominasragrite $[VO(H_2O)_5][(SO_4)]$; minasragrite: $[VO(SO_4)(H_2O)_4](H_2O)$.

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## REFERENCES

BALLHAUSEN, C.J., DJURINSKIJ, B.F. & WATSON, K.J. (1968): The polarized absorption spectra of three crystalline polymorphs of $VOSO_4$•$5H_2O$. *J. Am. Chem. Soc.* **90**, 3305-3309.

BROWN, I.D. & ALTERMATT, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr.* **B41**, 244-247.

COOPER, M.A. & HAWTHORNE, F.C. (2001): Structure topology and hydrogen bonding in marthozite, $Cu^{2+}[(UO_2)_3(SeO_3)_2O_2](H_2O)_8$, a comparison with guilleminite, $Ba[(UO_2)_3(SeO_3)_2O_2](H_2O)_3$. *Can. Mineral.* **39**, 797-807.

HAWTHORNE, F.C. (1985): Towards a structural classification of minerals: the $^{vi}M^{iv}T_2Ø_n$ minerals. *Am. Mineral.* **70**, 455-473.

________ (1990): Structural hierarchy in $M^{[6]}T^{[4]}Ø_n$ minerals. *Z. Kristallogr.* **192**, 1-52.

________ (1997): Structural aspects of oxide and oxysalt minerals. *In* Modular Aspects of Minerals (S. Merlino, ed.). *Eur. Mineral. Union, Notes in Mineralogy* **1**, 373-429.

________ & GRICE, J.D. (1990): Crystal-structure analysis as a chemical analytical method: application to light elements. *Can. Mineral.* **28**, 693-702.

________, KRIVOVICHEV, S.V. & BURNS, P.C. (2000): The crystal chemistry of sulfate minerals. *In* Sulfate Minerals – Crystallography, Geochemistry, and Environmental Significance (C.N. Alpers, J.L. Jambor & D.K. Nordstrom, eds.). *Rev. Mineral. Geochem.* **40**, 1-112.

IBERS, J.A. & HAMILTON, W.C., eds. (1992): *International Tables for X-ray Crystallography* **IV**. The Kynoch Press, Birmingham, U.K.

POUCHOU, J.-L. & PICHOIR, F. (1984): A new model for quantitative analysis. I. Application to the analysis of homogeneous samples. *La Recherche Aérosp.* **3**, 13-38.

________ & ________ (1985): "PAP" ($\phi\rho z$) procedure for improved quantitative microanalysis. *In* Microbeam Analysis – 1985. San Francisco Press, San Francisco, California (104-106).

SCHALLER, W.T. (1917): Minasragrite, a hydrous sulfate of vanadium. *J. Wash. Acad. Sci.* **7**, 501-503.

SCHINDLER, M., HAWTHORNE, F.C. & BAUR, W.H. (2000): Crystal-chemical aspects of vanadium: polyhedral geometries, characteristic bond valences and polymerization of $(VO_n)$ polyhedra. *Chem Mat.* **12**, 1248-1259.

SMITH, M.L. & MARINENKO, J. (1973): A reexamination of minasragrite. *Am. Mineral.* **58**, 531-534.

TACHEZ, M. & THÉOBALD, F. (1980): Structure du sulfate de vanadyle pentahydraté $VO(H_2O)_5SO_4$ β (variété orthorhombique). *Acta Crystallogr.* **B36**, 1757-1761.

________, ________, WATSON, K.J. & MERCIER, R. (1979): Redétermination de la structure du sulfate de vanadyle pentahydraté $VOSO_4$•$5H_2O$. *Acta Crystallogr.* **B35**, 1545-1550.

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