

## REVISION OF THE FORMULAE OF WERNERBAURITE AND SCHINDLERITE: AMMONIUM- RATHER THAN HYDRONIUM-BEARING DECAVANADATE MINERALS

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### ABSTRACT

Wernerbaurite (IMA 2012–064) and schindlerite (IMA 2012–063) from the St. Jude mine, Slick Rock district, San Miguel County, Colorado, USA, were described as hydronium-bearing decavanadate minerals with the formulae  $\{[\text{Ca}(\text{H}_2\text{O})_7]_2(\text{H}_2\text{O})_2(\text{H}_3\text{O})_2\}\{\text{V}_{10}\text{O}_{28}\}$  and  $\{[\text{Na}_2(\text{H}_2\text{O})_{10}](\text{H}_3\text{O})_4\}\{\text{V}_{10}\text{O}_{28}\}$ , respectively. Because these phases correspond to known synthetic phases with these formulae, the presence of  $\text{NH}_4$  in these minerals was not considered. Recent investigations of a similar phase discovered at a vanadium locality in the Fergana Valley of Kyrgyzstan showed it to contain  $\text{NH}_4$ , leading us to reanalyze the original electron-microprobe mounts of wernerbaurite and schindlerite, specifically seeking N; those analyses confirmed the presence of sufficient  $\text{NH}_4$  to replace the originally assigned  $\text{H}_3\text{O}$ . With the additional H sites included and O replaced by N at the  $\text{NH}_4$  sites, the structure refinement residual improved for wernerbaurite from  $R_1 = 3.41\%$  to  $R_1 = 3.26\%$  and for schindlerite from  $R_1 = 3.99\%$  to  $R_1 = 3.70\%$ . The newly assigned  $\text{NH}_4$  sites exhibited normal  $\text{NH}_4\text{-O}$  bond distances and coordination and reasonable bond-valence sums. The  $\text{H}_3\text{O}$  synthetic equivalents of both phases had been reported, as well as the  $\text{NH}_4$  synthetic equivalent of schindlerite. Subsequent to the publication of the original description of the minerals, the  $\text{NH}_4$  equivalent of wernerbaurite has also been reported.

*Keywords:* wernerbaurite, schindlerite, formula revision.

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## INTRODUCTION

The mines of the Slick Rock district have revealed numerous secondary vanadium minerals that result from oxidation of vanadium ore bodies that are exposed to near-surface conditions in the mining process; many of these new species contain the decavanadate anionic complex,  $(V_{10}O_{28})^{6-}$ , found in the pascoite family of minerals (Kampf *et al.* 2014). Two of these decavanadate-bearing minerals from the St. Jude mine, Slick Rock district, San Miguel County, Colorado, USA, wernerbaurite (IMA 2012–064) and schindlerite (IMA 2012–063), were described by Kampf *et al.* (2013) as hydronium-bearing decavanadate minerals with the formulae  $\{[Ca(H_2O)_7]_2(H_2O)_2(H_3O)_2\}\{V_{10}O_{28}\}$  and  $\{[Na_2(H_2O)_{10}](H_3O)_4\}\{V_{10}O_{28}\}$ , respectively. Because these phases correspond to synthetic hydronium-bearing compounds with the same formulae (Strukan *et al.* 1999, Zhang *et al.* 1985), the presence of  $NH_4$  in these minerals was not considered.

Recent investigations of a similar phase discovered in a black schist olistolite at the Hodza-Rushnai-Mazar vanadium mineral locality in the Fergana Valley of Kyrgyzstan (Karpenko *et al.* 2009, Karpenko 2010, Cooper *et al.* 2014) showed it to contain  $NH_4$ , leading the current authors to reanalyze the original electron-microprobe mounts of wernerbaurite and schindlerite, specifically seeking N to test for the presence of  $NH_4$ . The available Kyrgyzstan material does not yet provide sufficient material suitable for wet chemistry analysis, but crystallographic studies show it has a similar unit cell to wernerbaurite but with a smaller volume [930.77 Å<sup>3</sup> for the Kyrgyzstan material *versus* 963.55(12) Å<sup>3</sup> in wernerbaurite] and a provisional formula with two fewer water molecules than found in wernerbaurite  $[(NH_4)_2Ca_2[V_{10}O_{28}] \cdot 14H_2O$  in the Kyrgyzstan phase *versus*  $(NH_4)_2Ca_2[V_{10}O_{28}] \cdot 16H_2O$  for wernerbaurite, written in parallel format]. Infrared spectra obtained from the Kyrgyzstan mineral (sample

–KBr-microtablet) show molecular water (1625 cm<sup>-1</sup>) and a decavanadate cluster (957, 836, 819, 741, 595, 524 cm<sup>-1</sup>) in the presence of the ammonium group (1402 cm<sup>-1</sup>). In addition, since the original submission of the paper on wernerbaurite and schindlerite, the synthetic analog of wernerbaurite, containing  $NH_4$ , has been synthesized (Du *et al.* 2015).

## METHODS

*Chemical Analysis*

Kampf *et al.* (2013) described the analysis of specimens of wernerbaurite and schindlerite. Specimens in those original microprobe mounts were re-analyzed for N; analytical conditions were 15 KeV accelerating voltage, 10 nA beam current, and a 10 μm beam diameter. Nitrogen was analyzed with a 60 Å W/Si multilayer pseudocrystal (Cameca PC-1) that provides sufficient peak intensities and suppresses spectral interferences by higher order X-ray lines of heavier elements such as Al  $K\alpha(IV)$ . The sample and N standard (synthetic AlN) were carbon-coated at the same time to ensure an equivalent thickness of the carbon layer. Nitrogen was counted for 40 s on peak; background was measured for 20 s on each side of the peak. X-ray intensities for N  $K\alpha$  and Na  $K\alpha$  were monitored during each spot analysis. There was no systematic change in N count rate with time, but there was a small but observable decline in Na intensity that was measured and to which a “time zero” correction was applied using Probe for EPMA software. Raw X-ray intensities were corrected for matrix effects with a  $\phi(\rho z)$  algorithm (Pouchou & Pichoir 1991). Table 1 reports the original electron microprobe analyses of wernerbaurite (12 from three crystals) and schindlerite (21 from nine crystals) along with new analyses for  $(NH_4)_2O$  (11 for wernerbaurite and three for schindlerite).

TABLE 1. CHEMICAL ANALYSES OF WERNERBAURITE AND SCHINDLERITE

Const.	wernerbaurite					schindlerite					Standard
	wt.%	Range	S.D.	Norm.	Ideal	wt.%	Range	S.D.	Norm.	Ideal	
$(NH_4)_2O$	2.16	0.98–3.45	0.89			4.27	4.13–4.49	0.19			AlN
$(NH_4)_2O^*$				3.70	3.82				7.57	8.29	
$K_2O$	0.10	0.05–0.13	0.03	0.09		1.37	1.19–1.69	0.14	1.31		sanidine
$Na_2O$	0.37	0.13–0.91	0.25	0.33		4.08	3.47–4.87	0.36	3.90	4.94	albite
CaO	8.76	8.16–9.25	0.32	7.73	8.24	0.08	0.02–0.19	0.04	0.08		diopside
SrO	0.16	0.04–0.30	0.07	0.14		0.10	0.00–0.16	0.10	0.10		Sr titanate
$V_2O_5$	75.76	74.25–77.72	1.09	66.81	66.78	75.80	73.16–81.60	2.32	72.44	72.42	Y vanadate
$H_2O^*$				21.21	21.17				14.61	14.35	
Total				100	100				100	100	

\* Based on the structure.

TABLE 2. NH<sub>4</sub>-O BOND DISTANCES (Å) AND VALENCES (*vu*) FOR WERNERBAURITE AND SCHINDLERITE

wernerbaurite			schindlerite					
NH <sub>4</sub> -O10	2.787(3)	0.22	NH <sub>4</sub> 1-O9	2.855(3)	0.18	NH <sub>4</sub> 2-O13	2.901(3)	0.16
NH <sub>4</sub> -O2	2.900(3)	0.16	NH <sub>4</sub> 1-O12	2.917(3)	0.15	NH <sub>4</sub> 2-O14	2.939(3)	0.15
NH <sub>4</sub> -O13	2.940(3)	0.15	NH <sub>4</sub> 1-O2	2.935(3)	0.15	NH <sub>4</sub> 2-OW5	3.000(4)	0.12
NH <sub>4</sub> -OW2	3.035(3)	0.11	NH <sub>4</sub> 1-O5	3.014(3)	0.12	NH <sub>4</sub> 2-O7	3.085(4)	0.10
NH <sub>4</sub> -O4	3.161(3)	0.08	NH <sub>4</sub> 1-O4	3.028(3)	0.11	NH <sub>4</sub> 2-O10	3.088(4)	0.10
NH <sub>4</sub> -OW5	3.167(4)	0.08	NH <sub>4</sub> 1-OW2	3.055(4)	0.11	NH <sub>4</sub> 2-O8	3.159(4)	0.08
NH <sub>4</sub> -O10	3.179(3)	0.08	NH <sub>4</sub> 1-OW4	3.063(4)	0.10	NH <sub>4</sub> 2-O11	3.214(4)	0.07
<NH <sub>4</sub> -O>	3.024	Σ <sub>v</sub> 0.88	NH <sub>4</sub> 1-OW1	3.094(4)	0.10			
			<NH <sub>4</sub> 1-O>	2.995	Σ <sub>v</sub> 1.02	<NH <sub>4</sub> 2-O>	3.055	Σ <sub>v</sub> 0.78

### Crystal structure

The original X-ray intensity data obtained under experimental conditions described by Kampf *et al.* (2013) were used to refine the wernerbaurite and schindlerite atomic arrangements with NH<sub>4</sub> replacing H<sub>3</sub>O. The details of the data collection and conditions of refinement are reported in that work. Table 2 reports NH<sub>4</sub>-O bond lengths for wernerbaurite and schindlerite. The final atomic positions, atomic-displacement parameters, and observed and calculated structure factors have been deposited as cif files for the two phases.

## RESULTS

### Chemical Analysis

The average of three new analyses of Na<sub>2</sub>O in schindlerite (3.82% ± 0.14) agrees with the value originally reported in Kampf *et al.* (2013) of 4.08% ± 0.33. There was a large variation in (NH<sub>4</sub>)<sub>2</sub>O for wernerbaurite, which is generally inversely related to Na<sub>2</sub>O (11 new analyses = 0.83% ± 0.67, slightly higher than measured originally but within the analytical range). The (NH<sub>4</sub>)<sub>2</sub>O values for both minerals were about half of what is predicted by the structure determination. The nature of the structure suggests that NH<sub>4</sub><sup>+</sup> is weakly bonded and may be easily lost, along with H<sub>2</sub>O, under vacuum either initially during carbon coating of the sample or introduction into the microprobe chamber. Consequently, for the empirical formula, the (NH<sub>4</sub>)<sub>2</sub>O and H<sub>2</sub>O contents were calculated by stoichiometry based upon the structure, with K<sup>+</sup> sharing the NH<sub>4</sub><sup>+</sup> sites in each structure. The high analytical total after addition of calculated (NH<sub>4</sub>)<sub>2</sub>O and H<sub>2</sub>O is attributed to the loss of these constituents under vacuum. Consequently, normalized analytical values are provided in the table. We acknowledge the possibility that some H<sub>3</sub>O<sup>+</sup> may substitute for NH<sub>4</sub><sup>+</sup> in the structures of wernerbaurite and schindlerite, which could be partly responsible for

the much lower than ideal (NH<sub>4</sub>)<sub>2</sub>O values obtained by EPMA; however, given the amounts of (NH<sub>4</sub>)<sub>2</sub>O obtained by EPMA, the likelihood of significant NH<sub>4</sub><sup>+</sup> loss under vacuum, our success in locating four H sites surrounding the N sites in the structures, and the improved refinements obtained with the additional H sites included and N rather than O at the NH<sub>4</sub> sites (see below), it is clear that NH<sub>4</sub><sup>+</sup> must be significantly dominant over any H<sub>3</sub>O<sup>+</sup> in these structures.

For wernerbaurite, the empirical formula (based on V<sup>5+</sup> = 10 and O = 44) is {(NH<sub>4</sub>)<sub>1.93</sub>K<sub>0.03</sub>Sr<sub>0.02</sub>Σ<sub>1.98</sub>(Ca<sub>1.88</sub>Na<sub>0.14</sub>)Σ<sub>2.02</sub>(H<sub>2</sub>O)<sub>16</sub>}{V<sub>10</sub>O<sub>28</sub>}. The simplified (ideal) formula of wernerbaurite is {(NH<sub>4</sub>)<sub>2</sub>[Ca<sub>2</sub>(H<sub>2</sub>O)<sub>14</sub>](H<sub>2</sub>O)<sub>2</sub>}{V<sub>10</sub>O<sub>28</sub>}. For schindlerite, the empirical formula (based on V<sup>5+</sup> = 10 and O = 38) is: {(NH<sub>4</sub>)<sub>3.65</sub>K<sub>0.35</sub>Σ<sub>4.00</sub>(Na<sub>1.58</sub>Ca<sub>0.02</sub>Sr<sub>0.01</sub>H<sub>0.36</sub>)Σ<sub>2.00</sub>(H<sub>2</sub>O)<sub>10.00</sub>}{V<sub>10</sub>O<sub>28</sub>}. Note that this formula includes 0.36 H<sup>+</sup> added for charge balance; however, the structure refinement is consistent with full occupancy by Na. It is possible that some Na was lost under vacuum along with NH<sub>4</sub> and H<sub>2</sub>O. The simplified (ideal) formula of schindlerite is {(NH<sub>4</sub>)<sub>4</sub>Na<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub>}{V<sub>10</sub>O<sub>28</sub>}.

Considering the likely loss of some NH<sub>4</sub> under vacuum (see below), we confirmed the presence of sufficient NH<sub>4</sub> to replace the originally assigned H<sub>3</sub>O. It is also worth pointing out that the presence of organic matter, which provided a reducing environment for the original deposition of U and V oxides in the deposit, is the likely source of the NH<sub>4</sub> in these secondary phases.

### Crystal structure

In light of the revised chemical formulae of wernerbaurite and schindlerite, we also reexamined the difference-Fourier maps from the structure refinements of both and were able to locate the additional H sites associated with the NH<sub>4</sub> groups. With the additional H sites included and O replaced by N at the NH<sub>4</sub> sites, the residual for the structure refinement improved for wernerbaurite from R<sub>1</sub> = 3.41% (for 3440

$F_o > 4\sigma F$  reflections) to  $R_1 = 3.26\%$  (for 3434  $F_o > 4\sigma F$  reflections) and for schindlerite from  $R_1 = 3.99\%$  (for 2888  $F_o > 4\sigma F$  reflections) to  $R_1 = 3.70\%$  (for 2890  $F_o > 4\sigma F$  reflections). Furthermore, as is seen in Table 2, the newly assigned  $\text{NH}_4$  sites exhibit normal  $\text{NH}_4\text{-O}$  bond distances and coordination and reasonable bond-valence sums. For wernerbaurite, all atom sites refined to full occupancy by their ideal constituents, giving the structural formula  $\{(\text{NH}_4)_2[\text{Ca}_2(\text{H}_2\text{O})_{14}(\text{H}_2\text{O})_2]\{\text{V}_{10}\text{O}_{28}\}$ . For schindlerite, one of the two  $\text{NH}_4$  sites was refined with joint occupancy by 0.83 N and 0.17 K, and all other sites refined to full occupancy by their ideal constituents, providing the structural formula  $\{[(\text{NH}_4)_{3.66}\text{K}_{0.34}]\Sigma_4\text{Na}_2(\text{H}_2\text{O})_{10}\}\{\text{V}_{10}\text{O}_{28}\}$ . The amount of substitution of K for  $\text{NH}_4$  provided by the structure refinement is almost exactly what is indicated by the chemical analysis.

Whereas only the  $\text{H}_3\text{O}$  analogue of wernerbaurite had been reported as a synthetic phase (Strukan *et al.* 1999) at the time of the original mineral descriptions, since that submission the synthetic phase  $\{(\text{NH}_4)_2[\text{Ca}_2(\text{H}_2\text{O})_{14}(\text{H}_2\text{O})_2]\{\text{V}_{10}\text{O}_{28}\}$  has been prepared and described, including the crystal structure (Du *et al.* 2015). Its structure is almost identical with that of wernerbaurite as now refined, as expected from natural and synthetic analogues.

Both  $\text{H}_3\text{O}$  and  $\text{NH}_4$  synthetic equivalents of schindlerite have been reported, the latter by Fratzky *et al.* (2000).

#### ACKNOWLEDGMENTS

This study was funded, in part, by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County and by grant NSF-MRI 1039436 from the National Science Foundation to JMH. Jim Fisher, General Mine Superintendent, Denison Mines, allowed us to obtain specimens for study. The authors are grateful for the reviews of Henrik Friis, Mark Welch, and Jakub Plášil.

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Received July 17, 2015. Revised manuscript accepted January 12, 2016.