SHORTER COMMUNICATIONS

THE *X*-RAY DIFFRACTION POWDER PATTERN OF VANADINITE

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An attempt (Berry, 1959) to index the observed *x*-ray diffraction powder data for vanadinite, $Pb_5(VO_4)_3Cl$, recorded on A.S.T.M. Card No. 2-0708, by means of the unit cell data of Trotter & Barnes (1958), showed unsatisfactory agreement between obviously comparable values of *d*(obs.) and *d*(calc.). Because the powder and single-crystal data had been obtained with the use of specimens from different localities, the possibility arose of measurable variations in unit cell dimensions depending, for example, on differences in composition such as the V:As ratio. For this reason powder photographs were taken of eight specimens from five localities as follows:

(1) Apache mine, near Globe, Arizona; deep orange-red crystal,
(2) Same, but from different area of host rock,
(3) Mammoth mine, Tiger, Arizona; orange crystal,
(4) Same locality; yellow crystal,
(5) Eisenkappel, Carinthia, Austria; several small, amber to pale orange, crystals,
(6) Old Yuma mine, Tucson, Arizona; orange crystal,
(7) Abenab mine, Southwest Africa; yellow fragment from outer edge of large crystal,
(8) Same but orange-red fragment from centre of same large crystal.
(Specimens 6, 7, and 8 were kindly supplied by Dr. L. G. Berry.)

In each case the specimen was ground in a mortar, and then taken up in a capillary tube (Corning special glass 0707) of 0.30 mm. outer diameter, 0.08 mm. wall thickness, by suction (Matthews, 1954; Barnes, 1954) to ensure cylindrical samples of equal and uniform cross-section. The diffraction patterns were recorded in a camera of 114.59 mm. diameter, with Straumanis film mounting, and Cu$K\alpha$ (λ = 1.5418 Å) radiation. In each case the same set of fifteen lines (selected on the basis of maximum ease of measurement) was measured, with a device equipped with a vernier reading to 0.05 mm., from -2θ to $+2\theta$ (across the hole in the transmission area of the film), by two individuals each of whom measured each film twice with a sufficient interval of time between measurements of a given film to avoid bias. Film shrinkage corrections, although very small, were applied in all cases. The differences among the four values of 2θ observed for each line were not statistically significant. The means for each specimen, with their estimated standard deviations

(σ), are listed in Table 1; for any given line no individual value exceeds about 2σ. Thus, within the accuracy of measurement of the films, no significant differences were found for the 2θ values of the powder reflections from vanadinite specimens from widely separated localities and of various shades of colour from yellow to deep orange-red.

TABLE 1. VALUES OF 2θ (°) FOR 15 SELECTED LINES IN THE POWDER PATTERNS OF 8 SPECIMENS (UNDILUTED) OF VANADINITE

	I	II	III	IV	V	VI	VII	VIII	mean	σ
1	19.99	19.94	20.03	20.07	20.02	20.06	19.96	20.04	20.01	.04
2	21.19	21.15	21.12	21.19	21.13	21.17	21.09	21.16	21.15	.03
3	26.45	26.43	26.46	26.44	26.45	26.49	26.41	26.49	26.45	.02
4	29.24	29.22	29.19	29.23	29.18	29.27	29.17	29.23	29.22	.03
5	30.04	29.99	30.00	30.01	30.00	30.05	29.98	30.03	30.01	.02
6	42.91	42.92	42.89	42.89	42.90	42.97	42.90	42.95	42.92	.03
7	44.18	44.16	44.18	44.15	44.17	44.24	44.22	44.23	44.19	.03
8	46.69	46.66	46.70	46.71	46.63	46.68	46.67	46.72	46.68	.03
9	47.70	47.68	47.74	47.72	47.67	47.74	47.74	47.74	47.72	.03
10	49.68	49.72	49.62	49.62	49.74	49.78	49.66	49.61	49.68	.06
11	57.27	57.26	57.29	57.30	57.28	57.42	57.32	57.32	57.31	.05
12	66.57	66.49	66.62	66.67	66.44	66.63	66.63	66.70	66.59	.08
13	67.90	67.83	67.92	67.93	67.82	67.92	67.93	67.98	67.90	.05
14	68.85	68.75	68.83	68.92	68.73	68.97	68.90	68.90	68.86	.08
15	73.30	73.39	73.41	73.50	73.30	73.38	73.47	73.48	73.40	.08

Although there was no reason to doubt the validity of the unit cell dimensions ($a = 10.331 \pm 0.001$ Å, $c = 7.343 \pm 0.001$ Å) reported by Trotter & Barnes (1958) from an application of the method of Farquhar & Lipson (1946) to measurements of back-reflection oscillation photographs, two crystals from the same specimen as that employed for the structure investigation (Apache mine, near Globe, Arizona) were examined on an XRD-5 spectrogoniometer equipped with a single crystal orienter (Furnas, 1957) and a scintillation counter; Cu radiation was employed for one crystal, and Mo radiation for the other. Both crystals were mounted with c along the ϕ-axis of the goniostat so that values of 2θ for the $h0.0$ reflections were obtained at $\chi = 0°$, and those for the $00.l$ reflections at $\chi = 90°$. Within the sphere of reflection of the radiation employed, and providing the reflection was not forbidden by the space group, was of adequate intensity, and there was clear resolution of α_1 and α_2, 2θ for α_1 and α_2 of all orders of h and $\bar{h}$ were determined with $\chi = 0°$, and $\phi = 0°$ and $180°$, respectively, while 2θ for α_1 and α_2 (and for β in the case of Cu) of all orders of l were determined with $\chi = 90°$ and $\phi = 0°, 90°, 180°$, and $270°$. The zero 2θ value was difficult to establish accurately because of relatively high background, and spurious broad peaks (presumably arising from assorted absorption effects) in the very small ($<11°$) 2θ region, but it was estimated to be not greater than 0.01° and hence no zero correction was applied to the observed values of 2θ for the reflections examined.

Each reflection was scanned by hand. The counts for a fixed number of seconds were recorded, with the counter stationary, at intervals of 0.01° in 2θ. They were plotted against 2θ and the peak position was taken as the mid-point of a horizontal line intersecting both sides of the profile where the slopes were approximately the same. The peak positions were recorded to 0.001° in 2θ. The following measurements were made with the first crystal and Cu radiation ($K\alpha_1 = 1.54050$ Å, $K\alpha_2 = 1.54434$ Å, $K\beta = 1.39217$ Å): 4 each of $K\beta$, $K\alpha_1$, $K\alpha_2$, for $00.l$ with $l = 4, 6, 8$ (odd orders forbidden by the space group), (maximum $2\theta \approx 114.6°$); 2 each ($h0.0$, $\bar{h}0.0$) of $K\alpha_1$ and $K\alpha_2$, for $h0.0$ with $h = 4$ to 10, inclusive, (with the exception of $\bar{7}0.0$ which was very weak), (maximum $2\theta \approx 119.5°$). The following measurements were made with the second crystal and Mo radiation ($K\alpha_1 = 0.70926$ Å, $K\alpha_2 = 0.71354$ Å): 4 of $K\alpha_1$ for 00.4, and 4 each of $K\alpha_1$ and $K\alpha_2$ for $00.l$ with $l = 6, 8, 10, 12, 16$, (maximum $2\theta \approx 102.1°$); from 2 to 10 each of $K\alpha_1$ and $K\alpha_2$ for $h0.0$ (including $\bar{h}0.0$) with $h = 8, 9, 10, 12, 14, 15, 22$ (maximum $2\theta \approx 121.5°$). All 2θ values of the peak positions were converted to d's and thence to corresponding values of the appropriate axial lengths, c or a. In the case of a calculated from the measurements obtained with Mo radiation, the means of the values obtained for each order of $h0.0$ were all in the range 10.325 Å to 10.326 Å, so that the final value of a was taken as the mean of all values for all orders observed, with the result, $a = 10.325_2$ Å with an estimated standard deviation of 0.001_7 Å. The absorption coefficient of vanadinite for Mo$K\alpha$ radiation is about 730 cm^{-1} and that for Cu$K\alpha$ radiation is about 1400 cm^{-1}, and the setting of both crystals was such that the effect of absorption would be expected to be most noticeable when $\chi = 90°$. Thus, although the 2θ values observed in the determination of a with Mo radiation were not affected significantly by absorption, each of the three other series of measurements showed a systematic increase (greatest in the two with Cu radiation) in the calculated values for the appropriate axial length with increasing values of 2θ. Plotting c (Mo radiation), and c and a (Cu radiation) against $\frac{1}{2}[(\cos^2\theta/\sin\theta) + (\cos^2\theta/\theta)]$ (see Azároff & Buerger, 1958, pp. 236–239, 321–323), in each case gave a straight line with satisfactorily low scatter of observed points. Extrapolation to $\frac{1}{2}[(\cos^2\theta/\sin\theta) + (\cos^2\theta/\theta)] = 0$ showed $c = 7.342_8$ Å (Cu) and 7.342_5 Å (Mo), and $a = 10.324_9$ Å (Mo); from the graphs the accuracy is estimated as probably better than ±0.001 Å in each case. Taking the means of both values for each axial length, therefore, $a = 10.325 \pm 0.001$ Å and $c = 7.343 \pm 0.001$ Å. The latter is in exact agreement with the results of Trotter & Barnes (1958), while the former is lower by 0.006 Å. The plots and extrapolations on which the original determinations were based have been re-examined and there appears to be no obvious reason for altering the earlier value of 10.331 ± 0.001 Å for *a*. It is concluded, therefore, that the discrepancy must arise from some small, undetected, systematic error in one of the determinations. It has, of course, no significant effect on the interatomic distances calculated for vanadinite (Trotter & Barnes, 1958).

Powdered vanadinite does not give an ideal diffraction pattern; resolution of $K\alpha_1$ and $K\alpha_2$ is poor, and the diffraction lines are neither as narrow nor as sharp as might be expected from the geometry of the collimator, camera, and specimen. In addition, the powder diffraction photographs of the undiluted mineral exhibit a number of miscellaneous absorption effects in the small 2θ region, the most prominent of which is a fairly sharp, broad, and intense halo with a peak position at $2\theta \approx 8.1°$, for cylindrical samples of 0.2 mm. diameter, and $2\theta \approx 8.7°$ for those of 0.7 mm. diameter, together with a band of medium intensity having a sharp cut-off at $2\theta \approx 11.8°$ in the case of the thinner specimens, and a broad halo with a peak position at $2\theta \approx 12.6°$ in the case of the thicker ones. These effects vanish when the specimens are highly diluted and their diameters are kept small. Two diluted samples (one from the Apache mine, Arizona, and one from Eisenkappel, Austria), in which absorption was negligible, gave powder patterns in different cameras which both contained two very-weak, sharply defined, arcs at $2\theta \approx 9.2°$ and 10.0°; these remain unaccounted for except that the latter could correspond to the 10.0 reflection.

The effect of absorption on the observed 2θ values was examined by diluting vanadinite powder with five to seven parts by volume of powdered gum tragacanth,[1] and taking up the mixtures in capillary tubes of 0.2 mm. diameter. The observed 2θ values for these samples were in excellent agreement with those calculated from the unit cell constants. On the other hand, the observed 2θ values for undiluted vanadinite powder in 0.2 mm. capillaries (Table 1) showed an increase of about 0.1° in the range $20° < 2\theta < 75°$, while the increase in the observed 2θ values for undiluted samples in 0.7 mm. capillaries was much greater and decreased systematically from about 0.8° to 0.4° over the same range, and, in addition, the relative intensities of the first few lines ($2\theta < 30°$) were greatly reduced, and intense scattered radiation darkened the back-reflection area of the film. Finally, values of 2θ calculated from the spacings and the wave-length recorded on A.S.T.M. Card No. 2-0708 (vanadinite) are of comparable magnitude with corresponding values

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[1] Flour and corn starch, sometimes suggested for this purpose, proved to be unsatisfactory because both contributed additional lines to the powder pattern of the vanadinite.

TABLE 2. X-RAY DIFFRACTION POWDER DATA FOR VANADINITE, $Pb_5(VO_4)_3Cl$, (indexed for $d > 1.490$ Å). Cu $K\alpha$ ($\lambda = 1.5418$ Å); Ni filter; camera dia. 114.59 mm.; Straumanis film mounting; camera cut-off approx. 15 Å; I/I_1 by eye estimation and comparison with intensity scale; d(calc. 1) from $a = 10.331$ Å, $c = 7.343$ Å, d(calc. 2) from $a = 10.325$ Å, $c = 7.343$ Å; asterisks indicate lines probably present but too weak for accurate measurement.

I/I_1	d (obs.)	d (calc. 1)	d (calc. 2)	$hk.l$
<1	*	8.947	8.942	10.0
<1	*	5.676	5.675	10.1
15	5.161	5.166	5.162	11.0
30	4.468	4.473	4.471	20.0
40	4.218	4.225	4.223	11.1
10	3.817	3.820	3.819	20.1
15	3.675	3.672	3.672	00.2
60	3.384	3.397	3.396	10.2
		3.382	3.380	21.0
85	3.068	3.072	3.070	21.1
100	2.988	2.992	2.992	11.2
		2.982	2.980	30.0
2	2.836	2.838	2.837	20.2
5	2.760	2.763	2.762	30.1
8	2.579	2.583	2.581	22.0
5	2.485	2.487	2.486	21.2
		2.481	2.480	31.0
2	2.435	2.436	2.435	22.1
2	2.351	2.361	2.361	10.3
		2.351	2.350	31.1
12	2.313	2.315	2.314	30.2
10	2.237	2.237	2.235	40.0
15	2.210	2.212	2.212	11.3
—	—	2.147	2.147	20.3
		2.140	2.138	40.1
35	2.111	2.112	2.112	22.2
30	2.054	2.056	2.055	31.2
		2.052	2.051	32.0
40	1.980	1.983	1.982	21.3
		1.977	1.976	32.1
30	1.950	1.952	1.951	41.0
35	1.910	1.910	1.909	40.2
<1	*	1.892	1.892	30.3
		1.887	1.886	41.1
20	1.837	1.836	1.836	00.4
5	1.789	1.798	1.798	10.4
		1.792	1.791	32.2
		1.789	1.788	50.0
—	—	1.776	1.776	22.3
3	1.737	1.742	1.742	31.3
		1.738	1.738	50.1
		1.730	1.730	11.4
10	1.723	1.724	1.723	41.2
		1.722	1.721	33.0
10	1.692	1.698	1.698	20.4
		1.691	1.690	42.0
10	1.675	1.676	1.675	33.1
1	1.647	1.651	1.651	40.3
		1.648	1.647	42.1
20	1.610	1.613	1.613	21.4
		1.608	1.608	50.2
		1.607	1.606	51.0
20B	1.566	1.573	1.572	32.3
		1.570	1.569	51.1
		1.563	1.563	30.4
		1.559	1.558	33.2
1	1.539	1.536	1.535	42.2
<1	*	1.526	1.526	41.3
1	1.494	1.496	1.496	22.4
		1.491	1.490	60.0
1B	1.466			
3	1.432			
2	1.420			
12	1.406			
6	1.380			
12	1.365			
7	1.346			
20	1.336			
6	1.291			
2	1.275			
1	1.257			
5	1.244			
5	1.237			
10	1.207			
10	1.193			
5	1.184			
4	1.129			
5	1.115			
3	1.106			
5	1.094			
6	1.077			
2	1.069			
6	1.056			
5	1.025			
1	1.006			
10	0.996			
2BB	0.943			
5B	0.930			
2BB	0.894			
1BB	0.883			
3BB	0.875			

(plus additional broad diffuse lines out to $2\theta \approx 155°$)

observed for the larger, highly absorbing, samples over the 2θ range examined but individual values differ erratically by about ±0.3°. It is apparent, therefore, that any specimen suspected of containing vanadinite should be heavily diluted with powdered gum tragacanth, or some other inert material which does not itself give rise to powder diffraction lines, before an *x*-ray diffraction powder photograph is taken for identification purposes.

Indexed *x*-ray diffraction powder data for vanadinite, when absorption is negligible, are presented in Table 2. Values of *d*(calc.) were calculated for both sets of unit cell data (Trotter & Barnes, 1958, and the present note) by an IBM 650 computer with a programme written by Dr. F. R. Ahmed.

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X-RAY METHOD FOR RAPID DETERMINATION OF SULFUR AND COBALT IN LOELLINGITE

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One of the common constituents in arsenide-type ores is a loellingite-safflorite [(Fe,Co)As_2] solid solution which often contains 1 or 2 per cent sulfur. In other occurrences, such as in pegmatites, the loellingite may be the pure iron end member, or more often contains some sulfur with