

A Reexamination of Minasragrite¹

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Abstract

Minasragrite from type specimens from Cerro de Pasco, Peru, has been restudied in relation to current knowledge of vanadium sulfate compounds. New crystallographic, chemical and synthetic studies show that the mineral is identical with the stable form of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ described by Ballhausen, Djurinskij, and Watson (1968). The crystals are monoclinic, space groups $P2_1/a$, with $a = 12.947(2)\text{\AA}$, $b = 9.748(1)\text{\AA}$, $c = 7.005(1)\text{\AA}$, $\beta = 110.93(1)^\circ$. The specific gravity is (meas) 2.03(10), or (calc, assuming 4 formula units per unit cell) 2.036. The optics are biaxial negative with $n_\alpha = 1.513$, $n_\beta = 1.536$, $n_\gamma = 1.545$; pleochroism is in shades of blue with absorption $X > Y > Z$.

Crystallographic data are reported for the synthetic compound $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$, which is monoclinic, space group $P2_1/a$, with $a = 12.224(2)\text{\AA}$, $b = 7.416(1)\text{\AA}$, $c = 7.394(1)\text{\AA}$, $\beta = 108.85(1)^\circ$, and cell contents of 4 formula units.

Introduction

Minasragrite, a blue vanadyl sulfate from Minasragra near Cerro de Pasco, Peru, was described briefly by Schaller in 1915 and in more detail in 1917. Minasragrite occurs in an efflorescence on patronite as minute crystals, spherulites, and granular masses. Schaller suggested the formula $(\text{V}_2\text{O}_2)\text{H}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$ based upon an analysis of the efflorescence, after subtracting the proportion of melanterite, morenosite, gypsum, and patronite necessary to combine with the FeO, NiO, CaO, and insoluble matter found in the analysis. Schaller reported approximate values for the indices of refraction. These were later refined by Larsen (1921, p. 110). Still later, Palache (1934) described the habit of the crystals.

Until now, although minasragrite has appeared to be a discrete mineral species, its chemical nature has not been clearly defined. In this paper, we show that the mineral corresponds uniquely to the well-known vanadyl sulfate pentahydrate, $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, as previously suggested by us (Lindberg, Marinenko, and Breger, 1966).

Optical Characterization

Reexamination of Schaller's type material, consisting of mixed efflorescent minerals on patronite, shows blue vanadyl sulfate crystals identifiable as minasragrite from their optical properties: biaxial

negative, $2V$ medium-large, $n_\alpha = 1.513(2)$, $n_\beta = 1.536(2)$, $n_\gamma = 1.545(2)$, $B = .032$. The pleochroism is in shades of blue, with absorption $X > Y > Z$. Schaller reported that minasragrite was biaxial negative, but he recorded indices of refraction which correspond to biaxial positive character: $n_\alpha = 1.515$, $n_\beta = 1.525$, $n_\gamma = 1.545$, $B = .030$. Our measurements are in fairly good agreement with those of Larsen (1921, p. 110): $n_\alpha = 1.518(3)$, $n_\beta = 1.530(3)$, $n_\gamma = 1.542(3)$, $B = .024$.

X-ray Diffraction Studies

Minasragrite is monoclinic with space group $P2_1/a$. X-ray powder diffraction data are given in Table 1. Identical powder patterns were obtained from discrete crystals and from fine-grained spherulitic masses, both obtained from the type specimen. The material X-rayed represents the color range pale aquamarine to vivid cobalt blue. Refinement of the unit cell parameters from the powder diffraction data by the least squares method of Evans *et al.* (1963) gives: $a = 12.947\text{\AA} \pm .002\text{\AA}$, $b = 9.748 \pm .001$, $c = 7.005 \pm .001$, $\beta = 110^\circ 56' \pm 1'$; volume = 825.7\AA^3 . These parameters are consistent with those reported previously from measurements of Weissenberg and Buerger precession patterns (Lindberg *et al.*, 1966).

Palache (1934) obtained the elements $a:b:c = 0.7196:1:0.6656$, $\beta = 110^\circ 57'$ by optical goniometry. This is in good agreement with the elements $c:b:a/2 = 0.7186:1:0.6641$, $\beta = 110^\circ 56' 1/2'$ transformed for comparison from the X-ray diffrac-

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TABLE 1. X-ray Powder Diffraction Data for Minasragrite, $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}^*$

hkl	d(calc)	d(obs)	I	I_s	hkl	d(calc)	d(obs)	I	I_s	d(obs)	I
110	7.589	7.607	12	w	402	2.786	2.764	2	a	2.152	3
001	6.543	6.551	8	w	131	2.733			mw	2.125	3
200	6.046	6.049	20	mw	022	2.716	2.715	8	m	2.106	3
111	5.618	5.615	4	mw	221	2.685			nd	2.086	2
201	5.534	5.530	4	mw	412	2.662	6.663	2	vw	2.073	2
011	5.432	5.431	60	m	322	2.646	2.645	2	nd	1.999	4
210	5.138	5.135	100	s	420	2.569	2.566	6	vw	1.988	4
020	4.874				331	2.561				1.974	12
211	4.812				321	2.547				1.956	2
120	4.523	4.514	4	vw	330	2.530				1.943	2
111	4.463	4.483	8	w	202	2.524	2.524	10	m	1.927	2
121	3.976	3.975	8	m	511	2.502				1.912	2
021	3.909	3.907	70	ms	122	2.496	2.497	4	mw	1.896	2
311	3.826	3.826	35	m	231	2.473				1.871	6
201	3.813				212	2.444	2.442	10	w	1.856	1
220	3.795	3.792	3	w	040	2.437				1.820	3
310	3.725	3.725	17	mw	401	2.433				1.809	3
221	3.658	3.658	24	ms	422	2.406				1.789	3
211	3.551	3.553	3	m	140	2.389	2.389	2	mw	1.767	2
121	3.506	3.509	17	m	132	2.377	2.377	2	ms	1.744	2
202	3.437	3.438	12	s	232	2.361	2.361	2	mw	1.731	2
112	3.284	3.284	6	mw	411	2.361				1.703	2
002	3.271				510	2.347				1.677	2
212	3.241				203	2.335				1.672	2
401	3.217	3.218	2	vw	512	2.328				1.642	6
321	3.164	3.163	4	nd	032	2.305	2.305	3	m	1.629	2
130	3.138	3.139	6	mw	141	2.297				1.609	2
320	3.106				521	2.287				1.596	2
012	3.101	3.103	2	mw	431	2.286				1.583	2
411	3.055	3.054	2	mw	041	2.284				1.557	2
400	3.023	3.022	14	ms	213	2.271	2.270	6	ms	1.536	2
221	3.003				332	2.262				1.497	3
312	2.997	2.996	14	m	240	2.260				1.460	3
131	2.938				222	2.241				1.370	2
031	2.910	2.911	6	ms	113	2.233	2.234	4	mw	1.352	3
410	2.887	2.888	2	w	313	2.230				1.295	3
230	2.862	2.860	2	w	241	2.230				1.253	4
311	2.857				430	2.213	2.213	2	w		
122	2.837	2.836	14	m	331	2.199	2.197	4	nd		
222	2.809	2.808	2	m	141	2.195					
112	2.786				003	2.180	2.183	1	mw		

*Sample from Minasragra, Cerro de Pasco, Peru.

Debye-Scherrer method, Al internal standard, radiation $\text{CrK}\alpha$, $\lambda=2.2909 \text{ \AA}$. Single crystal intensities (I_s) from precession and Weissenberg patterns; s=strong, m=medium, w=weak, v=very, a=absent, nd=not determined.

tion results. Transformations are: Smith to Palache, 001/010/ $\frac{1}{2}$ 00; Palache to Smith 002/010/100.

Reflections suggesting the possible presence of a partially dehydrated phase, $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$, were looked for but not observed either in patterns from the analysis sample or in patterns from other mineral grains in the efflorescence. We obtained a pattern for synthetic $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ that corresponds to that reported for synthetic $(\text{V}^{5+}\text{O})_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ by Hanawalt, Rinn, and Frevel (1938; A.S.T.M. powder data file no. 1-0323). Hanawalt's suggested formula for the vanadyl sulfate differs from Schaller's suggested formula for minasragrite $(\text{V}^{4+}\text{O})_2\text{H}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$ only in relation to the valence of vanadium, that is, one atom of oxygen. Our synthetic sample yields (in wt. percent) 39.4 percent VO_2 , 37.1 percent SO_3 , and 23.6 percent H_2O (J. Marinenko, analyst; V^{4+} determined titrimetrically with permanganate); theoretical wt. percent for $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ are 38.2 percent, 36.9 percent, and 24.9 percent, respectively. Synthetic $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ is monoclinic, space group $P2_1/a$. Unit cell dimensions obtained from Buerger precession patterns and refined by least squares analysis of the powder diffraction data are: $a = 12.224 \text{ \AA} \pm .002 \text{ \AA}$, $b =$

$7.416 \pm .001$, $c = 7.394 \pm .001$, $\beta = 108^\circ 51' \pm 1'$; volume = 634.3 \AA^3 ; $a:b:c = 1.6483:1:0.9970$. Our measured powder data are listed in Table 2.

Tudo (1965), in a general study of vanadyl(IV) sulfate hydrates, has reported data for $\text{VOSO}_4 \cdot n\text{H}_2\text{O}$ with $n = 1, 3, 4, 5$ and 6. (His unindexed powder data have been included in section 19 of the Powder Diffraction File of the Joint Committee on Powder Diffraction Standards as cards no. 1412, 1413, 1414, 1415 and 1416). Tudo's data for $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ appear to correspond to ours, although his spacings are consistently smaller by about 0.8 percent. His data for $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ do not at all correspond to ours.

Ballhausen, Djurinskij, and Watson (1968), in a spectroscopic study of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, have found and characterized three polymorphs of this hydrate. They give unit cell data as follows (estimated errors in parentheses):

Form:	Stable	Unstable I	Unstable II
Space group:	$P2_1/c$	$Pm\bar{m}n$ or $Pm2_1n$	$Pm\bar{m}m$ or $Pmn2_1$
$a, \text{ \AA}$	6.99(3)	16.12(7)	7.23
$b, \text{ \AA}$	9.73(3)	21.12(10)	9.33
$c, \text{ \AA}$	12.98(4)	12.22(5)	6.18
β	110.9 (3)		
Z	4	20	2

Clearly (when the a and c axes are interchanged), their "Stable Form" corresponds to minasragrite.

TABLE 2. X-ray Powder Diffraction Data for Synthetic $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}^*$

hkl	d(calc)	d(obs)	I	hkl	d(calc)	d(obs)	I	d(obs)	I
001	6.998	7.006	12	400	2.892	2.892	6	2.180	10
110	6.243	2.241	50	112	2.848	2.847	3	2.040	9
		6.112	2	411	2.815	2.815	21	0.027	2
200	5.784	5.780	70	311	2.776			1.979	4
201	5.396	3.399	25	321	2.707			1.940	2
111	5.123	5.108	2	402	2.698	2.699	12	1.926	7
011	5.089			410	2.694			1.917	12
210	4.561	4.563	100	221	2.682			1.898	6
211	4.363	4.363	70	320	2.673	2.670	6	1.877	3
111	4.301			202	2.640	2.638	12	1.766	2
201	3.884	3.887	12	122	2.618	2.619	6	1.749	3
020	3.708	3.709	18	222	2.562	2.572	9	1.719	5
		3.650	2	022	2.545			1.701	3
202	3.543			412	2.535			1.677	3
120	3.531	3.532	4	212	2.487	2.487	18	1.653	7
002	3.499			203	2.456	2.455		1.639	4
311	3.494	3.497	42	130	2.417			1.573	4
211	3.441			401	2.412	2.417	9	1.559	7
310	3.421	3.426	6	322	2.399			1.542	4
112	3.308			122	2.371	2.371	9	1.508	4
121	3.285	3.286	36	421	2.352			1.449	6
021	3.276			131	2.334			1.392	3
212	3.197	3.198	6	003	2.333			1.381	4
012	3.164	3.166	12	213	2.331	2.330	18	1.347	6
220	3.122			031	2.331			1.308	3
221	3.056	3.058	18	321	2.329				
401	3.042			113	2.322				
121	3.034	3.032	9	511	2.322				

*Debye-Scherrer method, Al internal standard, radiation $\text{CrK}\alpha$, $\lambda=2.2909 \text{ \AA}$.

These authors have also carried out a full crystal structure analysis of this phase, which will be discussed below. We have made no attempt to reconcile the powder data reported by Tudo (1965) for $VOSO_4 \cdot 5H_2O$ with the other polymorphs reported by Ballhausen *et al* (1968).

Chemistry

A new sample of minasragrite was hand-picked from the type material for chemical, spectrographic, and thermal analyses. The various minerals of the efflorescence were first separated at the grain boundaries by means of ultrasonic vibrations, using carbon tetrachloride as a dispersing medium. It is estimated that our sample is 99 percent minasragrite, 0.6 percent patronite (water-insoluble vanadium sulfide), 0.2 percent potash alum, and 0.1 percent each of gypsum and melanterite. The microspectrographic analysis of this sample by C. L. Waring showed a major vanadium content, approximately 0.1 percent K, and 0.01 percent each of Na, Ca, Al, and Fe.

The microchemical analysis, including the specific gravity determination, was accomplished on a 45 mg sample. Classical volumetric and gravimetric methods were applied for all chemical determinations. The specific gravity was determined using carbon tetrachloride as the displacement liquid in a specially constructed micropycnometer.

The chemical analysis of the new sample is compared with Schaller's previous analysis in Table 3. Schaller's sample "necessarily contained all the minerals of the efflorescence, which were separated from the patronite by cold water" (Schaller, 1917). Total sulfate in Schaller's sample was distributed among minasragrite, melanterite, morenosite, and gypsum; total water was calculated by difference. The sulfate of any mineral present in the efflorescence but not accounted for in the distribution of sulfate between phases would be allotted to the sulfate in the minasragrite fraction; the cations combined with such a sulfate would be included in the H_2O by difference. Octahedra of potash alum occur in the efflorescence. It is suggested (see Table 3) that excess sulfate in Schaller's minasragrite fraction be allotted to potash alum, and that the K_2O and Al_2O_3 necessary to form potash alum be subtracted from the water by difference. In the proposed recalculation of Schaller's analysis, water by difference is low, since 5.75 percent water is required to maintain the ratios $V_2O_4 : SO_3 : H_2O = 1 : 2 : 10$.

A thermogravimetric analysis of minasragrite was

TABLE 3. Chemical Analyses and Calculations

A. Minasragrite, hand-picked sample						
Component	Calc. comp., ¹	Analyses, ²		Atomic Ratios ³		
	wt. perc.	wt. perc.				
V_2O_5		3.0		V	4.01	
V_2O_4	32.77	29.8		S	4.08	
SO_3	31.63	32.0		H	39.14	
H_2O	35.60	34.5		O	40.00	
Ins. in H_2O		0.6				
Total	100.00	99.9				
Spec. grav.	2.036	2.03±0.10				
B. Minasragrite plus admixed sulfates (Schaller, 1917)						
Component	Analysis ⁴	Minasragrite ⁵	Melanterite	Morenosite	Gypsum	Insoluble
V_2O_4	5.29	5.29				
FeO	0.97		0.97			
NiO	1.92			1.92		
CaO	0.46					0.46
SO_3	10.92	7.12	.08	2.06		0.66
Ins. in H_2O	66.16					66.16
H_2O by diff.	14.28	9.06	1.68	3.24	0.30	
Total	100.00 =	21.47	+ 3.73	+ 7.22	+ 1.42	+ 66.16
C. Suggested recalculation of minasragrite fraction of Schaller sample						
Component	Analysis	Potash alum ⁶	Minasragrite ⁷			
V_2O_4	5.29		5.29			
SO_3	7.12		2.01		5.11	
" H_2O by diff."	9.06	K_2O	0.59			
		Al_2O_3	0.64			
		H_2O	2.71		5.12	
Total	21.47 =		5.95		+15.52	

Notes: 1. Calculated composition for $VOSO_4 \cdot 5H_2O = V_2O_4 \cdot 2SO_3 \cdot 10H_2O$.

2. J. Marinenko, analyst.

3. Ratios calculated to total oxygen = 40. V_2O_5 assumed to represent $V_2O_4 + H_2O$ as a result of oxydation during sample preparation.

4. Analysis by W. T. Schaller.

5. Ratios calculated by Schaller, $V_2O_4 : SO_3 : H_2O = 1.02 : 2.86 : 16.17$.

6. Excess $SO_3 > 1/2 V_2O_4 : SO_3 = 1 : 1$ calculated to potash alum; K_2O , Al_2O_3 ,

H_2O to form potash alum deducted from " H_2O by diff".

7. $V_2O_4 : SO_3 : H_2O = 1 : 2 : 9.26$. Entire error of dividing SO_3 and H_2O among minasragrite, melanterite, morenosite, gypsum, and potash alum is allotted to the " H_2O by diff." in minasragrite.

made by F. O. Simon of the U.S. Geological Survey. His conclusions are: "Minasragrite starts to lose water at 70°C.² The loss appears to be complete at 150°C although this is masked to some extent by an inflection in the curve (150° – 250°C) which is presumed to correspond to the oxidation of V^{4+} to V^{5+} . The onset of the loss of SO_3 is also masked by the oxidation of vanadium, but it appears to begin at 250°C and is complete at 600°C. There is no loss in weight from 600° to 920° (maximum temperature attained). The final weight corresponds to what would be expected for a residue of V_2O_5 ."

Discussion

We first suggested the formula $V(OH)_2SO_4 \cdot 4H_2O$ as an alternate formula to $VOSO_4 \cdot 5H_2O$ (Lindberg, Marinenko, and Breger, 1966) to show

² During hand-picking, the temperature of 70°C may have been occasionally exceeded in the heat of the microscope lamp. Some grains liberated water, becoming sticky, first dissolving in the ambient film of water, then solidifying. The sample was then discarded and hand-picking was resumed on a new sample.

that some of hydrogens were involved in bonding. In 1968, Ballhausen, Djurinskij, and Watson described the polarized absorption spectra of three polymorphs of $\text{VO}(\text{H}_2\text{O})_4\text{SO}_4 \cdot 5\text{H}_2\text{O}$ of which their "stable phase," $\text{VO}(\text{H}_2\text{O})_4\text{SO}_4 \cdot \text{H}_2\text{O}$, is identifiable from their unit cell data as a synthetic minasragrite. Previously a crystal structure had been proposed for $\text{VO}(\text{H}_2\text{O})_4 \cdot 5\text{H}_2\text{O}$ by Palma-Vittorelli *et al* (1956), but the distances from the free water molecule to the coordinated water molecules in their structure are too short to be plausible: $\text{H}_2\text{O}(2) - \text{H}_2\text{O}(5) = 1.57\text{\AA}$ and $\text{H}_2\text{O}(4) - \text{H}_2\text{O}(5) = 2.38\text{\AA}$. Unfortunately, this structure determination cannot be accepted as reliable.

In their report of the pentahydrate polymorphs, Ballhausen, Djurinskij, and Watson (1968) briefly describe a complete structure analysis of the "stable phase." This study clearly shows the presence of SO_4 tetrahedra, a VO group forming one vertex of an octahedron containing one SO_4 and 4 H_2O ligands, and one uncoordinated H_2O molecule. The oxygen atoms of the VO and SO_4 groups, and of the $5\text{H}_2\text{O}$ molecules, are all further linked together by a complex network of hydrogen bonds.

In view of the correspondence of the crystallographic properties, the new chemical data, and the thorough characterization of the synthetic compound $\text{VO}(\text{H}_2\text{O})_4\text{SO}_4 \cdot \text{H}_2\text{O}$ by Ballhausen *et al*, we believe that the identity of minasragrite with this compound and its validity as a mineral species are now firmly established.

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References

- BALLHAUSEN, C. J., B. F. DJURINSKIJ, AND K. J. WATSON (1968) The polarized absorption spectra of three crystalline polymorphs of $\text{VO}(\text{H}_2\text{O})_4 \cdot 5\text{H}_2\text{O}$. *J. Amer. Chem. Soc.* **90**, 3305-3309.
- EVANS, H. T., JR., D. E. APPLEMAN, AND D. S. HANDWERKER (1963) The least squares refinement of crystal unit cells with powder diffraction data by an automatic computer indexing method. *Amer. Crystallogr. Ass. Meet., Cambridge, Mass., Prog. Abstr.*, p. 42.
- HANAWALT, J. D., H. W. RINN, AND L. K. FREVEL (1938) Chemical analysis by X-ray diffraction. *Indus. Eng. Chem., Anal. Ed.*, **10**, 457-512.
- LARSEN, E. S., JR. (1921) The microscopic determination of the nonopaque minerals. *U.S. Geol. Surv. Bull.* **679**, p. 155.
- LINDBERG, M. L., JOHN MARINENKO, AND I. A. BREGER (1966) Mineralogy of minasragrite. In, Geological Survey Research, 1966, *U.S. Geol. Surv. Prof. Pap.* **550A**, A150.
- PALACHE, CHARLES (1934) Contributions to crystallography: claudetite, minasragrite, sampsonite, native selenium, indium. *Amer. Mineral.* **19**, 194-205.
- PALMA-VITTORELLI, M. B., M. U. PALMA, D. PALUMBO, AND F. SGARLATA (1956) Evidence for a double covalent bond from paramagnetic resonance, optical absorption, and X-ray data. *Nuovo Cimento*, **3**, 718-930.
- SCHALLER, WALDEMAR T. (1915) Four new minerals. *J. Washington Acad. Sci.* **5**, 7.
- (1917) Minasragrite, a hydrous sulfate of vanadium. *J. Washington Acad. Sci.* **7**, 501-503.
- TUDO, JOSEPH (1965) Sur l'étude du sulfate de vanadyle et de sa réduction par l'hydrogène sulfuré: les sulfures de vanadium. *Rev. Chim. Minerals*, **2**, 53-117.

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