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VERNADSKITE DISCREDITED: PSEUDOMORPHS OF ANTLERITE AFTER DOLEROPHANITE*

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ABSTRACT

Vernadskite crystals from Vesuvius, Italy, are shown to be pseudomorphs of antlerite, $Cu_3(SO_4)(OH)_4$, after dolerophanite. Experimental work indicates that these pseudomorphs were formed by the action of moisture from fumaroles on crystals of dolerophanite.

Indexed *x*-ray powder data are given for synthetic and natural dolerophanite and antlerite.

INTRODUCTION

During a mineralogical investigation of specimens recently obtained from the walls and ceiling of the abandoned Ecton mine in Pennsylvania, several unidentified copper sulfate minerals were observed. In order to attempt to identify them, *x*-ray powder diffraction patterns were taken of a number of rare copper sulfate minerals. Among these was a pattern of vernadskite (originally spelled vernadskijte and vernadskyte by Zambonini, 1910) obtained from crystals from the only known specimen in the United States. This micromount-sized specimen from Vesuvius, Italy, was the gift of Zambonini to the late Colonel Washington A. Roebling. It was accompanied by the original label on which Zambonini had written, "part of the original lot." The minerals associated with the vernadskite crystals on this tiny specimen were found to be dolerophanite, anglesite, and conichalcite.

Vernadskite was described by Zambonini as a basic hydrated sulfate of undetermined crystal system. It was found as an alteration product of dolerophanite which had formed during the eruption of Vesuvius in October, 1868. The mineral was said to occur there as aggregates of pale-green birefringent crystals in close association with dolerophanite. The hardness of vernadskite was reported to be $3\frac{1}{2}$; the specific gravity, >3.3. The formula given for vernadskite, $4CuO \cdot 3SO_3 \cdot 5H_2O$ ($=Cu_4(SO_4)_3(OH)_2 \cdot 4H_2O$), was derived by Zambonini from the following chemical analysis made by Serra (in per cent): CuO 49.15, SO_3 37.01, H_2O [13.84], total [100.00]. Zambonini suggested that vernadskite was produced by the action of acid vapors from the fumaroles on dolerophanite, with the following reaction taking place:

dolerophanite — vernadskite

$$2Cu_2(SO_4)O + H_2SO_4 + 4H_2O \rightarrow 3CuSO_4 \cdot Cu(OH)_2 \cdot 4H_2O$$

* Publication authorized by the Director, U. S. Geological Survey.

Vernadskite Discredited (=Antlerite)

Sample preparation of "vernadskite" crystals for an x-ray powder diffraction pattern revealed the presence of included remnants of a light-brown, glassy mineral, thus necessitating very careful handpicking of the material for the powder spindle. The x-ray powder pattern obtained from the carefully selected fragments of "vernadskite" was that of antlerite, $Cu_3(SO_4)(OH)_4$; from the minute, light-brown, glassy inclusions, that of dolerophanite.

Closer re-examination of the "vernadskite" crystals on the specimen indicated that they are pseudomorphs of antlerite after dolerophanite. Several crystals were found that were partly dolerophanite and partly antlerite, where the change to antlerite was incomplete.

Experiments then were performed to show that dolerophanite may be converted to antlerite by the reaction of moisture with dolerophanite. Crystals of dolerophanite from Vesuvius, Italy (USNM R8317), averaging 1.00 mm. by 0.50 mm. by 0.25 mm. in size, changed to antlerite slowly and incompletely in distilled water at room temperature over a period of three days. They were completely converted when left immersed in distilled water in an oven at 80° C. for 12 hours, and also when placed in a dry vessel in the presence of a moist atmosphere in an oven at 80° C. for 24 hours. The results of these experiments were checked by means of x-ray powder patterns; in each case a pattern of antlerite was obtained. The experimental work indicates that the following reaction must have taken place near the fumaroles at Vesuvius to result in the formation of these pseudomorphs:

$$\underset{\text{dolerophanite}}{2Cu_2(SO_4)O} + 2H_2O \rightarrow \underset{\text{antlerite}}{Cu_3(SO_4)(OH)_4} + CuSO_4\ (\text{soluble})$$

Synthesis of Dolerophanite, Antlerite, and Hydrocyanite

Dolerophanite was synthesized so that sufficient material would be available for carrying on experimental work that would check the validity of the proposed reaction. Dolerophanite was easily synthesized (Binder, 1936) by placing finely-powdered $Cu(SO_4)\cdot 5H_2O$ in an open porcelain crucible in a muffle furnace for one hour at a temperature about 660° C. Synthetic dolerophanite produced in this manner is orange-brown. At a temperature about 640° C. synthetic hydrocyanite (chalcocyanite), $CuSO_4$ (Hey, 1955), was formed; it is pale greenish gray in color.

When distilled water, hot or cold, was added to the synthetic dolerophanite, the orange-brown powder immediately turned light green. The light-green residue gave the powder pattern of antlerite. The pale-blue filtrate was brought to dryness in an oven at 80° C.; the x-ray powder

TABLE 1. *X*-RAY POWDER DATA FOR DOLEROPHANITE, $Cu_2(SO_4)O$

MONOCLINIC, $C2/m$

$a=9.355\pm0.010$ Å, $b=6.312\pm0.005$, $c=7.628\pm0.005$, $\beta=122°17\tfrac{1}{2}'$[1]

Borchardt and Daniels (1957)[3]		Present Study[2]							
Synthetic $Cu_2(SO_4)O$		Synthetic $Cu_2(SO_4)O$ [f. 14347]		Vesuvius, Italy USNM R6084; [f. 14391]					
Measured		Measured		Measured		Calculated			
I	*d*	I	*d*	I	*d*	*d*	*hkl*		
78	6.46	50	6.451	50	6.443	6.447	001		
6	4.91	2	4.937	2	4.935	4.933	110		
25	4.75 band	13	4.755	11	4.760	4.757	$\bar{1}11$		
14	4.63	6	4.659	2	4.659	4.658	$\bar{2}01$		
4	4.02[4]	4	3.950	2	3.956	3.954	200		
100	3.63	100	3.617	100	3.623	3.619	$\bar{2}02$		
15	3.41	9	3.408	4	3.408	3.407	111		
						3.238	$\bar{1}12$		
8	3.29	4	3.220	2	3.228	3.224	002		
16	3.15	13	3.153	9	3.156	3.157	020		
21	2.83	8	2.840	8	2.835	2.835	021		
						2.796	022		
47	2.78	30	2.776	21	2.776	2.774	201		
8	2.67	3	2.680	2	2.678	2.677	$\bar{3}12$		
94	2.62	50	2.614	42	2.615	2.612	$\bar{2}21$		
34	2.54	25	2.546	18	2.546	2.543	$\bar{2}03$		
10	2.47[4]	4	2.468	4	2.468	2.466	220		
		1	2.431	1	2.432	2.432	310		
8	2.38[4]	4	2.381	4	2.377	2.379	$\bar{2}22$		
		4	2.365			2.362	112		
6	2.32[4]	4	2.324	2	2.331	2.328	$\bar{4}02$		
						2.266	$\bar{1}13$		
						2.258	$\bar{4}01$		
52	2.25	35	2.254	30	2.256	2.255	022		
						2.254	$\bar{3}13$		
5	2.14	4	2.151	2	2.151	2.149	003		
						2.137	$\bar{3}11$		
						2.128	$\bar{4}03$		
		1	2.087	1	2.087	2.084	221		
26	2.02	18	2.028	13	2.028	2.033	130		
						2.024	202		
						2.020	$\bar{1}31$		
10	1.97	9	1.979	4	1.979				
4	1.86	2	1.870	1	1.868				
7	1.82	4	1.821	3	1.819				
23	1.76	13B	1.769	13	1.767				
5	1.70	3	1.709	1	1.704				

[1] Single-crystal data obtained in this study from a crystal of dolerophanite from Vesuvius, Italy (USNM R6060).

[2] Films corrected for expansion B=broad. Camera diameter, 114.59 mm. Nickel-filtered copper radiation ($\lambda=1.5418$ Å). Lower limit of 2θ measurable: approximately 7° (12.6 Å).

[3] Camera diameter, 114.59 mm. Nickel-filtered copper radiation. The relative intensities listed are the ratios of peak heights obtained on a diffractometer trace. The designated bands appeared as a broad line in the *x*-ray photograph but were resolved in a diffractometer trace.

[4] These lines correspond to intense lines in the $CuSO_4$ or CuO *x*-ray pattern and were thought to be due to the presence of these materials as impurities.

TABLE 1 (*continued*)

Borchardt and Daniels (1957)[3]		Present Study[2]					
Synthetic $Cu_2(SO_4)O$		Synthetic $Cu_2(SO_4)O$ [f. 14347]		Vesuvius, Italy USNM R6084; [f. 14391]			
Measured		Measured		Measured		Calculated	
I	*d*	I	*d*	I	*d*	*d*	*hkl*
15	1.67	13	1.678	6	1.678		
4	1.64	2	1.648	6	1.642		
7	1.62 }						
11	1.61 } band	8	1.616	4	1.615		
14	1.60 }	6	1.600	4	1.600		
16	1.58	9	1.579	6	1.579		
		5	1.574	3	1.573		
5	1.55	2	1.556	1	1.556		
5	1.53	3	1.535	2	1.534		
4	1.51	3	1.510	2	1.512		
9	1.48 } band	4	1.480	2	1.482		
15	1.47 }	8	1.469	4	1.469		
7	1.45	2	1.450	2	1.448		
		3	1.430				
8	1.41	4	1.407	3B	1.407		
17	1.39	8	1.389	6	1.387		
		2	1.374	3	1.374		
		2	1.366	1	1.366		
		2	1.343	3	1.342		
		2	1.321	2	1.321		
		2	1.304	2	1.305		
		2	1.293	2	1.292		
		1	1.277	1	1.278		
		2	1.248	2	1.245		
		2	1.233	2	1.232		
		< 1	1.219	< 1	1.217		
		< 1	1.203				
		1	1.188	< 1	1.188		
		1	1.176	1	1.178		
		3	1.166	3	1.166		
				1	1.136		
		4B	1.129	3	1.128		
		2	1.116	1	1.116		
		1	1.106	1	1.106		
		2	1.095	2	1.094		
		2	1.080	2	1.079		
		1	1.062	1B	1.065		
		1	1.052	1	1.052		
		1	1.041	1	1.041		
				1	1.029		
		1B	1.026	1	1.025		
		3B	1.013	2B	1.013		
		2B	1.000	2B	1.001		
		Plus additional weak lines all with I<1.					

data for this dried salt was identical with those given in the ASTM card file for the compound $Cu(SO_4) \cdot H_2O$. When the dried salt was subjected to a temperature of 100° C. for 24 hours, the *x*-ray powder pattern remained unchanged. When the temperature was raised to 150° C. and the

TABLE 2. X-RAY POWDER DATA FOR ANTLERITE, $Cu_3(SO_4)(OH)_4$
ORTHORHOMBIC, *Pnam*
$a=8.24$ Å, $b=11.99$, $c=6.03$[1]

de Wolff (1955)[2]		Present Study[3]							
Synthetic $Cu_3(SO_4)(OH)_4$		Synthetic $Cu_3(SO_4)(OH)_4$ [f. 14347]		"Vernadskite" = Antlerite Vesuvius, Italy USNM R6084; [f. 14353]		Antlerite Chuquicamata, Chile USNM C5472; [f. 15077]			
Measured		Measured		Measured		Measured		Calculated	
I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	d_{hkl}	*hkl*
11	6.80	11	6.792	11	6.795	11	6.792	6.789	110
26	6.01	30	6.021	30	6.018	35	6.026	6.030	001
								5.995	020
23	5.40	21	5.405	18	5.406	15	5.405	5.385	011
100	4.86	100	4.858	100	4.855	100	4.853	4.847	120
9	4.52	6	4.517	6	4.519	6	4.515	4.509	111
8	4.13	11	4.125	9	4.127	11	4.122	4.120	200
								3.897	210
16	3.79	13	3.785	13	3.783	15	3.788	3.778	121
77	3.60	71	3.597	71	3.604	71	3.597	3.596	130
31	3.40	25	3.401	25	3.401	25	3.403	3.403	201
								3.396	220
9	3.34	7	3.339	6	3.339	6	3.333	3.331	031
								3.272	211
16	3.09	13	3.084	13	3.089	15	3.089	3.089	131
								3.015	002
18	3.00	21	2.998	21	3.003	21	3.003	2.998	040
								2.959	221
								2.869	230
		3	2.819	3	2.827	3	2.823	2.817	140
12	2.762	9	2.765	9	2.763	9	2.763	2.756	112
9	2.698	9	2.698					2.694	022
77	2.683	60	2.683	71	2.683	71	2.683	2.677	310
								2.591	231
85	2.566	71	2.564	71	2.564	71	2.567	2.560	122
								2.552	141
26	2.503	21	2.501	21	2.502	21	2.502	2.497	320

[1] X-ray crystallographic data obtained by Richmond (Palache, 1939) by the Weissenberg method on a crystal from Remolinos, Vallenar, Chile. Original kX values have been converted to Ångstrom units by the present author.

[2] Camera diameter, 114.6 mm. Copper radiation ($\lambda=1.5418$ Å). Intensities determined by photometer (Guinier camera).

[3] Films corrected for expansion. B = broad. Nickel-filtered copper radiation ($\lambda=1.5418$ Å). Lower limit of 2θ measurable: approximately 7° (12.6 Å).

TABLE 2 (*continued*)

de Wolff (1955)[2]		Present Study[3]							
Synthetic $Cu_3(SO_4)(OH)_4$		Synthetic $Cu_3(SO_4)(OH)_4$ [f. 14347]		"Vernadskite" =Antlerite Vesuvius, Italy USNM R6084; [f. 14353]		Antlerite Chuquicamata, Chile USNM C5472; [f. 15077]			
Measured		Measured		Measured		Measured		Calculated	
I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	d_{hkl}	*hkl*
								2.447	331
6	2.439							2.439	202
13	2.430	9	2.433	11	2.430	9	2.428	2.423	240
4	2.398	2	2.395	3	2.392	2	2.392	2.384	212
7	2.315							2.311	132
4	2.307	7	2.307	7	2.307	9	2.307	2.307	321
								2.303	150
13	2.259	9	2.259	9	2.259	11	2.259	2.255	222
								2.249	241
								2.229	051
								2.224	330
								2.151	151
69	2.131	50	2.129	50	2.127	60	2.127	2.126	042
								2.119	331
6	2.083	3	2.083	3	2.080	2	2.083	2.079	232
								2.073	250
18	2.065	9	2.062	9	2.065	11	2.062	2.060	400
								2.058	142
20	2.034	21	2.034	15	2.034	15	2.034	2.030	410
								2.025	340
								2.010	003
4B	2.004	6	2.006	6	2.004	6	2.002	2.002	312
2	1.951								
9	1.946	13	1.947	11	1.946	13	1.945		
7	1.927	3	1.926	4	1.925	3	1.929		
3	1.893	3	1.892	3	1.893	3	1.892		
12	1.835	9	1.834	11	1.833	8	1.833		
15	1.814	11	1.818	13	1.814	9	1.813		
2	1.801								
1	1.758	2	1.760	1	1.761	2	1.762		
6	1.711	3	1.712	3	1.711	2	1.712		
9	1.687	5	1.684	3	1.687	4	1.687		
3	1.667	2	1.669	2	1.668	2	1.669		
16	1.634	15	1.634	15	1.634	18	1.634		
6	1.617	4	1.618	4	1.617	4	1.618		
2	1.599	2	1.596	2	1.595	2	1.593		
13	1.566	11	1.566	13	1.567	9	1.568		

TABLE 2 (*continued*)

de Wolff (1955)[2] Synthetic $Cu_3(SO_4)(OH)_4$		Present Study[3] Synthetic $Cu_3(SO_4)(OH)_4$ [f. 14347]		"Vernadskite" = Antlerite Vesuvius, Italy USNM R6084; [f. 14353]		Antlerite Chuquicamata, Chile USNM C5472; [f. 15077]			
Measured		Measured		Measured		Measured		Calculated	
I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	d_{hkl}	hkl
15	1.551	15	1.557	13	1.554	13	1.551		
4	1.525	3	1.527	3	1.526	3	1.526		
12	1.511	9	1.512	7	1.512	6	1.513		
9	1.500	9	1.499	9	1.499	9	1.499		
21	1.481	21	1.482	15	1.483	18	1.483		
2	1.467	2	1.469	2	1.464	2	1.469		
2	1.455	2	1.455	3	1.455	3	1.454		
9	1.438	6	1.438	5	1.436	6	1.438		
1	1.426								
4	1.390	4	1.392	4	1.390	4	1.391		
1	1.365	2	1.363	2	1.364	3	1.361		
3	1.360								
7	1.316	7	1.318	6	1.317	8	1.318		
1	1.281	2	1.281	2	1.280	2	1.282		
3	1.277	3	1.277	4	1.277	4	1.277		
		1	1.251	1	1.254	1	1.253		
		1	1.236	1	1.237	1	1.237		
		1	1.224	1	1.224	1	1.224		
		2	1.215	2	1.214	2B	1.213		
		2	1.200	2B	1.200	2B	1.199		
		2	1.170	2B	1.168	2B	1.170		
		1	1.152	1	1.153	1B	1.154		
		1	1.130	1	1.131	1B	1.131		
		5	1.107	5	1.107	6	1.107		
		2	1.082	1	1.083	1	1.083		
		3	1.073	2	1.074	2	1.073		
		3	1.065	3	1.065	2	1.065		
		3	1.060	2	1.060	2	1.060		
		2	1.051	2	1.051	2	1.050		
		3	1.026	3	1.028	2B	1.027		
		3	1.012	2	1.011	2B	1.012		
		2	0.9995	2	0.9993	3B	0.9991		
		2	0.9878	1	0.9880	1	0.9878		
		2	0.9813			2	0.9810		
		4	0.9723	3	0.9723	3	0.9723		
		Plus additional weak lines all with $I<3$.							

dried salt was held at this temperature for 24 hours, a pattern of $CuSO_4$, synthetic hydrocyanite, was obtained.

X-Ray Data for Dolerophanite and Antlerite

All the *x*-ray powder films made in connection with this study were taken with Cu/Ni radiation ($\lambda = 1.5418$ Å) in Debye-Scherrer powder cameras (114.59 mm. diameter) using the Straumanis and Wilson techniques. Measurements made on the patterns of dolerophanite and antlerite necessitated correction for expansion. Intensities were estimated visually by direct comparison with calibrated intensity film strips of successive step line-exposures related to each other by a factor of $\sqrt{2}$. Interplanar spacings listed in the tables were calculated down to values of $d_{hkl} \geq 2.000$ Å.

A single-crystal *x*-ray study of dolerophanite from Vesuvius, Italy (USNM R6060), was made with a quartz-calibrated Buerger precession camera using Mo/Zr radiation ($\lambda = 0.7107$ Å). Film measurements were corrected for both vertical and horizontal shrinkage. The cell constants derived from single-crystal *x*-ray examination are given in Table 1; these data are in excellent agreement with those cited by Richmond and Wolfe (1940) for Vesuvius material.

No indexed *x*-ray powder data have previously been published for dolerophanite. Table 1 presents observed and calculated interplanar spacings obtained in this study for synthetic and natural dolerophanite. These are compared with the data given by Borchardt and Daniels (1957) for the compound $Cu_2(SO_4)O$ and were found to be in good agreement.

Indexed *x*-ray powder data for synthetic and natural antlerites are given in Table 2, which lists observed and calculated interplanar spacings, the latter down to $d_{hkl} = 2.002$ Å. These were found to be in excellent agreement with the data obtained by de Wolff (1955) for synthetic antlerite.

Acknowledgments

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