CRYSTAL-STRUCTURE REFINEMENTS OF VANADINITE AND PYROMORPHITE

YONGSHAN DAI AND JOHN M. HUGHES

Department of Geology, Miami University, Oxford, Ohio 45056, U.S.A.

ABSTRACT

The crystal structures of vanadinite [$Pb_5(VO_4)_3Cl$] and pyromorphite [$Pb_5(PO_4)_3Cl$] have been refined to R = 0.022, 0.021, respectively, using three-dimensional X-ray data. The atomic arrangement of pyromorphite is confirmed as an apatite isostructure. In the structures the Pb polyhedra show little response to the tetrahedral substitution, with average Pb–O bond lengths that agree to within 0.02 Å. The XO_4 tetrahedra yield bond lengths typical of VO_4 and PO_4 tetrahedra, and X–O bond angles with the crystallographic axes are similar to within 2°. The atomic arrangement responds to the tetrahedral substitution of P for V by contraction along a due to variations in X–O(1,2) bond lengths, yielding a predictive relationship between the a axial parameter and tetrahedral occupancy in the two minerals. The distortion of the VO_4 tetrahedron in vanadinite reported in an earlier film study was not confirmed, suggesting that immiscibility between vanadinite and other Pb-bearing apatites results from differential size of tetrahedral cation and not differential distortion in the tetrahedra.

Keywords: lead-containing apatites, crystal structures, vanadinite, pyromorphite.

SOMMAIRE

Nous avons affiné la structure cristalline de la vanadinite $Pb_5(VO_4)_3Cl$ et de la pyromorphite $Pb_5(PO_4)_3Cl$ jusqu'à un résidu R de 0.022 et 0.021, respectivement, en utilisant des données de diffraction X tridimensionnelles. Dans le cas de la pyromorphite, la structure est celle de l'apatite. Les polyèdres de coordinence du Pb varient peu avec la substitution dans la position tétraédrique; la longueur moyenne de la liaison Pb–O dans les deux structures concorde, à 0.02 Å près. Les tétraèdres XO_4 possèdent des longueurs de liaisons typiques des tétraèdres VO_4 et PO_4, et les angles entre X–O et les axes cristallographiques concordent, à 2° près. L'agencement des atomes dépend de l'atome dans la position tétraédrique; une substitution du P au V cause une contraction le long de a due aux variations des liaisons X–O(1,2), ce qui permet de prédire la proportion des deux atomes dans cette position à partir du paramètre a. La distorsion du tétraèdre VO_4 dans la vanadinite, proposée dans une étude antérieure fondée sur des clichés de diffraction, n'est pas retenue. La lacune de miscibilité entre vanadinite et les autres membres plombifères du groupe de l'apatite résulterait du décalage en dimension de l'atome à coordinence tétraédrique et non pas des différences en degré de distorsion des tétraèdres.

(Traduit par la Rédaction)

Mots-clés: groupe de l'apatite, membres plombifères, structure cristalline, vanadinite, pyromorphite.

INTRODUCTION

The lead-containing apatites have a general formula $Pb_5(XO_4)_3Y$, where Y is a halide and X is a pentavalent tetrahedrally coordinated cation. Despite the abundance of museum-quality specimens, X-ray studies of the lead-containing apatites (Y = Cl; X = V for vanadinite, P for pyromorphite and As for mimetite) are rare; seemingly high-quality specimens generally do not give crystals suitable for X-ray studies. In addition, such minerals present serious experimental difficulties because the scattering is so dominated by a single, highly absorbing element. Thus, despite more than 100 spectroscopic studies on these minerals, high-quality crystal-structure studies are lacking. As part of a larger study of the apatite group of minerals, we present here details of the crystal structures of vanadinite and pyromorphite, the two hexagonal end-members in pyromorphite–mimetite–vanadinite ternary system.

PREVIOUS WORK

In a study of synthetic lead-bearing apatites, Baker (1966) found that contrary to the viewpoints in classical textbooks, all compositions in the ternary system vanadinite–pyromorphite–mimetite could be synthesized at temperatures between 60 and 80°C. Subsequently, Cockbain (1968a,b) showed discontinuities in the solid solutions between any two of the minerals in the system; this result is of interest because the tetrahedral cation occupies a single, crystallographically unique site. He suggested that the results of Baker (1966) may be attributed to an intergrowth of the minerals. Later studies of Fortsch & Freiburg (1970), Levitt & Condrate (1970) and White (1984) further supported the results of Cockbain.

The crystallography of the lead-containing

apatites was studied by Hendricks *et al.* (1932). To date, details of the three-dimensional arrangement of atoms in pyromorphite have not been reported, although the mineral has logically been assumed to crystallize as an apatite isostructure. The first three-dimensional structure analysis of one of the lead-bearing apatites was reported in this journal by Trotter & Barnes (1958), who refined the structure of vanadinite to $R = 12\%$ using visual estimates of intensities from films. They reported an extremely distorted VO_4 tetrahedron, with O–V–O angles varying between 94 and 121°, atypical among orthovanadate structures. As structural differences have been suggested as a cause for the immiscibility in the lead-bearing apatite system (Cockbain 1968a), it is obvious that modern structure refinements and comparisons of vanadinite and pyromorphite are overdue.

EXPERIMENTAL

Euhedral single crystals of vanadinite and pyromorphite were examined using the precession method. The systematic absences are consistent with space group $P6_3/m$, confirming the results of Hendricks *et al.* (1932). No reflections characteristic of a monoclinic superstructure (*cf.* mimetite: Fortsch & Freiburg 1970, Brenner *et al.* 1970) were noted. Further details concerning the crystals are given in Table 1.

Intensity data were collected on a CAD4 diffractometer utilizing graphite-monochromated $MoK\alpha$ radiation. Intensities were measured using a θ–2θ scan technique, with θ scan widths $\omega = 1.0 + 0.34 \times \tan\theta$. A prescan of each peak during data collection was used to determine counting time for final scan, with a maximum time of 150 seconds per reflection. One third of the total counting time was spent determining background on both sides of a peak. Three intensity standards were monitored every 5 hours, and three orientation standards were monitored every 150 reflections for vanadinite and every 250 reflections for pyromorphite. No significant deviation of standards was noted.

Intensity data were collected for a quadrant of reciprocal space to $2\theta = 50°$. Because of the high linear-absorption coefficients of these two minerals (Table 1), the absorption corrections were carried out for all reflections in two steps. Firstly, an empirical technique was used based on the intensity data obtained from 360° psi scans at 10° intervals for five reflections of each mineral. Following isotropic refinement using all data, the data sets were corrected using the method of Walker & Stuart (1983) as implemented in program DIFABS. Subsequently, the equivalent reflections were averaged, and the reflections with intensity lower than $3\sigma_I$ were considered as unobserved.

STRUCTURE REFINEMENT

Neutral-atom scattering factors (Cromer & Waber 1974), including terms for anomalous dispersion, were used in the refinement. The starting positional parameters and isotropic temperature-factors of vanadinite and pyromorphite were taken from Trotter & Barnes (1958) and Sokolova *et al.* (1982), respectively. During the refinement, the anisotropic thermal parameters of O(1) of vanadinite and O(2) of pyromorphite refined to nonpositive definite values; thus anions in both structures were refined with isotropic thermal parameters. The final refinements of the structures were undertaken by refining positional parameters, scale factors, anisotropic temperature-factors of cations and isotropic temperature-factors of anions and an isotropic extinction-factor with total of 28 parameters for each structure.

The atomic coordinates and equivalent isotropic displacement-factors for the two minerals are listed in Table 2. Table 3 lists selected bond-lengths for all

TABLE 1. CRYSTAL DATA AND RESULTS OF STRUCTURAL REFINEMENTS

	VANADINITE	PYROMORPHITE
Dimensions(mm):	0.08 x 0.08 x 0.1	0.12 x 0.12 x 0.16
Source:	New South Wales, Australia	Globe, Arizona, U.S.A.
Color:	light orange	dark green
Space group:	$P6_3/m$	$P6_3/m$
Cell dimensions:		
Least squares:		
$\underline{a}$:(Å)	10.319(5)	9.977(1)
$\underline{b}$:	10.313(8)	9.976(1)
$\underline{c}$:	7.337(3)	7.351(2)
α:(°)	89.98(5)	89.96(2)
β:	90.03(3)	89.97(2)
γ:	120.08(5)	119.99(1)
Idealized:		
$\underline{a}$:(Å)	10.3174	9.9764
$\underline{c}$:	7.3378	7.3511
Absorption μ(MoKα) (cm^{-1}):	753	773
Composition*:	$Pb_{4.97}V_{3.01}O_{11.98}Cl_{1.02}$	$Pb_{5.05}P_{2.97}O_{12.00}Cl_{1.00}$
# Data collected:	1363	1282
# Unique data:	436	410
R_{merge}(%):	2.8	2.1
# Data >$3\sigma_I$:	283	245
R(%):	2.2	2.1
R_w(%):	2.4	2.2
Goodness-of-fit:	0.955	0.934
Peaks on difference map (e/Å^3):		
(+):	1.279	1.795
(−):	1.295	1.977

* Conditions of analysis: JEOL microprobe, 15 kV, 60 nA, ZAF corrections. Standards: V metal (V), PbS (Pb), apatite (P, Cl). Formula basis: O + Cl = 13. Analyst: John W. Drexler, University of Colorado.

TABLE 2. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC

DISPLACEMENT-FACTORS IN VANADINITE AND PYROMORPHITE

Atom	x	y	z	$U_{eq}(Å^2)$
		VANADINITE		
Pb(1)	1/3	2/3	0.0077(2)	0.0135
Pb(2)	0.25484(8)	0.01209(8)	1/4	0.0152
V	0.4097(3)	0.3840(3)	1/4	0.0068
O(1)*	0.333(1)	0.497(1)	1/4	0.0032
O(2)*	0.599(1)	0.485(1)	1/4	0.0039
O(3)*	0.359(1)	0.269(1)	0.065(1)	0.0060
Cl*	0	0	0	0.0048
		PYROMORPHITE		
Pb(1)	1/3	2/3	0.0048(1)	0.0084
Pb(2)	0.25429(9)	0.00536(9)	1/4	0.0108
P	0.4104(5)	0.3787(5)	1/4	0.0049
O(1)*	0.343(1)	0.490(1)	1/4	0.0032
O(2)*	0.590(1)	0.475(1)	1/4	0.0022
O(3)*	0.359(1)	0.274(1)	0.084(1)	0.0046
Cl*	0	0	0	0.0038

* Atoms denoted were refined isotropically.

TABLE 3. SELECTED BOND-LENGTHS (Å) AND BOND ANGLES (°)

FOR VANADINITE AND PYROMORPHITE

VANADINITE

Pb(1)-O(1)a*	2.49(1)	Pb(2)-O(1)c	3.20(1)	
-O(1)b	2.49(1)	-O(2)b	2.34(1)	
-O(1)c	2.49(1)	-O(3)a	2.68(1)	
-O(2)d	2.76(1)	-O(3)e	2.58(1)	
-O(2)e	2.76(1)	-O(3)j	2.68(1)	
-O(2)f	2.76(1)	-O(3)h	2.58(1)	
-O(3)d	2.95(1)	-Cla	3.1569(7)	
-O(3)e	2.95(1)	-Clg	3.1569(7)	
-O(3)f	2.95(1)			
Mean	2.73	Mean	2.80	

V-O(1)a	1.70(2)	O(1)a-V-O(2)a	111.3(6)
-O(2)a	1.69(1)	O(1)a-V-O(3)a	113.1(5)
-O(3)a	1.70(1)	O(1)a-V-O(3)j	113.1(5)
-O(3)j	1.70(1)	O(2)a-V-O(3)a	106.8(5)
		O(2)a-V-O(3)j	106.8(5)
Mean	1.70	O(3)a-V-O(3)j	105.4(5)

PYROMORPHITE

Pb(1)-O(1)a	2.558(7)	Pb(2)-O(1)c	3.08(2)
-O(1)b	2.558(7)	-O(2)b	2.35(2)
-O(1)c	2.558(7)	-O(3)a	2.64(1)
-O(2)d	2.68(1)	-O(3)e	2.66(1)
-O(2)e	2.68(1)	-O(3)j	2.64(1)
-O(2)f	2.68(1)	-O(3)h	2.66(1)
-O(3)d	2.894(7)	-Cla	3.1113(8)
-O(3)e	2.894(7)	-Clg	3.1113(8)
-O(3)f	2.894(7)		
Mean	2.71	Mean	2.78

P-O(1)a	1.56(1)	O(1)a-P-O(2)a	109.5(9)
-O(2)a	1.56(1)	O(1)a-P-O(3)a	111.8(5)
-O(3)j	1.52(1)	O(1)a-P-O(3)j	111.8(5)
-O(3)j	1.52(1)	O(2)a-P-O(3)a	108.3(5)
		O(2)a-P-O(3)j	108.3(5)
Mean	1.54	O(3)a-P-O(3)j	107.1(7)

* Symmetry-equivalent positions: a. x,y,z; b. -y,x-y,z;
c. y-x,-x,z; d. -x,-y,-z; e. y,y-x,-z; f. x-y,x,-z;
g. -x,-y,1/2+z; h. y,y-x,1/2+z; i. x-y,x,1/2+z;
j. x,y,1/2-z; k. -y,x-y,1/2-z; l. y-x,-x,1/2-z.

cation polyhedra and bond angles for the XO_4 tetrahedra in the minerals. The anisotropic thermal parameters of cations in Table 4, bond angles of Pb polyhedra in Table 5, and observed and calculated structure-factors in Table 6 have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

DISCUSSION OF THE STRUCTURES

The atomic arrangement of vanadinite as determined by Trotter & Barnes (1958) is in principle confirmed, although significant deviations from their reported structure have been found. Their average Pb(1)–O bond length is 0.13 Å shorter than ours, our Pb(2)–O(2) and Pb(2)–O(3a) bond lengths are respectively 0.20 Å and 0.21 Å shorter than theirs, and the difference of average V–O length is 0.04 Å. We attribute these differences to the use of more modern equipment and techniques in the present study, as all our bond-length values are within six σ of their values, using their standard deviations. The crystal structure of pyromorphite is also confirmed as an isostructure of vanadinite. The reader is referred to the paper of Trotter & Barnes (1958) for the description of the vanadinite structure, as the structure will not be reviewed in detail here. However, as the structures of lead-containing apatites have significance in understanding solid solution in the system (Cockbain 1968a), we will compare the two structures in detail.

Vanadinite and pyromorphite are chemically similar except for the tetrahedrally coordinated cation, and the crystal structures reflect that similarity. In each structure Pb(1) bonds to six oxygen atoms [3 × O(1), 3 × O(2)] in the form of an approximate trigonal prism, with three longer bonds to oxygen atoms [3 × O(3)] through the prism faces. Adjacent Pb(1)–O_9 "prisms" share pinacoidal faces at the mirror planes ($z = 1/4$ and 3/4) to form Pb(1)–O_9 polyhedral chains parallel to c. In the two structures, average Pb(1)–O bond lengths differ by only 0.02 Å, analogous Pb(1)–O bond lengths are similar to within 0.08 Å, and Pb(1)–O bond angles with the crystallographic axes are also similar to within 2.5°.

In both structures, Pb(2) lies in the mirror planes at $z = 1/4$, 3/4 and bonds to two oxygen atoms within the plane [O(1), O(2)], four oxygen atoms in the $12a$ general positions [4 × O(3)], and two Cl atoms located on the hexad at 0,0,0 and 0, 0,1/2 positions. The average bond-lengths for the Pb(2) polyhedron are similar to within 0.02 Å; the largest deviation occurs in the weak Pb(2)–O(1) bonds, 3.20 Å and 3.08 Å, respectively, in the structures of vanadinite and pyromorphite.

The major structural difference between vanadinite and pyromorphite occurs in the XO_4 tetrahedra, which are occupied by V^{5+} (0.59 Å radius) in vanadinite and P^{5+} (0.35 Å radius) in pyromorphite. Analogous angles of all X–O bonds

with the crystallographic axes are similar to within 2° between the two structures, although the average bond-lengths differ by 0.16 Å. The similar orientation of the two tetrahedra yields an explanation for the observed linear relationship between tetrahedral occupancy and the a axial parameter (Fortsch & Frieburg 1970). In each structure, X–O(1) and X–O(2) bonds lie in the mirror plane parallel to [001], but the X–O(3) bonds are about 55° from the plane. Tetrahedral substitutions thus cause a to vary mainly by the differences in X–O(1) and X–O(2) bond lengths between the tetrahedra; addition of the differential components of X–O(1) and X–O(2) bonds parallel to the a axis in each unit cell accounts for all but about 0.02 Å of the 0.34 Å difference in a between the structures. This observation provides a structural basis for the previously observed variation in the a cell parameter.

As compared to the findings of Trotter & Barnes (1958), the three-dimensional structure refinement reported herein yields a more regular VO_4 tetrahedron typical of orthovanadate structures, with O–V–O bond angles varying from 105.4 to 113.1°. The PO_4 tetrahedron in pyromorphite structure shows only slight distortion, with O–P–O angles varying from 107.1 to 111.8°. Thus, the cause of immiscibility cannot be a result of varying degrees of tetrahedral distortion, but more likely the large difference in size between V^{5+} and P^{5+}.

In our study of the lead-containing apatites, we have isolated both hexagonal and monoclinic specimens of mimetite. We will report the structure of monoclinic mimetite in a later study.

REFERENCES

BAKER, W.E. (1966): An X-ray diffraction study of synthetic members of the pyromorphite series. *Am. Mineral.* **51**, 1712-1721.

BRENNER, P., ENGEL, G. & WONDRATSCHEK, H. (1970): Blei-Apatite mit Uberstruktur. *Z. Kristallogr.* **131** S., 206-212.

COCKBAIN, A.G. (1968a): The crystal chemistry of the apatites. *Mineral. Mag.* **36**, 654-660.

———— (1968b): Lead apatite solid-solution series. *Mineral. Mag.* **36**, 1171-1173.

CROMER, D.T. & WABER, J.T. (1974): *International Table for X-ray Crystallography.* Vol. **IV**. The Kynoch Press, Birmingham, England.

FORTSCH, E. & FREIBURG, I. B. (1970): Untersuchungen an Mineralien der Pyromorphit-gruppe. *Neues Jahrb. Mineral., Abh.* **113**, 219-250.

HENDRICKS, S.B., JEFFERSON, M. E. & MOSLEY, V.M. (1932): The crystal structures of some natural and synthetic apatite-like substances. *Z. Kristallogr.* **81**, 352-369.

LEVITT, S.R. & CONDRATE, R.A., SR. (1970): The vibrational spectra of lead apatites. *Am. Mineral.* **55**, 1562-1575.

SOKOLOVA, E. V., EGOROV-TISMENKO, YU. K. & YAKHONTOVA, L. K. (1982): Crystal structure of rare arsenates - duftite and mimetite. *Vestn. Mosk. Univ., Ser. 4 Geol.,* 50-56 (in Russ.).

TROTTER, J. & BARNES, W.H. (1958): The structure of vanadinite. *Can. Mineral.* **6**, 161-173.

WALKER, N. & STUART D. (1983): An empirical method for correcting diffractometer data for absorption effects. *Acta Crystallogr.* **A39**, 158-166.

WHITE, J.S. (1984): Vanadinite from Touissit, Morocco, and comments on endlichite. *Mineral. Rec.* **15**, 347-350.