Canadian Mineralogist
Vol. 29, pp. 369-376 (1991)

THE CRYSTAL STRUCTURES OF MIMETITE AND CLINOMIMETITE, $Pb_5(AsO_4)_3Cl$

YONGSHAN DAI AND JOHN M. HUGHES,
Department of Geology, Miami University, Oxford, Ohio 45056, U.S.A.

PAUL B. MOORE
Department of the Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637, U.S.A.

ABSTRACT

The crystal structure of two specimens of mimetite [$Pb_5(AsO_4)_3Cl$] and that of its monoclinic ($P2_1/b$) dimorph, the new mineral species clinomimetite, have been refined to $R = 0.027$, 0.031, and 0.040, respectively. In the hexagonal phase, the Cl atom is located at the (0,0,0) special position, in contrast to a disordered Cl proposed earlier; thus mimetite is isostructural with vanadinite and pyromorphite. The previous conjecture on the cause of monoclinic character in clinomimetite, likened to that in chlorapatite, is not supported by our structural data. The monoclinic phase is pseudohexagonal ($b \approx 2a$; $\gamma \approx 120°$) and similar in atomic arrangement to mimetite. The largest difference between the dimorphs occurs in the positions of the O(3) atoms. The shifts of O(3) in clinomimetite, relative to positions in the hexagonal phase, are consistent with a change in locus of the $Pb(1)^{2+}$ $6s^2$ lone-pair electrons, which are not constrained by symmetry in the monoclinic phase. The redistribution of the lone-pair electrons in Pb(1) cation columns is considered a possible cause for the phase transition from hexagonal to monoclinic symmetry in $Pb_5(AsO_4)_3Cl$. The cation structures of mimetite and clinomimetite are well represented by the atomic arrangement in the Mn_5Si_3 intermetallic phase. Finnemanite, $Pb_5(AsO_3\square)_3Cl$, is an arsen*ite,* and represents a phase transitional between the analogous intermetallic phase Pb_5As_3 and the fully oxidized equivalents, mimetite and clinomimetite. The further insertion of oxygen atoms into finnemanite results in the $Pb_5(AsO_4)_3Cl$ dimorphs. The chemical bonds in finnemanite also reflect the transitional relationship between the intermetallic phase and mimetite, clinomimetite.

Keywords: crystal structures, lone-pair electrons, mimetite, clinomimetite.

SOMMAIRE

La structure cristalline de deux spécimens de mimétite [$Pb_5(AsO_4)_3Cl$] et d'un cristal de son dimorphe monoclinique ($P2_1/b$), pour lequel nous proposons le nom *clinomimétite,* a été affinée jusqu'à un résidu R de 0.027, 0.031 et 0.040, respectivement. Dans la phase hexagonale, l'atome Cl est situé sur la position spéciale (0,0,0), plutôt que sur une position désordonnée, proposition antérieure. La mimétite est donc isostructurale avec vanadinite et pyromorphite. L'explication qui avait été acceptée du caractère monoclinique de la clinomimétite, comparée à la chlorapatite, n'est pas retenue. La phase monoclinique est pseudo-hexagonale ($b \approx 2a$; $\gamma \approx 120°$), et l'agencement des atomes ressemble à celui de la mimétite. La différence la plus importante implique l'atome O(3). Les déplacements de cet atome dans la clinomimétite, relativement aux positions dans la phase hexagonale, concordent avec un changement de site de la paire d'électrons isolés $6s^2$ sur l'atome $Pb(1)^{2+}$. Ceux-ci ne sont pas contraints par opération de symmétrie dans la phase monoclinique. La redistribution de cette paire d'électrons dans les colonnes d'atomes Pb(1) serait une cause possible de la transition entre formes hexagonale et monoclinique de $Pb_5(AsO_4)_3Cl$. L'agencement des cations dans ces deux polymorphes est bien représenté par celui de la phase intermétallique Mn_5Si_3. La finnemanite, $Pb_5(AsO_3\square)_3Cl$, est un *arsenite,* et représente une phase transitionnelle entre les composés intermétalliques Pb_5As_3 et les équivalents pleinement oxydés, mimétite et clinomimétite. L'insertion d'atomes d'oxygène additionnels dans la structure de la finnemanite produit celle des dimorphes de $Pb_5(AsO_4)_3Cl$. Les liaisons de la finnemanite illustrent aussi la relation de transition qui existe entre la phase intermétallique et la paire mimétite, clinomimétite.

(Traduit par la Rédaction)

Mots-clés: structure cristallines, paires d'électrons isolés, mimétite, clinomimétite.

INTRODUCTION

Mimetite, $Pb_5(AsO_4)_3Cl$, is an end member in the ternary system pyromorphite–vanadinite–mimetite. By analogy with other apatite-group minerals that crystallize in space group $P6_3/m$, mimetite was presumed to be hexagonal (Hendricks *et al.* 1932). Since this early report, a monoclinic dimorph having space group $P2_1/b$ ($b = 2a$; $\gamma = 120°$) has been reported for both synthetic and natural samples (Keppler 1968, 1969, Brenner *et al.* 1970, Förtsch & Freiburg 1970). Keppler (1968, 1969) used both a precession camera equipped with a furnace and an optical heating-stage to show that the phase transition between the monoclinic and hexagonal dimorphs is rapid and reversible at temperatures ranging from 98 to 120°C in different samples, yet most natural samples of $Pb_5(AsO_4)_3Cl$ are hexagonal at standard

TABLE 1. CRYSTAL DATA AND RESULTS OF STRUCTURE REFINEMENTS

	MIMETITE	CLINOMIMETITE
Dimensions (mm):	0.09 x 0.08 x 0.08	0.14 x 0.12 x 0.11
Location:	Durango, Mexico	Johanngeorgenstadt, Erzgebirge, Sachsen, Germany (USNM B13647)
Cell parameters:		
Least squares:		
a: (Å)	10.212(2)	10.189(3)
b:	10.210(2)	20.372(8)
c:	7.419(4)	7.46(1)
α: (°)	90.01(2)	89.96(8)
β:	90.00(3)	90.01(8)
γ:	120.02(1)	119.88(3)
Constrained:		
a: (Å)	10.2110	10.1891
b:	10.2110	20.3723
c:	7.4185	7.4564
γ: (°)	120	119.8827
μ_1 (Mo*K*α) (cm^{-1}):	777.3	803.1
Composition:	$[Pb_{9.75}Ca_{0.32}]_{\Sigma 10.07}[As_{5.71}Si_{0.13}S_{0.13}P_{0.01}]_{\Sigma 5.98}Cl_{2.18}O_{23.91}$	$Pb_{9.99}[As_{5.74}Si_{0.07}S_{0.06}P_{0.14}]_{\Sigma 6.01}Cl_{2.18}O_{23.91}$
Theta limit:	0-25°	0-25°
Scan type:	θ/2θ	θ/2θ
Scan time (seconds):	< 150	< 120
Standards:		
Intensity:	3 per 5 hours	3 per 5 hours
Orientation:	3 per 250 reflections	3 per 500 reflections
# Data collected:	1344	2622
# Unique data:	429	2622
R_{merge} (%):	3.2	----
# Data > 3 σ_I:	232	1182
R (%):	2.7	4.0
R_w (%):	3.0	3.4
Goodness-of-fit:	0.83	1.62
Peaks on difference map (e/Å^3):		
(+) :	2.329	2.763
(−) :	1.432	2.660

temperature and pressure. To address this paradox and to elucidate the nature of the hexagonal–monoclinic phase transition, we have studied ten "mimetite" samples from different localities. Each was examined at room temperature by optical methods and long-exposure precession photographs; one of these samples exhibits the monoclinic superstructure that requires doubling of *b* axis.

Fifty years after the first description of the mimetite structure by Hendricks *et al.* (1932), Sokolova *et al.* (1982) studied the three-dimensional atomic arrangement in the phase. They refined the structure to R = 14.2%, and attributed such a high residual to the lack of absorption correction for their intensity data. In this paper, we present refinements of the atomic arrangement of the hexagonal and monoclinic dimorphs of $Pb_5(AsO_4)_3Cl$ and comment on the mechanism of the transition between the phases. The name *clinomimetite* for the monoclinic dimorph of $Pb_5(AsO_4)_3Cl$ has been approved by the International Mineralogical Association Commission on New Minerals and Mineral Names.

EXPERIMENTAL

X-ray intensity data for mimetite ($P6_3/m$) and clinomimetite ($P2_1/b$) were measured on an Enraf–Nonius CAD4 diffractometer utilizing Zr-filtered Mo*K*α and graphite-monochromated Mo*K*α radiation for mimetite and clinomimetite, respectively. Unit-cell parameters were refined (no symmetry constraints) using diffraction angles from 25 automatically centered reflections. The refined and constrained cell-parameters and crystal data are given in Table 1, which records details of data collection and structure refinement.

Intensity data were reduced to structure factors and corrected for Lorentz and polarization effects. Because of the high value of the linear absorption-coefficients of the crystals (Table 1), absorption corrections were carried out in two steps. First, an empirical psi-scan technique was employed using data obtained from 360° scans for five reflections. The data were further corrected for absorption using the method of Walker & Stuart (1983), as implemented in program DIFABS. Subsequently, the symmetry-equivalent reflections of the hexagonal crystal were averaged, and for both structures the reflections with intensities lower than $3\sigma_I$ were considered unobserved. Observed reflections were weighted proportional to σ_I^{-2}, with a term to downweigh intense reflections.

STRUCTURE REFINEMENT

Crystal-structure calculations were carried out using the SDP set of programs (Frenz 1985). Full-matrix least-squares refinements were undertaken by refining positional parameters, scale factor, anisotropic temperature-factors of cations and isotropic temperature-factors of anions, and an isotropic extinction factor. Neutral atomic scattering factors, including terms for anomalous dispersion, were used in the refinement.

Mimetite

The starting positional parameters and isotropic thermal parameters of mimetite were taken from Sokolova *et al.* (1982). Using their model, with Cl released in a (0,0,*z*) position, refinement of the atomic arrangement did not converge; the Cl atom was found to have an unusually large isotropic thermal factor. Subsequently, the Cl was fixed at (0,0,0), as in vanadinite and pyromorphite, and the structure routinely refined to R = 0.027 and R_w = 0.030. The positional parameters and equivalent isotropic displacement-factors are listed in Table 2, and selected bond-lengths are included in Table 3. Table

4 and 5 contain the anisotropic thermal parameters and the observed and calculated structure-factors; they have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

During the preparation of this manuscript, Dai and Hughes became aware of an independent refinement of the mimetite structure undertaken by the third author, who kindly shared his data. This second data-set led to the refined atomic positional parameters that also are included in Table 2. The two independent refinements are in good agreement, with the largest difference in positional parameters at 3.5σ. Because the conclusions drawn in this work are independent of the mimetite structure used, we report in detail only the data on the mimetite from Durango, Mexico (Dai & Hughes data).

Moore's specimen was obtained from the American Museum of Natural History (#40361, Tsumeb, Namibia), and was ground to a sphere of 0.085 mm radius. Its minor element chemistry is not known. The intensities of unique data to $2\theta = 60°$ were collected using a θ–2θ scan technique (705 data); the 442 independent data with $I > 2\sigma_I$ were used in the refinement procedures. Using standard full-matrix refinement procedures, the final R factor converged at 0.031. Complete details of data collection and refinement are available from the authors.

Clinomimetite

The reversible phase-transition between mimetite and clinomimetite, and the parameters of the monoclinic cell ($b \approx 2a$, $\gamma \approx 120°$) attest to the strong pseudohexagonal character of the monoclinic phase. In fact, seemingly good least-squares refinement could be obtained in the hexagonal space-group. Such a least-squares refinement in $P6_3/m$, based on 279 "hexagonal" reflections collected in the monoclinic cell, yielded $R = 0.042$, and $R_w = 0.048$. The final structure-refinement in space group $P2_1/b$ was based on 1182 observed reflections, of which 265 occur only in the monoclinic system. The starting positional and isotropic thermal parameters were derived from the mimetite of Sokolova *et al.* (1982), cast into the monoclinic cell, and the atomic arrangement refined to $R = 0.040$ and $R_w = 0.034$. The positional parameters and equivalent isotropic displacement-factors are given in Table 2. To facilitate analysis of the differences between the mimetite and clinomimetite structures, the positional parameters in the monoclinic cell as calculated from parameters of the hexagonal structure also are included in Table 2. Selected bond-lengths are included in Table 3, and the anisotropic thermal parameters in Table 4, and the observed and calculated structure-factors in Table 6 have been submitted for deposit.

TABLE 2. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT-FACTORS IN MIMETITE AND CLINOMIMETITE

Atom	x	y	z	U_{eq}*(Å^2)
		MIMETITE**		
Pb(1)	1/3	2/3	0.5070(3)	0.0143
	1/3	2/3	0.5070(2)	0.0187
Pb(2)	0.0047(1)	0.2511(1)	1/4	0.0149
	0.00450 (9)	0.25102(9)	1/4	0.0208
As	0.3837(3)	0.4091(3)	1/4	0.0059
	0.3843(2)	0.4095(2)	1/4	0.0110
O(1)	0.495(2)	0.328(2)	1/4	0.0218
	0.494(2)	0.332(2)	1/4	0.0241
O(2)	0.486(2)	0.604(2)	1/4	0.0166
	0.485(2)	0.598(2)	1/4	0.0380
O(3)	0.275(2)	0.359(2)	0.067(3)	0.0409
	0.268(2)	0.358(2)	0.075(2)	0.0561
Cl	0	0	0	0.0205
	0	0	0	0.0236
		CLINOMIMETITE***		
$Pb(1)_A$	0.6694(1)	0.41415(7)	0.0071(2)	0.0144
	2/3(0.028)	0.4167(0.052)	0.0070(0.001)	
$Pb(1)_B$	0.3367(1)	0.58059(7)	0.5059(2)	0.0142
	1/3(0.035)	0.5833(0.055)	0.5070(0.008)	
$Pb(2)_A$	0.0045(1)	0.37558(6)	0.2364(3)	0.0143
	0.0047(0.002)	0.3756(0.000)	1/4(0.101)	
$Pb(2)_B$	0.2527(1)	0.37298(6)	0.7383(3)	0.0157
	0.2511(0.016)	0.3732(0.004)	3/4(0.087)	
$Pb(2)_C$	0.2466(1)	0.74861(6)	0.2723(2)	0.0137
	0.2464(0.002)	0.7477(0.019)	1/4(0.166)	
As_A	0.3840(3)	0.4545(2)	0.2545(9)	0.0161
	0.3837(0.003)	0.4546(0.002)	1/4(0.034)	
As_B	0.4103(3)	0.2633(2)	0.7533(8)	0.0150
	0.4091(0.012)	0.2627(0.012)	3/4(0.025)	
As_C	0.0248(3)	0.5580(2)	0.2449(9)	0.0123
	0.0254(0.006)	0.5582(0.004)	1/4(0.038)	
$O(1)_A$	0.494(2)	0.413(1)	0.250(6)	0.0194
	0.495(0.010)	0.414(0.020)	1/4(0)	
$O(1)_B$	0.331(2)	0.667(1)	0.760(6)	0.0272
	0.328(0.031)	0.667(0)	3/4(0.075)	
$O(1)_C$	0.839(2)	0.504(1)	0.249(6)	0.0156
	0.833(0.061)	0.503(0.020)	1/4(0.007)	
$O(2)_A$	0.486(2)	0.5486(9)	0.232(4)	0.0074
	0.486(0)	0.552(0.069)	1/4(0.134)	
$O(2)_B$	0.603(2)	0.310(1)	0.742(6)	0.0382
	0.604(0.010)	0.309(0.020)	3/4(0.060)	
$O(2)_C$	0.109(2)	0.505(1)	0.278(4)	0.0145
	0.118(0.092)	0.507(0.041)	1/4(0.209)	
$O(3)_A$	0.256(2)	0.422(1)	0.089(4)	0.0240
	0.275(0.194)	0.430(0.163)	0.067(0.164)	
$O(3)_B$	0.619(3)	0.710(2)	0.052(4)	0.0410
	0.641(0.224)	0.708(0.041)	0.067(0.112)	
$O(3)_C$	0.085(3)	0.599(1)	0.050(4)	0.0286
	0.084(0.010)	0.613(0.285)	0.067(0.127)	
$O(3)_D$	0.288(3)	0.440(1)	0.449(4)	0.0312
	0.275(0.132)	0.430(0.204)	0.433(0.119)	
$O(3)_E$	0.651(2)	0.705(1)	0.415(3)	0.0029
	0.641(0.102)	0.708(0.061)	0.433(0.134)	
$O(3)_F$	0.084(2)	0.623(1)	0.407(3)	0.0141
	0.084(0)	0.613(0.204)	0.433(0.194)	
Cl	0.008(1)	0.2505(9)	0.490(2)	0.0204
	0(0.082)	1/4(0.010)	1/2(0.075)	

* $U_{eq} = 1/(6\pi^2)\Sigma_i\Sigma_j\beta_{ij}a_ia_j$ (Fischer & Tillmanns 1988), where $a_1 = a$, $a_2 = b$ and $a_3 = c$.

** The atomic coordinates in the second row for each atom are P.B. Moore's data.

*** For the monoclinic structure, the calculated atomic coordinates from the equivalent hexagonal atoms are listed below the refined coordinates. The numbers in the parentheses following the calculated coordinates are the differences (Å) between the calculated (hexagonal) and the refined (monoclinic) positions.

DISCUSSION OF THE STRUCTURES

In their refinement of the atomic arrangement of mimetite, Sokolova *et al.* (1982) suggested that the

TABLE 3. BOND LENGTHS (A) IN MIMETITE AND CLINOMIMETITE

MIMETITE

Pb(1)-O(1) x3	2.50(1)	Pb(2)-O(1)	3.06(3)
-O(2) x3	2.74(2)	-O(2)	2.33(3)
-O(3) x3	2.94(1)	-O(3) x2	2.57(2)
Mean:	2.73	-O(3) x2	2.76(2)
		-Cl x2	3.146(1)
		Mean$_{oxy}$:	2.68
As-O(1)	1.70(2)		
-O(2)	1.72(2)		
-O(3) x2	1.67(2)		
Mean:	1.69		

CLINOMIMETITE

Pb(1)$_A$-O(1)$_A$	2.53(4)	Pb(1)$_B$-O(1)$_A$	2.46(4)
-O(1)$_B$	2.40(4)	-O(1)$_B$	2.61(4)
-O(1)$_C$	2.54(3)	-O(1)$_C$	2.54(3)
-O(2)$_A$	2.73(2)	-O(2)$_A$	2.81(3)
-O(2)$_B$	2.72(4)	-O(2)$_B$	2.71(4)
-O(2)$_C$	2.94(2)	-O(2)$_C$	2.66(2)
-O(3)$_A$	3.12(3)	-O(3)$_D$	2.69(3)
-O(3)$_B$	2.79(2)	-O(3)$_E$	3.00(2)
-O(3)$_C$	2.68(3)	-O(3)$_F$	3.18(3)
Mean:	2.72	Mean:	2.74

Pb(2)$_A$-O(1)$_B$	3.08(2)	Pb(2)$_B$-O(1)$_C$	3.08(2)	Pb(2)$_C$-O(1)$_A$	3.03(2)
-O(2)$_C$	2.33(2)	-O(2)$_A$	2.33(1)	-O(2)$_B$	2.38(3)
-O(3)$_A$	2.51(2)	-O(3)$_A$	2.79(3)	-O(3)$_B$	2.41(3)
-O(3)$_C$	2.48(3)	-O(3)$_B$	3.04(4)	-O(3)$_C$	3.12(3)
-O(3)$_D$	2.97(3)	-O(3)$_D$	2.48(3)	-O(3)$_E$	2.85(2)
-O(3)$_F$	2.81(3)	-O(3)$_E$	2.52(2)	-O(3)$_F$	2.47(2)
-Cl	3.19(2)	-Cl	3.11(1)	-Cl	3.14(2)
-Cl	3.11(2)	-Cl	3.20(1)	-Cl	3.14(2)
Mean$_{oxy}$:	2.70	Mean$_{oxy}$:	2.71	Mean$_{oxy}$:	2.71
As$_A$-O(1)$_A$	1.72(2)	As$_B$-O(1)$_B$	1.71(2)	As$_C$-O(1)$_C$	1.65(1)
-O(2)$_A$	1.67(2)	-O(2)$_B$	1.70(2)	-O(2)$_C$	1.69(2)
-O(3)$_A$	1.67(3)	-O(3)$_B$	1.63(3)	-O(3)$_C$	1.63(3)
-O(3)$_D$	1.69(3)	-O(3)$_E$	1.67(2)	-O(3)$_F$	1.67(2)
Mean:	1.69	Mean:	1.68	Mean:	1.66

Cl atom occupies a disordered position at (0,0,0.572), although the high residual value and large B value for the Cl atom (4.3 Å^2) in their study invited further examination. The present study failed to support their disordered Cl model for the hexagonal structure, but instead suggests that mimetite is isostructural with vanadinite and pyromorphite, with the Cl located at (0,0,0) and (0,0,½). Thus the reader is referred to Trotter & Barnes (1958) and Dai & Hughes (1989) for detailed descriptions of the lead-bearing apatite structures.

The monoclinic structure of clinomimetite was explained by Keppler (1968, 1969) and Förtsch & Freiburg (1970) as resulting from ordering of the Cl atoms in the [0,0,z] anion columns, as in monoclinic chlorapatite (Mackie *et al.* 1972). Chlorapatite and mimetite are not, however, strictly analogous. In chlorapatite, Ca(2) [= Pb(2) in mimetite] bonds to *one* Cl atom in the [0,0,z] anion column; in the monoclinic variety, that Cl is ordered above or below the z = ¼ b-glide plane. In mimetite, however, the larger Pb(2) bonds to *two* Cl atoms, equidistant above and below the mirror, at (0,0,0) and (0,0,½). Thus the reduction of symmetry to monoclinic, if resulting from ordering of Cl in (0,0,z) positions, would shorten one Pb(2)–Cl bond but necessarily lengthen the other by an equivalent amount, having little effect on Pb(2) bond valence. Our structural data, as noted above, suggest that Cl occupies the special position at (0,0,½) in the hexagonal structure, and Cl in clinomimetite occupies the position (0.008,0.2505,0.490), essentially equivalent to (0,0,½) in the hexagonal space-group. The positional shift of Cl along c, unconstrained in $P2_1/b$, is less than 0.075 Å from the equivalent position in the hexagonal structure, and the temperature factors of Cl in both hexagonal and monoclinic structures are well behaved, with $B \approx 1.6$ Å^2. The refinement of the monoclinic structure thus does not support the previous conjecture for the cause of the monoclinic character.

Among the cations in clinomimetite, As^{5+} has the smallest positional shift from its analogous positions in the hexagonal structure (Table 2). The maximum shift is in the z direction ($\approx$0.038 Å). The average bond-lengths of the three nonequivalent tetrahedra in the monoclinic structure are similar to each other within ± 1σ and to those in the hexagonal structure within ± 1.5σ. The O–As–O angles range from 102 to 113°, slightly larger than those in the tetrahedron in the hexagonal structure, which vary from 106 to 113°.

In both the hexagonal and monoclinic structures, Pb(2) bonds to six oxygen and two chlorine atoms to form irregular, "side-coordinated" Pb(2)–O_6Cl_2 polyhedra. Based on the similarity of the Pb(2) polyhedra in the two structures, we suggest that the orientation of the 6s^2 lone pairs of Pb(2) in the monoclinic structure is similar to that in the hexagonal structure, the latter constrained by symmetry to lie in the z = ¼ mirror plane.

In mimetite, Pb(1) bonds to nine oxygen atoms [3 × O(1), 3 × O(2), 3 × O(3)] in the form of a tricapped trigonal prism (Fig. 1), similar to the Ca(1)–O_9 polyhedron in chlorapatite. In contrast to chlorapatite, however, the Pb(1)–O_9 polyhedron must accommodate the 6s^2 lone-pair electrons associated with Pb^{2+}. If we assume no positional disorder of Pb(1), which is not suggested by thermal parameters, symmetry in the hexagonal phase demands accommodation of the lone pair along the 3-fold axis, pointing toward either the O(1) or O(2) triangles in the mirror planes. The perimeter of the O(2) triangle is 1.22 Å larger than that of the O(1), and the Pb(1)–Pb(1) distance through the center of the O(2) triangle is 3.83 Å, 0.21 Å longer than the Pb(1)–Pb(1) distance through the center of the O(1) triangle. These observations suggest that the lone pair of Pb(1) is directed toward the O(2) triangle. In the monoclinic structure, Pb(1) atoms bond to nine oxygen atoms with topology similar to that of the Pb(1) polyhedron in the hexagonal structure, but the

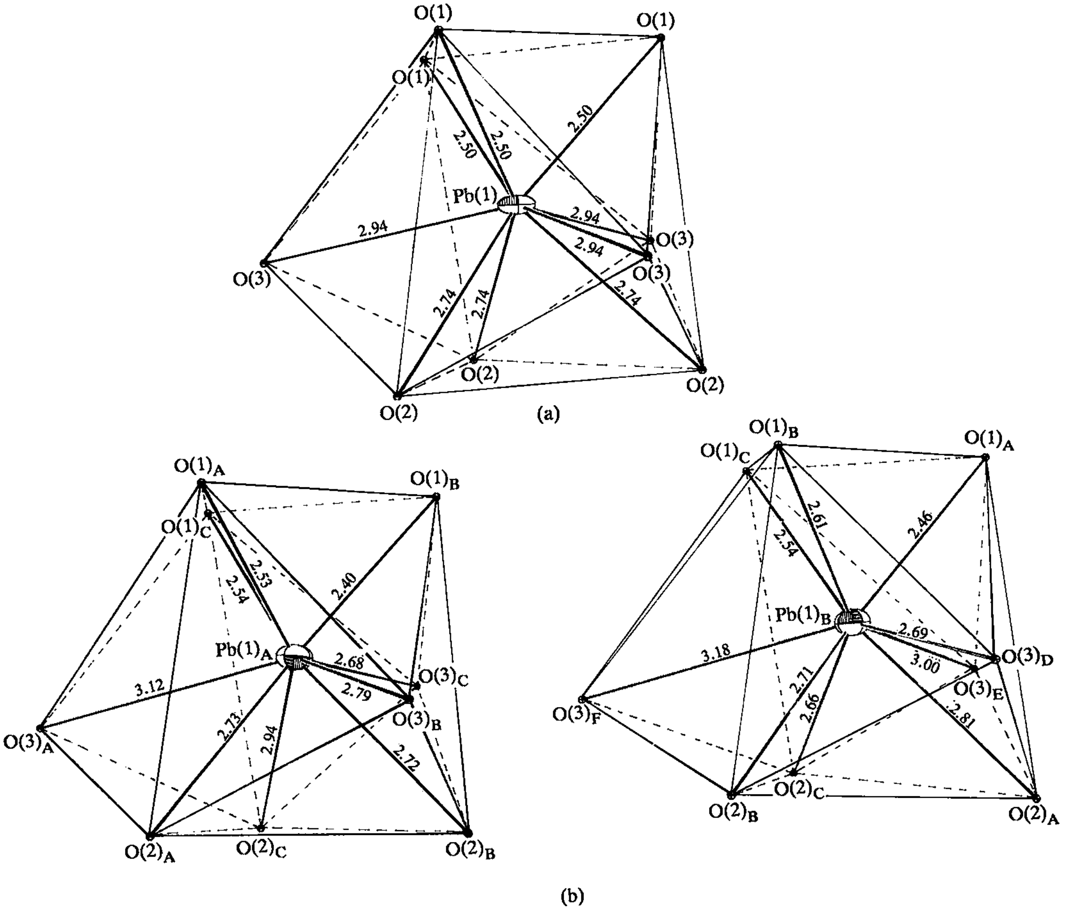

FIG. 1. Perspective diagrams for Pb(1) polyhedra in mimetite (a) and clinomimetite (b). For each polyhedron, the *c* axis is vertical, and the longest Pb(1)-O(3) bond is approximately in the plane of the page.

equivalent Pb(1) atoms occupy two nonequivalent general positions with point symmetry 1 in clinomimetite. Thus there is no symmetry constraint on the distribution of the $6s^2$ lone-pair electrons.

As noted in Table 2, the largest difference in positions of analogous atoms between the hexagonal and monoclinic dimorphs occurs in the O(3) atoms. In the hexagonal phase the O(3) atoms are trigonally disposed near the equatorial plane of the tricapped trigonal prism (Fig. 1), with Pb(1)-O(3) bond lengths of 2.94 Å (× 3). In the $Pb(1)_A$-O_9 polyhedron of clinomimetite, two of the hexagonally equivalent Pb(1)-O(3) bonds shorten considerably (2.79, 2.68 Å) and one lengthens to 3.12 Å. In the $Pb(1)_B$-O_9 polyhedron of clinomimetite, two Pb(1)-O(3) bond lengths increase (3.18, 3.00 Å), and one shortens to 2.69 Å. In all cases, the bond valence on the central Pb is maintained, with bond-valence sums of 2.00, 2.08, and 1.96 for the Pb(1) in the hexagonal dimorph and the $Pb(1)_A$ and $Pb(1)_B$ in the monoclinic dimorph, respectively (constants from Brown 1981). The shifts in position of the O(3) atoms in the monoclinic phase with respect to the hexagonal phase are consistent with a shift in position of the Pb^{2+} $6s^2$ lone-pair electrons, no longer constrained by symmetry in the monoclinic phase.

Although structure analysis does not yield direct information on the locus of the lone-pair electrons, indirect information on their location can be gained by analyzing lone-pair – bond-pair interactions through cation–anion bond lengths (Moore 1988). Figure 1 displays the $Pb(1)_A$ and $Pb(1)_B$ polyhedra in clinomimetite, and illustrates the changes in Pb(1)-O(3) bond lengths enumerated above. In the $Pb(1)_A$ polyhedron the lengthening of the $Pb(1)_A$-$O(3)_A$ bond and the concomitant shortening of $Pb(1)_A$-$O(3)_B$ and -$O(3)_C$ bonds suggest that the $6s^2$ lone pair has shifted toward $O(3)_A$ from the [0,0,*z*] direction in the hexagonal phase. Similarly, the change in $Pb(1)_B$–O(3) bond lengths, particularly the 0.24 Å increase of $Pb(1)_B$–$O(3)_F$ relative to the hexagonal phase, suggests a shift of the lone pair toward $O(3)_F$. The changes in Pb(1) coordination thus suggest that a result of the phase transformation, if not the cause of the transition, is a redistribution of the lone-pair electrons associated with Pb(1).

The differences in transition temperature observed in different crystals by Keppler (1968, 1969), Förtsch & Freiburg (1970) and Brenner *et al.* (1970) suggest that deviation from stoichiometry as well as differences in physical conditions of formation could affect this transition. The chemical formulas in Table 1 show that the extents of substitutions at tetrahedral sites are similar in our mimetite and clinomimetite, whereas those at the Pb sites differ. The clinomimetite crystal contains only Pb, but the hexagonal phase contains about 0.3 Ca atoms/unit cell. Rouse *et al.* (1984) showed that in hedyphane, $Pb_3Ca_2(AsO_4)_3Cl$, essentially complete ordering of the calcium occurs into the Ca(1) site. If the pattern of ordering is similar for substituent Ca in mimetite, the substitution of Ca^{2+} for Pb^{2+} in the Pb(1) cation columns would reduce the concentration of the $6s^2$ lone pairs along the 3-fold axis in mimetite. It may be that the relative saturation of the Pb(1) columns with lone pairs causes the low-temperature phase transition, explaining the range of transition temperatures observed in different samples. A suggested area of future research is a detailed microprobe study of mimetite to determine the relationship between chemistry and symmetry.

In a detailed analysis of the lone-pair effect and its relationship to the magnetoplumbite structure, Moore *et al.* (1989b) demonstrated that lone-pair – bond-pair interactions have many interesting implications, and suggested that variations in lone-pair – bond-pair interactions with temperature can induce phase transitions. It may be that mimetite is an example of a phase transition caused by changes in lone-pair – bond-pair interactions with temperature.

RELATIONSHIP OF MIMETITE AND CLINOMIMETITE TO THE Mn_5Si_3 AND FINNEMANITE STRUCTURES

Mn_5Si_3

Traditional rules of crystal chemistry urge mineralogists to view crystal structures of oxysalts as examples of anion packing with cations occupying the interstices. Upon comparing the structures of the oxysalts with those of analogous intermetallic compounds, however, O'Keeffe & Hyde (1985), Moore *et al.* (1989a, b) and Moore (1989) suggested that in some oxysalts, *cations* may play an important part in the atomic arrangements rather than just filling the interstices among anions.

TABLE 7. RELATIONSHIP BETWEEN MIMETITE AND Mn_5Si_3 STRUCTURES

MIMETITE			Mn_5Si_3*			Δ**(Å)
	Pb(1)			Mn(1)		0.05
1/3	2/3	0.5070	1/3	2/3	1/2	
	Pb(2)			Mn(2)		0.14
0.0047	0.2511	1/4	0	0.2358	1/4	
	As			Si		0.23
0.3837	0.4091	1/4	0.401	0.401	1/4	

* The atomic position data for Mn_5Si_3 are from Aronsson (1960).

** used as defined in Moore (1989), is the distance between the analogous atoms in the structures computed from the mimetite cell.

The similarity between cation positions in the apatite structure and the Mn_5Si_3 intermetallic phase has been noted by O'Keeffe & Hyde (1985). A comparison of the coordinates of the three unique cations in mimetite with those of the atoms in the intermetallic compound Mn_5Si_3 [a = 6.910 Å, c = 4.814 Å, $P6_3/mcm$ (Aronsson 1960)] shows remarkable agreement; the *largest* difference between the analogous atomic positions is 0.23 Å [scaled to the mimetite cell, Table 7; because of the structural similarity between the $Pb_5(AsO_4)_3Cl$ dimorphs, all comparisons of mimetite in this section hold for clinomimetite as well].

In the cell of the intermetallic phase, atoms occupy four layers parallel to (001) at z = 0, ½, ¼ and ¾. The mimetite structure can be pictured as the Mn_5Si_3 structure diluted by insertion of anions into the four intermetallic atom layers [Cl, O(3) at or near z = 0, ½; O(1), O(2) at z = ¼, ¾]. This insertion of anions leads to anisotropic increases in a and c because the anions join the cation layers parallel to (001).

Moore *et al.* (1989a, b) found that many oxysalt structures can be deduced from their related intermetallic phases by different anion insertions. In a trial refinement of the mimetite structure using our intensity data and fixed positions of Pb(1), Pb(2) and As derived from the Mn_5Si_3 structure, we obtained R = 24% *without refining cation positions or including anions in the refinement.* This approach clearly demonstrates that the cation arrangement in mimetite is well represented by that in the Mn_5Si_3 intermetallic phase, and invites further comparison of the structures of oxysalts and intermetallic phases.

Finnemanite [$Pb_5(AsO_3\square)_3Cl$]

The Mn_5Si_3 structure represents the mimetite structure devoid of anions, and thus all metals necessarily exist as neutral atoms. The mimetite structure is the oxygen-stuffed equivalent of the intermetallic phase, in which all metals exist in the fully oxidized state. Finnemanite, $Pb_5(AsO_3\square)_3Cl$, is an arsen*ite* and represents a phase transitional between the intermetallic phase and the fully oxidized equivalent, mimetite. In finnemanite, three-fourths of the oxygen atoms present in mimetite have been "inserted" into the analogous intermetallic structure.

Finnemanite (space group $P6_3/m$; a = 10.322 Å, c = 7.055 Å; Effenberger & Pertlik 1979) can be considered as an oxygen-deficient [O(1)-deficient] mimetite. The atomic arrangement in finnemanite is strikingly similar to that in mimetite; the largest difference between the analogous atomic positions in the two structures is 0.29 Å (scaled to mimetite cell). Despite the absence of O(1) from the finnemanite structure, the cation coordination polyhedra are identical to those in mimetite, save that O(1) is replaced by a vacancy [*i.e.*, Pb(1)-$O_6\square_3$, Pb(2)-$O_5\square Cl_2$, As-$O_3\square$]. The presence of the "O(1) vacancies" in the finnemanite structure leads to local concentrations of metallic bonding as [$\square$-$Pb(1)_2Pb(2)As^{3+}$] metallic clusters, where the vacancy is "coordinated" by two Pb(1), one Pb(2) and one As^{3+} in a distorted tetrahedron.

The nature of the chemical bonds in finnemanite also reflects its transitional nature between the intermetallic phase Mn_5Si_3 and mimetite. In the Mn_5Si_3 structure, metallic bonds are dominant, in contrast to the ionic–covalent bonds in mimetite. The finnemanite structure, however, contains both metallic and nonmetallic bonds. Although the oxygen content and chemical bonding are different among Mn_5Si_3, finnemanite and mimetite, the atomic arrangement of the metals in the structures is remarkably insensitive to these differences, and their isostructural relationship is maintained. It is also interesting to conjecture that solid solution may exist between mimetite and finnemanite. The presence of the O(1) vacancies and reduced As (As^{3+}) in mimetite may also affect the phase transition between mimetite and clinomimetite.

ACKNOWLEDGEMENTS

We gratefully acknowledge support of the U.S. National Science Foundation through grants EAR–8717655 and CHE–8418897 (Hughes), and EAR–8707382 (Moore). We thank Dr. Pete J. Dunn of the U.S. National Museum for providing several samples of mimetite, and Dr. George E. Harlow of the American Museum of Natural History for supplying P.B.M. with the Tsumeb material. The serendipitous independent conclusions of mimetite studies by Y.D. and J.M.H. on one hand, and P.B.M. on the other, obviated any need for two separate publications. P.B.M. acknowledges Dr. Elmer O. Schlemper of the University of Missouri and Dr. Pradip K. Sen Gupta of Memphis State University who collected the data, and refined the mimetite. Thorough reviews of the manuscript were provided by Carl Francis, Joel D. Grice and an anonymous reviewer.

REFERENCES

ARONSSON, B. (1960): A note on the compositions and crystal structures of MnB_2, Mn_3Si, Mn_5Si_3 and $FeSi_2$. *Acta Chemica Scandinavica* **14**, 1414-1418.

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

BROWN, I.D. (1981): The bond-valence method: an empirical approach to chemical structure and bonding. *In* Structure and Bonding in Crystals II (M. O'Keeffe & A. Navrotsky, eds.). Academic Press, New York (1-30).

DAI, YONGSHAN & HUGHES, J.M. (1989): Crystal-structure refinements of vanadinite and pyromorphite. *Can. Mineral.* **27**, 189-192.

EFFENBERGER, H. & PERTLIK, F. (1979): Die Kristallstruktur des Finnemanits, $Pb_5Cl(AsO_3)_3$, mit einem Vergleich zum Strukturtyp des Chlorapatits, $Ca_5Cl(PO_4)_3$. *Tschermaks Mineral. Petrogr. Mitt.* **26**, 95-107.

FISCHER, R.X. & TILLMANNS, E. (1988): The equivalent isotropic displacement factor. *Acta Crystallogr.* **C44**, 775-776.

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

FRENZ, B.A. (1985): Enraf–Nonius Structure Determination Package. *In* SDP Users, Guide. Version 4. Enraf-Nonius, Delft, The Netherlands.

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.

KEPPLER, U. (1968): Monokliner Mimetesit, $Pb_5(AsO_4)_3Cl$. *Neues Jahrb. Mineral. Monatsh.*, 359-362.

______ (1969): Zum Modifikationswechsel chlorhaltiger Apatite. *Neues Jahrb. Mineral. Monatsh.*, 64-67.

MACKIE, P.E., ELLIOTT, J.C. & YOUNG, R.A. (1972): Monoclinic structure of synthetic $Ca_5(PO_4)_3Cl$, chlorapatite. *Acta Crystallogr.* **B28**, 1840-1848.

MOORE, P.B. (1988): The joesmithite enigma: note on the $6s^2$ Pb^{2+} lone pair. *Am. Mineral.* **73**, 843-844.

______ (1989): Perception of structural complexity: fillowite revisited and α-iron related. *Am. Mineral.* **74**, 918-926.

______, SEN GUPTA, P.K. & LE PAGE, Y. (1989b): Magnetoplumbite, $Pb^{2+}Fe_{12}^{3+}O_{19}$: refinement and lone-pair splitting. *Am. Mineral.* **74**, 1186-1194.

______, ______ & SCHLEMPER, E.O. (1989a): Kornerupine: chemical crystallography, comparative crystallography, and its cation relation to olivine and to Ni_2In intermetallic. *Am. Mineral.* **74**, 642-655.

O'KEEFFE, M. & HYDE, B.G. (1985): An alternative approach to non-molecular crystal structures, with emphasis on the arrangements of cations. *Structure and Bonding* **16**, 77-144.

ROUSE, R.C., DUNN, P.J. & PEACOR, D.R. (1984): Hedyphane from Franklin, New Jersey and Långban, Sweden: cation ordering in an arsenate apatite. *Am. Mineral.* **69**, 920-927.

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.

Received February 27, 1990, revised manuscript accepted July 15, 1990.