

ANORTHOMINASRAGRITE, $V^{4+}O(SO_4)(H_2O)_5$, A NEW MINERAL SPECIES FROM TEMPLE MOUNTAIN, EMERY COUNTY, UTAH, U.S.A.: DESCRIPTION, CRYSTAL STRUCTURE AND HYDROGEN BONDING

MARK A. COOPER AND FRANK C. HAWTHORNE[§]

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

JOEL D. GRICE

Research Division, Canadian Museum of Nature, Ottawa, Ontario K1P 6P4, Canada

PATRICK HAYNES

P.O. Box 1531, Cortez, Colorado 81321, U.S.A.

ABSTRACT

Anorthominasragrite, $V^{4+}O(SO_4)(H_2O)_5$, is a new mineral species from Temple Mountain, Emery County, Utah, U.S.A. It occurs as blue-green crusts and spherical granular aggregates (up to ~1 mm across) in a fossil (Triassic) tree; individual crystals are <0.1 mm and are intimately intergrown. Anorthominasragrite has a white 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 2.12 g/cm³. Anorthominasragrite is biaxial positive, with α 1.548, β 1.555, γ 1.574, all ± 0.002 , $2V(\text{obs.}) = 86(1)^\circ$, $2V(\text{calc.}) = 63^\circ$, non-pleochroic, $X \wedge c \approx 18^\circ$ (in β obtuse), $Y \approx a$, $Z \wedge b \approx 19^\circ$ (in γ obtuse). Anorthominasragrite is triclinic, space group $P\bar{1}$, a 7.548(3), b 7.805(2), c 7.821(3) Å, α 79.03(4), β 71.94(3), γ 65.31(3)°, V 397.1(2) Å³, $Z = 2$. The strongest seven lines in the X-ray powder-diffraction pattern [d in Å(hkl)] are: 6.617(100)(100), 7.053(80)(010), 4.116(80)($\bar{1}10$), 3.712(80)(121,002,211), 3.206(70)(221), 2.934(50)($\bar{1}\bar{1}2$, $\bar{1}02$), 5.314(30)(011). Chemical analysis with an electron microprobe gave VO_2 33.93, SO_3 30.78, H_2O (calc.) 35.52, sum 100.23 wt.%; the amount of H_2O was determined by crystal-structure analysis. The resulting empirical formula on the basis of 10 anions (including 5 H_2O) is $V_{1.04}S_{0.98}O_5(H_2O)_5$; the end-member formula is $V O(SO_4)(H_2O)_5$. Anorthominasragrite is the triclinic polymorph of $V O(SO_4)(H_2O)_5$. The crystal structure of anorthominasragrite was solved by direct methods and refined to an R index of 3.2% for 673 observed ($|F_o| > 5\sigma F$) reflections measured with an automated four-circle X-ray diffractometer using $MoK\alpha$ X-radiation. There is one V site occupied by V^{4+} and surrounded by three O atoms and three (H_2O) groups in an octahedral arrangement, with one short vanadyl bond (1.587 Å), four similar equatorial bonds (<2.013 Å), and one longer V–O bond (2.253 Å) *trans* to the vanadyl bond. The structure consists of $(V^{4+}\phi_6)$ (ϕ : unspecified anion) octahedra and (SO_4) tetrahedra that corner-share O^{2-} vertices to form $(V^{4+}O)_2(H_2O)_6(SO_4)_2$ groups [as in bobjonesite, $V^{4+}O(SO_4)(H_2O)_3$], with two additional isolated (H_2O) groups.

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

SOMMAIRE

L'anorthominasragrite, $V^{4+}O(SO_4)(H_2O)_5$, est une nouvelle espèce minérale découverte au mont Temple, comté d'Emery, Utah, aux États-Unis. Elle se présente en encroûtements bleu-vert et en aggrégats sphériques atteignant ~1 mm de diamètre dans un arbre fossilisé d'âge triassique; les cristaux individuels sont moins de 0.1 mm et intimement enchevêtrés. L'anorthominasragrite possède un rayure blanche, un éclat vitreux, et semble sans fluorescence en lumière ultra-violette, sans clivage et sans plan de séparation. La dureté de Mohs est environ 1, et la densité calculée est égale à 2.12 g/cm³. L'anorthominasragrite est biaxe positive, avec α 1.548, β 1.555, γ 1.574, tous ± 0.002 , $2V(\text{obs.}) = 86(1)^\circ$, $2V(\text{calc.}) = 63^\circ$, non-pléochroïque, $X \wedge c \approx 18^\circ$ (β obtus), $Y \approx a$, $Z \wedge b \approx 19^\circ$ (γ obtus). Il s'agit d'un minéral triclinique, groupe spatial $P\bar{1}$, a 7.548(3), b 7.805(2), c 7.821(3) Å, α 79.03(4), β 71.94(3), γ 65.31(3)°, V 397.1(2) Å³, $Z = 2$. Les sept raies les plus intenses du spectre de diffraction (méthode des poudres) [d en Å(hkl)] sont: 6.617(100)(100), 7.053(80)(010), 4.116(80)($\bar{1}10$), 3.712(80) (121,002,211), 3.206(70)(221), 2.934(50)($\bar{1}\bar{1}2$, $\bar{1}02$), et 5.314(30)(011). Une analyse chimique avec une microsonde électronique a donné: VO_2 33.93, SO_3 30.78,

[§] E-mail address: frank_hawthorne@umanitoba.ca

H₂O (calc.) 35.52, total 100.23% (poids); la quantité de H₂O a été déterminée par ébauche de la structure cristalline. La formule empirique qui en résulte, exprimée sur une base de 10 anions (y inclus 5 H₂O) est V_{1.04}S_{0.98}O₅(H₂O)₅, et la formule idéale est V O (SO₄) (H₂O)₅. L'anorthominasragrite est le polymorphe triclinique de V O (SO₄) (H₂O)₅. Sa structure cristalline a été résolue par méthodes directes et affinée jusqu'à un résidu *R* de 3.2% pour 673 réflexions observées ($|F_o| > 5\sigma F$), mesurées avec un diffractomètre automatisé à quatre cercles utilisant un rayonnement MoK α . Il y a un site V où loge le V⁴⁺, entouré de trois atomes d'oxygène et trois groupes (H₂O) dans un agencement octaédrique, avec une liaison vanadyle courte (1.587 Å), quatre liaisons équatoriales semblables (<2.013 Å), et une liaison V–O plus longue (2.253 Å) en position *trans* par rapport à la liaison vanadyle. La structure contient des octaèdres (V⁴⁺φ₆) (φ: anion non spécifié) et des tétraèdres (SO₄) qui partagent des vertex O²⁻ pour former des groupes (V⁴⁺O)₂ (H₂O)₆ (SO₄)₂ [comme c'est le cas dans la bobjonesite, V⁴⁺O (SO₄) (H₂O)₃], avec deux groupes (H₂O) additionnels isolés.

(Traduit par la Rédaction)

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

INTRODUCTION

The Temple Mountain region of Utah contains some novel vanadium sulfate minerals associated with fossil trees of Triassic age. Recently, as a result of the successful solution and refinement of its crystal structure, we identified anorthominasragrite as a new mineral species.

Anorthominasragrite, orthominasragrite (Hawthorne *et al.* 2001) and minasragrite (Schaller 1917, Smith & Marinenko 1973) are triclinic, orthorhombic and monoclinic, respectively, and are polymorphs of V⁴⁺O (SO₄) (H₂O)₅. The new mineral and mineral name were approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (IMA 2001-040). The name denotes its relation to minasragrite: it is the triclinic polymorph of V⁴⁺O (SO₄) (H₂O)₅. The holotype specimen of anorthominasragrite is stored in the collection of the Canadian Museum of Nature, Ottawa, Canada, catalogue number CMNMC 83924.

PARAGENESIS

Anorthominasragrite 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. Anorthominasragrite occurs in a silicified tree that is approximately 46 cm wide by 30 cm high, with an undetermined length; there is a rim of coal around the tree that is 6–25 mm thick. Anorthominasragrite occurs with orthominasragrite (Hawthorne *et al.* 2001) and bobjonesite (Schindler *et al.* 2003), and a full description of the paragenesis is given in those papers.

PHYSICAL PROPERTIES

Anorthominasragrite occurs as blue-green crusts and spherical granular aggregates (< 1 mm across) of irregu-

lar grains. Individual grains are <0.1 mm and are intimately intergrown crystals. The grains are pale blue (paler blue than orthominasragrite), the streak is white, the luster vitreous, and no cleavage or parting was observed. The Mohs hardness is difficult to measure 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 of identical appearance; the calculated density is 2.12 g/cm³.

Optical properties were measured with a Bloss spindle stage for the wavelength 590 nm using a gel filter. Anorthominasragrite is biaxial (+) with indices of refraction α 1.548, β 1.555, γ 1.574, all $\pm$ 0.002, (+)2*V*(meas.) 86(1)°, 2*V*(calc.) 63°. The optical orientation is $X \wedge c \approx 18^\circ$ (in β obtuse), $Y \approx a$, $Z \wedge b \approx 19^\circ$ (in γ obtuse), and there is no observed 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 5 nA, and a beam diameter of 20 μ m. The following standards were used: VP₂O₇ (V) and anhydrite (S). The crystals broke down rapidly under the electron beam. The data were reduced and corrected by the *PAP* method of Pouchou & Pichoir (1984, 1985). The presence and quantity of (H₂O) 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 (H₂O) groups] *pfu* (per formula unit).

X-RAY POWDER DIFFRACTION

The powder-diffraction pattern was recorded with a Debye-Scherrer camera using Ni-filtered CuK α X-radiation. Table 2 lists the X-ray powder-diffraction data and refined unit-cell dimensions for anorthominasragrite. The unit-cell dimensions were also deter-

mined using a Bruker *P4* automated four-circle diffractometer (Table 3).

SINGLE-CRYSTAL DIFFRACTION

A small crystal was attached to a glass fiber and mounted on a Bruker *P4* automated four-circle diffractometer equipped with a serial detector and MoK α X-radiation. Eight reflections visible on a three-h rotation photograph were automatically aligned, and the cell dimensions and orientation matrix were determined by least-squares refinement of the setting angles; the values are given in Table 3. A total of 1127 reflections was measured to $45^\circ 2\theta$ using a fixed scan speed of $0.3^\circ 2\theta/\text{min}$, with index ranges $7 \leq h \leq 8$, $8 \leq k \leq 7$, $0 \leq l \leq 8$; no significant diffraction was present beyond $2\theta = 45^\circ$. The data were corrected for Lorentz, polarization and background effects, and reduced to structure factors. Psi-scan data were collected for two strong reflec-

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

VO ₂	33.93	V ⁴⁺	1.04
SO ₃	30.78		
H ₂ O	(35.52)	S ⁶⁺	0.98
Sum	100.23	O	5
		H ₂ O	5

* Calculated on the basis of 5 oxygen atoms and 5 (H₂O) groups.

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR ANORTHOMINASRAGRITE

<i>l</i> _{est}	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>	<i>l</i> _{est}	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>	<i>l</i> _{est}	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>
20	7.437	7.417	0	0	1	30	2.555	2.556	1	3	1	5 B	1.809*	1.814	3	4	1
80	7.053	7.074	0	1	0	10B	2.493*	2.509	1	2	1	"	"	1.804	1	4	2
100	6.617	6.625	1	0	0	"	"	2.487	2	3	1	20	1.779	1.780	4	3	1
10	5.732	5.732	1	0	1	5	2.438	2.441	3	2	1	"	"	1.779	3	4	2
30	5.314	5.309	0	1	1	10	2.385	2.385	3	1	0	"	"	1.778	1	4	1
5	4.976*	4.948	0	1	1	10	2.360	2.358	0	3	0	20	1.765	1.764	3	1	1
80	4.116	4.111	1	1	0	"	"	2.358	2	1	2	"	"	1.763	0	1	4
10	3.787	3.782	1	2	0	"	"	2.357	3	1	2	5	1.748	1.748	0	4	1
80	3.712	3.721	1	2	1	20B	2.308*	2.322	3	2	2	5	1.733	1.732	3	2	2
"	"	3.709	0	0	2	"	"	2.315	3	2	0	10	1.693	1.695	4	1	3
"	"	3.707	2	1	1	"	"	2.312	2	3	2	"	"	1.694	0	4	1
10	3.420	3.426	1	1	1	"	"	2.300	1	3	2	"	"	1.692	0	2	4
10	3.383	3.384	0	1	2	"	"	2.295	2	2	3	10	1.678	1.677	1	0	4
5	3.287	3.284	0	2	1	20	2.242	2.240	1	1	3	5	1.658	1.661	2	1	3
70	3.206	3.207	2	2	1	10	2.205	2.208	3	0	0	"	"	1.656	4	0	0
20B	3.091*	3.101	1	2	1	"	"	2.204	2	0	2	"	"	1.656	3	4	3
"	"	3.079	2	2	0	5	2.133	2.133	2	3	1	10	1.641	1.642	0	4	2
50	2.934	2.934	1	1	2	20	1.990	1.990	2	1	3	10	1.617	1.618	4	1	1
"	"	2.929	1	0	2	10	1.950	1.949	1	3	2	"	"	1.615	3	2	0
10	2.873	2.884	2	1	1	"	"	1.948	3	1	1	10	1.606	1.607	4	4	1
"	"	2.866	2	0	2	5	1.926	1.929	0	3	2	"	"	1.603	4	4	2
10	2.819	2.823	1	1	2	"	"	1.923	2	2	1	10	1.577	1.577	4	0	3
5	2.717	2.717	1	2	0	10	1.892	1.891	2	4	0	10	1.552	1.554	2	1	5
10	2.640	2.636	2	1	0	5B	1.852*	1.861	2	4	2	10	1.531	1.532	1	4	1
10	2.585	2.595	1	2	1	"	"	1.855	2	2	4	"	"	1.531	1	4	1
"	"	2.579	1	1	3	"	"	1.850	4	1	1	10	1.505	1.505	3	5	2

114.6 mm Debye-Scherrer powder camera; Cu radiation, Ni filter ($\lambda = 1.5418 \text{ \AA}$). Intensities visually estimated; not corrected for shrinkage and no internal standard. B = broad line. Calculated powder pattern from single-crystal refinement was used to aid indexing. Observed lines marked with an asterisk were not used for unit-cell parameter refinement. Indexed with a 7.548(3), b 7.805(2), c 7.821(3) $\text{\AA}$, α 79.03(4), β 71.94(3), γ 65.31(3)°, V 397.1(2) $\text{\AA}^3$.

tions, and the intensity data were corrected for absorption effects by modeling the crystal as an ellipsoid; of the 1035 symmetrically distinct reflections, 673 were considered as observed ($|F_o| > 5\sigma F$).

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 3, and are expressed as percentages. The Bruker SHELXTL PLUS (PC version) system of programs was used for this work.

The structure was solved by direct methods in the space group $P\bar{1}$. Two cation sites were identified by a combination of site-scattering values and local stereo-

chemistry. All anions were assumed to be oxygen ($Z = 8$), and the scattering power of cations indicated that the two cation sites are occupied by V ($Z = 23$) and S ($Z = 16$). The local stereochemistry is in accord with this assignment. The structure refined rapidly to an R index of ~4% for a model with anisotropic-displacement factors for all non-hydrogen atoms. At this stage, a difference-Fourier map allowed identification of some of the H-atom sites. The hydrogen bonding in anorthominasragrite is more complicated than that in the previously described vanadium sulfate hydrates. Therefore, we first examined the hydrogen bonding in the earlier structures to help establish more rigorous crystal-chemical criteria to unravel the complete hydrogen-bonding pattern for anorthominasragrite. Full-matrix least-squares refinement of all atoms (with fixed isotropic-displacement factors for all the H atoms) converged to an R index of 3.2%. Positional and displacement parameters for the constrained refinement are given in Table 4, selected interatomic distances are listed in Table 5, details of the hydrogen bonds are listed in Table 6. Observed and calculated structure-factors are available from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

HYDROGEN BONDING IN THE PREVIOUSLY DETERMINED VANADIUM SULFATE HYDRATES

Known vanadium sulfate hydrates $V^{4+} O (SO_4)_x (H_2O)_x$ ($0 \leq x \leq 6$) are listed in Table 7; the structural

TABLE 3. MISCELLANEOUS INFORMATION FOR ANORTHOMINASRAGRITE

a (Å)	7.533(2)	crystal size (µm)	20 x 20 x 50
b	7.792(2)	radiation	MoKα/Gr
c	7.818(2)	No. of reflections	1127
α (°)	78.96(2)	No. of unique reflections	1035
β	71.86(2)	No. $ F_o > 5\sigma F $	673
γ	65.41(2)	R_{merge} %	1.1
V (Å ³)	395.5(2)	R_{obs} %	3.2
D_{calc} (g/cm ³)	2.12	wR_{obs} %	3.8
Space Group	$P\bar{1}$		
Cell content:	2 [V O (SO ₄) (H ₂ O) ₂]		
$R = \Sigma(F_o - F_c) / \Sigma F_o $			
$wR = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o ^2]^{1/2}$, $w = 1$			

TABLE 4. ATOM POSITIONS AND DISPLACEMENT FACTORS IN ANORTHOMINASRAGRITE

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
V(1)	0.12488(18)	0.70127(17)	0.81162(16)	0.0146(7)	0.0130(7)	0.0131(8)	0.0001(5)	-0.0019(5)	-0.0058(5)	0.0139(6)
S(1)	-0.0759(3)	0.4323(2)	0.7700(2)	0.0184(10)	0.0151(11)	0.0119(10)	0.0007(8)	-0.0044(8)	-0.0088(9)	0.0144(8)
O(1)	-0.0080(7)	0.2446(7)	0.7111(6)	0.030(3)	0.018(3)	0.021(3)	-0.002(2)	-0.009(2)	-0.013(2)	0.021(2)
O(2)	-0.1980(7)	0.4410(7)	0.9629(6)	0.017(3)	0.024(3)	0.010(3)	0.001(2)	-0.000(2)	-0.010(2)	0.017(2)
O(3)	-0.2048(7)	0.5789(7)	0.6653(6)	0.027(3)	0.023(3)	0.014(3)	0.005(2)	-0.009(2)	-0.010(2)	0.022(2)
O(4)	0.1068(7)	0.4700(7)	0.7551(6)	0.024(3)	0.019(3)	0.018(3)	-0.007(2)	-0.000(2)	-0.009(2)	0.021(2)
O(5)	-0.1087(7)	0.8167(7)	0.8944(7)	0.019(3)	0.028(3)	0.027(3)	-0.007(2)	-0.005(2)	-0.008(2)	0.025(2)
OW(1)	0.2351(8)	0.8909(7)	0.8350(7)	0.030(3)	0.020(3)	0.024(3)	-0.003(2)	-0.007(2)	-0.015(3)	0.023(2)
OW(2)	0.1474(8)	0.8043(8)	0.5510(7)	0.035(3)	0.030(3)	0.017(3)	0.004(2)	-0.014(2)	-0.019(3)	0.024(2)
OW(3)	0.4535(7)	0.5275(7)	0.6937(7)	0.013(3)	0.020(3)	0.025(3)	-0.000(2)	-0.006(2)	-0.005(2)	0.020(2)
OW(4)	-0.3629(8)	0.9818(7)	0.6052(7)	0.029(3)	0.030(3)	0.035(3)	0.007(3)	-0.005(3)	-0.017(3)	0.032(3)
OW(5)	0.5236(8)	0.1867(8)	0.9212(8)	0.031(3)	0.025(3)	0.048(4)	-0.003(3)	-0.007(3)	-0.005(3)	0.037(3)
H(1)	0.325(10)	0.883(13)	0.906(10)	0.05*						
H(2)	0.163(11)	1.027(2)	0.814(12)	0.05*						
H(3)	0.113(13)	0.774(12)	0.453(8)	0.05*						
H(4)	0.214(12)	0.893(9)	0.496(11)	0.05*						
H(5)	0.563(9)	0.568(12)	0.685(11)	0.05*						
H(6)**	0.495(21)	0.407(10)	0.766(16)	0.05*						
H(7)**	0.460(34)	0.528(34)	0.567(9)	0.05*						

* Fixed during refinement.

** Site occupancies: H(6) = 0.6, H(7) = 0.4.

complexity of this relatively simple chemical system is quite surprising. Prior to the discovery of anorthominasragrite, the structures of four vanadium sulfate hydrates ($x \geq 3$) were known (Table 7).

Bond valence associated with the V–O bond

The short vanadyl bond is a very strong bond, and one significant issue with the structures of the vanadium sulfate hydrates is whether the bond-valence requirements of the vanadyl O-atom are met solely by V^{4+} (*i.e.*, is there a [1]-coordinated O-atom?), or whether this O-atom is a hydrogen-bond acceptor. For example, there have been two different hydrogen-bonding schemes proposed for the orthorhombic polymorph of V^{4+} O (SO_4) (H_2O)₅ (orthominasragrite) (Tachez & Théobald 1980b, Hawthorne *et al.* 2001). Hawthorne *et al.* (2001) reported a V–O distance of 1.580(6) Å and assigned two weak hydrogen bonds to this vanadyl O-atom. Tachez & Théobald (1980b) reported a slightly longer V–O distance [1.591(5) Å] and did not assign any hydrogen bonds to the vanadyl O-atom. In the case of the triclinic polymorph of V^{4+} O (SO_4) (H_2O)₅ reported here (anorthominasragrite), the V–O distance [1.587(4) Å] falls between the two values reported for the orthorhombic polymorph. It is of interest to be able to accurately assess the need for hydrogen bonding at the vanadyl O-atom in these structures. What vanadyl bond-length is required to completely satisfy the bond-valence requirements of the vanadyl O-atom? Assessment of the vanadyl bond associated with V^{4+} in [1 + 4 + 1] coordination for well-refined structures gave a range of distances, 1.48 to 1.74 Å, with a mean at 1.60 Å (Schindler *et al.* 2000). Using the bond-valence parameter of Brown & Altermatt (1985), the minimum V^{4+} –O distance, 1.48 Å, gives a bond valence of 2.27 *vu*; is this reported distance, 1.48 Å, too short? Is the bond-valence curve of Brown & Altermatt (1985) overestimating the bond-valence contribution? If the bond-valence parameter is accurate, an observed distance of 1.527 Å would provide the necessary 2.00 *vu* needed to satisfy the bond-valence requirements of the vanadyl O-atom.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) IN ANORTHOMINASRAGRITE

S–O(1)	1.450(6)	V–O(2) <i>a</i>	1.997(5)
S–O(2)	1.499(4)	V–O(4)	2.002(6)
S–O(3)	1.460(5)	V–O(5)	1.587(4)
S–O(4)	1.489(7)	V–OW(1)	2.031(7)
<S–O>	1.475	V–OW(2)	2.024(5)
		V–OW(3)	2.253(4)
		<V–O>	1.982

a: $\bar{x}, \bar{y}+1, \bar{z}+2$.

We decided to further investigate very short vanadyl bonds in 10 well-refined structures ($R \leq 6\%$) containing 12 independent vanadyl bonds (≤ 1.65 Å) (Table 8). All of the compounds are anhydrous and fully ordered, and seven of the ten structures were published after 1985. The vanadyl (V–O) bond-length was plotted against the bond-valence received by the vanadyl O-atom from other neighboring cations (black circles, Fig. 1). The data point with an incident valence of 0 *vu* is from the *only* compound in which the vanadyl O-atom must be [1]-coordinated; the other eleven data-points are for vanadyl O-atoms receiving one or two additional weak bonds from Na, Mg, K, Ca or V^{4+} (Table 8). Linear regression gave an intercept value of 1.563(6) Å. Using the bond-valence curve of Brown & Altermatt (1985), a V^{4+} –O distance of 1.563 Å gives a bond valence of 1.82 *vu*; the curve of Zachariasen (1978) gives a value of 2.04 *vu*. Hence we have adopted the curve of Zachariasen (1978) for all bond-valence calculations involving V^{4+} and O in this paper, and the curves of Brown &

TABLE 6. DETAILS OF HYDROGEN BONDS, (Å) (°), IN ANORTHOMINASRAGRITE

OW(1)–H(1)	0.98(9)	H(1)–OW(5) <i>j</i>	1.89(9)
OW(1)–H(2)	0.98(3)	H(2)–O(1) <i>b</i>	1.86(6)
OW(1)–OW(5) <i>j</i>	2.847(10)	OW(1)–H(1)–OW(5) <i>j</i>	164(7)
OW(1)–O(1) <i>b</i>	2.787(6)	OW(1)–H(2)–O(1) <i>b</i>	156(8)
H(1)–H(2)	1.54(11)		
H(1)–OW(1)–H(2)	104(8)	OW(5) <i>j</i> –OW(1)–O(1) <i>b</i>	127.4(3)
OW(2)–H(3)	0.98(9)	H(3)–O(1) <i>c</i>	1.76(9)
OW(2)–H(4)	0.98(9)	H(4)–OW(4) <i>g</i>	1.70(9)
OW(2)–O(1) <i>c</i>	2.723(9)	OW(2)–H(3)–O(1) <i>c</i>	169(6)
OW(2)–OW(4) <i>g</i>	2.673(9)	OW(2)–H(4)–OW(4) <i>g</i>	171(6)
H(3)–H(4)	1.56(15)		
H(3)–OW(2)–H(4)	106(7)	O(1) <i>c</i> –OW(2)–OW(4) <i>g</i>	106.1(2)
OW(3)–H(5)	0.98(9)	H(5)–O(3) <i>d</i>	1.74(8)
OW(3)–H(6)	0.98(8)	H(6)–OW(5)	1.88(9)
OW(3)–H(7)	0.98(14)	H(7)–OW(3) <i>e</i>	2.01(9)
OW(3)–O(3) <i>d</i>	2.702(9)	OW(3)–H(5)–O(3) <i>d</i>	166(7)
OW(3)–OW(5)	2.847(7)	OW(3)–H(6)–OW(5)	170(6)
OW(3)–OW(3) <i>e</i>	2.962(10)	OW(3)–H(7)–OW(3) <i>e</i>	164(10)
H(5)–H(6)	1.51(15)		
H(5)–OW(3)–H(6)	101(10)	O(3) <i>d</i> –OW(3)–OW(5)	99.1(2)
H(5)–H(7)	1.52(28)		
H(5)–OW(3)–H(7)	102(10)	O(3) <i>d</i> –OW(3)–OW(3) <i>e</i>	95.2(2)
OW(4)–O(3)	2.858(7)		
OW(4)–OW(4) <i>h</i>	2.916(14)	O(3)–OW(4)–OW(4) <i>h</i>	98.2(3)
OW(4)–OW(5) <i>i</i>	2.906(9)	O(3)–OW(4)–OW(5) <i>i</i>	115.0(2)
OW(5)–O(5) <i>a</i>	3.016(8)		
OW(5)–OW(3)	2.847(7)	O(5) <i>a</i> –OW(5)–OW(3)	104.8(2)
OW(5)–OW(4) <i>f</i>	2.906(9)	O(5) <i>a</i> –OW(5)–OW(4) <i>f</i>	101.6(3)

a: $\bar{x}, \bar{y}+1, \bar{z}+2$; *b*: $\bar{x}, \bar{y}+1, \bar{z}$; *c*: $\bar{x}, \bar{y}+1, \bar{z}+1$; *d*: $\bar{x}+1, \bar{y}, \bar{z}$; *e*: $\bar{x}+1, \bar{y}+1, \bar{z}+1$; *f*: $\bar{x}+1, \bar{y}-1, \bar{z}$; *g*: $\bar{x}, \bar{y}+2, \bar{z}+1$; *h*: $\bar{x}-1, \bar{y}+2, \bar{z}+1$; *i*: $\bar{x}-1, \bar{y}+1, \bar{z}$; *j*: $\bar{x}+1, \bar{y}+1, \bar{z}+2$.

Altermatt (1985) for all other bonds. It should be noted that some of the incident bond-valence contributions to the vanadyl O-atom in Figure 1 include long *trans bonds* to V^{4+} ; if one uses the curve of Brown & Altermatt

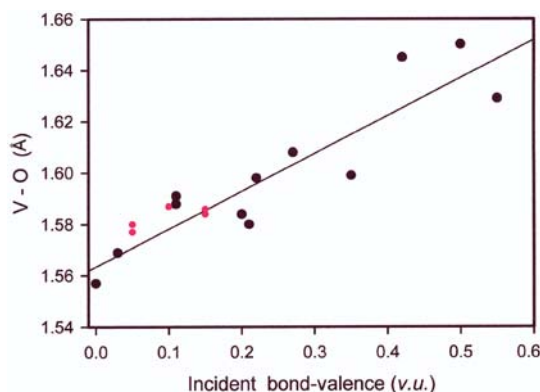


FIG. 1. Variation in V–O (vanadyl) bond-length as a function of bond valence incident at the vanadyl O-atom from adjacent cations (omitting V of the vanadyl bond) calculated from the curve of Zachariasen (1978) for V^{4+} –O and Brown & Altermatt (1985) for all other bonds; black circles: anhydrous V^{4+} -bearing structures; red circles: vanadium sulfate hydrate structures $V^{4+} O (SO_4) (H_2O)_x$, $3 \leq x \leq 6$.

(1985) to plot the relevant data-points, the resulting regression line is only marginally affected [the intercept passes through 1.559(7) Å]. The data in Figure 1 provide convincing evidence for a satisfied vanadyl O-atom at 1.563 Å from a V^{4+} cation. The observed vanadyl bond-lengths for the refined structures of the vanadium sulfate hydrates $V^{4+} O (SO_4) (H_2O)_x$ [$3 \leq x \leq 6$] range from 1.576(3) to 1.591(5) Å and have associated bond-valences ranging from 1.96 to 1.87 *vu*, respectively (Table 9). We recognize that these values may be slightly high, as the curve of Zachariasen (1978) seems to slightly overestimate the bond valence for a fully saturated vanadyl bond (*i.e.*, 1.563 Å $\equiv$ 2.04 *vu*). All of the vanadyl O-atoms of the vanadium sulfate hydrates are therefore marginally bond-valence-deficient from the V^{4+} contribution alone, and must receive at least one weak hydrogen-bond. However, the final decision to assign such hydrogen bonds will need to involve additional criteria: (1) the positions of H atoms, if located, (2) reasonable (H_2O) geometry, and (3) reasonable geometries for hydrogen-bond acceptors. Proposed schemes of hydrogen-bonding for the previously reported vanadium sulfate hydrates $V^{4+} O (SO_4) (H_2O)_x$ [$3 \leq x \leq 6$], using the bond-valence curves recommended above, are presented in Figures 2–6.

For several of the structures, H positions were reported at distances too close (generally 0.7 to 0.9 Å) to the donor O-atom (O_D). It is well known that H positions refined freely using X-ray intensity data will typi-

TABLE 7. VANADIUM SULFATES OF THE FORM $V^{4+} O (SO_4) (H_2O)_x$.

x	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)	Symmetry	Z	D _{calc} (g cm ⁻³)	Ref.	Mineral Name
0	6.261	6.261	4.101				160.8	<i>P4/n</i>	2	3.37	[1]*	(polymorph α)
0	7.376	6.269	7.082				327.5	<i>Pnma</i>	4	3.31	[2]*	(polymorph β)
0	?	?	?	?	?	?	?	?	?	?	[3]	(polymorph γ)
1	9.54	6.36	7.20				436.9	orth	4	2.75	[4]	
1	6.26	6.26	6.10				239.0	orth?	2	2.51	[5]	
1	11.2	6.27	7.10				498.6	orth	4	2.41	[6]	
1.5	7.77	6.07	6.34				299.0	orth	2	2.11	[4]	
2	6.29	6.29	6.92				273.8	orth?	2	2.41	[7]	
2	8.913	8.93	7.80		92.4		620.3	mono	4	2.13	[8]	
2	7.75	6.92	6.29				337.3	orth	2	1.96	[4]	
3	8.980	9.026	7.776				630.3	<i>P2₁2₁2</i>	4	2.29	[8]	
3	7.387	7.401	12.046		106.57		631.2	<i>P2₁/n</i>	4	2.28	[9]*	(syn-bobjonesite)
	7.3940	7.4111	12.0597		106.55		633.5	<i>P2₁/n</i>	4	2.28	[10]*	bobjonesite
5	7.533	7.792	7.818	78.96	71.86	65.41	395.5	<i>P</i> $\bar{1}$	2	2.12	[11]*	anorthominasragrite
5	6.976	9.716	12.902		110.90		816.9	<i>P2₁/c</i>	4	2.06	[12]*	(syn-minasragrite)
5	7.234	9.304	6.184				416.2	<i>Pmn2₁</i>	2	2.02	[13]*	(syn-orthominasragrite)
	7.242	9.319	6.192				417.9	<i>Pmn2₁</i>	2	2.01	[14]*	orthominasragrite
5	16.12	21.12	12.22				4160.4	<i>Pm</i> $\bar{3}$ <i>n</i>	20	2.02	[15]	
6	7.473	10.137	6.202	101.90	95.54	92.12	456.8	<i>P</i> $\bar{1}$	2	1.97	[16]*	(syn-stanleyite)

* Structure refinement.

References: [1] Longo & Arnett (1970); [2] Boghosian *et al.* (1995); [3] Tundo & Laplace (1977); [4] Tachez & Théobald (1976); [5] Ladwig (1969); [6] Tundo (1965); [7] Tachez *et al.* (1982b); [8] Schneider *et al.* (1982); [9] Tachez & Théobald (1980a); [10] Schindler *et al.* (2003); [11] this work; [12] Tachez *et al.* (1979); [13] Tachez & Théobald (1980b); [14] Hawthorne *et al.* (2001); [15] Bailhausen *et al.* (1968); [16] Tachez & Théobald (1980c).

cally refine too close to O_D . We have therefore derived bond valences for hydrogen bonding based on the distance between the donor O-atom and acceptor O-atom (O_D-O_A) using the plot of $O_A...H$ bond-valence versus O_D-O_A from Brown & Altermatt (1985). Bond valences for the hydrogen bonds were defined at 0.05 *vu* increments that correspond to the following ranges in O_D-O_A : 0.25 *vu* (2.56–2.66 Å), 0.20 *vu* (2.66–2.80 Å), 0.15 *vu* (2.80–2.94 Å), 0.10 *vu* (2.94–3.05 Å), 0.05 *vu* (3.05–3.23 Å). The proposed hydrogen-bonds were examined for the vanadium sulfate hydrates, paying particular attention to the region surrounding the vanadyl O-atom. The resulting relation between vanadyl bond-length and incident bond-valence (*via* hydrogen bonding) for the vanadium sulfate hydrates, $V^{4+}O(SO_4)(H_2O)_x$ [$3 \leq x \leq 6$], is listed in Table 9 and shown in Figure 1 with red circles. There is good overall agreement between (1) both the bond-valences for hydrogen in vanadium sulfate hydrates and weak bonds from the cation (anhydrous vanadium sulfate structures) to the vanadyl oxygen, and (2) the V–O distance.

Monoclinic $V^{4+}O(SO_4)(H_2O)_3$ (bobjonesite): At an observed distance of 1.577(3) Å, the vanadyl oxygen at O(1) is nearly satisfied (1.95 *vu*) from the V^{4+} contribution alone (*cf.* Figs. 1, 2a). There are three crystal-structure refinements reported for the monoclinic polymorph of $V^{4+}O(SO_4)(H_2O)_3$: (1) a single-crystal X-ray study of the synthetic compound (Tachez & Théobald 1980a), (2) a powder neutron-diffraction study of the deuterated synthetic compound (Tachez *et al.* 1982a), and (3) a single-crystal X-ray study of bobjonesite (Schindler *et al.* 2003). All three structural models are in close agree-

ment (Fig. 3a) for the non-H positions, but there are significant differences for the H-atom positions belonging to the (H_2O) group H(1)–O(2)–H(2), which forms a *trans* bond with the V^{4+} cation. This distinction is shown in Figure 3b, where H-atom positions for the three studies are plotted relative to the mean positions for the non-H sites. The H positions of the two latter studies (Position II) agree with each other, and are displaced in a clockwise fashion relative to the positions indicated in the earliest study (Position I). The details of the different hydrogen-bonding geometries are given in Table 10. For Position II, the H atom at H(2) is closer to the acceptor O(7), and forms a straighter hydrogen-bond. For Position I, the H atom at H(1) forms a nearly symmetrical bifurcated hydrogen-bond to O(1) and O(7). For Position II, there is a pronounced asymmetry in the bifurcated geometry of this hydrogen-bond from H(1), with a possible weak interaction between H(1) and O(1). Position II must be favored as the more likely arrangement on both experimental and crystal-chemical grounds. We cannot rule out a weak hydrogen-bond contribution to O(1), so we retain the bifurcated hydrogen-bond from H(1) (Fig. 2a) and note that the bond geometry is rather extreme (Table 10), *i.e.*, close to the geometrical limits for such an interaction. The details of the hydrogen-bonding are of key interest, as in this particular compound, the vanadyl O-atom is very nearly satisfied from the V^{4+} cation alone. As all the other vanadium sulfate structures contain longer vanadyl bonds, we anticipate that all these structures will contain at least one weak hydrogen-bond to the vanadyl O-atom.

Orthorhombic $V^{4+}O(SO_4)(H_2O)_5$ (orthominasragrite): The next shortest vanadyl bond [1.580(6) Å] occurs in orthominasragrite (Hawthorne *et al.* 2001), the orthorhombic polymorph of $V^{4+}O(SO_4)(H_2O)_5$ (Table 9). The local environment in the vicinity of the vanadyl O-atom O(1) is shown in Figure 4. Hawthorne *et al.* (2001) assigned two weak hydrogen-bonds from H-atoms [H(1) and H(2)] lying on the mirror plane ($x = 0$) to the vanadyl O-atom at O(1). They noted that the H(1)–O(2)–H(2) angle of 62° is unreasonably small, and proposed a disordered hydrogen-bond model involving

TABLE 8. SELECTED COMPOUNDS WITH SHORT VANADYL ($V^{4+}=O$) BONDS

Compound	$V^{4+}=O$ (Å)	O–X (Å)	X	Ref.
$V^{3+}_2(V^{4+}O)(P_2O_7)_2$	1.557	–	–	(1)
$Zn_2(V^{4+}O)(PO_4)_2$	1.569	2.950	V^{4+}	(2)
$(V^{4+}O)SiP_2O_8$	1.591	2.492	V^{4+}	(3)
$K_4(V^{4+}O)_3(SO_4)_5$	1.580	2.704	K	(4)
"	1.584	2.726	K	(4)
"	1.588	3.044	K	(4)
"		3.574	K	(4)
$\beta-(V^{4+}O)(SO_4)$	1.598	2.271	V^{4+}	(5)
$Ca(V^{4+}O)_2(PO_4)_2$	1.599	2.121	V^{4+}	(6)
$CaV^{4+}_4O_9$	1.608	2.446	Ca	(7)
$Na(V^{4+}O)(AsO_4)$	1.629	2.167	V^{4+}	(8)
"		2.338	Na	(8)
$Ca(V^{4+}_2O_6)$	1.645	2.540	x2 Ca	(9)
$MgV^{4+}_4O_9$	1.650	1.947	Mg	(10)

X = Additional weakly bonded cations.

References: (1) Johnson *et al.* (1988), (2) Lii & Tsai (1991), (3) Rice *et al.* (1976), (4) Fehrmann *et al.* (1989); (5) Boghosian *et al.* (1995), (6) Lii *et al.* (1992), (7) Bouloux & Galy (1973), (8) Haddad *et al.* (1992), (9) Onoda & Nishiguchi (1996), (10) Bouloux *et al.* (1976).

TABLE 9. STEREOCHEMICAL DETAILS OF VANADYL O-ATOMS IN VANADIUM-SULFATE HYDRATES $V^{4+}O(SO_4)(H_2O)_x$ [$3 \leq x \leq 6$]

x	sym.*	mineral	V–O (Å)	V–O (vu)	Hydrogen bond (vu)	Fig.	Ref.
3	M	syn-bobjonesite	1.576(3)	1.96	–	–	(1)
3	M	bobjonesite	1.577(3)	1.95	0.05	2a	(2)
5	O	orthominasragrite	1.580(6)	1.93	0.05	2b	(3)
5	O	syn-orthominasragrite	1.591(5)	1.87	–	–	(4)
5	M	syn-minasragrite	1.584(1)	1.91	0.15	2c	(5)
5	T	anorthominasragrite	1.587(4)	1.89	0.10	8	(6)
6	T	syn-stanleyite	1.586(2)	1.90	0.15	2d	(7)

* Symmetry: T = triclinic, M = monoclinic, O = orthorhombic. References: (1) Tachez & Théobald (1980a), (2) Schindler *et al.* (2003), (3) Hawthorne *et al.* (2001), (4) Tachez & Théobald (1980b), (5) Tachez *et al.* (1979), (6) this work, (7) Tachez & Théobald (1980c).

H(1) and H(2) [H(2) is labeled as H2* and H(1) is absent in Fig. 4]. Further evaluation of this disordered model reveals that a reasonable (H₂O) geometry cannot occur for any local configuration. The earlier structural model of Tachez & Théobald (1980b) for the synthetic analogue was based on a single ordered H(2) site lying

off the mirror plane (*i.e.*, H1* in Fig. 4), gave a reasonable (H₂O) geometry [an H(2)–O(2)–H(2)' angle of 106°], and resulted in moderate hydrogen-bond-valence directed toward the O-atom at O(5). From a geometrical standpoint, the model of Tachez & Théobald (1980b) is preferred. From a bond-valence perspective, the O(1)

(a) Bobjonesite

	V	S	H1	H2	H3	H4	H5	H6	Σ
O(1)	1.95		0.05						2.00
O(2)	0.22		0.85	0.80	0.15				2.02
O(3)	0.47				0.85	0.80			2.12
O(4)	0.45						0.80	0.80	2.05
O(5)	0.51	1.50							2.01
O(6)	0.51	1.46							1.97
O(7)		1.54	0.10	0.20			0.20		2.04
O(8)		1.58				0.20		0.20	1.98
Σ	4.11	6.08	1.00	1.00	1.00	1.00	1.00	1.00	

(b) Orthominasragrite

	V	S	H1	H2	H3	H4	H5	H6	Σ
O(1)	1.93			0.05					1.98
O(2)	0.25		0.85	0.95					2.05
O(3) x2	0.47				0.80	0.80			2.07
O(4) x2	0.49						0.80	0.80	2.09
O(5)		x2 1.50	0.15		0.20	0.20			2.05
O(6)		1.56						0.20	1.96
O(7)		1.47					0.20	x2	1.87
Σ	4.10	6.03	1.00	1.00	1.00	1.00	1.00	1.00	

FIG. 2. Bond-valence tables for (a) bobjonesite, (b) orthominasragrite, (c) synthetic minasragrite, and (d) synthetic stanleyite, calculated as in Figure 1.

TABLE 10. DETAILS OF HYDROGEN BONDING IN MONOCLINIC $V^{4+}O(SO_4)(H_2O)_3$

	Position I	Position II	
	Tachez & Théobald (1980a)	Tachez <i>et al.</i> (1982a)	Schindler <i>et al.</i> (2003)
O(2)–H(1)	0.81(13)	1.00(1)	0.98(2)
H(1)··O(1)	2.49(14)	2.66(2)	2.56(3)
H(1)··O(7)'	2.42(15)	2.05(2)	2.13(2)
O(2)–H(1)··O(1)	128(14)	101(1)	112(3)
O(2)–H(1)··O(7)'	128(14)	158(1)	148(3)
O(2)–H(2)	0.99(10)	1.00(1)	0.98(3)
H(2)··O(7)	1.88(9)	1.81(1)	1.81(2)
O(2)–H(2)··O(7)	149(9)	168(1)	169(3)
H(1)–O(2)–H(2)	114(12)	102(1)	97(3)

[illegible][illegible]

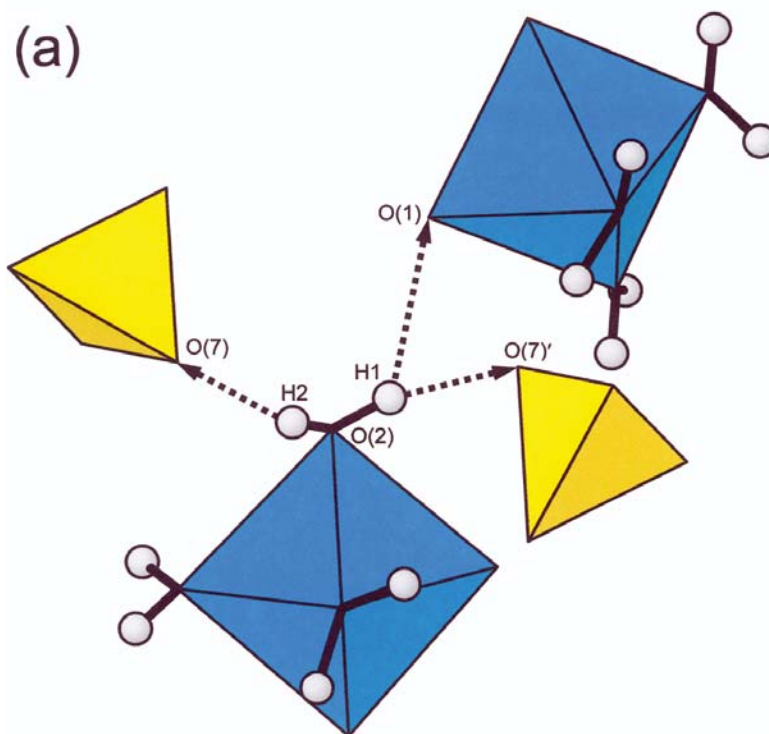
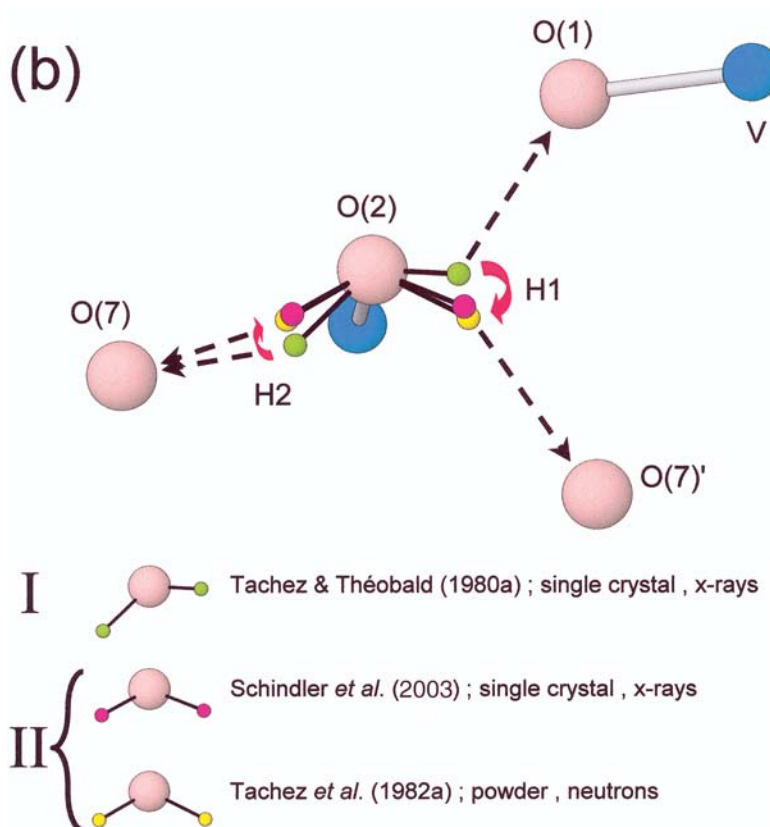


FIG. 3. Perspective view of the arrangement of atoms in bobjonesite. (a) View of the ($V\phi_6$) (blue) and (SO_4) (yellow) polyhedra with associated (H_2O) groups (H atoms shown as grey circles); O_D-H bonds are shown as full lines and $H \cdots O_A$ bonds are shown as broken lines. (b) Perspective view of the different models for the hydrogen-bond arrangement; large pink circles: O atoms; blue circles: V atoms; small red, yellow and green circles: H atoms. The red arrows indicate the sense of rotation of the (H_2O) group from position I to position II.

ambiguity in H-position labeling, we have relabeled the two positions (Fig. 4) as follows: (1) the ordered H-position on the mirror plane is $H2^*$; (2) the disordered H-position off the mirror plane is $H1^*$. To arrive at the most reasonable geometry, the $H1^*$ and $H2^*$ positions were refined using the soft constraint that they remain 0.98 Å from the donor O-atom [O(2)], the positional parameters for the well-resolved $H2^*$ position were then fixed, and the constraint that the separation between $H1^*$ and $H2^*$ remain at 1.55(1) Å was imposed. These constraints were necessary in order to achieve a fully convergent refinement that includes the more poorly resolved $H1^*$ site. This new model for the hydrogen bonding in orthominasragrite provides: (1) a weak hydrogen-bond to the vanadyl O-atom at O(1), (2) a moderately strong hydrogen-bond to O(5), (3) satisfactory incident bond-valence sums at all sites (Fig. 2b), and (4) (H_2O) groups and hydrogen-bonds with reasonable geometries (Fig. 4).

Monoclinic $V^{4+}O(SO_4)(H_2O)_5$ (minasragrite): A vanadyl-bond length of 1.584 Å was observed by Tachez *et al.* (1979) for this structure (Table 9). The H-atom positions reported for the isolated (H_2O) group at O(10) are consistent with a simple hydrogen-bonding scheme involving a hydrogen bond of moderate bond-valence directed toward the vanadyl O-atom at O(1) (Fig. 2c). For this arrangement, typical bond-angles are observed (Fig. 5).

$V^{4+}O(SO_4)(H_2O)_6$ (stanleyite): The vanadyl bond observed for triclinic $V^{4+}O(SO_4)(H_2O)_6$ is 1.586 Å, and has a bond valence of 1.90 *vu* (Fig. 2d). The reported H-atom positions for the isolated (H_2O) group at O(7) are shown in Figure 6. A bifurcated hydrogen-bond from H(12) is directed toward two symmetry-related vanadyl O-atoms [O(1) and O(1)']. The O(7)–O(1)' distance is rather long [3.37 Å], and the bond valence of the associated hydrogen-bond from H(12) to O(1)' must be very small (*i.e.*, < 0.05 *vu*); we have therefore ex-



cluded this contribution in the bond-valence table (Fig. 2d). The O(7)–O(1) distance is 2.88 Å, and we have assigned a bond valence of 0.15 *vu* for the associated hydrogen-bond from H(12) to O(1).

Summary

Details of the hydrogen bonding for the four previously determined vanadium sulfate hydrate structures are given in the bond-valence tables (Figs. 2a–2d), and the various hydrogen-bond acceptors are summarized in Figure 7. There are up to three types of acceptor O-atoms present: O_V = vanadyl O-atom; O_T = terminal sulfate O-atom; and O_B = bridging O-atom. For all structures, O_V is mildly bond-valence-deficient considering bonds from the V⁴⁺–O interaction alone, providing strong justification for a weak hydrogen-bond directed toward O_V. The terminal O-atom of the (SO₄) group, O_T, receives either two or three hydrogen bonds. The bridging O-atom, O_B, that is corner-shared by V⁴⁺ and S, may receive a single hydrogen-bond. There are up to three types of (H₂O) groups present: W_E = equatorial (H₂O) group, W_T = *trans* (H₂O) group, and W_I = iso-

lated (H₂O) group. None of the structures contain hydrogen bonds directed toward any equatorial (H₂O) group (W_E). Those containing isolated (H₂O) groups have two hydrogen bonds directed toward the W_I groups. There may be a single hydrogen-bond directed toward a *trans* (H₂O) group (W_T).

DESCRIPTION OF THE STRUCTURE OF ANORTHOMINASRAGRITE

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 1.475 Å, close 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 1.587 Å, four intermediate-length V–O bonds in the range 1.997–2.031 Å and approximately orthogonal to the short V–O bond, and one long bond of 2.253 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 $[1 + 4 + 1]$ geometry is characteristic of $^{[6]}V^{4+}$, as discussed by Schindler *et al.* (2000).

Identity of the anions

The bond-valence table (Fig. 8) indicates that the V^{4+} cation bonds to three (H_2O) groups, OW(1), OW(2) and OW(3). The O(1), O(3) and O(5) atoms receive 1.60, 1.56 and 1.89 *vu* from the S and V atoms, and hence these anions must be O atoms. The O(2) and O(4) atoms each bond to both V^{4+} and S, with incident bond-valence sums of 1.92 and 1.95 *vu* from these cations; hence O(2) and O(4) also are O atoms. There are two

other anions in the structure, OW(4) and OW(5); these do not bond to the principal cations of the structure, and hence they must be isolated (H_2O) groups. Details of the hydrogen-bonding scheme are given in Table 6 and Figures 8 and 9. Hydrogen-bond valences were assigned in the same manner as for the other vanadium sulfate hydrates.

H sites located from difference-Fourier maps

Well-resolved electron-density peaks from the difference-Fourier map were assigned to H-positions for the (H_2O) groups at OW(1), OW(2) and OW(3). The H-positions H(1) through H(4) are fully ordered and belong to OW(1) and OW(2) (Fig. 8). Hydrogen atoms at

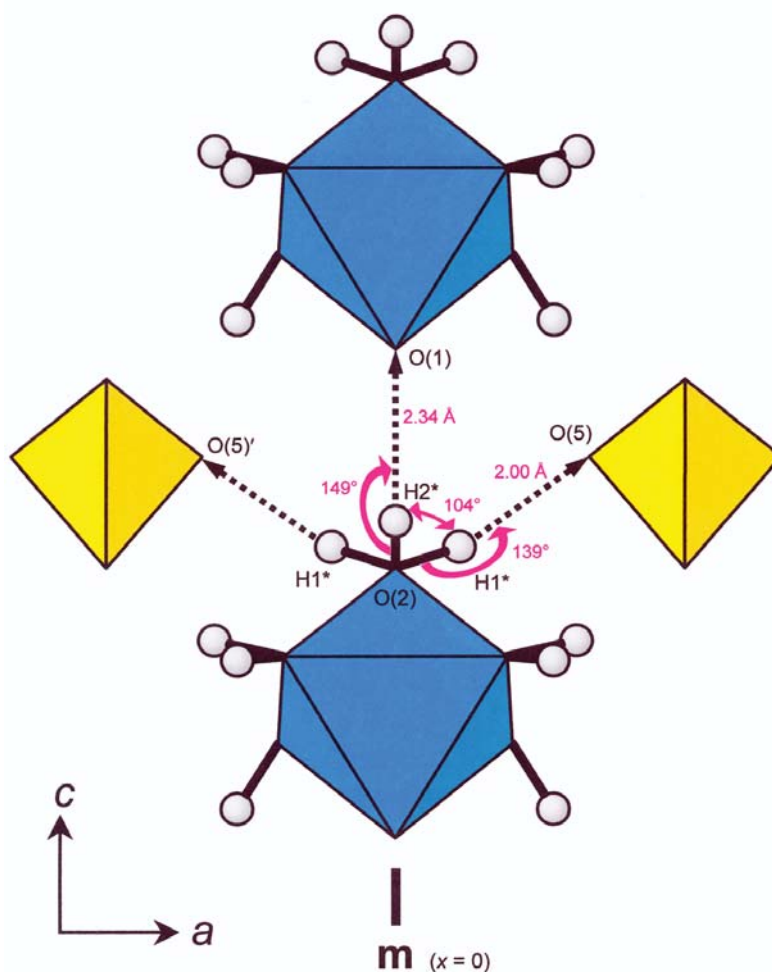


FIG. 4. The hydrogen-bond arrangement in orthominasragrite showing the H1* and H2* sites derived in the present study, together with the resulting bond-lengths and angles. Legend as in Figure 3a.

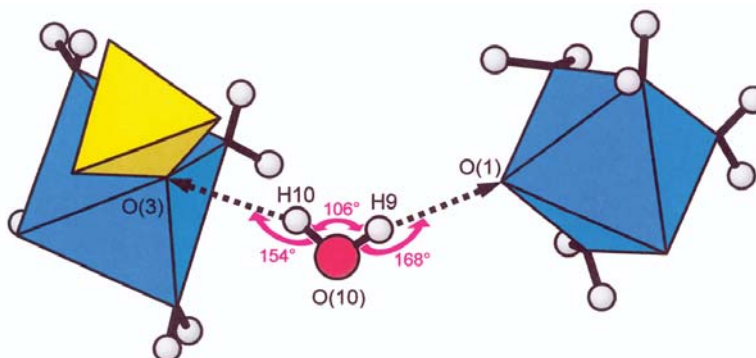


FIG. 5. The hydrogen-bond arrangement around the O(10) anion in minasragrite, showing the associated bond-angles. Legend as in Figure 3a.

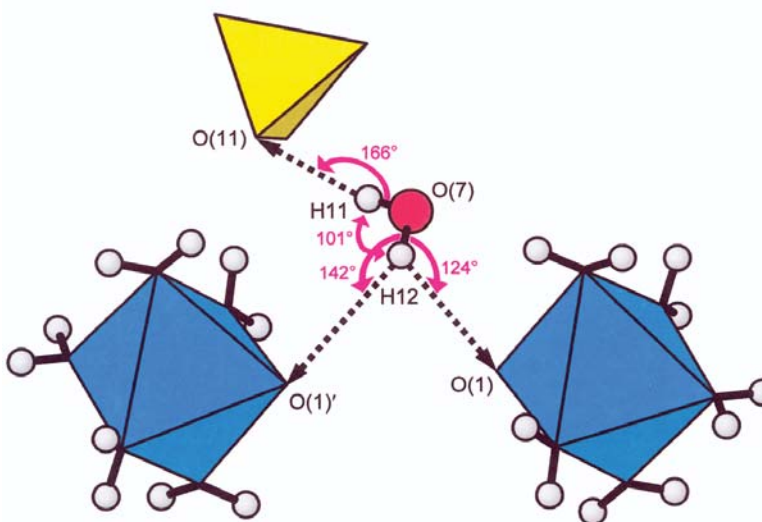


FIG. 6. The hydrogen-bond arrangement around the O(7) anion in synthetic stanleyite, showing the associated bond-angles. Legend as in Figure 3a.

H(1) and H(4) form hydrogen bonds with the isolated (H_2O) groups OW(5) and OW(4), respectively. Hydrogen atoms at H(2) and H(3) form hydrogen bonds to a terminal O-atom of the (SO_4) group, O(1). Three significant electron-density peaks [H(5), H(6) and H(7)] were located near the O-atom at OW(3); these peaks conform to the H-atoms of a positionally disordered (H_2O) group. Site-occupancy refinement of H(5), H(6) and H(7) showed that the H(5) site is fully occupied, and that the H(6) and H(7) sites are each approximately half occupied. The H(5) site is fully ordered with a hydrogen bond to the terminal O(3) atom of the (SO_4)

group. Where the H(6) site is occupied, a hydrogen bond is formed with the O-atom at OW(5); where H(7) is occupied, a neighboring OW(3)' site, related through the center of symmetry, receives a hydrogen bond. The geometry and associated hydrogen-bond angles at the OW(3) site, namely H(5)–OW(3)–H(7) [OW(3) in Figs. 8 and 9], H(5)–OW(3)–H(6) [OW(3)' in Figs. 8 and 9] and the OW(3) (H_2O)-groups are reasonable (Table 6). In the final refinement model, the H(5), H(6) and H(7) occupancies were fixed at 1.0, 0.6 and 0.4, respectively. All H positions [H(1) through H(7)] were refined with the soft constraint that O–H is approximately equal to

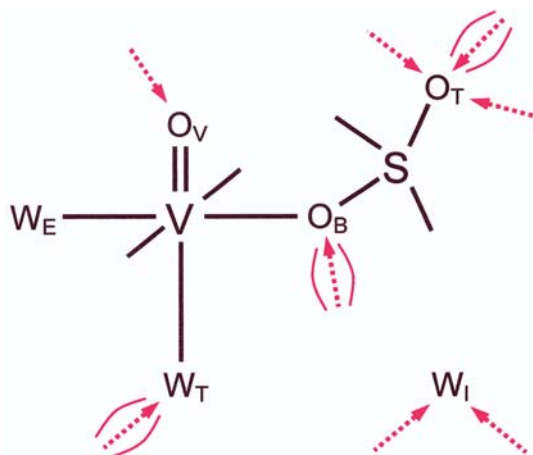


FIG. 7. Summary of the possible hydrogen-bond linkages in vanadium sulfate hydrates; V and S denote cation sites, O_B denotes the anion bridging between the $(V\phi_6)$ and (SO_4) polyhedra, O_V is the vanadyl O-atom, O_T is a terminal O-atom, W_E is an equatorial (H_2O) group, W_T is a *trans* (H_2O) group, W_I is an isolated (H_2O) group. Broken red lines denote required hydrogen-bonds; broken red lines in parentheses indicate possible hydrogen-bonds.

0.98 Å. Note that in Figure 8, all bold entries are associated with fully ordered sites; positionally disordered H-sites and their associated hydrogen-bond valences appear as non-bold entries. The use of non-bold and non-italicized labels and entries, in combination with those that are non-bold and italicized, allows easier identification of inter-dependent local hydrogen-bonding associated with the disordered H-positions (as is apparent when comparing Figs. 8 and 9).

Inferred H positions

Hydrogen positions could not be reliably located in the difference-Fourier map for the isolated (H_2O) groups at OW(4) and OW(5). In Figures 8 and 9, the associated H-positions [H(8)] through [H(13)] are enclosed in square brackets to denote that those sites are inferred, rather than located on difference-Fourier maps. After assigning hydrogen bonds for the H-atoms at H(1) through H(7), it is clear from the bond-valence table (Fig. 8) that the following anions (bonded to either V^{4+} or S^{6+}) are still bond-valence-deficient: O(3), O(5) and OW(3). On the basis of the analysis of hydrogen bonding in the other vanadium sulfate hydrates (Fig. 7), we expect that (1) at least two hydrogen-bonds are directed toward the terminal O-atom of the (SO_4) group at O(3), (2) a weak hydrogen-bond is directed toward the

Anorthominasragrite

	V	S	H1	H2	H3	H4	H5	H6	H7	[H8]	[H9]	[H10]	[H11]	[H12]	[H13]	Σ
O(1)		1.60		0.20	0.20											2.00
O(2)	0.52	1.40														1.92
O(3)		1.56					0.20			0.15						1.91
O(4)	0.51	1.44														1.95
O(5)	1.89												0.10			1.99
OW(1)	0.47		0.85	0.80												2.12
OW(2)	0.48				0.80	0.80										2.08
OW(3)	0.23						0.80	0.85	0.90							1.98
OW(3)'									0.10							2.08
OW(4)						0.20				0.85	0.85	0.85				2.05
OW(4)'											0.15					2.05
OW(5)			0.15					0.15				0.15	0.90	0.85	0.85	2.05
Σ	4.10	6.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	

FIG. 8. Bond-valence table for anorthominasragrite; bold entries denote ordered arrangements, and non-bold entries denote positionally disordered arrangements. Legend as in Table 2.

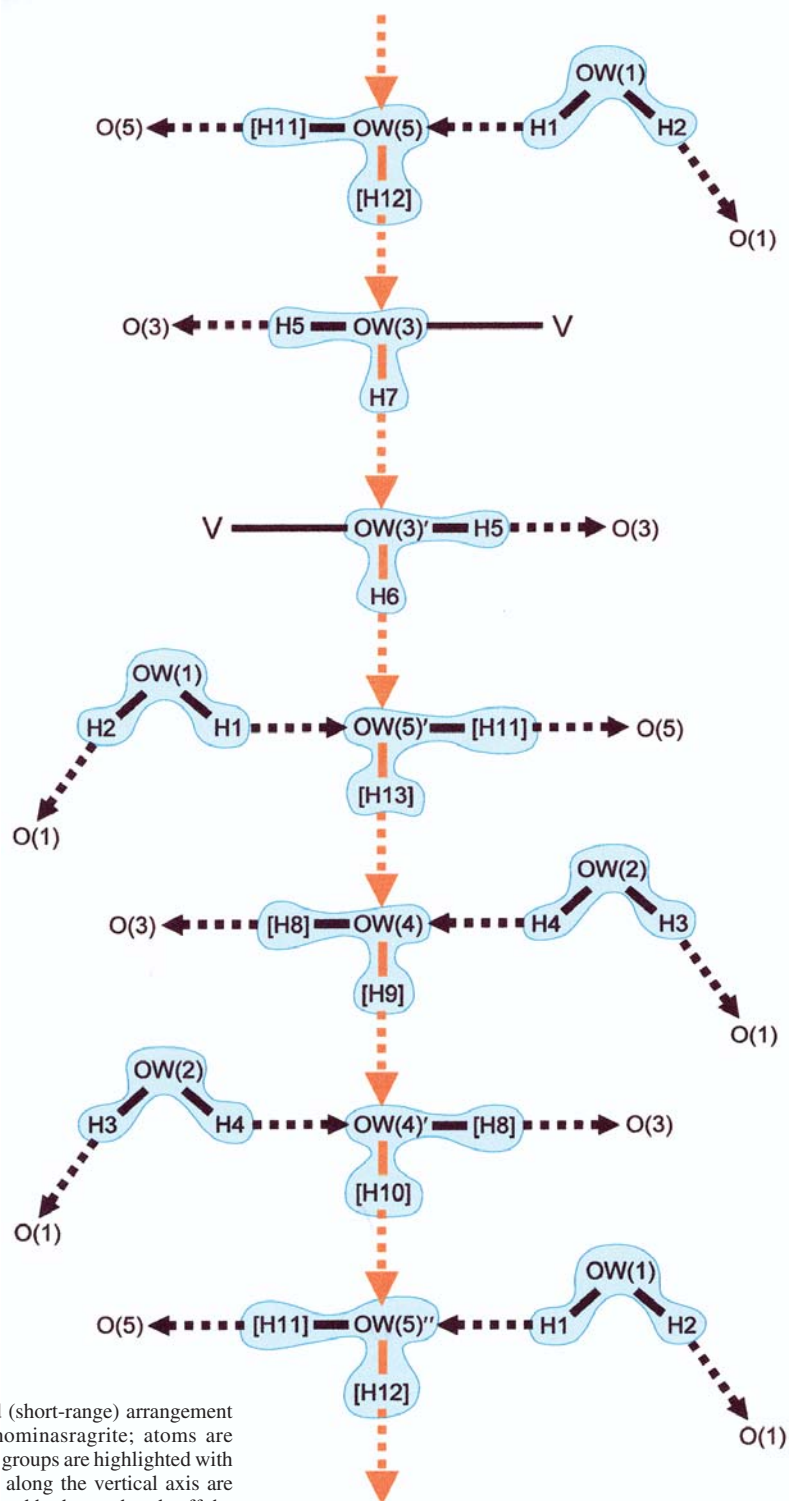


FIG. 9. Sketch of locally ordered (short-range) arrangement of hydrogen bonds in anorthominasragrite; atoms are shown by their symbols, (H₂O) groups are highlighted with blue shading, hydrogen bonds along the vertical axis are shown as broken orange lines, and hydrogen bonds off the vertical axis are shown as broken black lines.

vanadyl O-atom at O(5), (3) a possible hydrogen-bond is directed toward the *trans* (H₂O) group at OW(3), and (4) two hydrogen-bonds are directed toward the isolated (H₂O) groups at OW(4) and OW(5).

The inferred H-positions, [H(8)] through [H(13)], were developed from the following considerations: (1) The remaining bond-valence requirements for each bond-valence-deficient anion must be satisfied *via* hydrogen bonds from (H₂O) groups with reasonable geometries (*i.e.*, reasonable O_A–OW–O_A angles and O_D–O_A distances). (2) The patterns of hydrogen bonding in the previously determined vanadium sulfate hydrates should apply to the disordered hydrogen-bonding in anorthominasragrite. (3) Hydrogen bonding involving disordered H-positions must satisfy local bonding requirements; hydrogen bonding need not adhere to long-range symmetry. (4) Hydrogen bonds must emanate from OW(3) in two distinct ways.

Details of short-range hydrogen-bonding

A locally ordered arrangement of hydrogen bonding in anorthominasragrite is shown in Figure 9, in which the (H₂O) groups are highlighted with blue shading. The disordered H-positions [H(6), H(7), H(9), H(10), H(12) and H(13)] associated with the (H₂O) groups OW(3), OW(4) and OW(5) are presented in a locally ordered configuration along the vertical axis of Figure 9. All H-positions lying either to the left or right of the vertical axis are fully ordered. Note that the hydrogen bonding along the vertical axis (shown in orange) is necessarily unidirectional. Near the top of Figure 9, the (H₂O) group at OW(3) is shown associated with the H(5) and H(7) sites. The H-atom at H(7) is hydrogen-bonded to a nearby OW(3)' anion, which is related to the first OW(3) site by a center of symmetry (note that the *short-range* stereochemical details need not conform to the *long-range* symmetry, *i.e.*, the center of symmetry). The (H₂O) group at OW(3)' is associated with H-atoms at the H(5) and H(6) sites. The positional disorder between the H(6) and H(7) sites *must* occur because two neighboring H(7) sites (related by a center of symmetry) would approach each other too closely. The same condition also exists between the neighboring OW(4) and OW(4)' sites related through a center of symmetry (Fig. 9). The hydrogen-bond arrangement in anorthominasragrite does not conform to $\bar{1}$ symmetry. This distinction in local hydrogen-bonding as a function of H-disorder can be followed through the bond-valence table (Fig. 8) by differentiating italicized from non-italicized entries.

Structure topology

The structural unit in anorthominasragrite is a $[(V^{4+}O)_2(SO_4)_2(H_2O)_6]$ group, formed by corner-sharing of (SO₄) tetrahedra and (V ϕ_6) octahedra about an inversion center (Fig. 10a). This same structural unit is

also present in bobjonesite, the monoclinic polymorph of $V^{4+}O(SO_4)(H_2O)_3$ (Tachez & Théobald 1980a, Schindler *et al.* 2003) (Fig. 10b). The stagger of the $(V^{4+}O)_2(SO_4)_2(H_2O)_6$ groups differs between the two structures; in anorthominasragrite, they are all oriented in the same sense (Fig. 11a), whereas in bobjonesite, successive rows of $[(V^{4+}O)_2(SO_4)_2(H_2O)_6]$ groups along [010] are related by 2₁-screw axes along *b* (Fig. 11b). Openings among adjacent $[(V^{4+}O)_2(SO_4)_2(H_2O)_6]$ groups in anorthominasragrite contain the isolated (H₂O) groups OW(4) and OW(5) that provide additional structural cohesion *via* hydrogen bonding (Fig. 11a).

The formulae and structures of vanadium sulfate hydrates

From the above comparison of anorthominasragrite, $V^{4+}O(SO_4)(H_2O)_5$, and bobjonesite, $V^{4+}O(SO_4)(H_2O)_3$, it is not apparent from their simple formulae that they are structurally similar. All the vanadium sulfate hydrates contain V^{4+} octahedrally coordinated by (1) a vanadyl O-atom, (2) a *trans* (H₂O) group, and (3) four equatorial anions that are either (H₂O) groups or O-atoms that also bond to an S-atom. A more informative formula can be written by identifying the structural unit in brackets [*i.e.*, including (H₂O) groups bonded to V^{4+}], and the interstitial complex in braces [*i.e.*, including isolated (H₂O) groups] (Table 11).

From the new formulae, the various linkages between structural components are immediately apparent. Each V^{4+} is coordinated by one vanadyl O-atom and *x* (H₂O) groups. The remaining $(5-x)$ anions bonded to V^{4+} are O-atoms of the (SO₄) group, as shown in Figure 12. The structures of bobjonesite and anorthominasragrite are based on a $[V^{4+}O(SO_4)(H_2O)_3]$ cluster that bonds to a neighboring identical cluster to form a $[(V^{4+}O)_2(SO_4)_2(H_2O)_6]$ group, with an additional two isolated (H₂O) groups in anorthominasragrite (Figs. 12a, b). In minasragrite, a $[V^{4+}O_2(H_2O)_4]$ octahedron links to a single (SO₄) group to form a $[V^{4+}O(SO_4)(H_2O)_4]$ group, with a single additional isolated (H₂O) group (Fig. 12c). The orthominasragrite and stanleyite structures are based on isolated $[V^{4+}O(H_2O)_5]$ and (SO₄) groups, with one isolated (H₂O) group in stanleyite (Figs. 12d, e).

The structures of the vanadium sulfates

The crystal structures of two of the three polymorphs of anhydrous vanadium sulfate (*x* = 0) have been determined (Table 7). These structures contain –S–O–V– chains with additional weaker connections *via* short-vanadyl – long-*trans* bonds (V=O–V). The α -structure consists of sheets of corner-sharing (V ϕ_6) octahedra and (SO₄) tetrahedra that further connect *via* interlayer V=O–V linkages (Longo & Arnott 1970). The –S–O–V– chains in the β -structure form a three-dimensional

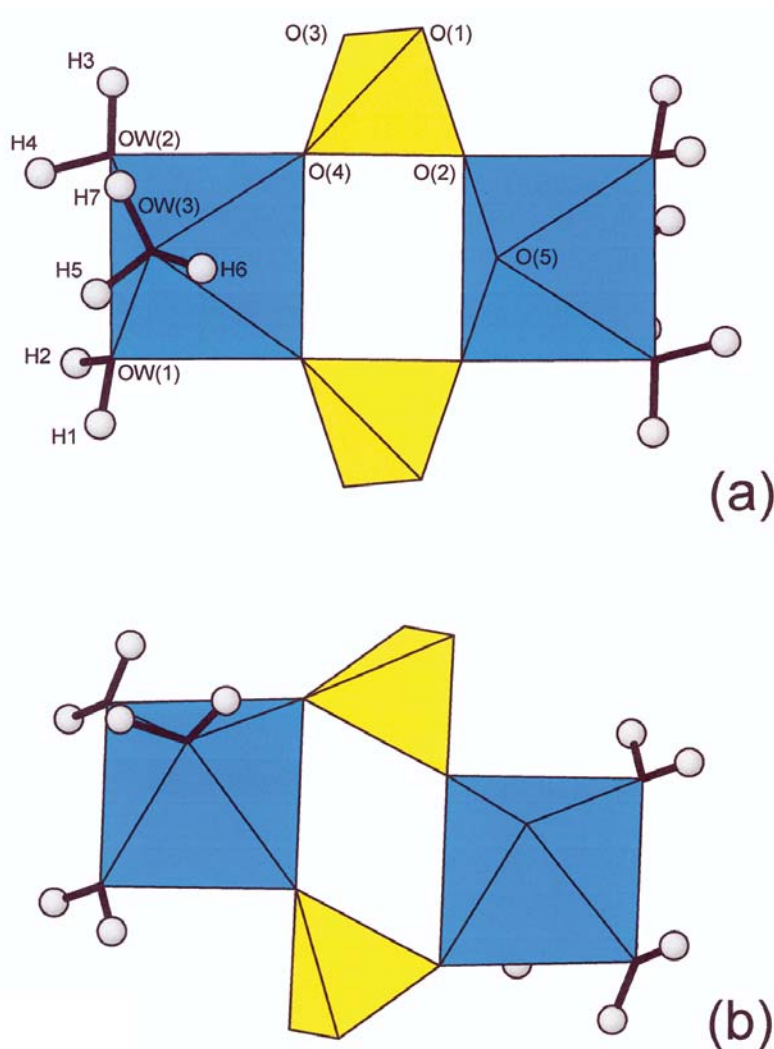


FIG. 10. Perspective views of the structural units in (a) anorthominasragrite, (b) bobjonesite. Legend as in Figure 3a.

network (Boghosian *et al.* 1995). There are seven reported compounds in the range ($1 \leq x < 3$) (Table 7), but none are of known structure as yet. Tachez & Théobald (1976) proposed that (1) for $x < 3$, the structures are based on $-S-O-V-$ chains and belong either to the α - $VO(SO_4)$ or to the β - $VO(SO_4)$ family of structures; (2) for $x \geq 3$, the structures contain fragmented units of $(V\phi_6)$ octahedra and (SO_4) tetrahedra that are linked by hydrogen bonds. For the $x < 3$ structures, if the V^{4+} is constrained to be in $[1 + 4 + 1]$ coordination, (H_2O) groups can occur as (1) a distant *trans* ligand bonded to a single V^{4+} , or (2) isolated (H_2O) groups. In Figure 13, we show the number of (H_2O) groups in the formula

unit as a function of the calculated density for the vanadium sulfate hydrates in Table 7. There are two well-established trends. For $x < 3$, there is a rapid decrease in calculated density with increasing number of (H_2O) groups, as compared to the ($x \geq 3$) compounds. This behavior is consistent with simple insertion of (H_2O) groups between $-S-O-V-$ chains for ($x < 3$) compounds and with major structural rearrangement involving $(V\phi_6)$ octahedra, (SO_4) tetrahedra and (H_2O) groups for ($x \geq 3$) compounds. For the orthorhombic polymorph of $V^{4+}O(SO_4)(H_2O)_3$, Schneider *et al.* (1982) proposed a structural model based on sheets of corner-sharing $(V\phi_6)$ octahedra and (SO_4) tetrahedra, somewhat resem-

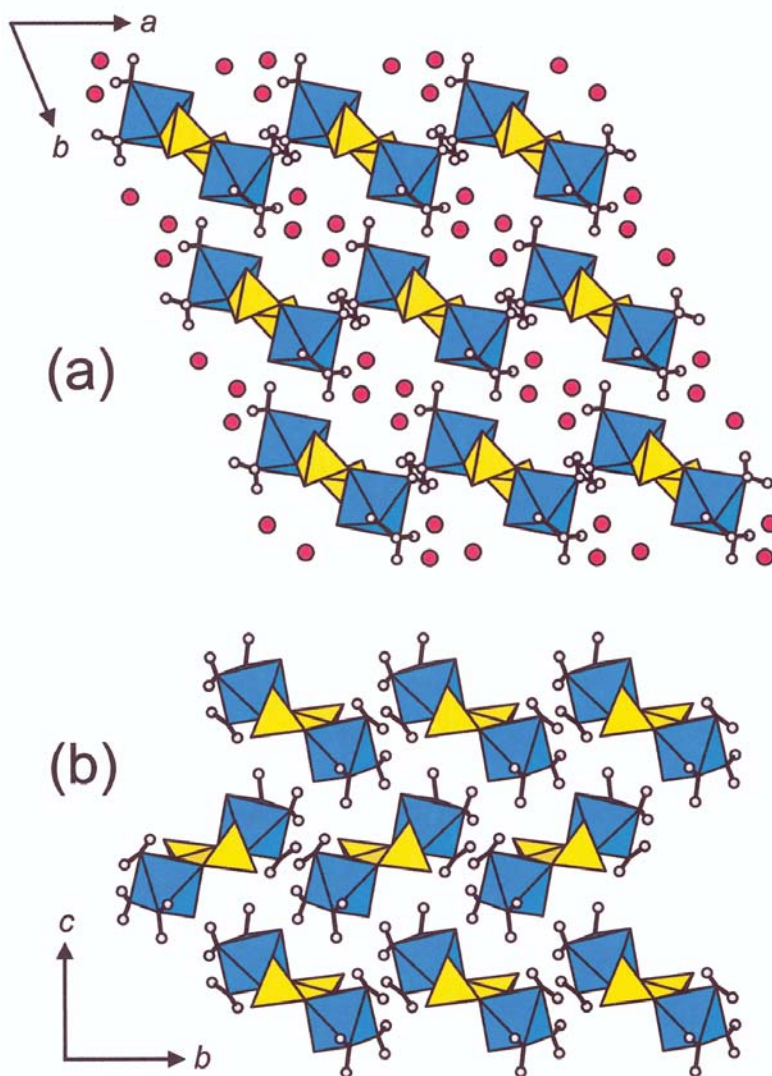


FIG. 11. The crystal structures of (a) anorthominasragrite and (b) bobjonesite; legend as in Figure 3a. In anorthominasragrite, the isolated (H₂O) groups are shown as red circles.

bling the structure of α -VO(SO₄), with interstitial (H₂O) groups. Moreover, they noted that the measured H₂O content varies among samples, from $x = 2.4$ to $x = 3.5$. In Figure 13, we have plotted the data (open circles) of Schneider *et al.* (1982) for $x = 2.4, 3.0, 3.5$ and their reported cell parameters. It is interesting that for $x = 3$, the data fall within the ($x \geq 3$) field, very near the position for the monoclinic polymorph of V⁴⁺ O (SO₄) (H₂O)₃. This suggests the following question: Is it structurally feasible to order three interlayer (H₂O) groups between sheets of corner-sharing (V ϕ_6) octahedra and

(SO₄) tetrahedra and produce a density analogous to that of the fundamentally different monoclinic polymorph?

ACKNOWLEDGEMENTS

We thank John M. Hughes and an anonymous referee for their comments on this paper. This work was supported by the Natural Sciences and Engineering Research Council of Canada in the form of a Canada Research Chair and Discovery, Equipment, Major Installation and Major Facilities Access Grants to FCH.

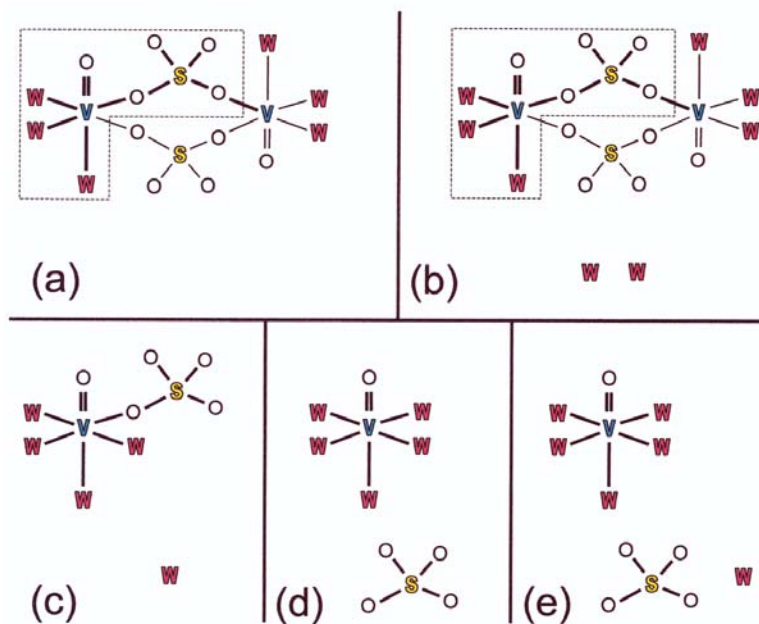


FIG. 12. A sketch of the different polyhedron-connectivities in the structures of the vanadium sulfate hydrates, $V^{4+} O (SO_4) (H_2O)_x$, $3 \leq x \leq 6$: (a) bobjonesite, (b) anorthominasragrite, (c) minasragrite, (d) orthominasragrite, (e) stanleyite. The V^{4+} , S, O and (H_2O) groups are indicated by the letters V, S, O and W, respectively.

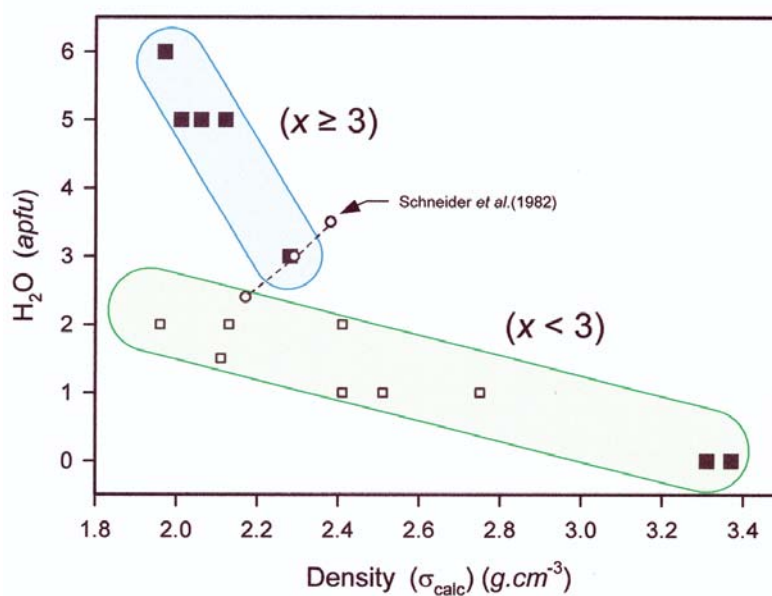


FIG. 13. The variation in (H_2O) content (x) as a function of density in the $V^{4+} O (SO_4) (H_2O)_x$ structures; the blue shading encompasses structures with $x \geq 3$, and the green shading encompasses structures with $x < 3$. Black squares: known structures; hollow squares: unknown structures; hollow circles: orthorhombic polymorph of $V^{4+} O (SO_4) (H_2O)_3$ (Schneider *et al.* 1982).

REFERENCES

- BALLHAUSEN, C.J., DJURINSKII, B.F. & WATSON, K.J. (1968): The polarized absorption spectra of three crystalline polymorphs of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$. *J. Am. Chem. Soc.* **90**, 3305-3309.
- BOGHOSIAN, S., ERIKSEN, K.M., FEHRMANN, R. & NIELSEN, K. (1995): Synthesis, crystal structure redetermination and vibrational spectra of β - VOSO_4 . *Acta Chem. Scand.* **49**, 703-708.
- BOULOUX, J.C. & GALY, J. (1973): Structure cristalline de l'hypovanadate CaV_4O_9 . *Acta Crystallogr.* **B29**, 1335-1338.
- _____, MILOSEVIC, I. & GALY, J. (1976): Les hypovanadates de magnésium MgVO_3 et MgV_2O_5 . Structure cristalline de MgVO_3 . *J. Solid State Chem.* **16**, 393-398.
- 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.
- FEHRMANN, R., BOGHOSIAN, S., PAPTAEODOROU, G.N., NIELSEN, K., BERG, R.W. & BJERRUM, N.J. (1989): Crystal structure and infrared and Raman spectra of $\text{K}_4(\text{VO})_3(\text{SO}_4)_5$. *Inorg. Chem.* **28**, 1847-1853.
- HADDAD, A., JOUINI, T. & PIFFARD, Y. (1992): Preparation and crystal structure of NaVOAsO_4 . *Eur. J. Solid State Inorg. Chem.* **29**, 57-63.
- HAWTHORNE, F.C. & 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.
- _____, SCHINDLER, M., GRICE, J.D. & HAYNES, P. (2001): Orthominasragrite, $\text{V}^{4+}\text{O}(\text{SO}_4)(\text{H}_2\text{O})_5$, a new mineral species from Temple Mountain, Emery County, Utah, U.S.A. *Can. Mineral.* **39**, 1325-1331.
- IBERS, J.A. & HAMILTON, W.C., eds. (1992): *International Tables for X-ray Crystallography* IV. Kynoch Press, Birmingham, U.K.
- JOHNSON, J.W., JOHNSTON, D.C., KING, H.E., JR., HALBERT, T.R., BRODY, J.F. & GOSHORN, D.P. (1988): Structure and magnetic properties of $\text{V}_2(\text{VO})(\text{P}_2\text{O}_7)_2$. A mixed-valence vanadium (III,III,IV) pyrophosphate. *Inorg. Chem.* **27**, 1646-1648.
- LADWIG, G. (1969): Zur Bildung und Natur des α - VOSO_4 und seines 1-Hydrates, α - $\text{VOSO}_4 \cdot \text{H}_2\text{O}$. *Z. Anorg. Allg. Chem.* **364**, 225-240.
- LII, K.H., CHUEH, B.R., KANG, H.Y. & WANG, S.L. (1992): Synthesis and crystal structure of $\text{Ca}(\text{VO})_2(\text{PO}_4)_2$. *J. Solid State Chem.* **99**, 72-77.
- _____, & TSAI, H.J. (1991): Synthesis and crystal structure of $\text{Zn}_2\text{VO}(\text{PO}_4)_2$, a vanadyl (IV) orthophosphate containing a dimer of edge-sharing ZnO_5 square pyramids. *J. Solid State Chem.* **90**, 291-295.
- LONGO, J.M. & ARNOTT, R.J. (1970): Structure and magnetic properties of VOSO_4 . *J. Solid State Chem.* **1**, 394-398.
- ONODA, M. & NISHIGUCHI, N. (1996): Crystal structure and spin gap state of CaV_2O_5 . *J. Solid State Chem.* **127**, 359-362.
- POUCHOU, J.L. & PICOIR, F. (1984): A new model for quantitative analysis. I. Application to the analysis of homogeneous samples. *La Recherche Aérop.* **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).
- RICE, C.E., ROBINSON, W.R. & TOFIELD, B.C. (1976): Crystal structure of a condensed phosphatosilicate, oxovanadium (IV) diphosphatomonosilicate, $\text{VO}(\text{SiP}_2\text{O}_8)$. *Inorg. Chem.* **15**, 345-348.
- 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. Mater.* **12**, 1248-1259.
- _____, _____, HUMINICKI, D.M.C., HAYNES, P., GRICE, J.D. & EVANS, H.T., JR. (2003): Bobjonesite, $\text{V}^{4+}\text{O}(\text{SO}_4)(\text{H}_2\text{O})_3$, a new mineral species from Temple Mountain, Emery County, Utah, U.S.A. *Can. Mineral.* **41**, 83-90.
- SCHNEIDER, R., GÜNTHER, J.R., & OSWALD, H.R. (1982): Thermal dehydration and structural models of two new vanadyl sulfate hydrates. *J. Solid State Chem.* **45**, 112-118.
- SMITH, M.L. & MARINENKO, J. (1973): A reexamination of minasragrite. *Am. Mineral.* **58**, 531-534.
- TACHEZ, M. & THÉOBALD, F. (1976): Contribution à l'étude des hydrates du sulfate de vanadyle. *Rev. Chim. Minérale* **13**, 530-539.
- _____, & _____ (1980a): Liaisons hydrogène dans les cristaux de sulfate de vanadyle trihydraté ($\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$). Comparaison structurale de quatre sulfates de vanadyle hydratés. *Acta Crystallogr.* **B36**, 2873-2880.
- _____, & _____ (1980b): Structure du sulfate de vanadyle pentahydraté $\text{VO}(\text{H}_2\text{O})_5\text{SO}_4 \beta$ (variété orthorhombique). *Acta Crystallogr.* **B36**, 1757-1761.
- _____, & _____ (1980c): Structure du sulfate de vanadyle hexahydraté. *Acta Crystallogr.* **B36**, 249-254.
- _____, _____ & HEWAT, A.W. (1982a): Localization of hydrogen atoms by neutron profile refinement of

- vanadyl sulfate trihydrate, $\text{VOSO}_4 \cdot 3\text{D}_2\text{O}$. *Acta Crystallogr.* **B38**, 1807-1809.
- _____, _____ & LEHMANN, M.S. (1982b): Étude de la déshydratation in situ de $\text{VOSO}_4 \cdot 5\text{D}_2\text{O}$ en tube scellé de silice par diffraction de neutrons. *C.R. Acad. Sci., Sér. II.* **294**, 709-711.
- _____, _____, WATSON, K.J. & MERCIER, R. (1979): Redétermination de la structure du sulfate de vanadyle pentahydraté $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$. *Acta Crystallogr.* **B35**, 1545-1550.
- TUDO, J. (1965): Vanadyl sulfate and its reduction by hydrogen sulfide: vanadium sulfides. *Rev. Chim. Minérale* **2**, 53-117.
- _____ & LAPLACE, G. (1977): Mise en évidence d'une troisième forme du sulfate de vanadyle $\gamma\text{-VOSO}_4$. *C.R. Acad. Sci. Paris, Sér. C* **284**, 675-677.
- ZACHARIASEN, W.H. (1978): Bond lengths in oxygen and halogen compounds of *d* and *f* elements. *J. Less-Common Met.* **62**, 1-7.

Received January 15, 2003, revised manuscript accepted July 21, 2003.

