AN X-RAY DIFFRACTION STUDY OF SYNTHETIC MEMBERS OF THE PYROMORPHITE SERIES

W. E. BAKER, *Broken Hill Division, The University of New South Wales, Australia.*

ABSTRACT

Twenty-five compounds within the composition field covered by the pyromorphite series were prepared by simple hydrous synthesis at 60–80° C. X-ray powder diffraction examination was used to record compositional differences and to examine the solid solution characteristics of the series. Contrary to the views expressed in modern texts, complete solid solution between the end members was found to exist. Cell dimensions for the pure compound $Pb_5(PO_4)_3Cl$ were found to be $a = 9.987$ Å, $c = 7.330$ Å; for $Pb_5(AsO_4)_3Cl$ $a = 10.251$ Å, $c = 7.442$ Å and for $Pb_5(VO_4)_3Cl$ $a = 10.323$ Å, $c = 7.346$ Å.

INTRODUCTION

Although there is considerable literature on the pyromorphite series, which includes minerals varying in composition between the end members pyromorphite $Pb_5(PO_4)_3Cl$, mimetite $Pb_5(AsO_4)_3Cl$ and vanadinite $Pb_5(VO_4)_3Cl$, there is a number of features that require further study. Several texts (Palache *et al.*, 1951; Berry and Mason, 1959; Dennen, 1959) comment on solid solution characteristics of the series. There is reported to be complete solution between pyromorphite and mimetite but incomplete solution between vanadinite and the former two minerals. These views are apparently based upon analysis of minerals of the series, since there are no experimental data applicable to solid solution studies.

Many of the published x-ray data for members of the series are not supported by chemical analysis, and this limits their usefulness. Barnes (1962) noted a lack of agreement between single crystal and powder data for vanadinite. He examined a number of vanadinite specimens by the film method to see if the discrepancy could possibly be related to differences in composition, but found no significant variations in their diffraction patterns. In order to supplement data on solid solution in the series and to examine the variations of x-ray data with phosphate, arsenate and vanadate ion content, a number of compounds covering a wide range of compositions between the end members were synthesized.

EXPERIMENTAL PROCEDURES

Syntheses of compounds related to pyromorphite have a very long history and many of the early procedures are noted by Mellor (1936). More recently Jaffe (1951) has abstracted the literature referring to the synthesis of apatites which are closely related to pyromorphite. Fusion methods are predominant in these syntheses, and the wet methods do not simulate the natural formation particularly closely.

The method developed for the present study is extremely simple and has proved quite effective. A dilute (about 0.2% W/V) solution of sodium ortho-phosphate, arsenate or vanadate or mixtures of these salts was added dropwise through a microburette to a concentrated solution of lead chloride at 60-80° C. which was continuously stirred. Each synthesis required approximately 12 hours to complete during which time the initially precipitated lead ortho-salt reacts with the lead chloride to yield the required compound.

$$3Pb_3(XO_4)_2 + PbCl_2 \xrightarrow{\text{aq}} 2Pb_5(XO_4)_3Cl$$
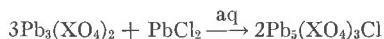
The method was used to produce 25 synthetics, the composition of which was controlled by the sodium ortho-salt solution made up from A.R. grade chemicals. To check that the syntheses were possible at lower temperatures, two of them (17 and 20) were duplicated at 30° C. At this lower temperature the reaction was given five days to run to completion. These compounds will be detailed later when their pertinent x-ray data are considered.

The pure end members were examined by x-ray diffraction over a 2θ range 15°–90° using a Philips PW1050 diffractometer unit with a copper target and a scanning rate of $\frac{1}{4}°$ per minute. Silicon powder was used as an internal standard. The observed spacings are compared with those

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR SYNTHETIC PYROMORPHITE

		Unit Cell Dimensions	$a = 9.987$ Å $c = 7.330$ Å			$a:c = 0.734$	
d_{obs}	I/I_1	hk.l	d_{calc}	d_{obs}	I/I_1	hk.l	d_{calc}
4.994	8	11.0	4.993	1.564	4	50.2	1.564
4.326	20	20.0	4.324	1.553	4	51.0	1.553
4.132	45	11.1	4.135	1.547	8	30.4	1.546
3.726	2	20.1	3.725	1.540	6	32.3	1.540
3.668	7	00.2	3.664	1.519	8	51.1	1.519
3.377	27	10.2	3.374	1.515	9	33.2	1.515
3.271	36	21.0	3.269	1.399	1	40.4	1.398
2.985	100	21.1	2.985	1.384	1	52.0	1.385
2.959	100	11.2	2.957	1.376	1	33.3	1.376
2.885	60	30.0	2.883	1.360	2	52.1, 42.3	1.361, 1.358
2.497	2	22.0	2.497	1.346	2	32.4	1.346
2.440	1	21.2	2.440	1.341	5	60.2	1.342
2.266	6	30.2	2.266	1.338	6	21.5	1.338
2.195	16	11.3	2.195	1.325	2	43.2	1.326
2.162	7	40.0	2.162	1.318	1	61.0	1.319
2.063	34	22.2	2.063	1.315	8	41.4	1.315
2.007	18	31.2	2.007	1.312	7	51.3	1.311
1.983	9	32.0	1.984	1.297	2	61.1	1.298
1.957	21	21.3	1.957	1.296	8	52.2	1.296
1.915	23	32.1	1.915	1.248	2	44.0	1.248
1.886	21	41.0	1.886	1.220	1	42.4	1.220
1.861	26	40.2	1.862	1.205	1	52.3	1.205
1.833	9	00.4	1.833	1.199	1	62.0	1.199
1.721	1	11.4	1.720	1.187	1	11.6	1.187
1.711	1	31.3	1.712	1.185	1	51.4	1.185
1.688	2	20.4	1.687	1.180	1	44.2, 32.5	1.182, 1.179
1.678	4	41.2	1.678	1.171	2	70.2, 53.2	1.171
1.633	8	42.0	1.634	1.145	1	21.6	1.144
1.623	5	33.1	1.623	1.098	1	22.6	1.097
1.599	6	21.4	1.598	1.089	1	63.0, 31.6	1.090, 1.089

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR SYNTHETIC MIMETITE

d_obs	I/I₁	hk.l	d_calc	d_obs	I/I₁	hk.l	d_calc
		Unit Cell Dimensions	$a = 10.251$ Å $c = 7.442$ Å			$a:c = 0.726$	
d_{obs}	I/I_1	hk.l	d_{calc}	d_{obs}	I/I_1	hk.l	d_{calc}
5.126	3	11.0	5.125	1.664	6	33.1	1.665
4.440	18	20.0	4.439	1.626	5	21.4	1.627
4.222	17	11.1	4.221	1.602	7	50.2	1.603
3.813	2	20.1	3.813	1.574	15	32.3, 30.4	1.574, 1.575
3.723	9	00.2	4.721	1.558	9	51.1	1.559
3.434	18	10.2	3.433	1.553	10	33.2	1.553
3.355	38	21.0	3.356	1.529	2	42.2	1.529
3.058	100	21.1	3.059	1.422	2	52.0	1.422
3.013	90	11.2	3.012	1.407	2	33.3	1.407
2.962	66	30.0	2.960	1.396	3	52.1	1.396
2.853	2	20.2	2.851	1.374	5	60.2, 32.4	1.375, 1.374
2.560	2	22.0	2.562	1.359	6	43.2	1.359
2.492	1	21.2	2.492	1.342	10	41.4, 51.3	1.342, 1.341
2.423	1	22.1	2.423	1.327	6	52.2	1.328
2.337	3	31.1	2.337	1.281	3	44.0	1.281
2.315	2	30.2	2.316	1.233	2	52.3	1.233
2.233	6	11.3	2.233	1.201	5	{ 32.5	{ 1.202
2.220	6	40.0	2.220			{ 53.2, 70.2	{ 1.200
2.110	30	22.2	2.111	1.176	2	71.0	1.176
2.053	10	31.2	2.053	1.109	1	31.6	1.108
2.037	5	32.0	2.037				
1.994	22	21.3	1.995				
1.964	18	32.1	1.965				
1.936	18	41.0	1.937				
1.905	20	40.2	1.907				
1.860	8	00.4	1.860				
1.786	2	32.2	1.787				
1.747	2	31.3, 11.4	1.748, 1.749				
1.718	4	41.2, 20.4	1.718, 1.719				
1.677	6	42.0	1.678				

calculated for the given unit cell data for synthetic pyromorphite, mimetite and vanadinite in Tables 1–3.

The approach to the solid solution study was made on the basis that it was as incomplete as the literature suggests. In producing the synthetics it was expected that when a selected composition fell outside the solid solution field, two or three components would crystallize. It was anticipated that this situation would show clearly in the x-ray diffraction records. None of the 25 compounds however yielded any sign of the presence of more than one component. To check that this result was not due to the inability of the diffraction method to differentiate between the small spacing differences involved, a possible two component mechanically mixed sample was examined. Figure 1 gives part of the diffraction patterns for a physical mixture of two compounds with phosphate to vanadate ratios of 3:2 and 2:3 and a single compound in which

TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR SYNTHETIC VANADINITE

		Unit Cell Dimensions	$a=10.323$ Å $c=7.346$ Å			$a:c=0.712$	
d_{obs}	I/I_1	hk.l	d_{calc}	d_{obs}	I/I_1	hl.l	d_{calc}
5.160	8	11.0	5.161	1.559	11	33.2	1.558
4.470	35	20.0	4.470	1.460	1	60.1	1.460
4.224	27	11.1	4.223	1.432	1	52.0	1.431
3.819	5	20.1	3.819	1.419	1	40.4	1.419
3.674	6	00.2	3.673	1.407	3	33.3	1.408
3.397	30	10.2	3.398	1.405	4	52.1	1.405
3.380	41	21.0	3.379	1.382	4	60.2	1.381
3.069	89	21.1	3.070	1.367	3	32.4	1.368
2.995	92	11.2	2.994	1.364	5	43.2	1.364
2.987	100	30.0	2.985	1.347	3	21.5	1.347
2.578	3	22.0	2.580	1.343	4	51.3	1.343
2.486	2	21.2	2.487	1.340	5	61.1	1.340
2.314	4	30.2	2.314	1.337	9	41.4	1.337
2.236	6	40.0	2.235	1.334	9	52.2	1.334
2.212	6	11.3	2.212	1.290	3	44.0	1.290
2.112	24	22.2	2.112	1.242	3	62.0	1.240
2.055	13	31.2	2.055	1.236	3	52.3	1.236
1.982	18	21.3	1.983	1.208	2	51.4	1.209
1.976	22	32.1	1.975	1.206	4	70.2, 53.2	1.206
1.952	18	41.0	1.951	1.191	4	11.6	1.191
1.909	16	40.2	1.909	1.184	2	71.0	1.184
1.836	8	00.4	1.836				
1.790	1	32.2	1.791				
1.723	3	41.2	1.723				
1.689	4	42.0	1.689				
1.675	4	33.1	1.675				
1.613	5	21.4	1.614				
1.607	8	50.2, 51.0	1.608, 1.606				
1.571	8	32.3	1.572				
1.569	11	51.1	1.569				
1.564	13	30.4	1.563				

the ratio is 1:1. This leaves no doubt that the number of components can be clearly recognized.

The composition changes between the various synthetics are reflected in the variation of d-spacings. From Tables 1–3 it can be seen that the order of cell dimension increase for a is pyromorphite-mimetite-vanadinite and for c is pyromorphite-vanadinite-mimetite. This is an ideal situation for the study of composition changes in a 3 component system by means of x-ray data. The spacings selected to examine the variation in a and c were 30.0 and 11.2 respectively. An accuracy in the determination of ± 0.001 Å was required, and this was readily attainable by use of silicon as internal standard and reduction of the scanning speed to $\frac{1}{8}°$ per minute. The compositions of the synthetics and the values of their 30.0 and 11.2 spacings are given in Table 4. The spacings are plotted against composition for the pairs pyromorphite-mimetite, mimetite-

vanadinite and pyromorphite-vanadinite in Figs. 2 and 3. The data for the three component system pyromorphite-mimetite-vanadinite are plotted in Fig. 4. In this figure the values for the 30.0 spacings are given on the left side of the diagram and the lines of equal spacing rise up to the right. The 11.2 spacings are given on the right with the lines of equal spacing rising to the left. Both 30.0 and 11.2 spacings are given on separate scales at the bottom of the figure.

DISCUSSION

The data obtained in this study do not support the existence of incomplete solid solution in the pyromorphite series. It is not thought that the
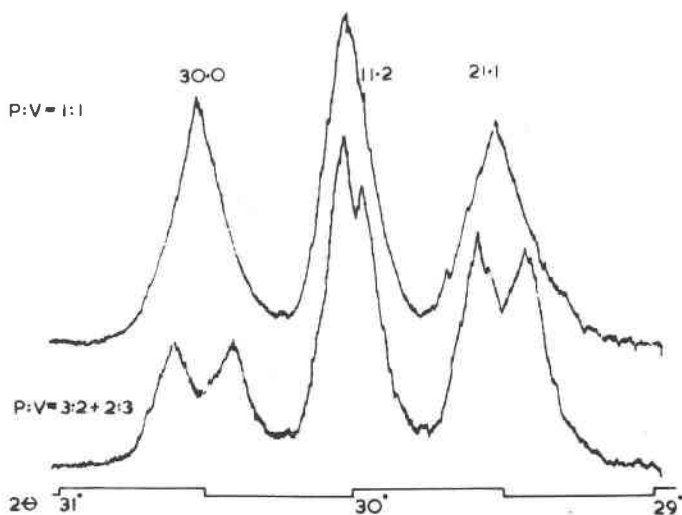
FIG. 1. Part of diffractometer traces for a two component mixture and a single compound in the system pyromorphite-vanadinite.

higher than normal surface temperatures of the syntheses (60–80° C. compared with 20–30° C.) were a critical factor in the attainment of complete solid solution in the synthetic system. Although low temperature synthesis was used as a check for only two compounds, there is no reason to expect that the others could not be similarly produced. The incomplete nature of solid solution in the pyromorphite series which has been widely recorded in the mineralogical texts, appears to be supported by published analysis of the included minerals. Wide variation in phosphate: arsenate ion ratios between pyromorphite and mimetite has been recorded, but apart from the species endlichite, with an arsenate: vanadate ion ratio of

about 1:1, little variation in the composition of vanadinite has been recorded.

There do not seem to be any crystallo-chemical reasons favoring incomplete solid solution. The minerals are essentially ionic, and the ideal

TABLE 4. 30.0 AND 11.2 INTERPLANAR SPACINGS FOR SYNTHETICS OF
THE PYROMORPHITE SERIES

Sample No.	Composition			Spacings (Å)	
	Pyr. :	Mim. :	Van.	30.0	11.2
1	100	0	0	2.885	2.959
2	0	100	0	2.962	3.013
3	0	0	100	2.987	2.995
4	80	20	0	2.900	2.970
5	60	40	0	2.916	2.981
6	40	60	0	2.931	2.992
7	20	80	0	2.946	3.002
8	0	80	20	2.967	3.009
9	0	60	40	2.972	3.006
10	0	40	60	2.977	3.002
11	0	20	80	2.982	2.999
12	80	0	20	2.906	2.966
13	60	0	40	2.925	2.974
14	40	0	60	2.945	2.981
15	20	0	80	2.965	2.988
16	80	10	10	2.902	2.968
17	60	20	20	2.920	2.978
18	45	45	10	2.930	2.987
19	45	10	45	2.936	2.981
20	33.3	33.3	33.3	2.943	2.989
21	20	20	60	2.959	2.992
22	20	60	20	2.951	2.999
23	10	10	80	2.974	2.993
24	10	45	45	2.965	3.000
25	10	80	10	2.957	3.006

Goldschmidt rules of substitution are thus applicable. The phosphate, arsenate and vanadate ions are large and can be appreciably deformed by the surrounding ions of the structure in which they occur. It is thus not possible to give fixed ionic radii for them, although for the purpose of comparison the radii of spheres based on the average bond lengths in the normal ortho-compounds ($P-O=1.53$ Å; $As-O=1.75$ Å; $V-O=1.75$ Å) can be used. This approach yields a value of 2.9 Å for the phosphate ion, 3.2 Å for the arsenate ion and 3.1 Å for the vanadate ion. With
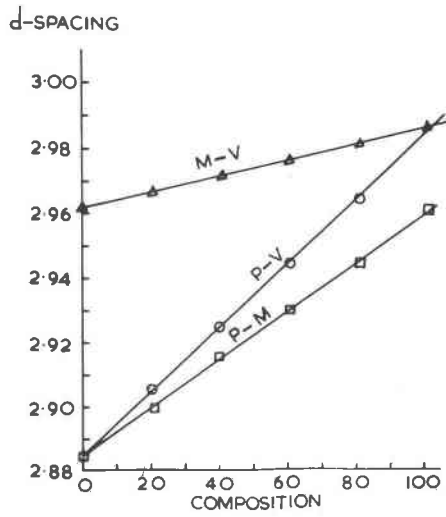
Fig. 2. Variation in 30.0 spacing with composition for synthetics of the
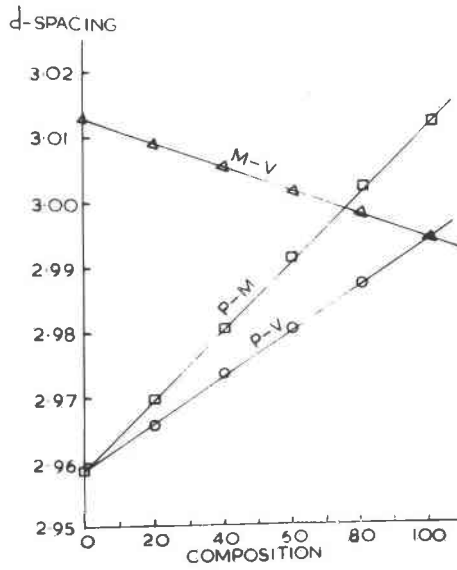pyromorphite series.

Fig. 3. Variation in 11.2 spacing with composition for synthetics of the
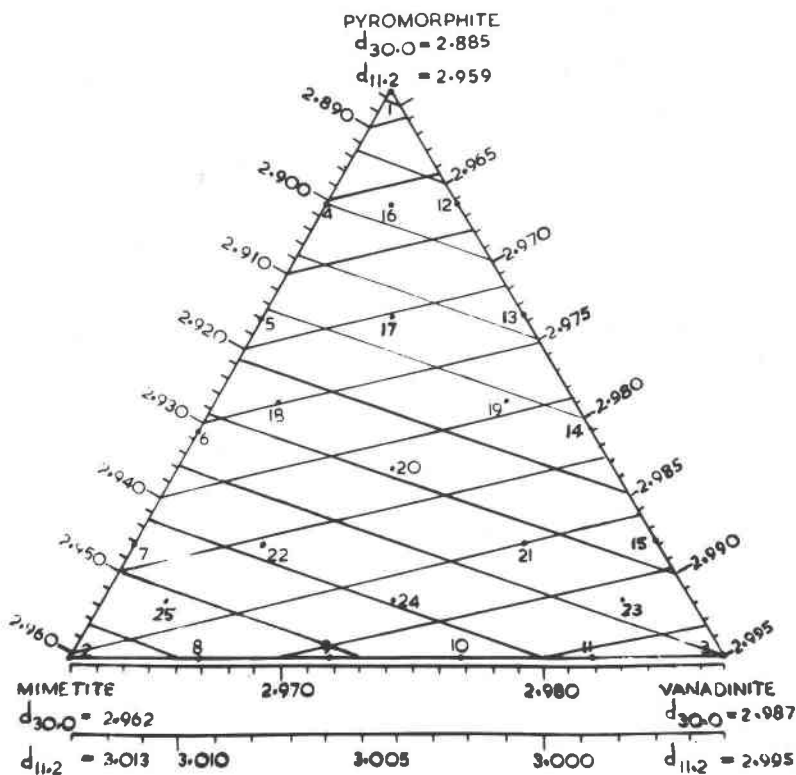pyromorphite series.

FIG. 4. Variation of 30.0 and 11.2 spacings with composition for the system pyromorphite-mimetite-vanadinite.

these values the size differences, expressed as percentages, in terms of the larger ion of the various pairs are about 9% for phosphate—arsenate, 3% for arsenate—vanadate and 6% for phosphate—vanadate. All these values are below the approximate Goldschmidt limit of 15% for complete solid solution. It is of interest to note that the greatest difference is for phosphate—arsenate, whereas it is for the system pyromorphite—mimetite that complete solution is known in the natural environment.

In view of these considerations it is possible that the literature is in error in claiming incomplete solid solution for the pyromorphite series. This being the case, the limited chemistry of the natural members of the series may only be a reflection of the availability of the particular ions at the time of mineral formation. The phosphate and arsenate ions are relatively common in the oxidized zone of lead deposits, and it is thus to be expected that a wide range of ion ratios could occur between pyro-

morphite and mimetite. Vanadium is less commonly associated with lead mineralization, and it would not be reasonable to expect a complete range of compositions between vanadinite and other minerals of the series.

The cell data calculated for the synthetic end members agree reasonably well with those given by Hendricks *et al.* (1932) and accepted by Palache *et al.* (1951). These data are compared in Table 5. The greatest discrepancy occurs between the data for pyromorphite. The presence of a small amount of calcium, for example, would considerably reduce the cell dimensions given for the pure lead compound. As the literature value is not supported by an analysis, this possible explanation of the discrepancy cannot be checked.

In his work on vanadinites Barnes (1962) found no variations in x-ray data for number of vanadinite specimens which were selected from various localities and were of variable color. In abstract (*Geoscience Abstract*

TABLE 5. CELL DIMENSIONS IN Å FOR MEMBERS OF THE PYROMORPHITE SERIES

Mineral	Synthetic		Hendricks *et al.* (1932)	
	a	c	a	c
Pyromorphite	9.987	7.330	9.95	7.31
Mimetite	10.251	7.442	10.24	7.43
Vanadinite	10.323	7.346	10.31	7.34

5-3107, 1963) the color variation of the vanadinite specimens has been taken as an index of such compositional variations as vanadate:arsenate ion ratio. It is thus reported that there is no variation in x-ray data for vanadinite with the replacement of vanadium by arsenic, although this interpretation is not made in the original paper.

The present work shows very clearly that the cell dimensions do change with composition. Reference to Fig. 4 shows that, with an accuracy in spacing determination of ± 0.001 Å, variations in terms of end member content of about 2% can be detected. In terms of the standard oxides of chemical analysis this represents variations in P_2O_5, As_2O_5 or V_2O_5 content of the order of 0.2%. It is not suggested however that Fig. 4 can be used as a guide to the composition of the natural species. No allowance is made for the substitution of calcium, barium and strontium for lead or for the substitution of bromide, fluoride, hydroxide and carbonate for chloride, all of which are known to occur in varying, though generally small, amounts. For the vanadinite specimens examined by Barnes (1962) it is possible that the color differences are the result of variation in composition. Since the measurements were made with a vernier read-

ing to 0.05 mm, no significance could be attached to the variations found in the several 2θ values determined for a number of specimens. It is evident from the study of the synthetics that a variation in 2θ of 0.05 degrees allows a considerable variation in composition.

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